Iodine Aspects of Severe Accident Management

Workshop Proceedings
Vantaa (Helsinki), Finland
18-20 May 1999

Organized in collaboration with

Fortum
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In implementing its programme, CSNI establishes co-operative mechanisms with NEA’s Committee on Nuclear Regulatory Activities (CNRA), responsible for the activities of the Agency concerning the regulation, licensing and inspection of nuclear installations with regard to safety. It also co-operates with NEA’s Committee on Radiation Protection and Public Health and NEA’s Radioactive Waste Management Committee on matters of common interest.
Workshop on Iodine Aspects of Severe Accident Management

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OECD Workshop on
Iodine Aspects of Severe Accident Management
Vantaa, Finland, 18-20 May 1999

SUMMARY AND CONCLUSIONS

INTRODUCTION AND OBJECTIVES

Following a recommendation of the OECD Workshop on the Chemistry of Iodine in Reactor Safety held in Würenlingen (Switzerland) in June 1996 (Summary and Conclusions of the Workshop, Report NEA/CSNI/R(96)7), the CSNI had decided to sponsor a Workshop on Iodine Aspects of Severe Accident Management, and their planned or effective implementation. The starting point for this conclusion was the realization that the consolidation of the accumulated iodine chemistry knowledge into accident management guidelines and procedures remained, to a large extent, to be done. The purpose of the meeting was therefore to help build a bridge between iodine research and the application of its results in nuclear power plants, with particular emphasis on severe accident management. Specifically, the Workshop was expected to answer the following questions:

- what is the role of iodine in severe accident management?
- what are the needs of the utilities?
- how can research fulfil these needs?

The Workshop was organized in Vantaa (Helsinki), Finland, from 18 to 20 May 1999, in collaboration with Fortum Engineering Ltd. It was attended by forty-six specialists representing fifteen Member countries and the European Commission. Twenty-eight papers were presented. These included four utility papers, representing the views of Electricité de France (EDF), Teollisuuden Voima Oy and Fortum Engineering Ltd (Finland), the Nuclear Energy Institute (USA), and Japanese utilities.

The papers were presented in five sessions:

- iodine speciation
- organic compound control
- iodine control
- modeling
- iodine management

A sixth session was devoted to a general discussion on iodine management under severe accident conditions.

The meeting was concluded, for interested participants, by technical tours of the VICTORIA and COPO research facilities and of the Loviisa Nuclear Power Plant.
CONCLUSIONS AND RECOMMENDATIONS

Role of Iodine in Severe Accident Management

The role of iodine in Severe Accident Management can be considered on three separate levels:

- the level of the expected operator actions that are governed by the SAM guidelines and procedures,
- the level of the emergency response organisation actions, and
- the level of the plant modifications for the mitigative measures,

A possible role of iodine management is the influence of gaseous iodine on the public protection needs when initiating the filtered containment venting. The means for reducing the gaseous iodine would be to increase the sump pH to clearly basic values provided that it is still compatible for long-term management operation.

The optimized filtered venting operation with respect to iodine reflects on all above levels. Some utilities might consider it beneficial to provide robust means to increase the sump pH and scrubber efficiency. Such measures might be passive or might require well-defined operator action to actuate.

Evaluation of possible delaying of manual filtered venting would be in most cases a task for the emergency response organization. The decision to delay filtered venting actuation would be based on estimated volatile iodine releases and consequent need for evacuation or sheltering. Such task is a typical interface between SAM and the emergency response organization.

In many countries, however, the decision as regards the containment filtered venting actuation may incorporate other criteria. For example, in France, the decision to actuate containment filtered venting is made essentially on actual containment pressure criteria in order to avoid any risk of a gross containment failure. Such decision can be at least one day after the onset of the accident, once the offsite emergency measures to protect the public have been completed.

Needs of utilities

The safety significance of iodine, in case of accidents, has always been recognized by the industry, and more particularly by the utilities. A prudent engineering approach, based on conservative assumptions, has led to addressing all iodine relevant problems at the design level, and robust systems and components have been provided.

All such components and systems are used for plant safety assessment, and would thus be called upon, if available, in case of accident.

Design and acceptance criteria for such components and systems can vary from one country to another. However, as some countries have designed such systems to address in vessel core-melt scenarios, there is no need, on the utility side, for further development for such systems and components. Concerning accident management, as
was seen in the discussions which took place in the SESAM group (CSNI Senior Group of Experts on Severe Accident Management), critical decisions are made without factoring in iodine considerations, as the major concerns are to stop accident progression and prevent uncontrolled loss of containment integrity. Guidance is generally well established, and here again, no urgent need has been identified at the utility level.

Two issues, however, could be considered, for which data consolidation could be welcome:
- iodine behavior in the secondary side of SGs
- possibility for on-line measurement of iodine concentration inside containment.

This, however, should be understood as a need to summarize existing data for the former, evaluate the interest and feasibility for the latter, rather than a need for further extended development.

It should also be emphasized that the current trend towards electricity market deregulation will put pressure on utilities to decrease their generation costs. Although there is no evidence that utilities will all take the same actions to achieve this objective, there will be probably a trend to reassess the need for some regulatory constraints. Examples of such initiatives were given in the meeting for the U.S. regulatory context, utilities contemplating applications for charcoal removal in some filtration systems or for eliminating the need for post-accident sampling.

At last, considering the current lack of plans for future development of nuclear power, maintaining and transmitting knowledge could well become a critical issue in the near future. Although no precise need was identified during the meeting, as most presentations were clearly on progress in R&D, it could be wise to evaluate whether additional knowledge on iodine behavior is deemed necessary for the safety of currently operating plants in the years to come, and, in case yes, which level of knowledge would be adequate and how to maintain it.

Related issues such as the activities having the potential for attracting young graduates should be discussed in this perspective.

**Needs of regulators**

Regulators need information, knowledge, an adequate data base and competence in order to perform their duties. This is true in particular for assessing the iodine aspects of severe accident management.

Another reason for regulators to need knowledge on iodine behavior is when they either perform or review level 2 PSAs. Assessing the source term and the impact of accident management actions on the releases, requires adequate knowledge of the main fission product chemistry and phenomena in the containment. The needed accuracy depends on the uses of the PSA.
Deregulation puts pressure on utilities to reduce costs and to relax regulatory constraints. The regulators should be able to judge the acceptability of relaxation requests and their justification, and for that they will need up-to-date information.

Finally, during a real crisis situation, regulators may be called upon to take or recommend prompt decisions to protect the public, such as (1) is sheltering better than evacuation, (2) should the public be instructed to take potassium iodide tablets. Careful preparation may not be enough to take such decisions. A team of people knowledgeable in plant behavior in severe accident situations, and in iodine behavior in particular, may be needed.

**Improvement of predictive capabilities**

Presentations and discussion during the workshop brought up needs to finish tasks that are currently underway and would improve the predictions of iodine behavior. There is need for validated, fast-running models, integrated to plant codes, to predict iodine behavior, for design assist, safety analysis and accident response decision-making. Implicit is the need to complete and consolidate the current generation of experiments (i.e., PHEBUS) and the need for distillation of the knowledge into practical tools (i.e., IMOD) which is just entering fruition.

Specifically, there is also a need for reliable predictions of time-dependent airborne iodine species concentrations to establish qualification requirements for hydrogen recombiners.

**Progress made on major iodine chemistry safety issues since the 1996 Iodine Workshop**

**Homogeneous Phase Iodine Chemistry**

The sump pH is the most important parameter in determining the formation of volatile iodine in the aqueous phase, and the maintenance of a high pH could be an important accident management tool in many sequences. It is therefore important that the factors leading to the acidification of the sump are well understood and quantified.

Recent results on nitric acid formation confirm old calculations and experiments at laboratory scale. The effect of surface material on the nitric acid formation is recognized to be significant, but no experimental results were presented to quantify the extent of the surface effect.

Pyrolysis of cable insulation as a result of core melt can be extensive and produce HCl and Cl₂. This could have an impact on pH and filtering and scrubbing on severe accident management, but plant-specific evaluations should be considered. Significant progress has been made on understanding and modeling the effect of organic materials on pH decrease. The radiolysis of organic solvent dissolved from painted surfaces could lead to acid production in the containment sump.
The sump temperature is confirmed to be of secondary importance in determining iodine volatility as the result of further data obtained on hydrolysis and partition coefficient of various organic iodides.

In the gas phase, organic iodine could be higher than originally expected, in particular at low oxygen content, in presence of chlorine and B₄C control rod material in the BWR case.

Rate of conversion of I₂ to IO₃⁻ by ozone is lower than previously thought, and is expected to be even lower if surface effects and the presence of H₂ are considered. However, further confirmation is needed.

Surface reactions

Reactions of iodine with structural surfaces are better understood in the area of organic iodide and acid production.

New data has been provided by PHEBUS FPT 1 tests on iodine/painted surfaces interactions.

Reactions with surfaces in the containment could affect the iodine volatility either by permanent trapping on the surface, or by changing the chemical form of iodine.

Significant progress has been made on Ag-I interaction. Good data and proper modeling have been obtained on the major mechanisms of Ag + I₂ reactions. Nevertheless, in addition to the importance of the Ag₂O + I⁻ reaction, there is still some debate on the stability of AgI and also Ag₂O in the presence of radiation. NOₓ and Cl⁻ may reduce AgI stability; this is to be confirmed by ongoing experiments.

Mass transfer

Overall gas-aqueous interfacial mass transfer uncertainties remain but they are generally considered to be of low impact on iodine source term evaluation.

Modeling of iodine chemistry

Significant progress has been achieved on simulation of intermediate scale tests using various models.

The experts expressed clear needs for further ISP activities focussing on iodine behavior under accident conditions.

The most significant development on modeling of iodine chemistry is the development of simple models that are flexible and readily understandable.

Availability of improved fast running integral codes will help better understand the interactions between severe accident phenomena and the effect of severe accident management measures on the iodine source term and will also aid decision making.
Iodine management

The progress made since the last Iodine Workshop includes the following:
• the effects of paints and cable insulation material are now widely acknowledged and there are calculation tools available so that those effects on pH evolution can be quantified,
• plant modifications to enhance pH control in plants that are most vulnerable to iodine volatilization have been initiated,
• the effects of chlorine on iodine behavior in scrubber filters have been identified and some plant modifications to mitigate these effects have already been made,
• the possibility of poisoning effect of gaseous iodine on catalysts has been restated.

Concluding remarks on the status

Iodine Speciation and Chemical Processes

Iodine behavior in containment is a complex interplay of sump radiolysis and surface chemistry reactions, strongly influenced by key parameters such as temperature, pH and composition of surface and solute materials.

Effects of pH on iodine volatility and the related effects of paints and cable insulation are now widely acknowledged and calculation tools predict iodine behavior with reasonable accuracy.

Modeling

ISP 41 was the first comparison exercise on iodine code. Mechanistic and semiempirical codes were capable of producing satisfactory results, but they showed sensitivity to user experience and selection of input data.

Simple iodine models, suitable for use in fast-running system codes, have shown ability to reproduce integral experimental results and are verified by mechanistic code calculations.

Iodine Control

Significant reduction in iodine releases can be obtained by controlling containment water pH and by filtering containment leakage.

Silver is an effective trap for molecular iodine. Experiments also indicate the probable high trapping efficiency of iodide by extensively oxidised silver aerosols, but uncertainties exist regarding knowledge of the surface state. Stability of AgI to radiation, especially in the presence of Cl\textsuperscript{−} and NO\textsubscript{2}, remains to be established, according to recent investigations. An experimental programme (PHEBUS Project - PSI) is addressing this issue.
HCl, arising from pyrolysis of cable insulation, in the absence of strong buffering can cause lowering of pH, increase of volatile iodide formation, and possible impairment of filtered venting scrubber systems by Cl₂.

In ice condenser designs, buffer chemicals (borax) in the ice provide efficient pH control, utilizing favorable mass transfer characteristics within containment.

Charcoal filters are shown to provide an effective and well-characterized barrier to iodine release from the vacuum building in CANDU plants.

New results

PHEBUS experiments have shown that significant amounts of gaseous iodine were transported in the primary circuit during certain phases of the test. The gaseous iodine injected at the break from the circuit was the main cause of the observed gaseous iodine fraction in the containment during the short term (several hours). In the middle term (a few days), the organic iodides are the dominant species. They result from the partial conversion of the iodine that reacted with the atmospheric paints.

General/Accident Management

Iodine aspects enter SAM issues at different levels, primarily at the interface with emergency response planning, safety assessment and possible plant modification design analysis. Should a severe accident happen, iodine issues would not drive accident management decisions. No additional research need was identified with respect to present regulatory requirements.

The Programme Committee points out, however, that further research may still be needed for other applications, such as risk assessment, emergency response planning, and to maintain capability and competence in the field of iodine chemistry and its application to nuclear reactor safety.

SESSION SUMMARIES

Introductory Session

There were two invited lectures to introduce the background and the objectives of the Workshop. The Chairman of the CAM, Mr. Jacques Duco explained the background of the current workshop and highlighted the conclusions from the 4th Workshop on the Chemistry of Iodine in Reactor Safety held on June 10-12, 1996 at Würenlingen, Switzerland. He stressed that it would be beneficial to review the progress made since that meeting and how the progress can be integrated into accident management.

Mr. Michel Vidard of EdF discussed the needs of the nuclear industry with respect to the iodine aspects of SAM. He concluded that the iodine aspects have been addressed in the design of existing plants using quite conservative assumptions and that no major modifications were expected for Accident Management. Remaining uncertainties are deemed manageable by utilities.
Session I: Iodine Speciation (Prepared by Professor J.O. Liljenzin, Chalmers University of Technology, Gothenburg, Sweden)

Five papers were presented at Session I. These can be divided into three groups according to the areas treated, see Table below.

The first two papers in the Table treated various aspects of the results from the PHEBUS FP tests FPT-0 and FPT-1 of importance for the iodine source term and initial iodine speciation. The current paradigm of release from the overheated core as CsI is questioned as measurements indicate that a fraction of the iodine is transported in a more volatile form during certain phases. Inl formation has been postulated, based on kinetic calculations, but no experimental evidence is available. Furthermore, elemental iodine is probably also emitted in non-negligible amounts from the primary system in these tests. Analysis of data indicates that kinetics might play a role in iodine speciation in the primary circuit. These observations may require future changes of the initial chemical form of iodine in many of the currently used severe accident analysis codes. This will then probably have an indirect effect on accident management as such codes are often used to predict the progression of severe accidents and the possible effects of planned management actions.

The second group of two papers described measurements of iodine reactions of importance in air filled containments, but also important for inerted P/S-containments during the start of reactor operation, i.e., before reduction in oxygen concentration is complete. Furthermore, these data are also of interest for both types of containments in case of severe accidents due to loss of cooling during refuelling and maintenance. An interesting observation by Evans et al. is the formation of organic iodides with higher

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<td>HCl from cable pyrolysis</td>
<td>- pH control - RI trapping in venting filters</td>
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molecular weight than CH₃I, and correspondingly lower volatility. Ozone induced oxidation of elementary iodine is effective in reducing the concentration of gaseous I₂, not only in irradiated dry air but also in the presence of steam.

The third group only comprises one paper which describes measurements of HCl release from a typical cable insulation, HYPALON, during pyrolysis in the absence of oxygen. The observed amounts of HCl per weight of insulation corroborates earlier scouting measurements made in the Swedish RAMA project in the 1980's. The effect of HCl on iodine behavior and management is threefold. Firstly the resulting very low pH of unbuffered water volumes will increase the fraction of iodine converted to organic iodides (RI). Secondly, radiolytic production of Cl₂ will lead to an increase of the fraction of iodine present as I₂. Thirdly, HCl will consume some of the amount of iodine removal reagents present in filtered venting scrubber systems, requiring higher initial amounts. From an accident management point of view this will require earliest possible injection of the proper amount of strongly alkaline liquids or buffer solutions into containments with initially unbuffered water.

Session II: Organic Compound Control (Prepared by Dr. J Clara Wren, AECL, Canada)

The session on organic compound control dealt primarily with organic iodide formation, which is of interest, because of the difficulty of filtering or scrubbing these species. Since the last iodine workshop, significant progress has been made in understanding the role of painted surfaces in formation of organic iodides, and a large data base has been accumulated on the formation of these species.

It is now well established that organic iodides may be formed as a result of the interaction of organic solvents "leached" from painted surfaces and I₂ in the aqueous phase. The general features of the process is well understood and a model has been developed.

The mechanism for organic iodide formation from interaction of I₂ on painted surfaces is not as well understood, however a significant effort has been made in performing experiments, compiling the data and developing an empirical model based on this mechanism.

Because the relative importance of the two processes (homogenous aqueous phase and heterogeneous surface) has not been established, quantifying organic iodide inventory with any certainty in containment under accident conditions, for those situations where surface reactions are expected to be important, is still somewhat problematic.

A suggested approach to address the issue of the quantification of organic iodide is to compare the predictions by each of these models, for a given series of reactor accident conditions. This will establish whether or not it is important to firmly identify a proper mechanism in quantifying the organic iodide production rate. If it is, additional work will be required to establish the mechanism for the heterogeneous formation route.
An additional influence of painted surfaces is their effect on pH of the sump when in contact with irradiated solutions. The radiolysis of organic solvents dissolved from painted surfaces could lead to significant quantities of acid being produced in the sump. The mechanism is now well understood and easily modeled. The impact of this study on SAM is in pH control during severe accidents.

Experiments have also been initiated on the homogeneous gas phase production of organic iodides from CH₄ and I₂, which could be an important route for formation in BWR reactor accident sequences. The new results indicate that the organic iodide formation under BWR conditions may be higher than originally expected. The effect of chlorine appears to be significant. Large amounts of B₄C in the control rods of some PWRs (EDF 1300 MW units) could also impact the organic iodide production during a severe accident.

In summary an extensive data-base now exists for the effect of organic components on iodine volatility, and modeling is reasonably well advanced. Additional effort is required to establish the organic iodide inventory in containment for situations in which the generation of organic iodides on surfaces is expected to be significant.

Session III: Iodine Control (Prepared by Dr. Didier Jacquemain, CEA, France)

Six papers were presented in Session III. These can be divided into two groups according to the areas treated.

The first four papers concerned research linked to the study of limitation of gaseous iodine formation due either to the effect of maintaining high pH’s or the efficiency and stability of iodine trap (namely reaction with Ag to form insoluble Ag I). Progress was made to quantify factors possibly leading to the acidification of the sump: release of HCl from cable insulation by pyrolysis in the BWR situation, determination of nitric acid formation under radiation in glassvials.

There is a consensus in saying that high pH should be maintained in the sump to reduce volatile iodine formation from the aqueous phase. However, uncertainties remain to quantify acid production under representative conditions: effect of surfaces on HNO₃ production, effect of released material from fuel degradation, production of CO₂ in case of core-concrete interactions.

Two papers described the substantial progress made to gain a firm understanding of Ag/I interactions in the sump. Modeling of AgI formation in the sump has reached a sufficient level of accuracy to model small scale (SIEMENS and AEAT) and intermediate scale (PHEBUS, RTF, AECL) experiments. The use of Ag/I modeling for the reactor case requires the knowledge of the Ag surface state (oxidation, aerosol size, morphology). There is still no firm understanding of the effect of dissolution of Ag oxides on the Ag/I reaction. There is a consensus in saying that Ag may be a very efficient iodine trap in plants where Ag-In-Cd control rod material are used, provided AgI is stable to radiation. Stability of AgI to radiation, especially in the presence of Cl- and NO₂, remains to be established according to recent investigations.
The last two papers described a technical proposal and a technical system to mitigate volatile iodine. A proposal was made to substitute NaOH by hydroxylamine which offers the potential advantage of reducing I$_2$ volatilization from acidic sump down to pH = 1.0 and could help to get rid of NO$_x$ and H$_2$O$_2$ to some extent. Substantial research work is still required to determine the stability and mitigation efficiency under accidental conditions. TEDA impregnated charcoal were shown to be adequate organic iodides filtering devices when used to temperature up to 80°C and relative humidities up to 70 %. Kinetics of uptake of organic iodides as well as desorption rates were established for those conditions. Since other work showed that organic iodides may contribute significantly and even be in some cases the major contributors to the volatile iodine fractions (PHEBUS situation) making adequate technical systems for the filtration of those compounds appears to be of importance. Additional research may be necessary to show that the results in this presentation could be applied to other reactor systems and different conditions.

Session IV: Modelling (Prepared by Mr. Salih Güntay, PSI, Switzerland)

Six papers that can be grouped in the following 2 categories were presented in this session:

1. Modelling and verification
2. Application of iodine chemistry for plant assessment in conjunction with an integral severe accident system code

Four papers were presented in the first category. The first presented NUPEC’s further modelling efforts to improve the IMPAIR3 code in the areas of hydrogen peroxide production and its reaction with iodine, production and reaction of dissolved oxygen, the effect of boric acid, and nitric acid production. Assessment performed using RTF Test RTF3b demonstrated the predictive capability of IMPAIR3.

The second paper presented the outcome of the ‘International Standard Problem ISP41’, which was recommended by the 1996 Workshop. Nine organisations participated in this exercise which was organised for the first time by the OECD in this field. The comparisons indicated that the mechanistic codes (LIRIC and MELCOR-I) reproduced the RTF test data successfully. The exercise also indicated the importance of the user experience in selecting the model parameters (rate constants) used by the empirical codes (IODE and IMPAIR3). It demonstrated the need to extend the validity of the models incorporated in such codes to cover a broader range of conditions affecting the iodine chemistry. The experts expressed clear needs for further ISP activities focussing at other significant aspects of the iodine chemistry.

The third and fourth papers in the first category provided new approaches to treat the iodine chemistry with a very few number of species or to treat species categorised in 6 groups. The simplification of the chemistry has been attempted to obtain fast running computer models but still to predict the gaseous iodine concentration with reasonable accuracy. The approaches taken by both Canadian and French organisations have used rate constants developed based on the extensive sensitivity analysis of the
comprehensive mechanistic models. Although further work is needed to complete the development, the demonstrated predictive capabilities have indicated possibilities for future roles of such models if they are incorporated in integral system codes. Availability of such improved fast running integral tools will help to better understand the interactions of the several severe accident phenomena and the effect of several accident management measures on the iodine source term and will also aid the decision making.

The fifth and the sixth papers of this session in the second category presented applications of detailed iodine chemistry using the IODE code with the initial and boundary conditions as predicted by the system codes, MAAP3b and MELCOR for a large PWR and a VVER-440, respectively. The importance of key parameters, like sump pH, spray operation, etc., on the iodine source term into the environment was shown. The papers highlighted the further needs to determine the sump pH based on the conditions evolving during the accident progression and for the pH control. Highlighted also is the need for a coupled treatment of iodine chemistry with the rest of severe accident phenomenology. This argument supported the goals of the further simplified iodine model development introduced above.

Session V: Iodine Management (Prepared by Mr. Timo Karjuned, STUK, Finland)

The original approach to iodine management in a number of countries (TID 14844) was to design nuclear power plants assuming that during an accident a large fraction (50 %) of core inventory is released into containment, where one half is rapidly deposited while the another half stays initially airborne. From the airborne iodine, most (91 %) in elemental form, 5 % appears as aerosols and 4 % in organic compounds. These assumptions lead to containment designs with a relatively stringent requirement for leak tightness and to control of containment leakage by ventilation and filtering.

As the knowledge concerning iodine behavior has expanded substantially over the years, some of the early assumptions are now viewed as overly conservative, as stated in the second paper presenting the U.S. industry perspectives on the iodine management by Mr. D. Modeen. He listed the following mitigating phenomena:

- iodine is released mainly in the form of aerosols,
- aerosol form of iodine is generally retained in containment more readily than the gaseous form,
- reevolving of iodine from the containment sump is prevented by maintaining neutral or alkaline pH,
- significant fraction of iodine released from the core is retained in the primary circuit.

The current plant designs and operating practices are considered to provide adequate protection of the public from severe accidents. Consequently, the industry is now pursuing regulatory relief from systems such as post-accident sampling system, which are judged to be costly and unnecessary. No uncertainties in accident management have been identified by the U.S. industry that would warrant further studies.
During the discussion following the presentation, Mr. J. Lee from NRC pointed out that the term "severe accident" is used in the U.S.A. to refer to accidents involving both core damage and pressure vessel rupture, which are considered to be beyond the current design basis. This may explain why further iodine studies are seen as unnecessary by the industry, while in practice the industry is pursuing many relaxations in the current operating practices on the basis that they do not significantly increase the risk related to design basis accidents, which thus include also core melt accidents without pressure vessel rupture. Consequently, further studies supporting the evaluation of these and similar applications are needed.

An example of such studies was given by Mr. R. Hamazaki, who presented results from both experimental and analytical studies concerning volatile iodine formation during a core melt accident in a Japanese BWR.

In the calculation presented by Mr. Hamazaki the containment water pH was assumed to be affected by nitric acid formation alone, and therefore the reduction in water pH during the sequence was only moderate from 7 to 6. As suppression pool water in BWRs is not buffered, any additional release of acids can lead to a more sudden and deep reduction. Such a reduction may result from cable insulation pyrolysis releasing large quantities of hydrochloric acid.

The release of hydrochloric acid with its potential consequences to iodine retention in containment and scrubber filter system was described in detail in presentation by Mr. H. Sjövall. Should the suppression pool water become acidic, not only iodine but also chlorine is vaporized. As chlorine may then be carried out to the scrubber filter, where it competes with iodine in the reactions involving also sodiumthiosulfate, the release of chlorine can lead to degradation of filter iodine retention capability. In order to prevent this the thiosulfate concentration in the filter has been increased to compensate all possible chlorine releases. Modifications are foreseen also in the containment water pH control system, of which capacity will be increased to compensate hydrochloric acid releases. Also possibilities to enhance organic iodide retention in the scrubber filter by suitable additives will be studied. In the discussion that followed it was pointed out by Prof. J. Liljenz in that water pH affects also the formation of precipitates due to containment material oxidation, which may reduce the efficiency of decay heat removal systems in the long run.

The effect of hydrochloric acid on containment sump water pH was also studied by Mr. T. Routamo. However, this effect was shown to be of minor importance at Loviisa VVER due to borax stored in the ice in the ice condensers, which provide efficient buffering capacity during an accident.

The general consensus among the workshop participants was that a significant reduction in the iodine releases can be obtained by controlling containment water pH and by reducing, collecting and filtering the containment leakage. In designs where the containment can be depressurized without venting, these means appear to be efficient enough so that no major modifications in plant systems and current operation practices are foreseen. However, further studies may be warranted, should the current release limits or operation practices be modified. For the designs that apply filtered venting as
a part of their severe accident management strategy the situation is less clear, since there the containment water pH has been found to be sensitive to chemicals, such as chlorine, that can be released during an accident. The same chemicals may also affect directly the iodine reactions either in the containment or in a scrubber filter enhancing iodine volatilization. Some modifications have already been made to accommodate these effects, and possibilities to enhance iodine management will be sought also in the future.

Session VI: Session chairmen’s summaries and general discussion (Prepared by Dr. Harri Tuomisto, Fortum Engineering Ltd, Finland)

The session chairmen reported the conclusions of their sessions as presented in the previous sections. There was an extensive discussion on these reports.

The chairman emphasized the need for broad considerations of various aspects concerning the role of iodine in the SAM. Prevention and mitigation of fission product releases and related environmental and health consequences is the final goal of SAM once the core degradation has started. The objective of the workshop is to discuss, whether additional measures with respect to the iodine should be taken. All such considerations should take into consideration the overall plant-specific approach to SAM and iodine aspects should not be treated in isolation from the other SAM measures. When national criteria exist for the allowable Severe Accident releases of fission products, the iodine releases are mainly relevant for evaluation of acute health effects and evacuation, sheltering and stable iodine distribution needs. It is obvious that there are large differences among various plant designs and the considerations have to be very plant specific.

For discussion it is useful to separate the role of iodine to the operator level (SAM guidelines and procedures), the emergency organization level (avoiding or timing of early evacuations) and plant modification level.

Allocation of resources on the iodine R&D should be compared with respect to the risk reduction potential of other relevant SAM research. Finally, remaining uncertainties are to be managed by applying sufficiently robust decisions and measures.

Dr. Jay Lee of NRC preferred to focus on iodine research for design basis accidents instead of looking measures for Management of Severe Accidents. Furthermore, it is to be expected that the regulatory bodies will need capabilities to evaluate safety cases that the utilities may present already in near future. Such safety cases would aim at relaxation of such overly strict requirements that may cause an unnecessary cost burden in the deregulated electricity market. He added that the plant life management may bring respective cases e.g. for allowing higher than existing leakage rates and increased timing for containment isolation.
PROGRAMME COMMITTEE

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Dr. Jacques Royen (OECD/NEA)
OPENING REMARKS

by
Jacques Royen
OECD Nuclear Energy Agency

It is a great pleasure to welcome you to this Workshop on Iodine Aspects of Severe Accident Management, on behalf of the OECD Nuclear Energy Agency and its Committee on the Safety of Nuclear Installations (CSNI).

First of all, I would like to thank all the people who have made this meeting possible. This Workshop is organised in collaboration with Fortum Engineering Ltd. I thank very much Fortum, represented here by Mr. Heikki Väyrynen, Vice-President for Nuclear Power, for their kind hospitality and the excellent arrangements made. Our gratitude goes more particularly to the organisers of the meeting, Harri Tuomisto and his team, Marja Kossila, Virpi Tiainen and Carolina Tuomisto, who have spared no effort to make this meeting a success. I add that we are very happy to hold the meeting in Vantaa: over the years the Nuclear Power Division of IVO - now called Fortum - has established itself as one of the leading lights in the field of reactor safety. The quality of its research work and its plant operation is recognised by everyone, and envied by many.

I take this opportunity to thank Electricité de France (EDF) who provide logistic assistance to the organisation of the meeting; Neige Martin has participated very effectively in the preparation of the Workshop, and I understand she will also help with the preparation of the Proceedings.

Our thanks are also due to the members of the Programme Committee of the meeting: Harri Tuomisto, Benoit De Boeck, Jacques Duco, Salih Güntay, Grant Koroll, Jan-Olov Liljenzin and Michel Vidard. They have evaluated the abstracts of the papers, made suggestions and remarks, organised the sessions. Some of them will also act as Session Chairmen. Together with the other Session Chairmen, Clara Wren, Didier Jacquemain and Timo Karjuneen, they will write, during the meeting, brief summaries of the highlights and major points of interest of the sessions. They will also prepare, immediately after the Workshop, a brief note on the Conclusions and Recommendations which can be drawn from the meeting.

Finally, I want to thank all the authors who contributed papers to the Workshop. Thank you also for providing advance copies to the Programme Committee and Session Chairmen. This has been a real help in preparing the sessions.
This meeting is your meeting. It follows four workshops, also held under the sponsorship of the CSNI, on the chemistry of iodine in reactor safety. Its purpose is to help build a bridge between iodine research and the application of its results in nuclear power plants, with particular emphasis on severe accident management. We have only been partially successful as industry participation in this meeting is limited. But I am convinced we shall be able to establish a constructive dialogue, leading to a better understanding of the needs and the possibilities. This Workshop is a first step.

Let me emphasise the essential importance of the discussion periods. A 10-minute discussion will be part of the presentation of each paper, and a general discussion will conclude every session. A general discussion will be held at the end of the Workshop. It will discuss the role and importance of iodine management in the overall severe accident management strategy, the needs of the utilities, and how research can fulfil these needs. I expect the discussion to be lively.

I wish you an excellent meeting, and a pleasant stay in Helsinki.
Mr. Chairman, Ladies and Gentlemen,

As the Chairman of the Task Group "Containment Aspects of Severe Accident Management" (CAM) of the COMMITTEE ON THE SAFETY OF NUCLEAR INSTALLATIONS (CSNI) of the NUCLEAR ENERGY AGENCY (NEA), I have the honor of shortly introducing this workshop on "Iodine Aspects of Severe Accident Management".

At its December 1996 meeting, the CSNI endorsed the proposal made by its Principal Working Group 4 on "Confinement of Accidental Radioactive Releases" (PWG4), to organize a meeting specially devoted to iodine chemistry aspects of severe accident management and their planned or effective implementation.

This task was given to two Task Groups of the PWG4 involved in these issues, the Task Group on "Fission Product Phenomena in the Primary Circuit and the Containment", chaired by Mr. Salih GÜNTHAY of the Paul SCHERRER Institute (PSI), and the Task Group CAM.

The Program Committee was rapidly constituted, with the participation of Dr. Harri TUOMISTO (Fortum Engineering Ltd., Finland), who agreed to be the Chairman of the meeting, Mr. Benoît De BOECK (AVN, Belgium), Chairman of PWG4, Dr. Grant KOROLL (AECL, Canada), Prof. Jan-Olov LILJENZIN (Chalmers University of Technology, Sweden), Mr. Salih GÜNTHAY (PSI, Switzerland), Mr. Michel VIDARD (EDF/SEPTEN, France), Dr. Jacques ROYEN (OECD/AEN) and myself.

The Program Committee met twice and selected twenty nine technical papers, which were regrouped in six sessions.

Fortum Engineering Ltd. proposed to host the workshop at Vantaa and Electricité de France (EDF) offered to provide additional logistic support: such initiatives were both highly valued and have to be presently acknowledged.
Such a proposal of a meeting specially devoted to iodine chemistry aspects of severe accident management resulted from the conclusions of the FOURTH CSNI WORKSHOP ON THE CHEMISTRY OF IODINE IN REACTOR SAFETY, held at the Paul SCHERRER Institute, Würenlingen (Switzerland) on June 10-12, 1996. By the fact, it was apparent, when time came to the conclusions, that the large accumulated knowledge on the chemistry of iodine, as presented during the sessions, had to be translated at the soonest, as far as achievable, into accident management guidelines and procedures.

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But, just before entering the technical sessions of the present workshop, let us go back to the conclusions of the June 1996 Workshop, to remind us where we were at that time: such conclusions will provide a reference point on key issues, which will enable us to assess the knowledge gained from recent research activities on these points. In addition, discussions should derive on how these progresses in research have been integrated, or could be better integrated, in the development of accident management procedures and guidelines.

At the Fourth OECD Workshop on the Chemistry of Iodine in Reactor Safety, about seventy experts from fourteen OECD Member countries attended the meeting, as well as experts from Latvia and the Commission of the European Communities.

Outlined below are specific conclusions arising from the technical presentations, in such major areas as the homogeneous phase chemistry, the surface reactions, the mass transfer, the modelling of iodine chemistry and its applications to analysis of severe accidents, and the accident management and mitigation. They constitute, I repeat, the starting point for the assessment of progresses, which have been made up to now. The description of such knowledge improvements and of their applications regarding accident management strategies, will constitute the focal point of this meeting.

Technical issue: Homogeneous Phase Iodine Chemistry

It was recognized that iodine chemistry, both in the liquid and the gaseous phase, can have an important impact on the volatility of iodine within the containment following an accident.

The sump pH is the most important parameter in determining the formation of volatile iodine in the aqueous phase, and the maintenance of a high pH could be an important accident management tool in many sequences.
It is therefore important that the factors leading to the acidification of the sump – nitric acid formation, radiolytic or thermal decomposition of organic materials from paint and cable insulation - are well understood and quantified, which was not exactly the case in 1996 for all conditions of interest.

The radiolytic oxidation of I\(^-\) to I\(_2\) appeared to be well understood at low pH, but some uncertainties remained regarding the mechanism in alkaline solution, particularly at very low iodine concentrations.

The sump temperature was assumed to be of secondary importance in determining iodine volatility, and its effect on inorganic iodine chemistry appeared to be adequately understood.

However, there remained a need for further data at accident-relevant temperatures, particularly concerning the hydrolysis rates and partition coefficients of organic iodides.

Gas phase iodine chemistry was generally well understood, particularly in dry air; however, there was a need for further data on the radiolytic oxidation of I\(_2\) to IO\(_3^-\) in steam atmospheres.

**Technical issue: Surface Reactions**

Reactions of iodine with structural or aerosol surfaces within the RCS were recognized as having the potential of changing the chemical form of the iodine, which could change the source term to the containment.

Reactions with steel surfaces were said generally well understood at high RCS temperatures, but were not as well understood at lower containment temperatures.

Reactions with aerosol particles were assumed to be thermodynamically controlled, and this approach seemed satisfactory at high temperatures.

Reactions with surfaces in the containment could affect the iodine volatility, either by permanent trapping on the surface, or by changing the chemical form of the iodine.

Silver aerosol could be an important trap in the aqueous phase. The important factors affecting this reaction were generally well understood, but further information was required on the effect of other anions (e.g. NO\(_3^-\), Cl\(^-\)) on the reaction kinetics, and on the radiation stability of the AgI product, particularly at high dose rates.
Data on the interaction of I\textsubscript{2} with Ag aerosol in the containment gas phase were limited but adequate, since this reaction would not have a large effect on iodine volatility.

**Organic paints** were recognized as a potential, efficient iodine sink; in addition, reaction with organic surface materials might generate volatile organic iodides and convert I\textsubscript{2} to less volatile species (I\textsuperscript{-} or soluble organic iodides).

There were many uncertainties still to be resolved in this area, in particular the kinetics of iodine absorption and desorption, and the mechanism of organic iodide formation.

The effects of paint type, ageing and prototypic conditions of dose rate and temperature on the reactions all needed to be addressed. In addition to direct reactions with iodide, organic materials leached from paint could have an important influence on the radiation chemistry of iodine, either via acid formation or by competition in radical reactions. More data were required before these effects could be quantified.

Reaction of organic iodine with inorganic paints (e.g. Zn primer) results in I\textsubscript{2} trapping and reduction of ionic species. Understanding of this reaction was generally considered adequate, except under condensing conditions where further data were required.

Reactions of gaseous iodine with dry steel surfaces would lead to temporary trapping of I\textsubscript{2}; this process was generally well understood but gas phase deposition and desorption rates needed to be further validated. Reaction with wet steel surfaces, in both the gas and water phases, leads in addition to the reduction of I\textsubscript{2} to I\textsuperscript{-}; quantification of this effect was estimated adequate.

Very few data existed on the reaction of iodine with bare concrete surfaces; nevertheless, such reactions would not be expected to have a significant impact on iodine volatility.

The decomposition of CsI to I\textsubscript{2} by hydrogen combustion was not well understood, and there was a poor agreement between the available data regarding the extent of decomposition and the influence of thermal-hydraulic conditions.

**Technical issue: Mass transfer**

The rate at which iodine is transferred between phases (sump, atmosphere, spray, bubbles, etc.) can have a significant impact on the gaseous species concentration.
Uncertainties remained as to the mass transfer rates:

- from the sump to the containment atmosphere, including the effect of sump boiling,
- from bubbles to the sump (pool scrubbing), including the effect of aerosol particles,
- from the containment atmosphere to the spray droplets, particularly the effects of pH and iodine species concentration in the spray droplets, and
- for deposition onto surfaces, including the effect of wet surfaces.

**Technical issue: Modelling of Iodine Chemistry and Application to Analysis of Severe Accidents**

Phenomenological and mechanistic modelling approaches were successfully applied in containment iodine behavior codes (IODE, IMPAIR 3 and LIRIC, INSPECT, respectively).

The codes were used to predict iodine behavior for given severe accident conditions.

The uncertainties in the predictions mainly stemmed from uncertainties in the modelling of several homogeneous and heterogeneous processes and mass transfer, as outlined above; in addition, there were uncertainties in the thermal-hydraulic and aerosol conditions which affect the chemistry of iodine and its transport behavior.

The thermodynamic database used in programs such VICTORIA was well established. However, the kinetic database, especially at high temperatures, and used in mechanistic codes, still needed further development.

The databases used in the phenomenological codes are valid only for the range of experimental conditions under which the integral tests were conducted; care should be given not to extrapolate beyond that range. More collaborative work was still needed to establish a common ground in comparison of the codes and the databases employed.

**Technical issue: Accident Management and Consequence Mitigation.**

The importance of pH of the reactor sump on iodine chemistry is well understood. Need for an adequate pH control was emphasised.
Current research was expected to improve the knowledge and decrease the uncertainties involved in several reactions and interactions.

However, there was a need to implement the results of the past and current iodine research into better definition of requirements on the efficiencies of the retention devices, accident management guidelines and procedures. To a large extent, this work remained to be done.

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It was apparent at the Workshop that the translation of the accumulated knowledge into accident management guidelines and procedures was, largely, still to be achieved.

Following that, the Programme Committee of the the Fourth OECD Workshop on the Chemistry of Iodine in Reactor Safety recommended that a meeting specially devoted to iodine chemistry aspects of severe accident management and their planned or effective implementation, bringing together researchers, regulatory bodies and utilities, be convened in the not too far distance.

Here we are now, in May 1999.

The papers proposed for this workshop still address, to a large part, experimental research: three sessions are devoted to Iodine speciation, Organic compound control and Iodine control. This cannot be avoided, considering the remaining phenomena to be clarified, as stated above, in an attempt to close the issues.

Progress in modelling will also be presented, and I wish that, in the technical conclusions of the Vantaa meeting, all the progresses made since a couple of years be highlighted, contributing to a sound basis for the iodine aspects of severe accident management.

Just a small number of papers were proposed for the session which was initially thought as the kernel of the workshop, "Iodine management" session: I am convinced that these valuable papers will initiate a large, open discussion in the last session "Iodine Management under Severe Accident Conditions" and in the general discussion, where utilities needs should be placed in front of the results and perspectives of the iodine research, basic or applied.

This should result in a better understanding, through technical exchanges between experts of various countries, of the needs and concerns of the different actors contributing to the nuclear safety chain. Such an international workshop, under the aegis of OECD and hosted by FORTUM, will surely contribute to enhance international cooperation in the iodine aspects of
severe accident management arena, ultimately contributing to further demonstrate the safety and environmental acceptability of nuclear power as an economic energy source.

Thank you for your attention.
THE NEEDS OF THE NUCLEAR INDUSTRY WITH RESPECT TO
IODINE ASPECTS OF
SEVERE ACCIDENT MANAGEMENT
A UTILITY PERSPECTIVE

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ABSTRACT

Iodine-related issues in case of accidents have always been factored in the design of nuclear units. After a brief analysis of the main assumptions used for designing the structures and components contemplated to limit the detrimental consequences of the presence of iodine during an accident, the situation utilities would have to face in case of severe accidents is described, stressing operator problems, priorities, and critical issues in interfacing with the authorities.

Recent progress in iodine behavior understanding is then discussed, with the objective of evaluating whether further development is needed, the conclusion being that current knowledge is already very substantial, and that there could be a need for restructuring available data on core-melt in case of Steam Generator Tube Rupture and on-line measurement of iodine concentration inside containment.

1. INTRODUCTION

When looking at utility needs related to any given problem, one has to deal with the following issues:
Has the problem under analysis been factored in the design of the plants, and if yes, how?

In case of component or system malfunction or during postulated accidents relevant to the issue under analysis, should specific utility constraints be considered to allow proper handling of the problem?

Through all debriefings made after training sessions, or drills, are there tangible indications that, in case of (very) perturbed situations relevant to the considered issue, the accident could be managed more easily or more efficiently?

For those potentially beneficial modifications which would have been identified, would the resources needed to develop and validate components or tools which could improve utility effectiveness be commensurate with any quantifiable benefit in terms of public protection.

In the paragraphs below, the following will be briefly reviewed:

Which iodine-related problems were factored in plant design, together with the general approach used to address the problem, and preliminary remarks on impacts for Accident Management,

How is Severe Accident Management currently contemplated at the utility level, and are iodine-related issues directly reflected in Severe Accident Management Guidelines?

Which consequences recent progress in the understanding of fission product release to and behavior in the containment could have on design practice and Severe Accident Management,

Is there a need for further development on iodine-related issues.

2. PLANT DESIGN

The need to address detrimental consequences of postulated accidents has always been recognized in the design process. Amongst detrimental consequences, those resulting from the release of fission products from the core to the containment, then to the environment, have been extensively dealt with by the regulatory bodies and the designers through:

specific requirements and/or acceptance criteria for the former,

design provisions allowing compliance with the above mentioned requirements and/or acceptance criteria for the latter.

Issues to be addressed in case of fission product release from the core are:

environmental consequences at and beyond site boundaries,

control room habitability,

control and detection of leakage from systems partly installed outside containment that might contain radioactive materials following an accident,

environmental conditions for safety-related systems and components,
• shielding of systems and components which might contain radioactive material after an accident, to permit adequate access to important areas and to protect important equipment from the radiation environment.

In the Design Basis, all above-mentioned issues were dealt with using a “Source Term”. Though the word itself is not always used, and there is no unique quantitative definition, one could say that the Source Term allows to characterize fission product release to the containment for an ideal sequence considered as a reasonable envelope of most credible events contemplated in the design. From a quantitative standpoint the Source Term specifies, for all relevant phases of an accident and all relevant fission products, a conservative estimate of the timing, percentage of release with respect to total core inventory, and speciation when appropriate.

It must be noted that, as noted above, the understanding of which accidents or sequences had to be reasonably enveloped could vary from country to country. In the US for instance the Source Term (TID 14844) was representative of the in-vessel phase of a core-melt scenario, while in other countries, like France, it was intended to envelope a Design Basis LOCA, i.e. without melting of the core. Despite these apparent differences, commonalities existed in the approach. In particular:

• use of conservative assumptions for both release timing, all releases being assumed to occur at time 0, and released fractions, which were bounding estimates of what could be released from the gap (case of the Design Basis LOCA), or during the in-vessel phase of a core-melt scenario. Also, as dose evaluation on neighbouring populations or plant personnel emphasized thyroid doses, conservatism was assumed in iodine speciation, as volatile species were thought dominant compared to aerosols.

• filtration system with redundant trains, incorporating in particular demisters and heaters to remove steam and droplet from the air entering the system and decrease its relative humidity, High Efficiency Particulate Air (HEPA) filters to remove aerosols and charcoal adsorbers to remove the most volatile forms of iodine, i.e. elemental and organic forms, followed by HEPA filters to stop charcoal fines if any.

• Doses to the surrounding populations were assessed against criteria factoring differences in the understanding of bounding scenarios.

Iodine-related issues were so extensively credited in the design, and many provisions allowed to adequately deal with part of the potentially detrimental consequences resulting from iodine release inside containment. As these provisions were relied upon for compliance with acceptance criteria, they were de facto considered for Emergency Operating Procedures implementation. Differences in the approach were more reflected in the magnitude of contemplated phenomena than in the qualitative understanding of these phenomena. At last, as even in the most conservative approaches only in-vessel scenarios were considered, and some collateral phenomena such as hydrogen burning were not addressed, there was a need to revisit previously accepted assumptions considering hypothetical needs for Severe Accident Management on one hand, recent progress on fission product release and behavior on the other hand.
3. ACCIDENT MANAGEMENT

In case of accident, the utility has to deal with two different sets of problems:

- at the operator level, there is a permanent need to terminate accident progression and limit consequences both on-site and beyond the site fences,

- at the management level, one of the most delicate issues would be interfacing with civil authorities. Two problems need to be dealt with:
  - feeding the Safety Authorities with reliable data concerning process parameters and system status to allow an independent assessment of the situation in the plant and of accident evolution,
  - providing local authorities with reliable information on radioactive releases, if any, to help decide whether there is a need for sheltering or evacuating people.

3.1 Operators

For operators, a Severe Accident would be a dynamic reality. Contrary to what happens at the design level or in Probabilistic Risk Assessments, where accident scenarios are postulated, and those leading to core degradation are well characterized (i.e. not only would the designer know that core degradation will occur, but also the root cause of this degradation would be part of the assumptions), the operator would be confronted with an unknown initial malfunction or failure.

As this is the basis for operator training, he would normally implement Emergency Operating Procedures whose main objective is to provide strategies allowing to reach a controlled state, i.e. a state where all safety functions can be adequately fulfilled. However, at some time into the accident, he would start to realize that, not only some of the proposed strategies are not practicable (this shouldn’t be new as part of training is based on defeating some success paths), but that, all proposed mitigative measures fail.

He would then progressively realize that his major problem is the loss of capability to fulfill one essential safety function, and that there will be accident progression, until this capability can be restored.

Depending on the root causes of the accident, which he would not necessarily know, the loss of capability could result from multiple component failure, leading to essential system failure, or system unavailability resulting from erroneous evaluation of the situation. In any case so, the priority, for the operator would be to restore the minimum capability allowing to stabilize the situation.

Restoring this capability would not, however, be straightforward.

- First, the operator would need to understand what went wrong to decide which kind of problem needs to be fixed. This would require an assessment of accident progression, together with additional verification aiming at the identification of the root cause of accident
progression. This could prove a very difficult task as the number of sensors is limited on one hand, and many of them could have failed due to the harsh environmental conditions.

- Assuming the cause of accident progression has been identified, fixing the problem could require intervention in contaminated or radiative areas. This can be contemplated only if repair operations have been carefully planned and operators adequately trained to limit doses to the operator below acceptably low values.

- Before deciding whether the problem is worth fixing, an evaluation of accident progression using different assumptions on the use of all available resources might be of interest as this would allow to choose which strategy, if practicable, would best fit with the time window needed for repair.

- In the most perturbed situations, containment integrity could also be challenged. Decisions would have to be made to limit mechanical loadings below acceptable values for instance through actuating the Containment Spray System, or to prevent a catastrophic failure in more extreme situations, for example through venting the containment. However, though the primary objective in such situations be to limit environmental consequences, and some of these actions would be beneficial for iodine management (through removal from the containment atmosphere or trapping in filtering systems), it appears difficult to claim that decisions would be made essentially for iodine management.

All above-mentioned considerations tend to show that, in case of severe accident, operator actions would be governed by the need to restore essential safety functions, in particular decay heat removal capability, limit challenges to the containment or prevent catastrophic containment failure, rather than trying to take specific action to manage iodine.

3.2 Management

At the management level, as indicated above, there would be a need to feed the Safety Authorities with as accurate as possible plant information to allow an independent assessment of plant status and accident evolution, and provide local Civil Authorities with reliable information on releases to allow making proper decisions for protecting the public and the environment.

For the former, the main issue is communication reliability: this is well beyond the scope of the paper and will not be dealt with. However assuming that communications work well, the possible side effect of the independent assessment, especially in the case of core-melt scenarios, is a significant discrepancy in the forecast of accident evolution. Not only could the evolution of plant status be contemplated differently by people on-site and the Safety Authorities, but even quite similar forecasts on plant process parameters evolution could lead to wide discrepancies in the evaluation of the quantity and speciation of fission products inside containment.

This discrepancy with on-site evaluations could create misunderstanding with the local Civil Authorities with potentially damaging consequences, the most important being a possible loss of confidence in the Utility capability to predict the evolution of the crisis.

There is so a need, on the utility side, for a knowledge-based evaluation capability of fission-product behavior on one hand, and for an harmonization of evaluation procedures
with the Safety Authorities if possible. Such improvement, however, is not likely to result in noticeable changes in Severe Accident Guidelines

4. RECENT PROGRESS

R&D programs implemented in the last few years have been aiming at the confirmation of some key assumptions made originally on one hand, identify first and then quantify problems relevant to scenarios with extensive core degradation including vessel meltthrough and ex-vessel phenomena.

Key assumption made in the past on fission product release to the containment were related to:

- timing,
- percentage of core inventory,
- speciation (for iodine)

Dealing with timing, all releases were assumed to occur at time 0 as this would maximize airborne activity inside containment. As a result, fast closing isolation valves, and low containment leak rate, were actually needed for compliance with dose acceptance criteria, which seemed beneficial for plant safety. For utilities however, this led to additional burden during periodic tests. However, it was obvious to most people that assuming releases at time 0 was overly conservative, and that a more pragmatic approach, though still conservative, could be retained, assuming some delay before cladding failure or melting of the core. This progress has not been backfitted everywhere, though it has a real potential for improving safety through eliminating the need for fast closing valves, and would relieve utility burden during periodic tests.

As to released quantities, deposition in circuits was not considered before. There seems now to be enough evidence to show that quantities released to the containment would be smaller than originally contemplated, though some resuspension or revaporation could well have to be considered in the long-term, without any foreseeable impact on accident management or consequences on the environment, as pressure inside containment would most likely be low at the time of revaporation and releases from an intact containment would consequently be low.

Concerning iodine speciation, there is now converging evidence that most iodine released to the containment is under the form of aerosols (NUREG/CR-5732). Moreover, in the absence of parasitic phenomena, these aerosols will be removed from the containment atmosphere, either after being dissolved in water pools, or after plating out on surfaces. It is recognized that part of the iodine in aqueous solutions could experience, under acidic conditions in pools, a radiation-induced conversion to elemental iodine. However, there is extensive evidence that controlling the solution pH to a value corresponding to basic conditions (above 7) would dramatically reduce this conversion. It so appears that the filtration systems, which were designed for more severe conditions are adequate for the new situation. The only issue at stake could be the possibility to eliminate, in some cases, charcoal adsorbers, as the amount of volatile species is quite small. This could relieve some burden from the utilities as these adsorbers contain flammable material and have only moderately
satisfactory operating records. This would not, however, change accident management in any way.

At last, possible detrimental consequences of ex-vessel phenomena could be mitigated through already contemplated decisions relevant to Severe Accident Management, e.g. through not preventing water from reaching the bottom part of the containment.

If one tried to briefly summarize progress in aerosol phenomena understanding, the following considerations would be stressed:

- most assumptions made originally were very conservative and led to system overdesign in many cases, and to very pessimistic evaluations of consequences

- use of progress in the understanding of the behavior of fission products, in particular iodine, would allow to make more realistic evaluations, in particular on the amount of airborne activity and the most penalizing chemical species. This should confirm Emergency Planning provisions in some countries or allow to contemplate the possibility to relieve the most constraining provisions (e.g. early warning, early evacuation) in other countries. On-line forecasts during accidents should also be more realistic.

There is, however, no new information which would lead to reconsideration of currently contemplated accident management provisions.

5. DO WE NEED MORE?

From the above considerations, it would appear that, on the utility side at least, there is no need for additional information. Before jumping to this conclusion, some questions must be addressed:

- first, iodine-related problems have been extensively addressed in the design of plants and adopted design provisions, even overdesigned, have been satisfactory to the utilities. Is overdesign an incentive for further R&D?

- Though significant amounts of money have been injected in R&D programs, uncertainties remain. In most cases, these uncertainties appear quite manageable, as further progress wouldn’t bring significant modifications to system design, and would not likely modify accident management strategies. However, the question which could be raised is whether there would be any benefit, for utilities, in uncertainty reduction.

With the current level of understanding, one could say that reducing uncertainties would require further development on very complex issues, developments which could only be contemplated if very significant amounts of money were injected in R&D programs. To be acceptable, such investments should be commensurate with the potential benefit anticipated improvements would bring to the utilities. In evaluating potential benefits, the credibility of anticipated results should be analyzed: in particular, expected improvements would have to be compared to the dispersion of already available results. Currently, it appears that, for most cases, there is no iodine-related problem which could justify new developments.

Two issues however, could be analyzed, due to questions raised by Safety Authorities in some countries:
• Iodine behavior in Steam Generators in case of core-melt resulting from a Steam Generator Tube Rupture, as there is a potential for simultaneously breaching all three barriers

• Direct measurement of the quantity of iodine suspended inside containment during an accident.

This doesn’t mean that new developments would be needed, but that related problems should be analyzed consolidating existing data, examining whether there are substantial results allowing to reasonably bound uncertainties for the former, or indications that the objective appears credible for the latter, evaluate, if needed, the cost of further development, and decide whether the expected benefit can match anticipated costs.

5. CONCLUSION

Iodine-related problems have been addressed in the design of current plants using sometimes very conservative assumptions. Significant progress on iodine behavior has resulted from R&D programs developed up to now. New results confirmed that systems were sometimes overdesigned, or evaluations were very pessimistic, but that no major modification was expected for Accident Management.

Remaining uncertainties are deemed manageable by utilities and do not justify new extensive development.

There could be a need to restructure and consolidate current knowledge on iodine behavior in Steam Generators in case of core-melt resulting from a Steam Generator Tube Rupture, and on the interest of on-line measurement of iodine concentration inside containment.
IODINE CHEMICAL KINETIC STUDY WITHIN
THE PHEBUS PRIMARY CIRCUIT

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ABSTRACT

This paper is concerned with the gaseous kinetic aspects within the primary circuit of the PHEBUS facility. The rate constants of the relevant gaseous reactions ruling the global behaviour of iodine have been estimated for lack of experimental data. The primary circuit is modelled as a straight pipe which has been divided in twelve parts of different size with the temperature ranging from 423 to either 1500 K or 1800 K. The configuration is close to the FPT0 conditions. Each segment of the circuit behaves as a plug flow reactor. The experimental fission products and structural materials release and the rate of propagation of the gaseous mixture, which are used as input data, are those observed in the FPT0 experiment.

The aim of this work is to check the validity of the underlying thermodynamic-equilibrium assumptions made in state-of-the-art fission-product transport codes by taking into account the dynamic of the system. This will deliver information on the possible role of non-equilibrium conditions within a nuclear facility during a severe accident.
1. INTRODUCTION

The PHEBUS F.P. project is an international co-operation program within the framework of nuclear reactor safety (Krischer, 1992; Schwarz, 1999). Integral experiments are carried out in the PHEBUS facility, in order to investigate the degradation of the core and the releases, transportation and deposition of the fission products from the overheated bundle to the containment.

The FPT0 and FPT1 experiments were designed to simulate a low-pressure cold leg rupture. These first two tests show that a fraction of the iodine released from the bundle reached the containment as gaseous specie. This volatile iodine has been detected but not identified in both experiments. The gaseous fraction in FPT1, performed at higher fission product concentrations, was considerably smaller than in FPT0. Estimating this amount is particularly important as the gaseous iodine, which enters into the containment, influences the source term evaluation.

Pre-calculations performed with different safety codes (SOPHAEROS, VICTORIA) were not able to predict this experimental result. Actually, these codes consider that all the species reach thermodynamic equilibrium instantaneously. In a dynamical system this condition is achieved if the species residence time within a volume is greater than the reaction times only. The gaseous iodine compound might arise from the chemical kinetic limitations occurring within the gas phase.

Hitherto, a limited number of researchers dealt specifically with this aspect and most of the investigations were focused on the study of the kinetic of caesium-iodine reactions (Wren 1983; Cronemberg 1988; Burón 1990). The conclusions of these studies suggested that calculations under thermodynamic equilibrium hypothesis were valid in presence of high concentration releases and/or at high temperature only.

This work focuses on the kinetic aspects within the primary circuit’s gas phase during the FPT0 test. Details about the test can be found elsewhere (Hanniet, 1998). Section 2 presents the different chemical reaction of the kinetic model. The remainder of the section gives the procedures to calculate the kinetic rate constant, the pre-exponential factor and the activation energy. Section 3 is concerned with the modelling of the circuit. Finally, in the last sections the results and conclusions of this modelling are given. Appendix I gives details on the kinetic theories that are considered.

2. KINETIC NETWORK MODEL

Modelling a reactive multi-component model is enormously complex since all the present species are able to react and participate in more reactions simultaneously. Unfortunately it is not possible to include in the kinetic model all the species involved and all the reactions occurring in the gas phase. The proposed kinetic model is restricted to a set of reactions which describes the iodine chemistry in the gas phase (Cronemberg, 1988). The adopted chemical system includes 39 reactions concerning 35 species, which are reported in tables 1, and the condensation reactions listed in table II.1 of appendix II. Radiolysis reactions have not been considered in this model.

The reactants in the feed stream are limited to the dominant species H₂, H₂O, the control rod components Ag, Cd, In and the fission products (FPs) I, Cs and Te. The last two species are chosen as they are the most reactive with respect to the iodine.

The elementary reactions in the kinetic model regard unimolecular and bimolecular steps and are written in the following general form:
\[
\begin{align*}
    & k_{f,1,x} \\
    & A + X \xrightarrow{\text{products}} \xrightarrow{k_{b,1,x}} X \\
    & k_{f,2} \\
    & A + B \xrightarrow{\text{products}} \xrightarrow{k_{b,2}} \text{products} + X \\
    & k_{f,2,x} \quad \text{or} \quad A + B + X \xrightarrow{\text{products + X}} \xrightarrow{k_{b,2,x}} X \\
\end{align*}
\]

where \( k_f \) and \( k_b \) are the corresponding forward and backward rate constants. The «foreign molecule» \( X \), which may be involved in the reaction but is assumed to remain unchanged, is needed either to excite the reagents or to remove the freed internal energy when products are formed. In the present study the foreign molecule corresponds with steam.

The rate laws for the stoichiometric equations (rI) and (rII) can be described by

\[
\begin{align*}
    R_A &= -\frac{d[A]}{dt} = k_{f,1,x} [A][X] - k_{b,1,x} \text{[products]}[X] = \frac{k_{f,1}}{[X]} [A][X] - \frac{k_{b,1}}{[X]} \text{[products]}[X] \\
    R_A &= -\frac{d[A]}{dt} = k_{f,2} [A][B] - k_{b,2} \text{[products]} \\
    R_A &= -\frac{d[A]}{dt} = k_{f,2,x} [A][B][X] - k_{b,2,x} \text{[products]}[X] = \frac{k_{f,2}}{[X]} [A][B][X] - \frac{k_{b,2}}{[X]} \text{[products]}[X]
\end{align*}
\]

The gas-kinetic data is too poor or not available in the literature to enable us to determine \( k \) as a function of temperature. Therefore, the rate constants must be estimated. These terms can be derived from considerations of the molecular structure or from thermodynamic relations.

2.1 Thermodynamic data

Estimate of the rate coefficients can be done from the thermodynamic properties of the reaction. By this way, the reverse rate constant can be obtained from eq. (1) provided that the forward rate constant and the standard Gibbs energy of the reaction are known.

\[
\frac{k_f}{k_b} = \exp\left(-\frac{\Delta G_R}{RT}\right) \tag{1}
\]

In table (II.2, appendix 2) are collected the standard enthalpies and the free Gibbs energies of formation at a reference temperature of 298 K as well as at stated temperature intervals. These data are obtained from several sources (JANAF 1974, 1975, 1978, 1985, 1996; Barin, 1993; Cordfunke, 1990; Ball, 1991; Mills, 1974; Oppermann, 1976; Jackson, 1971). However the thermodynamic data of some species are still uncertain, especially for the gaseous species CdI, TeI and TeI₂.

The standard Gibbs free energy of formation is given in the form of a 3rd degree power series in temperature. These values for the range 400 to 2000 K are listed in table (II.2).

\[
\Delta G_f^0 = \beta_0 + \beta_1 T + \beta_2 T^2 \quad 400 \leq T \leq 2000 \text{ K}
\]

The InI₂ and InI₃ species are not taken into account in the model because they are largely minor at all temperatures compared with InI.
2.2 Evaluation of the rate constants

The dependence of the rate constant on temperature is given by the Arrhenius-type relationship derived from the transition state theory

\[ k(T) = A'(T) \exp \left( \frac{-E_a}{RT} \right) = A T^n \exp \left( \frac{-E_a}{RT} \right) \]  \hspace{1cm} (2)

where \( A' \) and \( E_a \) are the pre-exponential factor and the activation energy respectively. The temperature dependence of \( A' \) is stated by the term \( T^n \).

The forward kinetic constant will be estimated as described in the next subparagraphs. The reverse constant is obtained from (1). But, the reverse approach can be undertaken. The backward constants can also be estimated through the Transition-State Theory and afterwards \( k_f \) deduced from eq. (1). In order to reduce the uncertainty associated to the introduced approximations, the final retained kinetic constants are the geometrical means of these two values.

2.2.1 Estimation of the pre-exponential factor

The Transition-State Theory is used to calculate the pre-exponential factor (see appendix I). The \( A' \) factor is calculated from the molecular partition functions

\[ A' = \left( \frac{RT}{h} \right) \frac{\left( f_{tr}^3 f_{rot}^3 f_{vib}^{3n_A + 3n_B - 4 - i} \right)_{AB^z}}{\left( f_{tr}^3 f_{rot}^3 f_{vib}^{3n_A - 3 - i} \right)_{A} \left( f_{tr}^3 f_{rot}^3 f_{vib}^{3n_B - 3 - i} \right)_{B}} \]  \hspace{1cm} (3)

where the subscripts \( tr, rot \) and \( vib \) indicate the translational, rotational and vibrational states respectively of the molecule. The contribution of the electronic molecular partition function has been omitted. The exponent \( i \) depends on the geometry of the molecule and is equal to 2 for the linear and to 3 for the non-linear case.

The \( f \) terms are inferred from the following properties of the considered molecule: diameter, molecular weight and the vibration frequencies (see eq. I.11, appendix I). The diameters were considered temperature independent. The \( d_{AB} \) values were obtained by summing up the single bond and metallic radii (Allen, 1987; Teatum, 1969), excepted for the species \( I_2, HI, H_2 \) and \( H_2O \) where the following data were used: \( d_{H}=5.16 \), \( d_{HI}=4.21 \), \( d_{H_2}=2.83 \) and \( d_{H_2O}=2.64 \) Å (Reid, 1988). The \( \nu \) values were taken from the literature (Nakamoto, 1986).

Usually it is not possible to calculate the rotational and vibrational factors of the activated complex, being the properties of \( AB^z \) unknown. Thereby the rotational and vibrational states of \( AB^z \) are considered equal to \( A \) or \( B \) specie. Hence eq. (3) becomes

\[ A' = \left( \frac{RT}{h} \right) \frac{\left( f_{tr}^3 \right)_{AB^z}}{\left( f_{tr}^3 \right)_{A} \left( f_{tr}^3 \right)_{B} \left( f_{rot} \right) f_{vib}^l} \]  \hspace{1cm} (4)

The exponent \( k \) and \( l \) are integers lying between -3 and 2 for \( k \), and 0 and 5 for \( l \). These exponents depend on the reaction type considered.

The pre-exponential values are calculated at 500 and 1000 K. Once these values are known, the \( A \) and \( x \) terms were determined. The results are summarised in the tables 2.
2.2.2 Estimation of the activation energy

The activation energy is complex to estimate but reasonable values are obtained in some particular cases. The following six reaction schemes are involved in the model.

\[
\begin{align*}
AB + X & \rightarrow A + B + X \quad \text{(sI)} \\
AB + B + X & \rightarrow AB_2 + X \quad \text{(sII)} \\
A + BC & \rightarrow AB + C \quad \text{(sIII)} \\
A + BCD & \rightarrow AC + BD \quad \text{or} \quad A + BCD & \rightarrow ABC + D \quad \text{(sIV)} \\
AB + CD & \rightarrow AC + BD \quad \text{(sV)} \\
AB + CD & \rightarrow ABC + D \quad \text{(sVI)} \\
ABC + DE & \rightarrow AD + BCE \quad \text{(sVII)}
\end{align*}
\]

- In the first type of reaction, X is either an atom or a molecule and the activation energy is supposed to be equal to the energy of dissociation of AB minus 3.7 kJ.mol\(^{-1}\). This value corresponds to the term \(\frac{3}{2}RT\), with \(T=298\) K.
- The activation energy of the reaction (sII) is generally neglected, as no bond has to be broken.

\[
\frac{E_a}{E_{A-B}} = \left(1 + \frac{\Delta H_r}{E_{A-B}}\right)^{-1} \left[1 + \left(1 + \frac{\Delta H_r}{E_{A-B}}\right)^{\frac{1}{p-1}}\right]^{-1}
\]  \quad (5)

\(\Delta H_r\) is the enthalpy of reaction, \(E_{A-B}\) is the bond energy formed and \(p\) is a parameter adjusted in a series of similar reactions. A mean value of \(p\) is 1.2. Eq. (5) is employed to calculate \(E_{a,f}\) or \(E_{a,b}\).

- The activation energy for the reaction (sIV) is the same as for (sIII).
- In the case of reaction (sV), the empirical relation (6) is used (Otozai, 1951)

\[
E_a = 0.65(E_{A-B} + E_{C-D}) - 0.35(E_{A-C} + E_{B-D})
\]  \quad (6)

- For reaction (sVI), the eq. (5) is employed by substituting \(E_{A-B}\) with \(E_{B-C}\).
- Assuming that the nature of the bond between the molecules BC is not modified, the reaction (sVII) and (sV) are similar and the relation is

\[
E_a = 0.65(E_{A-B} + E_{D-E}) - 0.35(E_{A-D} + E_{B-E})
\]  \quad (7)

If the simplified form of the Arrhenius equation is used, in other words that the difference in the mean heat capacities of reactants and products is negligible (\(\Delta C_p=0\)), the following relationship exists between the activation energies of the corresponding forward and reverse reaction

\[
E_{a,f} - E_{a,b} = \Delta H_r
\]  \quad (8)
The activation energy of the reverse reaction can be calculated with eq (8). In the case of (sIII), the value adopted for Ea,f is the mean value between Ea,f issued from (5) and Ea,f obtained by (8), knowing Ea,b and ∆Hr. The Ea values are gathered in tables 2. Knowing A, x and Ea, it is possible to model k in the temperature range 400-2000 K.

3. SIMPLE MODEL FOR THE PRIMARY CIRCUIT

The primary circuit was subdivided in 12 horizontal tubular elements. At unsteady-state, the general material balance performed over the i-th segment for the j-th compound may be written as:

$$\frac{\partial C_j^{(i)}}{\partial t} \, dV = F_j^{(i)} - \left( F_j^{(i)} + \frac{\partial F_j^{(i)}}{\partial V} \, dV \right) + R_j^{(i)} \, dV$$  \hspace{1cm} (9)

where the term on the left hand side denotes the accumulation, the first two terms on the right hand side account for increase due to inflow and outflow and the last term accounts for the rate of production due to the reactions.

Supposing that turbulent flow condition prevail, the axial and the radial diffusion relative the bulk flow are negligible and the gas mixture properties are considered uniform over any cross-section normal to its motion. Thereby each segment can be configured as a plug flow reactor (Levenspiel, 1972). Thus the differential form of equation (9) under these conditions takes the one-dimensional form (10).

$$\frac{\partial C_j^{(i)}}{\partial t} = -u \left( \frac{\partial C_j^{(i)}}{\partial x} \right) + R_j^{(i)}$$  \hspace{1cm} (10)

where u is the average velocity of the gaseous mixture throughout the segment. The residence time for all the species is computed by dividing the segment length by the average flow u. The amount of condensed species (see table II.1, appendix II) is subtracted from molar balance at the outlet of each segment. The energy and linear momentum transport equation are not performed, as the temperature is kept constant within the segment and no pressure drop is assumed throughout the segment.

4. APPLICATION OF THE KINETIC MODEL TO THE FPT0 TEST

The calculated linear velocity u lies between 4 and 30 m.s⁻¹ for the FPT0 test. The operating pressure is 1.9 bars. The geometrical and the operational conditions for the FPT0 experiment have been modelled as described in table 3, with a gradual temperature decrease along the pipe. As the temperature of the bundle is not constant, two temperature configurations are taken to see the influence of the temperature at the inlet of the primary circuit.

The points C and G of the circuit are equipped with instrumentation allowing the analysis of the species. Values at point G are taken as representative corresponds to the inlet of the containment.

The set of partial differential equations cannot be solved analytically and the calculations are performed using the Facsmile software (Malleson 1990).
Table 3. Geometrical configuration and temperature of each segment.

<table>
<thead>
<tr>
<th>Segment</th>
<th>Diameter [m]</th>
<th>Length [m]</th>
<th>Temperature [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Config. 1</td>
</tr>
<tr>
<td>1</td>
<td>0.073</td>
<td>0.137</td>
<td>1500</td>
</tr>
<tr>
<td>2</td>
<td>0.061</td>
<td>0.098</td>
<td>1400</td>
</tr>
<tr>
<td>3</td>
<td>0.048</td>
<td>0.785</td>
<td>1300</td>
</tr>
<tr>
<td>4</td>
<td>0.039</td>
<td>0.070</td>
<td>1200</td>
</tr>
<tr>
<td>5</td>
<td>0.030</td>
<td>2.220</td>
<td>1100</td>
</tr>
<tr>
<td>6</td>
<td>0.030</td>
<td>5.248</td>
<td>1000</td>
</tr>
<tr>
<td>7</td>
<td>0.038</td>
<td>0.791</td>
<td>973</td>
</tr>
<tr>
<td>8</td>
<td>0.030</td>
<td>3.187</td>
<td>973</td>
</tr>
<tr>
<td>9</td>
<td>0.020</td>
<td>1.480</td>
<td>700</td>
</tr>
<tr>
<td>10</td>
<td>0.020</td>
<td>1.480</td>
<td>500</td>
</tr>
<tr>
<td>11</td>
<td>0.020</td>
<td>6.259</td>
<td>423</td>
</tr>
<tr>
<td>12</td>
<td>0.030</td>
<td>5.213</td>
<td>423</td>
</tr>
</tbody>
</table>

All the fission products and structural materials are released within the time window 12000-18500 seconds. Concerning the steam, only $7.9 \times 10^{-2}$ moles are implied during this period of time.

Table (4) draws up the inventory of FPs and control rod materials present in the circuit. The total amounts of steam and hydrogen are respectively of 1688 and 55 moles during the test.

Table 4. Compounds released from the bundle in the FPT0.

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial bundle inventory (ibi) [g]</th>
<th>Release</th>
<th>Point G (423 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mass [g]</td>
<td>% of the ibi</td>
</tr>
<tr>
<td>Ag</td>
<td>476.8</td>
<td>58.6</td>
<td>12.3</td>
</tr>
<tr>
<td>Cd</td>
<td>29.8</td>
<td>14.0</td>
<td>47.0</td>
</tr>
<tr>
<td>Cs</td>
<td>$1.44 \times 10^{-1}$</td>
<td>$9.2 \times 10^{-2}$</td>
<td>64.3</td>
</tr>
<tr>
<td>I</td>
<td>$3.6 \times 10^{-2}$</td>
<td>$3.1 \times 10^{-2}$</td>
<td>86.5</td>
</tr>
<tr>
<td>In</td>
<td>89.4</td>
<td>8.8</td>
<td>9.8</td>
</tr>
<tr>
<td>Te</td>
<td>$4.7 \times 10^{-2}$</td>
<td>$4.4 \times 10^{-2}$</td>
<td>92.4</td>
</tr>
</tbody>
</table>

Figure (1) presents the steam molar flow injected in the bundle and the hydrogen flow resulting from the bundle degradation phase. In figures (2) and (3), the release of the FPs and control rod components are drawn as a function of time. All the compounds are supposed to be released from the bundle in their elementary forms.
5. RESULTS OF THE KINETIC CALCULATIONS

The kinetic model indicates that InI is the predominant gaseous iodine compound over the whole temperature interval as shown in fig. (4) and (5). From the results it seems that the temperature at the inlet has not an important influence on the gas composition, excepted for I.

At point C (973 K) all the iodine is under vapour form and about 99% of the iodine is present as the metallic indium iodide vapour. This result is consistent with the FPT0 test which establish that iodine was mainly transported in a vapour form at this point (Hanniet, 1998). The results of the Thermal Gradient Tube (TGT), devoted to provide information concerning the condensation temperatures of I species, can not be used. As the TGT sampling has be triggered 10 s after the core shut down, at 18148 s, the sampling is not representative of the release phases.

Between 500 and 423 K and with the given InI molar flow rate inside the pipe, most of InI condenses.

At point G (423 K), the vapour pressure of this compound governs the observed flow rate. About $2 \times 10^{-5}$ moles (~10% of the ibi) of InI still stay under vapour form at 423 K. In graph 6 is shown the cumulated gaseous fraction reaching the containment atmosphere as a function of time. In FPT0, it is difficult to know with accuracy the total percent of the unknown gaseous iodine specie flowing through G. The estimation is around 4% of the ibi. Thus, the kinetic result agrees rather well with it.

At the inlet of the containment, the other most present iodine species are I$_2$, HI and CdI$_2$ but in much lower proportion as can be seen in fig. (4) and (5). The amount of these two compounds differs significantly in the two configurations at point G. The values obtained, referred to the bundle inventory, are:

- Config. 1, 0.02% I$_2$, 0.01% HI, 0.04% CdI$_2$
- Config. 2, 0.33% I$_2$, 0.06% HI, 0.12% CdI$_2$

An important fact is that most of the reactions did not reach their equilibrium state at point C.

The thermodynamic codes predict that InI is predominant at high temperature (above 1200 K) and that CsI, CdI$_2$, I$_2$ are the main stable iodine compounds at lower temperature. The kinetic calculation shows that InI remains the main iodine compound. This is explained by the lack of time for achieving the decomposition reactions of InI.

6. CONCLUSIONS

A simple mono-dimensional transport model accounting for the main reactions was developed to predict the iodine time evolution within the primary circuit of the PHEBUS facility. A first attempt at validation was carried out for the operational conditions of the FPT0 test.

The kinetic system predicts that, at 1500 and 1800 K, almost all iodine available reacts with indium to form InI. The indium iodide remains the predominant gaseous iodine compounds when the temperature decreases until 423 K. For the FPT0 conditions, most of InI condenses between 500 and 423 K. At point G, about 10% of the ibi is still present in the gas phase.

This model is able to explain the presence of gaseous iodine at the inlet of the containment in accordance with the experimental data. The kinetic calculation also shows that many reactions do not reach their equilibrium at low temperature (below 1200 K).

However, no general conclusion can be drawn regarding the use of this model as predictive tool. The introduction of others compounds (Rb, Mo...), of radiolysis reactions, the
presence of aerosol particles and flow conditions might influence the gas composition at the outlet of the primary circuit.

ACKNOWLEDGMENTS

The authors are particularly grateful to the colleagues of the Nuclear Safety Unit for their helpful assistance. The first author wishes to thank the European Commission for the award of a Marie Curie fellowship. The CEA/IPSN in Cadarache is warmly thanked for providing the experimental data.

NOTATIONS

\( h \) Planck’s constant \([6.6242 \times 10^{-34} \text{ J s}]\)
\( d_{AB} \) collision radius between A and B, \( \frac{1}{2} (d_A + d_B) \) \([\text{m}]\)
\( E_a \) activation energy \([\text{J mol}^{-1}]\)
\( f \) partition function
\( F \) molar flow \([\text{mol s}^{-1}]\)
\( k \) kinetic constant \([\text{mol}^{-2} \text{ mol}^{-3} \text{ s}^{-1}]\)
\( M \) molecular weight \([\text{kg mol}^{-1}]\)
\( N \) Avogadro’s number \([6.02283 \times 10^{23} \text{ mol}^{-1}]\)
\( R \) universal gas constant \([8.31439 \text{ J K}^{-1} \text{ mol}^{-1}]\)
\( R_j \) rate of generation of compound j \([\text{mol m}^{-3} \text{ s}^{-1}]\)
\( t \) time variable \([\text{s}]\)
\( T \) absolute temperature \([\text{K}]\)
\( u \) linear velocity \([\text{m s}^{-1}]\)
\( x \) distance from entrance segment \([\text{m}]\)

REFERENCES


Table 1.1 Reaction mechanism rate constants and activation energies at 1000 K.

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Table 1.2 Reaction mechanism rate constants and activation energies at 1000 K.

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### Table 1.3  Reaction mechanism rate constants and activation energies at 1000 K.

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**Reaction**: Cd + Te + H$_2$O $\rightarrow$ CdTe + H$_2$O  
**Environment**: nonlinear complex

**Reaction**: In + Te + H$_2$O $\rightarrow$ InTe + H$_2$O  
**Environment**: nonlinear complex

**Reaction**: In + InTe + H$_2$O $\rightarrow$ In$_2$Te + H$_2$O  
**Environment**: nonlinear complex

### Table 2.1  Reaction mechanism rate parameters.

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Table 2.2 Reaction mechanism rate parameters.

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<th>x</th>
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<td></td>
<td>[kJ·mol⁻¹]</td>
</tr>
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</table>
Fig. 1  Steam and hydrogen flows injected to the inlet of the primary circuit.

![Graph showing molar flow vs time for H2O and H2](image)

**Fig. 2**  Control rod material flows injected to the inlet of the primary circuit.

![Graph showing molar flow vs time for Ag, Cd, and In](image)
Fig. 3  Fission product flows injected to the inlet of the primary circuit.

Fig. 4  Gaseous iodine speciation as a function of temperature in the primary circuit (config. 1).
Fig. 5 Gaseous iodine speciation as a function of temperature in the primary circuit (config. 2).

Fig. 6 Indium iodide vapour reaching the containment, % referred to the initial iodine bundle inventory.
APPENDIX 1: KINETIC THEORIES IN GASES

I.1 Molecular models

The kinetic theory is directly influenced by the intermolecular interactions existing between the molecules of the gas. Real gas equations of states (EOS) takes into account the intermolecular forces existing among the molecules and the non-zero volume of the molecules themselves. Each model is defined by the mutual potential energy \( U(r) \) between two molecules at the distance \( r \). Briefly, the principal models are described below, for further details refer to Amdur and Hammes (1966).

The roughest approximation to the intermolecular forces is done through the hard-sphere potential function \( U(r) \). The well-known Van der Waals EOS corresponds with the elastic hard spheres modelling with additional attractive forces. The gas obeys to the equation (I.1).

\[
\left( P + \frac{a}{V^2} \right) (V - b) = n R T \tag{I.1}
\]

Attractive and repulsive forces can exist within the gas. The equation of state is written on the virial form:

\[
P V = R T \left( 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \right) \tag{I.2}
\]

The virial coefficients \( B, C, D \) are function of the temperature only and are found experimentally or calculated from the intermolecular potential energy function.

I.2 Collision model theory

The hard-sphere collision theory allows the calculation of rate constants using the principle of the classical mechanics.

I.2.1 Unimolecular reactions

The following elementary physical reaction mechanism is used to explain unimolecular reactions:

\[
A + X \xleftrightarrow{} A^* + X \rightarrow \text{products} + X
\]

The energised molecule \( A^* \) decomposes if the vibrational energy exceeds the activation energy for the overall decomposition reaction. \( X \) is any molecule that transfer its kinetic energy into vibrational energy of \( A \) or receive kinetic energy from \( A \).

The microscopic theory of unimolecular reactions was built on the basis of three assumptions:

- the energy of activation is supplied by binary collisions in which the vibrational energy is available for activation
- for activation it is sufficient to have the minimum energy \( E_a \) in the molecule as a whole
- the probability of reaction is not increased if the energy of molecule exceeds \( E_a \)
For $E_a \gg RT$, the fraction $W$ of reactant molecules containing energy per mole in excess of $E_a$ is given (Benson, 1960 and 1976), for a system of molecules having $p/2$ vibrational modes, by (1.3).

$$W = \left( \frac{E_a}{RT} \right)^{\frac{p}{2} - 1} \frac{1}{\Gamma(p/2)} \exp\left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (1.3)

The higher order terms can be neglected for usual values. $\Gamma$ is the gamma function.

$$\Gamma\left(\frac{p}{2} + 1\right) = \int_0^\infty x^{p/2} e^{-x} \, dx \quad \text{and} \quad \Gamma(1/2) = \sqrt{\pi}$$  \hspace{1cm} (1.4)

$p/2$ has a maximum value of $(3n-6)$ for a nonlinear molecule made up of $n$ atoms or $(3n-5)$ for a linear molecule. It can be shown that:

$$k = k_\infty \left(1 + \frac{k_\infty \sqrt{\pi M}}{2 \pi d^2 W C \sqrt{RT}}\right)^{-1}$$  \hspace{1cm} (1.5)

where $k_\infty$ is the rate constant at infinite pressure.

The Rice-Ramsperger-Kassel's model (Kassel, 1932) considers that the reactant and reactional intermediate have the same frequency of vibration $\nu$ and $k_\infty$ is defined by:

$$k_\infty = \nu \exp\left( -\frac{E_c}{RT} \right)$$  \hspace{1cm} (1.6)

$E_c$ is the critical energy of dissociation. At rough estimates, $E_c$ can be supposed equal to the bond energy of the bond broken in the reaction. In general, R.R.K. theory provides satisfactory agreement with experiment.

\textbf{I.2.2 Bimolecular reactions}

Let us consider the following elementary bimolecular reaction: $A + B \rightarrow \text{products}

The total number of all $A\cdot B$ collision per unit of time and unit of volume is given by the frequency factor of collision $Z_{AB}$.

$$Z_{AB} = \frac{1}{\sigma} C_A C_B d_{AB}^2 N_A \sqrt{\frac{8 \pi RT}{M_{AB}}}$$  \hspace{1cm} (1.7)

$\sigma$ is the symmetry number, equals 2 if the nuclei are identical and is otherwise equal to 1. At a fixed temperature, $k$ is proportional to $Z$. Then, the rate is equal to:

$$R = -\frac{dC_A}{dt} = k_{AB} C_A C_B = Z_{AB} sf \exp\left( -\frac{E_a}{RT} \right)$$  \hspace{1cm} (1.8)

The calculated pre-exponential values are often much higher than the observed values and therefore corrected by a so-called steric (or probability) factor. This fudge factor reflects that the reacting molecules must be properly oriented if the two molecules want to react together. The sf-value lies between 0 and 1.
I.3 Transition-state theory

This theory which has extensively been developed by Eyring et al. (1940) was built in three steps. Firstly, a potential energy surface is used to obtain the energy of activation. Next, a rate equation is formulated between the reactants and the activated complex. Finally, the rate equation is got in terms of thermodynamic state functions characterising the transition state complex and the reactants.

I.3.1 Unimolecular reactions

The reactional path is $A \leftrightarrow A^\dagger \rightarrow \text{products}$.

$A^\dagger$ is the activated complex in thermal equilibrium with the system. The kinetic constant of the reaction can be explicit as a function of the equilibrium constant $K^\dagger$

$$k = \frac{RT}{h} K^\dagger$$  \hspace{1cm} (I.9)

$K^\dagger$ can be expressed in terms of partition functions, $f$, according to equation (I.10).

$$K^\dagger = \frac{f_{A^\dagger}}{f_A} \exp \left( \frac{-\Delta E^{0\dagger}}{RT} \right)$$  \hspace{1cm} (I.10)

$\Delta E^{0\dagger}$ is the difference in internal energy between the complex and the reactants at 0 K.

For a single molecule, the $f$-values are:

$$f_{tr} = \frac{\sqrt{2\pi MR T}}{Nh} \quad f_{rot} = \frac{\sqrt{8\pi^2 \hbar^2 RT}}{Nh\sqrt{\sigma}} \quad \frac{1}{f_{vib}} = 1 - \exp \left( -\frac{hN\nu}{RT} \right)$$  \hspace{1cm} (I.11)

$f_{tr}$, $f_{rot}$, $f_{vib}$ refer respectively to the translational, rotational and vibrational components. The electronic partition function did not take into account.

$\nu$ is the fundamental frequency of vibration for a harmonic oscillator, in $s^{-1}$.

At 298 K, the orders of magnitude for $f$ are:

$5 \times 10^{10} \leq f_{tr} \leq 10^{12} \text{ m}^{-1}, 10 \leq f_{rot} \leq 1000, 1 \leq f_{vib} \leq 10.$

For a linear molecule made of $n_A$ atoms, the partition function product is $f_A = f_{tr}^3 f_{rot}^2 f_{vib}^{3n_A - 5}$.

For a nonlinear molecule, one degree of vibration must be suppressed but one degree of rotation must be added, $f_A = f_{tr}^3 f_{rot}^2 f_{vib}^{3n_A - 6}$.

If it is assumed that $f_{A^\dagger} = f_A$, then $k = \frac{RT}{h} \exp \left( -\frac{E_A}{RT} \right)$.

I.3.2 Bimolecular reactions

The reactional path is $A + B \leftrightarrow AB^\dagger \rightarrow \text{products}$.

$AB^\dagger$ is the activated complex in thermal equilibrium with the system. As relationship (I.10) before, the equilibrium constant $K^\dagger$ can be calculated as a function of $f$-values according to equation (I.12).
\[ K^* = \frac{f_{AB}^z}{f_A f_B} \exp \left( -\frac{\Delta E^{0*}}{RT} \right) \]  

(I.12)

The expression of rotation component is:

\[ f_{\text{rot}}^3 = \frac{8 \pi^2 (2 \pi R T)^{3/2}}{N^3 h^3 \sigma} \sqrt{I_1 I_2 I_3} \]

and the vibrational partition function is the product of terms like equation (I.11) for all the degrees of freedom.

If A and B are nonlinear polyatomic molecules containing \( n_A \) and \( n_B \) atoms, the partition functions for the transition state complex can be written:

\[ f_{AB}^z = f_{\text{tr}}^3 f_{\text{rot}}^3 f_{\text{vib}}^{3n_A + 3n_B - 7} \]

If the complex is linear, the following term is obtained:

\[ f_{AB}^z = f_{\text{tr}}^2 f_{\text{rot}}^3 f_{\text{vib}}^{3n_A + 3n_B - 6} \]

In the simplest case of a reaction between two atoms, the collision model and the transition state theory provide the same expression for \( k \).

### I.4 Link between the two models

In comparing the two theories, it is possible to obtain the order of magnitude of the steric factor. All the partition functions were assumed to be equal for the three molecules A, B and AB. These approximate sf-values, reported in table (I.1) extracted from Benson (1960), clearly show that more than the reaction is complex less than the collision model is verified.

<table>
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<th>Type of reaction</th>
<th>Type of complex</th>
<th>Steric factor</th>
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</tr>
<tr>
<td>atom + linear molecule</td>
<td>linear</td>
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</tr>
<tr>
<td></td>
<td>nonlinear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^3)</td>
</tr>
<tr>
<td>atom + polyatomic molecule</td>
<td>nonlinear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^4)</td>
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<tr>
<td>two linear molecules</td>
<td>linear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^4)</td>
</tr>
<tr>
<td></td>
<td>nonlinear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^5)</td>
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<tr>
<td>linear + nonlinear molecule</td>
<td>nonlinear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^4)</td>
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<tr>
<td>two nonlinear molecules</td>
<td>nonlinear</td>
<td>((f_{\text{vib}}/f_{\text{rot}})^5)</td>
</tr>
</tbody>
</table>

### I.5 Kinetic rate constant as a function of temperature

The equilibrium constant is linked to the thermodynamic properties of the activated complex, \( \Delta G^{0*} = -RT \ln(K^*) = \Delta H^{0*} - T \Delta S^{0*} \).

\[ k = \frac{R T}{h} \exp \left( \frac{\Delta S^{0*}}{R} \right) \exp \left( -\frac{\Delta H^{0*}}{RT} \right) \]  

(I.13)

In deriving the previous equation, the following relationship is obtained:
\[
\frac{d(\ln k)}{dT} = \left( \frac{RT + \Delta H^0}{RT^2} \right)
\]

As in the most cases, \(\Delta H^0\) is much higher than \(RT\), \(k\) varies in accordance with the classical Arrhenius expression.

**NOMENCLATURE**

- \(C\) concentration \([\text{mol.m}^{-3}]\)
- \(d\) diameter of the molecule \([\text{m}]\)
- \(d_{AB}\) collision radius between \(A\) and \(B\), \(\frac{1}{2}(d_A+d_B)\) \([\text{m}]\)
- \(E_a\) activation energy \([\text{J.mol}^{-1}]\)
- \(f_r\) translational partition function per unit of volume \([\text{m}^{-1}]\)
- \(f_{rot}\) rotational partition function
- \(f_{vib}\) vibrational partition function
- \(h\) Planck's constant \([6.626\times10^{-34} \text{J.s}]\)
- \(I\) moment of inertia, \(M^2d^2\) \([\text{Kg.mol}^{-1}.\text{m}^2]\)
- \(k\) kinetic constant \([\text{mol}^{-x}.\text{m}^{3x}.\text{s}^{-1}]\)
- \(k_\infty\) kinetic constant at infinite pressure \([\text{s}^{-1}]\)
- \(K\) equilibrium constant
- \(M\) molecular weight \([\text{Kg.mol}^{-1}]\)
- \(M^*\) reduced mass, \(M_{AB}^* = \left( \frac{M_A M_B}{M_A + M_B} \right)\)
- \(N\) Avogadro's number, \([6.023\times10^{23} \text{mol}^{-1}]\)
- \(P\) pressure \([\text{Pa}]\)
- \(R\) universal gas constant \([8.314 \text{J.K}^{-1}.\text{mol}^{-1}]\)
- \(s_f\) steric factor
- \(T\) absolute temperature \([\text{K}]\)
- \(U\) potential energy of interaction between the gaseous molecules \([\text{J}]\)
- \(V\) volume of the gas phase \([\text{m}^3]\)
- \(W\) fraction of reactant molecules with a energy superior to \(E_a\)
- \(Z_{AB}\) collision frequency factor between molecule \(A\) and \(B\) \([\text{mol}^{-x}.\text{m}^{3x}.\text{s}^{-1}]\)
- \(\sigma\) symmetry number
- \(\nu\) frequency of vibration
- \(\Gamma\) gamma function

**REFERENCES**


### APPENDIX II: THERMODYNAMIC PROPERTIES

#### Table II.1 Reactions of condensation and Gibbs energies associated.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_R$ (1000 K)</th>
<th>$\Delta G_R$ (500-2000 K)</th>
<th>Range</th>
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<td>$\beta_1 \times 10^3$</td>
<td>$\beta_2 \times 10^5$</td>
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<td>-75.44</td>
<td>85.59</td>
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<td>-284.82</td>
<td>135.75</td>
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<td>In(g) ⇌ In(c)</td>
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<td>-237.11</td>
<td>103.85</td>
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<td>Cd(g) ⇌ Cd(c)</td>
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<td>-113.71</td>
<td>128.25</td>
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<td>Te(g) ⇌ Te(c)</td>
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<td>-212.30</td>
<td>156.15</td>
</tr>
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<td>-167.98</td>
<td>204.22</td>
</tr>
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<td>CsI(g) ⇌ CsI(c)</td>
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<td>-119.33</td>
<td>60.49</td>
</tr>
<tr>
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<td>-86.75</td>
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Table II.2  Standard Enthalpies and Gibbs energies of formations of the gaseous compounds.

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<th>Species</th>
<th>$\Delta H^\circ$ (298 K)</th>
<th>$\Delta G^\circ$ (298 K)</th>
<th>$\Delta G^\circ$ (400-2000 K)</th>
<th>$\beta_0$</th>
<th>$\beta_1 \times 10^3$</th>
<th>$\beta_2 \times 10^6$</th>
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Iodine Studies at the University of Toronto: 
*Piecing Together a Portrait of the 53rd Element*

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University of Toronto, Toronto, Canada, M5S 3E5

**ABSTRACT**

At the last Workshop, the rate of \( I_2(g) \) deposition on painted surfaces was described. Research since then has focused on evaluating and understanding the retention of \( I_2(g) \) on stainless steel. Experiments have been performed in which radio-labeled \( I_2(g) \) was deposited on samples of SS-316 and SS-304 tubing using surface temperatures of 25 to 90°C. Physical deposition predominates for \( I_2(g) \) concentrations below \( 10^9 \) M. At higher concentrations, a slow chemisorption process occurs for low humidity while rapid chemisorption with pitting corrosion occurs at high humidity. This study has revealed the complex nature of \( I_2(g) \) deposition on stainless steel and, in particular, that the process occurs through different mechanisms under different conditions. At present, we are constructing a new apparatus that will allow the rate of deposition on surfaces under condensing steam conditions to be investigated.

Recently, a program of bench scale experiments was completed in which iodine volatilization was measured for irradiated \( 10^4 \) to \( 10^6 \) M CsI solutions containing \( 10^{-3} \) to \( 10^{-6} \) M concentrations of various organics. Iodine volatilization increased by up to two orders of magnitude in the presence of alkyl chlorides and carbonyls while it decreased in the presence of aromatics. The organic iodides produced were identified and were related to the structure of the original organics added to the system. These results were used to develop and assess a semi-mechanistic model of the impact of organics on iodine volatility.

The air-water partitioning of different types of organic iodides has been studied for temperatures of 25 to 75°C using a bubble column. The values at 25°C are being used to develop a simple molecular structure based relationship for predicting the partition coefficient of most organic iodides. The temperature dependence is being interpreted in terms of enthalpies of vaporization and solubilization, the second of which is often unknown. This work should provide a basis for estimating the volatility of most organic iodides for the temperature range relevant to containment structures.

One of the remaining areas of uncertainty in relation to the mass transfer of iodine is the extent to which the interfacial transfer rate will be enhanced by rapid chemical reactions. Enhancement of the evaporation of \( I_2 \) from solutions containing \( I^- \) was measured for a range of concentrations and used to validate a finite difference approach to modeling this system. This approach has been extended to examine enhancement by radiolytic processes.

Over the last few years, we have developed mechanistic models in order to interpret and represent the many different aspects of iodine behaviour in containment. We are in the process of creating an integrated model that will combine all these separate models. Specifically, this model will represent the processes associated with the radiolysis of aqueous iodine solutions, the impact of organics and organic iodide formation, adsorption on surfaces, interfacial mass transfer and, gas phase radiolysis. This model will be used as a research tool to study the relative importance and interaction between these processes. We are currently improving our model of
gas phase radiolysis and applying this to explore the production of O$_3$ and NO$_x$, and the elimination of I$_2$(g).

INTRODUCTION

Considerable progress towards understanding iodine behaviour in containment has been achieved at the University of Toronto since the last Iodine Workshop. This work has involved bench scale experiments, typically focussing on individual aspects of the physical or chemical behaviour of iodine. The objective of this research program has been not only to characterize these individual aspects, but also to combine these “pieces” in order to develop an integrated picture of “how” iodine behaves. Within these studies, effort is also directed towards achieving an understanding of the underlying phenomena as it is not only the “how” but also the “why” that is of interest. Hence the objective of the program is to produce a “portrait” rather than a “picture”, in the sense that a portrait also provides insight into the underlying character of its subject.

This paper provides a brief overview of the research that our group has performed since the last Workshop. Specifically, the paper describes the experimental approaches and recent findings in the key areas of: adsorption on painted and steel surfaces, the impact of organics on volatility, organic iodide volatility, mass transfer, and modeling of these phenomena. Only limited information is presented here as the details of the experimental methodology and the results are available elsewhere [1,2,3,4,5,6,7,8,9,10].

RESULTS AND DISCUSSION

A) Impact of Organics on Iodine Volatility

Organic impurities may arise in containment from various sources such as paints, oils, and greases. The radiolysis of these organic compounds can significantly affect iodine volatility and speciation. In particular, radiolysis in the aqueous phase can result in the production of organic acids thereby decreasing solution pH and O$_2$ concentrations, conditions that favor higher I$_2$ production. Organics may also react with water radiolysis products, thereby competing with the rapid radiolytic interconversion between non-volatile I and volatile I$_2$. Finally, organic radicals produced through radiolysis can react with iodine species such as I$_2$ to form organic iodides.

Although the quantities and type of organic compounds vary somewhat for different paint types, certain compound classes are ubiquitous. Carbonyl compounds (methyl ethyl ketone and methyl isobutyl ketone) are commonly used in the application of paints, whereas methylated aromatics (xylene and toluene) are present in thinners. Alcohols and halogenated hydrocarbons (trichloroethane) are also common additives. All of these species could be released into the aqueous pool in considerable quantities after an accident.

The impact of organics on the rate of iodine volatilization from irradiated solutions was investigated under a range of conditions. A bench-scale apparatus installed in the irradiation chamber of a Gammacell was used to provide continuous measurement of the volatilization of iodine from radio-labeled 10$^{-4}$ to 10$^{-6}$ M CsI solutions with pH values of 5 to 9. The rate of volatilization was determined in the presence of 10$^{-3}$ to 10$^{-6}$ M concentrations of various alkyl
halides, carbonyls and aromatics, three types of compounds most likely present in containment. In separate experiments, iodo-organics and molecular iodine in the gas and liquid phases of irradiated samples were analyzed using gas-chromatography/ mass spectrometry and UV spectrophotometry. The details of the methodology used in these experiments are provided elsewhere [1,4,7,8,11].

The impact of organics of different types was quite varied while that for organics of the same type was quite similar (FIGURE 1). Iodine volatilization increased by up to two orders of magnitude in the presence of alkyl chlorides and carbonyls while it decreased in the presence of aromatics. Gas and liquid phase analysis indicated that chloro-iodo organics and alkyl iodides are formed in the presence of alkyl chlorides and carbonyls respectively, while no volatile iodo-organics were observed in the presence of aromatics. Molecular iodine measurements indicated that I₂ concentration increases in the presence of alkyl chlorides and decreases in the presence of carbonyls and aromatics, for solutions of fixed pH.

![Volatilization at CsI Concentration of 10⁻⁶ M](image)

*Figure 1. The impact of various types of organics (10⁻³ M) on iodine volatilization rate for irradiated 10⁻⁶ M CsI, pH 5 solutions*

The impact of the organics also depended on the solution pH (FIGURE 2). At lower pH, higher rates of volatilization were observed both in the presence or absence of organics. However the magnitude of the pH effect differed amongst the organics: the alkyl halides augmented the impact of pH while the aromatic compounds suppressed it.

The results from this study provided strong support for a generic approach to predicting the impact of organics on iodine volatility. In particular, the results served as the basis for developing and assessing a semi-mechanistic model of the impact of organics on iodine volatility [1].
Figure 2. The effect of pH on iodine volatilization rate for different types of organics ($10^{-3} M$) in irradiated $10^{-2} M$ CsI solutions

B) Volatility of Organic Iodides

In this project a stripping apparatus filled with packing was used to determine Iodine Partition Coefficients (IPCs) for a range of alkyl iodides, aromatic iodides, phenolic iodides and iodoalcohols.

A novel aspect of the experimental procedure was the use of I-131 labeled iodoorganics. Using this radiochemical approach enabled partition coefficients to be measured by direct counting of aqueous and gaseous samples. Aqueous samples were collected from the stripping column and extracted with chloroform in order to measure the aqueous phase organic iodide concentration. To determine the gaseous concentration, air was bubbled through the column, such that the species being studied could reach equilibrium between the two phases. Subsequently the air was passed through an activated carbon filter onto which the labeled organic was adsorbed.

The IPC decreased as the molar volume increased for both iodoalkanes and iodoaromatics (FIGURE 3). Both the vapour pressure and aqueous solubility of organics should decrease with increasing molar volume. Hence, the IPC might not be expected to exhibit a significant dependence on molar volume. However, it appears that for iodoalkanes and iodoaromatics, the dependence of aqueous solubility outweighs that on vapour pressure, resulting in decreasing values for the IPC. One possible explanation for the strong dependence of aqueous solubility on molar volume is that as the molar volume increases it becomes more “difficult” for a cavity to be created within the aqueous solvent to accommodate the dissolution of the solute.

A relationship based on structural bond contributions was used to estimate IPC for organic iodides [6]. This approach had previously been used to predict the partitioning of organics in the environment but had not been applied to organic iodides in any detail. These calculated values were then compared to the experimental results, for the purpose of improving the model as it relates to organic iodides. The agreement for the iodoalkanes was quite good however divergence occurred for the large iodoaromatics. Specifically, the model provided a reasonable estimate of the IPC for iodobenzene and 2-iodotoluene, but not for 1-iodonaphthalene.
To estimate the effect of temperature on the IPC, it was assumed that like aqueous solubility and vapour pressure, the IPC would follow Clausius-Clapeyron type behaviour. If the IPC is defined as the ratio of aqueous solubility to vapour pressure and it is assumed that the effect of temperature on molar volume is negligible, the following equation can be obtained,

$$\ln(IPC') = \frac{\Delta H_{\text{HENRY}}}{R} \frac{1}{T} + \text{constant}$$

where IPC' = IPC/RT, and $$\Delta H_{\text{HENRY}} = \Delta H_{\text{EXCESS}}^{\text{SOLUTION}} - \Delta H_{\text{VAPORIZATION}}$$.

This relationship was tested against experimental data, as shown with iodomethane and 1-iodobutane (FIGURE 4).

Thus the data supported the assumption that the IPC follows Clausius-Clapeyron type behaviour. Using the graph and the above equation, $$\Delta H_{\text{HENRY}}$$ was determined to be approximately -22500 and -20700 J/mol for iodomethane and 1-iodobutane respectively. For iodomethane, the $$\Delta H_{\text{HENRY}}$$ value is very close in size to that for the enthalpy of vaporization,
which is approximately 27000 J/mol, showing that the excess enthalpy of solution is relatively small for this compound. In contrast, the enthalpy of vaporization for 1-iodobutane is approximately 39000 J/mol, so for this compound the excess enthalpy of solution makes a significant contribution to $\Delta H_{\text{Henry}}$. Thus, the knowledge of the enthalpy of vaporization alone is not enough to predict the relationship between the IPC and temperature for some organic iodides.

C) Enhancement of Mass Transfer by Rapid Chemical Reactions

A study was undertaken in order to provide experimental data needed to evaluate the model of enhancement proposed by Burns and Goodall [12]. This model was then extended in order to investigate the potential impact of radiation chemistry on the rate of iodine volatilization. Due to the rapid nature of radiolytic processes, the mean lifetime of many aqueous iodine species is much shorter than the characteristic time for mass transfer and consequently, mass transfer may be substantially enhanced.

The experiments were performed for a simple system in which I$_2$ gas was either absorbed into, or evaporated from, solutions containing different I$^-$ or S$_2$O$_3^{2-}$ concentrations. The system consisted of a 18 mL/s flow of I$_2$ in air impinging onto 100 mL of stagnant aqueous solution in a 250 mL Erlenmeyer flask. The value of $k_1$ was determined by measuring the rate of evaporation of water, using Trabold and Obot’s (1991) [13] method, corrected using the ratio of the diffusion coefficients of water and I$_2$ (0.23 and 0.085 cm$^2$/s respectively at 25°C) raised to the power 0.66 (Mackay and Yeun, 1983) [14].

These results were modelled using FACSIMILE by assuming that resistance to mass transfer in the aqueous phase was limited by a film, the thickness of which was determined based on the value of $k_1$ measured in the absence of reaction, and the diffusion coefficient of I$_2$ in water. This liquid film was subdivided into 19 zones with the 20th zone representing the bulk aqueous phase that was assumed to be perfectly mixed. The transport of chemical species between the zones was at a rate determined by the diffusion coefficient of the species (D$_i$) and the thickness of each zone. The impact of chemical reaction on mass transfer was represented by also including the rate of change in concentration of a species within each zone, due to formation or destruction through chemical processes. For example in the case of interfacial transfer of I$_2$ in acidic I$^-$ solutions, the rapid equilibrium between I$_2$ and I$^-$ was accounted for using forward and reverse rate constants of $5.6 \times 10^9$ M$^{-1}$s$^{-1}$ and $7.5 \times 10^6$ s$^{-1}$ respectively [15]. Further details of the experimental method and modelling approach are available elsewhere [3].

The enhancement of the rate of evaporation I$_2$ due to the rapid reaction with I$^-$ was measured by drawing air over I$_2$/I$^-$ solutions with known I$^-$ concentrations (FIGURE 5). The rate of I$_2$ evaporation was evaluated by collecting samples of the solutions and analysing for I$_2$ concentration at 350 nm using a Varian Cary 3 UV-Vis spectrophotometer. For each experiment, 4 to 6 samples were taken. Measurement of the rate of I$_2$ volatilization from solutions containing no I$^-$ allowed the value of $k_1$ for evaporation in the absence of reaction to be evaluated.

For solutions with I$^-$ concentrations below $1 \times 10^{-4}$ M, the overall mass transfer coefficient ($K_{OL}$) was constant and dependent on transfer through the liquid side film. At I$^-$ concentrations above $1 \times 10^{-3}$ M, the reaction between I$_2$ and I$^-$ ions significantly enhanced $K_{OL}$. At concentrations above 0.1 M, $K_{OL}$ approached an asymptotic value and the evaporation of I$_2$ was limited by the transfer of I$_2$ through the gas side film.
D) Deposition of Iodine on Stainless Steel

The adsorption of I_{2(g)} on stainless steel tubing was investigated in order to quantify the rate and extent of iodine deposition and understand the underlying mechanisms. The operating conditions considered included I_{2(g)} concentration, relative humidity and tube surface temperature (TABLE 1).

A gas stream containing I_{2(g)} labeled with radioactive I-131 was passed through 25.4 cm long, 0.64 cm OD, stainless steel tubing. The rate and extent of iodine retention were obtained by recording the gamma emission of I-131 deposited on the tubing (364.5 keV) using 2x2" NaI scintillation detectors connected to APTEC PC based multi-channel analyzer (MCA) cards. Two types of steel were examined in this study, SS-316L and SS-304L.
Table 1 Experimental parameters

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relative Humidity</th>
<th>Iodine Gas Phase Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>23, 40, 60, 90</td>
<td>Low: 0% &lt; RH &lt; 25%</td>
<td>High: 5x10⁻⁷ M &lt; [I₂]g &lt; 5x10⁻⁵ M</td>
</tr>
<tr>
<td></td>
<td>High: 75% &lt; RH &lt; 100%</td>
<td>Med.: 5x10⁻⁹ M &lt; [I₂]g &lt; 1x10⁻⁸ M</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Low: 5x10⁻¹¹ M &lt; [I₂]g &lt; 1x10⁻⁹ M</td>
</tr>
</tbody>
</table>

The results suggested that three different mechanisms were involved in the iodine deposition processes (FIGURE 6). Physical adsorption of I₂ predominated at low iodine concentrations regardless of relative humidity or tube temperature. Under these conditions a steady state loading was rapidly achieved and desorption was rapid.

![Image: Iodine Deposition Rate Vs [I₂]g](image)

**Figure 6. Plot of deposition rate Vs I₂(g) concentration for SS-316L**

A slow chemisorption process occurred for SS-316 under dry conditions with medium or high I₂(g) concentrations (>10⁻⁹ M). This process involve physical adsorption followed by a slow, rate limiting, chemical reaction on the surface. It is speculated that the rate of this surface reaction was limited by something other than the amount of physically adsorbed iodine, the availability of reactive sites, for example, as the deposition rate was only weakly dependent of the I₂(g) concentration. The other characteristic of this type of adsorption was the slow rate of desorption which indicated that the iodine was chemically bound to the steel surface. Deposition of 10⁻⁹ to 10⁻⁷ M I₂(g) on SS-304 occurred through this slow chemisorption process for both humid and dry conditions. It is suspected that for the SS-304, used in this study, higher I₂(g) concentrations, or surface iodine loadings, were required for the corrosion based adsorption process described below to be initiated.

At medium to high relative humidities and high I₂(g) concentration deposition occurred through a rapid pitting type corrosion process. This process was characterized by high rates of iodine deposition, slow and incomplete desorption, and the extent of adsorption being limited by the surface capacity. It is believed that I₂ initially reacted at defect sites to form hygroscopic FeI₂ which attracted more water propagating the reaction. The initial rate and extent of iodine deposition depended on several factors such as the number of available sites to initiate the reactions and how well these sites propagated under the relevant experimental conditions. Temperature played an important role in determining the extent of the surface reactions. At near ambient temperature (25°C), the propagation appeared to be inhibited resulting in an apparent

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maximum surface loading. At moderate temperature of 40° or 60°C and high humidity, however, no such inhibition occurred resulting in rapid and continuous iodine adsorption.

E) Adsorption of Iodine by Paint Under Condensing Conditions

Steam released into the containment following an accident will condense on painted surfaces forming droplets, rivers or a falling film of water. The presence of this water may significantly impact upon the value of this paint as a passive safety. In particular, the water may be effective in removing I$_2$(g), however much of the I$_2$ transferred into the condensate may flow down the containment walls to the pool rather than being retained by the paint itself. Furthermore, these films will provide a location for iodine to react with organic components released from the paint, potentially resulting in enhanced iodine volatility and increased organic iodide formation.

In this project, the adsorption of I$_2$(g) by paint under condensing conditions is being investigated both experimentally and through computer modeling. Several different types of paints are being studied including Carbozinc-11, Epoxy type Keeler & Long 4500, water based Ripolin, and polyurethane based paint. An apparatus suitable for this purpose has been designed and constructed (FIGURE 7). The centerpiece is a glass vessel with a cold finger to which a painted coupon is attached such that steam will condense on its surface (FIGURE 8). The rate of iodine adsorption by the paint is continuously monitored using $^{131}$I tracer. The condensation rate can be adjusted by varying the temperature of the incoming steam and the flow rate of cooling water through the cold finger. Condensate from the cold finger and condenser are collected to allow subsequent analysis for iodine and organics.

![Figure 7. Apparatus for Condensing Steam](image-url)
Some preliminary tests with steam condensation on a glass surface have shown that, initially, the condensate forms water droplets which eventually join to form a river of water falling under the influence of gravity. The formation of droplets, rather than continuous film may have been due to the relatively hydrophobic nature of the glass surface. It is possible that an organically coated surface would exhibit a similar pattern of condensation.

The study also covers the identification and quantification of the organics released to the condensing steam. Samples of the condensate will be analyzed using solid phase microextraction (SPME) to extract the organic compounds coupled with the use of GC/MS. As part of this work, the release of organic compounds from painted surfaces has been examined by immersing painted samples in water at temperatures between 25 to 90°C. Data obtained so far has supported the previous finding that the organics released are to a great extent determined by the types of organic solvents used in the thinner. Different paint manufacturers use different groups of organic solvents to thin the paint prior to application on the surface. Keeler & Long 4500, for example, has been shown to release isomers of xylene, as well as ethyl benzene and butyl acetate which constitute the thinner. In addition the presence of other types of organics has been detected.

A preliminary form of a FACSIMILE based computer model has been developed to simulate the chemistry within the falling water. The model utilizes known iodine reactions and additional data from the on-going studies at the University of Toronto. The program simulates the transfer of I₂(g) into the water film, its reaction within the aqueous film and the adsorption of iodine species by the painted surface (FIGURE 9). In another version of the model, the water film is assumed to be falling and collected in the “sump”. The amount of iodine collected in the sump as well as concentration of iodine retained by the surface as a function of time and height are also evaluated by the program.
F) Modeling of Gas Phase Radiolysis

Over the last few years, we have developed mechanistic models in order to interpret and represent the many different aspects of iodine behaviour in containment. We are in the process of creating an integrated model that will combine all these separate models. Specifically, this model will represent the processes associated with the radiolysis of aqueous iodine solutions, the impact of organics and organic iodide formation, adsorption on surfaces, interfacial mass transfer and, gas phase radiolysis. This model will be used as a research tool to study the relative importance and interaction between these processes.

As part of this work we are re-assessing our model of gas phase radiolysis. This model was originally based on the reaction set compiled by Sagert [16]. This re-assessment has resulted in the addition of reactions and the updating of rate constants. The G-values are still those proposed by Sagert for water saturated air at 40 °C but work is underway to develop a subroutine to adjust these values to alternate conditions. In addition, Arrhenius parameters are being collected in order to make the rate constants within the model temperature dependent.

The model was applied to the investigation of O3 and NOx formation, with a particular interest in conditions relevant to the PHEBUS experiments: 70% N2, 4.5% O2, 0.5% H2, 25% H2O, 2 atm pressure, 1200°C and 1 kGy/hr. In earlier work [17] the gaseous concentrations of O3 under these conditions was predicted to approach 5 ppmv while that of HNO3 increased linearly up to 20 ppmv after 5 hours. However, the model did not consider scavenging of OH by H2:

$$H_2 + OH \rightarrow H_2O + H \quad k = 4 \times 10^6 \text{L/mol}\cdot\text{s}, [18]$$

(1)

Through a sensitivity analysis, it was determined that with the inclusion of reaction (1) the hydrogen content in the air had a significant impact on both O3 and HNO3 concentrations (FIGURES 10 and 11). Specifically, increasing the initial hydrogen content lowered both O3 and HNO3 concentrations. The effect on nitric acid was most pronounced when the hydrogen content reached 0.5%, which represents the conditions prevailing in PHEBUS experiments, resulting in a constant HNO3 concentration of less than 2 ppmv. The trend with no hydrogen was the same as that reported in earlier work in which reaction 1 was omitted.
The model was also used to simulate the radiolytic elimination of I$_2$(g) using an initial I$_2$(g) concentration of 4x10$^{-6}$ M. The rate of elimination was approximately proportional to the dose rate (FIGURE 12). The model predicted that the major process for I$_2$(g) removal was through:

I$_2$ + OH $\rightarrow$ \[ \rightarrow \] I$_2$O$_3$

The initial rate of I$_2$ depletion was nearly equal to the initial rate of OH production. Hence the fractional rate of I$_2$(g) elimination was much faster for lower I$_2$(g) concentrations and at higher dose rates (FIGURE 12). The hydroxyl radical originated from the reaction of H$_2$O with ions,
such as N₂⁺, O₂⁺, and H₂O⁺, produced through the radiolysis of air. However, when the initial I₂(g) concentration was below 1x10⁻¹⁰ M the initial rate of iodine elimination decreased by approximately an order of magnitude. At these concentrations the competition between other species, such as NO₂, for OH became comparable. Finally, it was determined that the I₂(g) was eventually oxidized to form aerosol particulate I₂O₃.

**Figure 12. The Effect of Dose Rate on I₂ Fraction During the Radiolysis of Moist Air at 40 °C**

Our work on a gas phase radiolysis model is ongoing. At present, a subroutine is being developed to theoretically predict the gaseous concentrations of volatile organic compounds emitted from surrounding painted surfaces. As well, the deposition of ozone onto painted surfaces is being addressed based on literature concerning indoor air quality. Finally, further experimental data is needed in order to validate the model. In particular, measured O₃ and NOₓ concentrations under different conditions are required. In addition, the product from the radiolytic elimination of I₂(g) needs to be confirmed.

**CONCLUSIONS**

Although many conclusions can be drawn from these studies, only a few relating to accident management are presented here. It has long been known that maintaining basic pH following an accident will greatly reduce the re-volatilization of iodine and results presented here further support this. However, should acidic conditions arise, paints containing aromatic based solvents could act as a passive safety feature by reducing re-volatilization and decreasing the formation of volatile organic iodides. The presence of alkyl halides within containment should be avoided as much as possible, as these compounds increase the amount of volatile iodine in both organic and inorganic forms. A predominance of gaseous iodine in organic forms should, in general, be anticipated although I₂(g) may make a significant contribution under some conditions.

Sampling of I₂(g) concentrations using stainless steel sample line systems may represent a problem as significant line losses will likely occur, under humid conditions in particular. Radiolysis of moist air should result in the formation of significant amounts of NOₓ which could
reduce solution pH and hence increase iodine volatility. However, the presence of even a small amount of H₂ should, in theory, reduce the concentration of NOₓ and hence have a beneficial effect in terms of the release of iodine. In contrast, radiolytic elimination of I₂(g) may be significant but the impact of H₂ on the effectiveness of this removal pathway still needs to be explored.

REFERENCES


AN OVERVIEW OF THE IODINE BEHAVIOUR IN THE TWO FIRST PHEBUS TESTS FPT-0 AND FPT-1

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ABSTRACT

The PHEBUS F.P. program is a wide international effort to investigate, through a series of in-pile integral experiments, LWR severe accident phenomena, in particular bundle degradation and the subsequent release and transport of radioactive materials up to the containment. Two tests simulating a low pressure cold leg break under a steam-rich environment have already been successfully performed: FPT-0 with trace irradiated fuel and FPT-1 with re-irradiated BR3 fuel. Both tests have provided experimental data of high interest, particularly concerning iodine release from the fuel bundle, transport in the reactor coolant system and behaviour in the containment.

The analysis of FPT-1, currently in progress, shows that the results exhibit common features and differences with the previous test FPT-0. In both tests, highest gaseous iodine fractions are obtained after Zicaloy-oxidation phases; the amount measured in FPT-1, referred to the initial bundle inventory, is however significantly lower than in FPT-0. The fast deposition of iodine in the sump as insoluble AgI observed in FPT-0 appears to be considerably slowed down in FPT-1 to a point that iodine re-volatilisation from the sump, which was inhibited in FPT-0, becomes possible in FPT-1. The results of both tests indicate
that the gaseous iodine in the long term is produced by release of organic iodides from the painted condenser surfaces.

The data obtained from the PHEBUS tests indicate that the current modelling in iodine chemistry codes is not fully adequate to model the observed phenomena. The comparison of modelling and experimental data has identified areas of necessary developments: modelling of thermodynamics and kinetics of chemical reactions in the reactor coolant system, of kinetics of organic iodides formation/decomposition and of Ag/I interactions in the containment. The later requires a more accurate knowledge of the Ag physical and chemical state in the containment (surface characteristics and oxidation state).

Implication of PHEBUS results for LWR iodine source term studies are briefly discussed.

INTRODUCTION

The PHEBUS FP program offers the first opportunity, through a series of in-pile integral experiments, for evaluation of fission product behaviour in the presence of mixtures of radioactive and non-radioactive materials (structural and control rod materials), gas effluents (H₂O/H₂ mixtures), radiation fields, temperatures and pressures prototypic of LWR severe accident conditions (Krischer, 1992; Von der Hardt, 1994). The first PHEBUS test, FPT0, performed in December 1993 with trace-irradiated fuel in the presence of silver-indium-cadmium control rod material and essentially under oxidising conditions, was intended primarily as a means to evaluate the adequacy of the test facility and test procedures to be used throughout the rest of the PHEBUS test program to study fission product behaviour. The FPT0 test has, however, provided indications and suggestions about issues that should be pursued in future tests in the program. This is certainly true in the case of iodine chemistry in the circuit and in the containment (Jacquemain, 1997). The second test FPT1, performed in July 1996, with a test bundle design and degradation scenario similar to that of FPT-0, should allow to check that the unexpected phenomena highlighted in FPT0 are reproduced with BR3 re-irradiated fuel, i.e.:

- the existence of significant amount of gaseous iodine in the cold leg of the primary circuit and in the containment early during the degradation phase,
- the correlation between bundle degradation events (fuel oxidation, material re-location pool formation) and the physical form and amount of iodine transported through the primary circuit,
- the low iodine retention in the primary circuit pipes but the high affinity of iodine for the containment walls both in the sump and in the atmosphere,
- the role played by control rod and structural material in iodine transport to the containment,
- the presence of Ag in large excess relative to iodine in the containment and the formation of insoluble and non-volatile iodine in the sump.

This paper presents an overview of the iodine data collected during the PHEBUS tests, with an emphasis on the gaseous iodine results in the experimental circuits and in the containment. Results concerning other aspects of PHEBUS results are described more
extensively in papers published elsewhere (Clément, 1998; Hanniet, 1998). The first section of
the paper will be devoted to a short description of the PHEBUS test facility and
instrumentation dedicated to fission products and gaseous iodine measurements. The second
and third section will give a description of the main results obtained in the PHEBUS circuit
and containment concerning gaseous iodine, in particular the released mass and kinetics of
release and the available information existing on the iodine forms in the circuit and the
containment. The fourth section will present a comparison of modelling and experimental
data performed with the iodine chemistry code IODE 4.2 developed at IPSN. The last section
will discuss implications of PHEBUS tests results for LWR iodine source term studies.

**THE PHEBUS FACILITY AND INSTRUMENTATION**

**Description of the facility**

We summarise here only the information necessary for the understanding of the paper.
For a more complete description concerning the test facility and the PHEBUS-FP project, see
Schwarz (1998). The facility was designed to simulate the reactor core, primary circuit with a
steam generator and the reactor containment of a LWR, the scaling factor being, for the three
parts, about 1/5000 as compared to a 900 MWe LWR (figure 1).

The test bundle comprised 20 light water reactor (LWR) fuel rods and one central
silver-indium-cadmium control rod with stainless steel cladding. Two Zircaloy grids are
located at 220 and 740 mm from the bottom of the fuel column. The test package, surrounded
by an insulating shroud and contained in a pressurised in-pile tube, is inserted into a
pressurized water loop located at the centre of the 40 MW PHEBUS reactor core. The bundle
was irradiated for a few days in the PHEBUS reactor. The objective of the irradiation is to
re-build in the test fuel the inventory in short-lived fission products such as I\(^{131}\), to induce
radiation doses large enough to study radiochemistry effects in the containment. The initial
bundle inventory and the obtained inventory of the main fission products are given in table 1
for the two tests. The main difference between the two tests arise from the difference in fuel
burn-up: the fission product inventories are much larger in FPT-1.

The upper plenum above the bundle is connected to an horizontal line made of Inconel
and heated to 700° C. It conveys the gases and aerosols leaving the test bundle to a U tube
simulating a PWR steam generator. In FPT-0 and FPT-1, the walls of the steam generator
model were maintained at 150°C, i.e. above the conditions of steam saturation for the
considered pressure. The outlet of the U tube is then connected to the model containment,
thus simulating a cold leg break.

After the experimental line at 150°C, a 10 m³ cylinder collects the aerosol, gas and
steam/hydrogen effluents conveyed by the circuit during the test, simulating a reactor
containment building in presence of a break in the primary circuit. Particular design features
of the containment vessel are a sump at the bottom (the sump is initially composed of 100 l of
water at pH = 5.0 (0.3 M boric acid, 1.75 \times 10^{-4} M NaOH)) and a group of three condensers in
the upper part (painted with RIPOLIN epoxy paint, currently used in EDF plants), which are
designed to control steam condensation and thus simulate the cold structures of a reactor
building. The outer vessel wall is heated to avoid steam condensation and subsequent aerosol
deposition on the containment walls.

\[1\] The fuel was 4.5 % enriched fresh UO\(_2\) for FPT-0. The irradiated fuel used in FPT-1 originates from the BR3
plant in Mol, Belgium. The average burn-up was of the order of 23 GWd/\(\text{tU}\).
Figure 1: Schematic representation of the PHEBUS test facility for FPT-0 and FPT-1. The 900 MWe LWR to PHEBUS scaling factor is close to 1/5000 for the 3 main modelled components of a reactor depicted in the figure (reactor core, primary circuit with a steam generator, containment).

Table 1: FPT-0 and FPT-1 initial bundle inventories for main elements of interest

<table>
<thead>
<tr>
<th>Element</th>
<th>FPT-0, mass (g)</th>
<th>FPT-1, mass (g)</th>
<th>Element</th>
<th>FPT-0, mass (g)</th>
<th>FPT-1, mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>9284.0</td>
<td>9163.0</td>
<td>Fe</td>
<td>179.8</td>
<td>173.9</td>
</tr>
<tr>
<td>Pu</td>
<td>-</td>
<td>47.6</td>
<td>Sn</td>
<td>50.6</td>
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<tr>
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<td>Ni</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ag</td>
<td>476.8</td>
<td>478.3</td>
<td>Cd</td>
<td>29.8</td>
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</tr>
<tr>
<td>In</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Re</td>
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<td>482.12</td>
<td></td>
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</tr>
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<td>Ba</td>
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<td>Mo</td>
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<td></td>
<td></td>
<td>0.036</td>
<td>1.12</td>
</tr>
</tbody>
</table>

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Fission products measurements

The evaluation of the amount of fission products and activation products in various parts of the facility is obtained by applying several techniques.

During the test, on-line γ spectrometers measured the activities of the numerous radionuclides released by the fuel. Three are located along the circuit (inlet of steam generator (SG), along the SG and outlet of the SG); one measures the activity of the containment atmosphere as well as that of the deposits on the containment walls and condensers, finally one measures the activity of the water in the sump (figure 1).

After the test, in FPT-1, the evaluation of the amount of fission products and activation products still present in the fuel region or deposited in the vertical channel was obtained post-test by quantitative γ-spectrometry of the test device (Cornu, 1997). In both tests, samplings of released materials were performed by a specific instrumentation placed in furnaces at specific points on the experimental line at 700°C (point C, figure 1) and on the experimental line at 150°C (point G, figure 1). Aerosols were collected on inertial impactors and filters. Gas capsules located downstream of filters and impactors were used to collect gas at point G. Thermal gradient tubes were used at point C to condense vaposurs.

The containment was strongly instrumented. Aerosols were collected on inertial impactors, filters and sequential sedimentation coupons. Gas capsules located downstream of filters or impactors and May-packs were used to sample the containment gas. May-packs allow for the discrimination of volatile iodine species on successive filtering stages (molecular iodine is chemi-sorbed on the "Knit-mesh" filter stage and organic iodine on the Zeolite filter stage). The different filter stages of one May-pack were γ scanned on-line during both tests. During FPT-1, a large gas capsule partially filled with Zeolite was also γ-scanned on-line.

All sampling instruments and sections of the main circuit component are recovered by remote handling as soon as the experimental installation is back to atmospheric pressure and room temperature. They are transferred to a hot cell under the « FP caisson » where first inspections and γ-scans are carried out, beginning with those samplers which have to be scanned for T131 analysis.

FPT-0 and FPT-1 test conditions

The first test of the programme, FPT-0, using fresh fuel, was performed from December 2 to 6, 1993. The second, FPT-1, with irradiated fuel, from July 26 to 30, 1996. Both experiments were operated under similar thermal-hydraulic conditions, the main difference between them being the burn-up of the test fuel. The test scenarios were divided in experimental phases as listed in table 2.

The experiments consisted first of 5 hour transients during which the inlet coolant (steam) flow varied between 0.5 g/s and 3 g/s in FPT-0 (2 g/s in FPT-1). The main objective was to investigate bundle degradation, fission product release and transport under low

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2 At point C, samplers were placed in 2 furnaces: one at 700°C upstream and one at 150°C downstream. At point G and in the containment, samplers are placed in furnaces at 150°C

3 Zeolite filters are composed of granulates of overall composition Na2O / Al2O3 / 2.5 SiO2, coated with silver Ag and lead Pb. Knit-mesh filters are composed of copper wires plated with silver. The mass composition of the filter is 90 % Cu -10 % Ag. In both filters, the active element is Ag.
pressure (0.2 MPa) and mainly oxidising (steam-rich) conditions. The bundle fission power was gradually increased until cladding rupture, oxidation, and fuel melting occurred. High temperatures reached during the transients resulted in Zircaloy and control rod absorber alloy melting, fuel liquefaction, material relocation, fuel melting and induced the release of hydrogen, aerosols and fission products. The transients were terminated by a core shut-down and a cooling of the bundle with steam. Experimental results concerning the bundle degradation in PHEBUS tests are described in detail in separate papers (Von der Hardt, 1995; Schwarz, 1998).

During the degradation phase, the containment vessel boundary conditions were adjusted in order to limit the relative humidity ratio to about 70 - 80%, avoiding uncontrolled steam condensation on the outer walls which could force fission product deposition on undesirable non-instrumented spots. The study of the aerosol settling and surface deposition in the containment lasted for 19 hours after the bundle degradation in FPT-0 and for about 60 hours in FPT-1 (table 2) during the so-called aerosol phase. The aerosol phase was followed by the washing of the elliptic bottom part of the containment. The washing was performed with the water of the sump to bring the settled aerosols into the sump. The objective of this experimental phase is to bring significant radioactive material into the sump to observe radiolytic effects during the following chemistry phase. It required a preparatory phase during which controlled temperatures were changed to avoid significant water vaporisation from the sump during the operation (table 2). After the washing, another preparatory phase was necessary to re-adjust temperatures to their desired level for the chemistry phase. This last experimental phase lasted for about 4 days in FPT-0 and about 1 day in FPT-1, during which the iodine chemistry in the containment atmosphere and the sump was studied. The objective is to measure iodine volatility on the long term and to provide some understanding on the processes at the origin of the formation of volatile iodine.

Table 2: Containment boundary conditions during experimental phases of the PHEBUS tests

<table>
<thead>
<tr>
<th>Phases</th>
<th>Duration (hours)</th>
<th>Containment temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FPT-0</td>
<td>FPT-1</td>
</tr>
<tr>
<td>Bundle degradation</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Core shut-down - Containment isolation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol phase</td>
<td>18.5</td>
<td>60</td>
</tr>
<tr>
<td>Preparatory phase</td>
<td>6</td>
<td>4.5</td>
</tr>
<tr>
<td>Washing</td>
<td>0.25</td>
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</tr>
<tr>
<td>Preparatory phase</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Chemistry phase</td>
<td>96</td>
<td>18</td>
</tr>
</tbody>
</table>

Containment depressurisation - end of experimental phases

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CURRENT UNDERSTANDING OF THE GASEOUS IODINE BEHAVIOUR IN FPT-0 AND FPT-1

Release from the fuel bundle and transport through the circuit hot leg

The degradation phase resulted in a large release of fission products and bundle and structural materials in the circuit and in the containment vessel as illustrated in figure 2 for 131I in FPT-1. In both tests, the highest release rates were measured during a first temperature escalation phase (first escalation of the Zr-oxidation reaction), then during the heat-up phase following the first escalation phase and finally during a second oxidation phase, occurring before the core shut-down (figure 2). The later phase probably corresponds to oxidation in lower parts of the test bundle, due to the downward movement of hot material.

The integral release fractions from the bundle for the main elements listed in table 1 proved to be very similar in both tests. Four kinds of nuclides can be distinguished:

- highly volatile nuclides (release fraction higher than 50%): Te, I, Cs, Sb and probably Cd4,
- release fraction in between 10 and 50%: structural material and fission products such as Mo, Ag, In, Sn, Fe and Co,
- release fraction lying between 1 and 10%: material such as W, Re, Mn, Ru,
- release fraction under 1%: material such as Ba, Sr, U, Nb, Zr and Ce.

In both tests, iodine was almost totally released from the fuel bundle during the degradation (about 86.5% of the initial bundle inventory in FPT-0), probably as a gas, considering the high temperatures reached in the fuel (Schwarz, 1998). In the vertical line above the bundle, gaseous iodine probably reacted partially with Ag, In, Cs or Rb to form a metal iodide vapour. The existence at this location of significant unreacted gaseous iodine fractions is unexpected for reducing conditions but predicted for oxidising conditions by thermodynamic evaluations performed for PHEBUS conditions (see for instance: Götzmann, 1996). A comparison of the iodine aerosol plus vapour mass flowing through the hot leg of the circuit (point C) with that flowing through the cooler zones of the circuit (steam generator deposits + flow through the cold leg (point G)) is presented in figure 2 and 3 for FPT-1. The results indicate a deficit in iodine flow at point C with respect to the flow through the cooler zones of the circuit amounting to more than 20% of the flow (measured in the cooler zones of the circuit) for the sampling performed during the early degradation phase at 11050-11349 s and for the sampling performed during the late degradation phase at 16766-16823 s. Thus, in the hot leg of the circuit (point C, 700°C), at least5 20% of the

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4 To be confirmed by post-test analyses for the FPT-1 test.
5 Deposits in the sampling line in between the filter at 700°C and the downstream filter at 150°C at point C were not measured but estimated assuming that the deposits were equivalent to those measured in the steam generator (figure 3 and next section). Under this hypothesis, the estimated deposits are certainly higher than the actual values (the surface and volume of the steam generator lines are larger than those offered by the sampling line). This is confirmed by the analysis of the sampling performed during the main release phase at 13809-14101 s (figure 3) which yields an excess of iodine flow representing 7% of the flow measured in the cooler zones of the circuit, an excess due to the overestimation of the deposits on the sampling line.
Figure 2: FPT-1 - (top) Sampling time-windows (thick lines) and corresponding non-condensed iodine fractions in the hot leg of the circuit (point C, 700°C); the measured evolution of hydrogen volume concentration in the circuit is shown, together with the evolution of the OLAM signal (on-line aerosol monitor, signal attenuations correspond to increase in the aerosol concentration in the circuit carrier gas) and the $^{131}$I flow rate signal. (bottom) Iodine flowrate data in the hot leg (point C, 700°C) and the cold leg (point G, 150°C) of the circuit. Note that two consecutive data points with the same value correspond to the start and the end-time of a given sampling. Thick lines on the top of the figure indicate sampling time-windows yielding information on gaseous iodine at point C and at point G. Steam and hydrogen flowrates in mol/s are given, showing that reducing conditions are reached only during the first oxidation phase.
total iodine flow was present as a form which could not be condensed on the 150 °C sampling systems during the early and late Zr-oxidation phase. This form may be attributed to gaseous iodine since metal iodide compounds would have been condensed in the sampling line and in the 150°C filter as evidenced by the sampling performed during the main release phase (sampling at 13809-14101 s, figure 3). No similar determination could be made for FPT-0 since for this test the instrumentation in the hot leg of the circuit did not include 150°C aerosol filtration systems. However, the presence of gaseous iodine fractions in the circuit hot leg in FPT-0 cannot be excluded.

Apparently, the conditions favouring the formation of gaseous iodine correspond to the conditions obtained during the Zr-oxidation phases. During the first oxidation phase in FPT-1, the carrier gas contains H₂ in molar excess with respect to steam. Reducing conditions in the circuit would be responsible for the presence of large fraction of gaseous iodine, a result which contradicts thermodynamic evaluations made to date for PHEBUS conditions (see, Götzzmann, 1996).

![Figure 3: FPT-1 - Comparison of the iodine mass flowing through the hot leg of the circuit with that flowing through the rest of the circuit (steam generator and cold leg) for the three 700°C + 150°C filters samplings. Characteristics of each sampled experimental phase (H₂/H₂O, Cs/I, Ag/I and Ag/Cs) molar ratios are given.](image)

During the second oxidation phase in FPT-1, the carrier gas still contains steam in molar excess with respect to hydrogen. Results however indicate that the Cs concentrations are lower during this late phase of the transient. The existence of significant gaseous iodine fraction at this time may be linked to these low Cs concentrations, an assertion which needs to be confirmed by thermodynamic evaluations.

It is also worth noting that the amount of iodine collected on the 700°C filter at point C in FPT-1 is significant. This fraction of condensed iodine at 700°C cannot be attributed to
known simple metallic iodide species but either to an unknown complex species or to iodine trapped in condensed matter. This fraction represents more than 10% of the total iodine flow on the sampling performed during the late oxidation phase.

The results obtained in the hot leg of the circuit for FPT-1 confirm the correlation existing between bundle degradation events (clad oxidation, material re-location, pool formation) and the physical form and amount of iodine transported through the circuit. More elements to establish this correlation are obtained with the containment sample data.

Steam generator deposits

Iodine was then transported up to the steam generator tube and deposited there more than other fission products and structural materials (in FPT-0, about 27% of the released iodine fraction against an average 15% for the other elements). The iodine deposition profile measured in FPT-1 indicate that most of the deposition occurred at the entrance of the hot leg of the steam generator (figure 4). This result may be interpreted either by wall and bulk condensation of a metal iodide vapour, or by chemisorption of gaseous iodine on Cd deposits (Cd deposits were found by post-test analyses to be very large at this location in FPT-0).

One cannot exclude here too the existence of significant unreacted gaseous iodine fractions. In the steam generator temperature range (700°C down to 150°C), reaction kinetics may limit the yields of reaction involving iodine and vapour or condensed metals. These limitations are more important when the reactive (here, fission products) concentrations are lower. Since in FPT-0 the fission products concentrations are significantly lower than in FPT-1 (cf. table 1), one could expect larger fractions of unreacted iodine in the FPT-0 circuits. Experimental results in the containment confirm this tendency (cf. next paragraphs).

![Graph](image)

**Figure 4**: FPT-1 - I$^{131}$ deposition profile in the hot leg of the steam generator. Iodine deposition profile is singular with respect to that measured for other nuclides in that iodine deposition is larger at the entrance of the hot leg.
Transport through the cold leg of the circuit

In the cold leg of the circuit (point G, 150°C), most of the iodine is apparently transported by aerosols. FPT-0 gas capsule data indicated that at least 2 % of the total iodine flow was present under a gaseous form after the main Zircaloy-oxidation phase and at the core shut-down. These low fractions measured do not exclude the possibility that temporarily gaseous iodine fractions may have been much higher. According to the first containment sampling performed after the oxidation phase, more than a third of the total iodine flow was present in FPT-0 under a gaseous iodine form during the oxidation phase (cf. next paragraph).

FPT-1 Zeolite gas capsule data at point G show no evidence of significant gaseous iodine fractions on the Zeolite, even during oxidation phases. However, a sampling performed during the first oxidation phase in the containment shows that the injected gaseous iodine is not efficiently trapped on a double Zeolite filter, a large fraction of it is found in the downstream gas space (at least 40%). Based on this data, the existence of an iodine species not tractable by Zeolite filtration at point G can be suspected. The gas space volume of the Zeolite gas capsule at point G being small and the gaseous iodine production being probably strongly time-dependent (according to hot leg and containment samplings), it is not surprising to find very little or no iodine in the gas space volume of those capsules.

Those cold leg samplings illustrate the difficulty encountered during PHEBUS tests to map time-dependent events with a limited number of samplings and to design an instrumentation dedicated to gaseous iodine determination, not knowing the species involved. FPT-1 results indicate that the gaseous iodine species present in the circuit may not be tractable by Zeolite filtration which excludes, a priori, the expected gaseous I₂ and HI species.

Transport to the containment and behaviour during the bundle degradation phase

More than half of the fuel inventories of iodine successfully negotiated passage through the PHEBUS circuit to reach the model containment (63 % in FPT-0). Much of this iodine was conveyed by aerosol particles that either settled on the containment bottom or deposited on the containment surfaces (by diffusiophoresis on the painted condenser and by an unidentified mechanism on the containment walls) over a period of a few hours.

In both tests, the measured gaseous iodine fractions are at their highest level at, or following, Zircaloy-oxidation phases (figure 5). In FPT-0, there was no sampling performed during the first oxidation phase. The first sampling performed about 30 minutes after this phase yielded a gaseous iodine fraction representing at least 6 33 ± 12 % of the containment inventory at that time. This result does not exclude the possibility that temporarily, earlier after the oxidation phase, the gaseous iodine fraction could have been even higher.

In FPT-1, there were samplings performed during the two oxidation phases. The sampling performed during the first oxidation phase indicated that a few percents of the containment inventory is gaseous at that time. At this time, about 40 % of the collected gaseous iodine is not retained on the double Zeolite filter of the apparatus, showing that a significant fraction of the gaseous iodine is not tractable by Zeolite filtration (which a priori

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6 Data uncertainties are discussed in Pantera (1998) and Jacquemain (1999) and are the results of data coherence and measurement accuracy analysis.
Figure 5: Gaseous iodine fraction at sampling times during the bundle degradation phase and the early aerosol phase. Evolution of the containment inventory is shown as an indication as full lines. Data uncertainties are discussed in Pantera for FPT-0 (1998) and Jacquemain for FPT-1 (1999).

Excludes for this fraction an identification with the expected HI, I₂ or organic iodides. Later samplings performed with the same apparatus do not exhibit anymore this specific iodine behaviour. The « unknown » species detected early during the test probably transforms quickly into another chemical species which is then efficiently retained on Zeolite. The
sampling performed during the second oxidation phase yields a gaseous iodine amount comparable to that obtained during the first oxidation phase.

After both oxidation phases in FPT-1, the gaseous iodine fraction decreases rapidly. Both decreases may be fitted mathematically by the same exponentially decaying function. A fast decrease which may be linked either to a diffusiophoresis of gaseous iodine (Weber, 1992) at the painted condensing surfaces and/or to a fast chemical transformation as mentioned earlier.

The volatile fraction of iodine originating from the primary circuit also disappeared in a few hours in FPT-0, probably due to deposition on the containment surfaces (cf. next section). It is however not possible to characterise precisely the gaseous iodine evolution during the bundle degradation phase in FPT-0 since only one measurement was performed during this phase.

**Behaviour after containment isolation (aerosol and chemistry phase)**

The evolution of the gaseous iodine fraction during the aerosol phase is different in the two tests. In FPT-1, the gaseous iodine fraction increases significantly immediately after containment isolation (by a factor of 2). It remains then more or less constant for about 5 hours. The increase may be attributed to a measured release of gaseous iodine from the painted condensing surfaces (figure 7). The release represents about a third of the iodine which was deposited on the condensing painted surfaces at the end of the bundle degradation phase. May-pack data (figure 9) indicate that, at this time, most of the iodine (75 %) is found on the Zeolite stage of the device, consistent with a release of organic iodide compounds. The released iodine may have two origins: either gaseous iodine which reacted directly with the paint during the test transient or formation of iodide ions, I⁻, by solubilisation in the condensed steam of the soluble iodine species initially transported by the aerosol and subsequent reaction with paint. No conclusion is possible from the experimental data on this question.

In FPT-0, the gaseous iodine fraction decreased exponentially during the aerosol phase (figure 6). No significant decrease of iodine activity on the painted condenser surfaces was measured. The data does not exclude however that a minor release, insignificant with respect to the total amount of iodine deposited, occurred during the long term phase.

For the long term, the gaseous iodine evolution in FPT-1 is probably determined by the more « soluble » behaviour of iodine, compared with FPT-0, noted during the bundle degradation phase and the aerosol phase. Indeed, the sump iodine volumic activity evolution measured during the aerosol phase (figure 8) indicates that the removal of iodine from the bulk volume of the aqueous phase is slow. It requires about 50 h. This removal process may be identified either as a slow reaction of iodide ions with Ag material and deposition of this material on the sump bottom, or by a slow deposition of an iodine suspension of the colloidal type on the sump bottom or by a slow deposition onto the sump surfaces. The later mechanism (of deposition onto the sump surfaces) was shown to be insignificant in containment mass balance evaluation presented in Garnier (1999). It is not possible to decide on the first two possibilities, actually a combination of both is probable.
Figure 6: Evolution of the gaseous iodine fraction in the containment of the two first PHEBUS tests. Confidence intervals on the values are discussed in Pantera (1998) and Jacquemain (1999).

Figure 7: FPT-1 comparison of the evolution of the gaseous iodine fraction in the containment atmosphere and of the evolution of the iodine fraction deposited on the painted condensing surfaces. A similar decrease of the activity was measured for two iodine isotopes $^{131}$I and $^{133}$I on the condensers. Other isotopes, such as $^{132}$Te given here as an example, do not exhibit the behaviour observed for iodine.
Figure 8: FPT-1 comparison of the evolution of the gaseous iodine fraction in the containment atmosphere (confidence intervals discussed in Jacquemain (1999)) and of the evolution of the iodine fraction in the containment sump (measured activity interpreted as volumic activity). The decrease in iodine volumic activity corresponds to a removal of iodine from the bulk volume of the aqueous phase.

TOTAL IODINE DISTRIBUTION ON SEQUENTIAL AND ON-LINE MAYPACK

Figure 9: FPT-1 - Distribution of gaseous iodine in the sequential and on-line May-packs as a function of experimental time. The gaseous iodine amount trapped in each type of iodine filter (successively Knit-mesh, silver Zeolite and KI impregnated charcoal) was normalised to the total gaseous iodine amount trapped in the May-pack device.
The evolution of the gaseous iodine fraction after the washing phase is different in the two tests. In FPT-1, a significant increase of the gaseous iodine fraction (by a factor close to 2) was measured (figure 6). This increase may be attributed to the formation and transfer to the containment atmosphere of volatile I₂ formed by radiolytic oxidation of soluble I⁻ ions. May-pack data indicate that at the washing 75% of the iodine is trapped on the Knit-mesh stage of the apparatus (figure 9), consistent with I₂ being the major gaseous iodine species at that time. After the washing, the I₂ contribution to the gaseous iodine fraction decreases regularly from 75% down to about 25%, probably due to a back-transfer of I₂ to the sump and subsequent slow reaction with Ag. The total gaseous iodine fraction remains however constant, indicating that contribution of the iodine species deposited on the Zeolite increases. This observation would indicate that a significant production of organic iodides compounds still occurs after the washing phase. However, no evolution of the iodine fraction deposited on the condensing surface of the condenser can be noted from figure 7. The release at that time may be too small to be observable.

In FPT-0, no increase in the gaseous iodine concentration was observed at the washing; the gaseous iodine fraction remained stable (figure 6) and represented only 0.063 ± 0.032% of the bundle inventory. These results were consistent with an efficient trapping of the iodine by Ag and the subsequent inhibition of volatile iodine formation by sump radiolysis. May-pack data indicated that most of the iodine was trapped on the Zeolite stage of the apparatus, consistent with organic iodides being the major gaseous iodine species at that time. This result was attributed to the release of organic iodides from the painted condenser surfaces.

For the long term evolution, the main difference between the two tests is probably determined, as mentioned earlier, by the more « soluble » behaviour of iodine noted in FPT-1. This difference in behaviour may be attributed to the large difference in between the Ag/I molar ratios determined in FPT-0 (~ 2500) and in FPT-1 (~ 50), this ratio being determinant for the kinetics of the reaction to form insoluble AgI. In short, AgI being formed quickly in FPT-0, the processes involving soluble iodide as a reactive species are strongly inhibited in this test, AgI formation being slower in FPT-1, those processes may become significant in the production of volatile iodine. Those processes are:

- reaction of I⁻ ions, formed by solubilisation in condensed steam of the soluble iodine species initially transported by the aerosol, with the paint of the condenser, leading to the release of volatile organic iodide compounds,

- radiolytic oxidation of I⁻ ions present in the sump, leading to the production in the sump and transfer to the containment atmosphere of molecular iodine I₂, subsequent reaction with painted condensors.

The FPT-1 data, taken as a whole, appear to be consistent with a slow Ag/I reaction process, allowing for the processes listed above to occur and determine the long term volatile iodine behaviour. FPT-0 data were consistent with a fast iodine trapping by silver, inhibiting those processes and the long term volatile iodine behaviour was essentially determined by the evolution of the gaseous iodine which was injected from the primary circuit during the bundle degradation phase. The results also show that organic iodides could very well be the major
contributor to the gaseous iodine fraction at the end of both tests. Those results have important applications for iodine chemistry code development and iodine source term evaluation as discussed in next sections.

IMPLICATIONS OF PHEBUS RESULTS FOR CONTAINMENT IODINE CHEMISTRY CODE DEVELOPMENT

The PHEBUS tests are the first opportunity for integral evaluation of iodine partitioning processes with prototypic mixes of radioactive and non-radioactive materials, radiation fields, temperatures and pressures. What is sought from the PHEBUS test results is a check that the current understanding of the chemistry of iodine as embodied in the computer codes is sufficient to predict adequately iodine concentrations in a reactor containment and the rates at which these concentrations are reached. In iodine chemistry codes, validated on the current knowledge of iodine chemistry, iodine concentrations and partitioning rates are determined from:

- deposition of soluble iodine aerosol (e.g., CsI) in the sump,
- formation of volatile forms of iodine (I₂ or organic iodides) from iodide ions I⁻ under radiation fields in the sump,
- transport of volatile iodine species from the sump into the bulk containment atmosphere,
- loss of iodine from the atmosphere by homogenous reaction or deposition on surfaces.

The PHEBUS test results indicate that the iodine behaviour in the containment cannot be described simply by those processes, mainly since the sump is not the only volatile iodine source.

On the short term (during the fission products release phase), PHEBUS results indicate that volatile iodine concentrations in the containment were essentially due to gaseous iodine injected by the primary circuit. Containment iodine chemistry codes consider that the iodine source to the containment is composed solely of condensed iodine aerosols. Calculations performed with the code IODE 4.2, developed at IPSN (Jacquemain, 1998), illustrate that during the main fission products release phase in PHEBUS tests, calculated gaseous iodine concentrations largely underestimate the actual ones (figure 10). Correct concentration levels may be temporarily obtained assuming an injection of gaseous molecular iodine I₂ in amounts corresponding to the experimentally measured ones (« I₂ injection effect » in figure 10).

On the long term, production of volatile forms of iodine can occur either in the aqueous phase or on painted surfaces in the model containment. Volatile iodine formation in the aqueous phase is known from laboratory studies to depend on the iodide concentration in the aqueous phase, the radiation dose to the aqueous phase, the temperature, the pH of the aqueous phase, and the presence of silver. The PHEBUS tests yielded results concerning the aqueous concentration of iodine, the effect of Ag, the solution pH that have implications on the modelling of severe reactor accident sequences in which the degradation results in a significant control rod material release to the containment. Substantial amounts of the released silver reached the PHEBUS model containment. Evidence to date from the reactor circuit is that silver was transported as mixed aerosol particles in the form of silver metal
within the reactor circuit. But, once it reached the reactor containment, it was oxidised by fairly powerful oxidising agents (probably, ozone and nitrous oxides produced by air radiolysis). When deposited in water, the partially oxidised silver could react with dissolved iodide I\(_2\) to form AgI(s), reducing substantially the aqueous iodine concentration and greatly reducing the rate of volatile iodine formation from the sump. The situation in the PHEBUS tests is, however, equivocal since the mechanisms which yielded the formation of AgI are not completely clarified.

Substantial efforts were made in the framework of the 4th EU Research Program on Severe Accident to improve the Ag/I formation modelling (Dickinson, 1997) and new models were implemented in European iodine chemistry codes such as IODE 4.2 (Jacquemain, 1998). These new models involve the silver oxidation state which was shown to be determinant in the Ag/I reaction kinetics. Calculations made for PHEBUS tests with IODE 4.2 show that the major difficulty in modelling the Ag/I reaction in the aqueous phase is to estimate from the experimental data parameters such as the silver specific surface and the Ag oxidation state. Indirect information may be obtained from aerosol size characterisation methods and post-test chemical analyses of the aerosol deposits\(^7\). The information on these parameters is however uncertain which could greatly affect the calculated concentration levels. IODE 4.2 calculations (figure 10) indicate that with a suitable choice of these parameters (silver specific surface of 100 m\(^2\)/kg and silver oxidised fraction of 10 % in weight\(^7\)), the increase in volatile iodine concentration after the washing phase in FPT-1 is correctly calculated. Sensitivity studies on those parameters showed that they are not influential in FPT-0 calculations (when varied in realistic ranges). The Ag/I molar ratio is so high in this experiment that the calculated Ag/I reaction is fast enough to inhibit the production of volatile iodine from the sump.

Models of organic iodide formation and behaviour under reactor accident conditions are not nearly as well developed as models of elemental iodine formation and behaviour. An effort of model development for these reactions is underway in the framework of the EU Research Program (Dickinson, 1997). Those reactions are not included in the current modelling of the IODE 4.2 code. This may explain why the volatile iodine concentrations calculated during the aerosol phase largely underestimate the experimental ones both in FPT-0 and FPT-1. Indeed, significant release of organic iodides probably occurred during those experimental phases.

In conclusion, a substantial work of development and validation of containment iodine chemistry codes is required to model the PHEBUS containment chemistry which occurred during FPT-0 and FPT-1, particularly in the field of Ag/I reaction modelling and models of organic iodides formation. The PHEBUS data base is however not sufficient, to date, to show that the necessary manipulations of the models can be extrapolated to reactor accident conditions. For instance, the amount of Ag released, its physical and chemical state may be strongly sequence-dependent. Results from several tests will have to be examined to have confidence in such extrapolation.

\(^7\) Aerosol mean median diametres are close to 3 μm in the containment, yielding a specific surface of the order of 100 m\(^2\)/kg. Those aerosols are composed partially of Ag (30 to 40 % in weight). Post-test analyses indicate that Ag aerosol material can be partially water-soluble (up to 10 % in weight), this water-soluble fraction was attributed by analysts to oxidised silver.
Figure 10: IODE 4.2 calculations and comparison with experimental data of the mass of iodine in suspension in the containment atmosphere (top) FPT-0 (bottom) FPT-1. Parameters retained for the Ag/I reaction modelling are a silver specific surface of 100 m²/kg, an oxidised Ag fraction of 10 % in weight. The Ag/I molar ratios determined experimentally are, respectively, close to 50 in FPT-1 and close to 2500 in FPT-0.
CONCLUSION

Implications of PHEBUS results for LWR iodine source term studies

The most important PHEBUS results for iodine source term studies are:

- the existence during Zircaloy-oxidation phases of significant fractions of gaseous iodine in the model circuit. Those fractions may be quite large (few tens %) in the hot leg of the circuit as indicated by FPT-1 results;
- the low production of gaseous iodine by sump radiolysis, due to the presence of Ag coming from the control rod;
- on the long term, organic iodides released from the painted condenser surfaces in the gas phase would dominate the volatile iodine fraction.

Those results have important implications when extrapolated to the reactor case. They would significantly impact on the late release of iodine in case of venting or in case of containment failure. Besides, organic iodides are more difficult to filter or otherwise remove from containment atmospheres than is elemental iodine. This also has substantial implications for reactor safety.

Future experiments

The PHEBUS data base will be extended with the FPT-2 test during which a significant reducing window will be maintained during bundle degradation. FPT-2 should thus help to correlate more definitely reducing conditions with gaseous iodine generation in the primary circuit. The following test FPT-3 will be performed with Boron carbide to study the impact of products resulting from the B$_4$C degradations on primary circuit chemistry and containment chemistry.

Concerning primary circuit chemistry, even if integral experiments, such as PHEBUS, prove more adequate to measure released fractions and chemical forms, the fact that chemical transformations in the primary circuit play an important role which can be different for different accidental sequences lead to the necessity to perform analytical studies to validate a primary circuit chemical model useful for the reactor case. Those analytical studies could involve the determination of gaseous iodine fractions and species as a function of location in a model circuit (conditions simulating a cold leg and a hot leg break), of reducing and oxidising conditions (various H$_2$/H$_2$O carrier gas mixtures), of fission products concentrations and of the presence of control rod material or not. Experimental programs to investigate those aspects are currently being discussed and may be proposed as programs to be performed in the framework of the next EU Research Program.

Concerning containment chemistry, experiments to study systematically the release of volatile organic iodides from reactor painted surfaces and other material such as liners, cables under representative conditions appear to be a priority. Besides, experiments to better delineate mechanisms of formation of gaseous iodine from water solutions in a range of conditions (effects of Ag, and B species, sump pH, irradiation, high temperature) needs to be pursued in separate effects experiments. In case of significant silver release, efforts should be made to determine for different reactor accident sequences, Ag aerosols oxidation state and specific surface. Some of those experiments are planned or already running in the framework of the PHEBUS project and EU programs.
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RADIOLYTIC OXIDATION OF MOLECULAR IODINE IN THE CONTAINMENT ATMOSPHERE

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ABSTRACT

In the severe accident containment atmosphere, radiation produces radicals and chemically reactive molecules such as ozone (O₃). Some of these species oxidize gaseous molecular iodine (I₂) into non-volatile iodine oxides, thereby reducing the inventory of volatile iodine in the containment atmosphere. The impact of radiation on gaseous I₂ chemistry is investigated by kinetic experiments under boundary conditions relevant to severe accidents. It is observed that I₂ decreases with time and radiation dose at room temperature, 80°C and 130°C. Iodine oxides (I₂O₅, I₄O₉) are formed as reaction products. Compared to steam-free conditions, presence of non-condensing steam does not significantly change the rate of the radiation-induced I₂ decrease. The relative I₂ decrease slows down with increasing initial I₂ concentration. Modelling of the experimental data reveals the important influence of the formation of the oxidizing species such as ozone on the I₂ decrease. The inclusion of radiation-induced I₂ oxidation derived from this study represents an important improvement of the current IMPAIR modelling of gas phase chemistry, and also of source term predictions.

1 INTRODUCTION

The prediction of the iodine source term to the environment, as well as the accident management measures, require an adequate knowledge of the radiiodine chemistry in the containment during severe accidents. The amount of volatile iodine species is influenced by a variety of chemical reactions depending on the specific boundary conditions. An important reaction is the oxidation of molecular iodine (I₂) in the containment atmosphere by chemically reactive species such as ozone (O₃) which are produced by radiolysis of the containment atmosphere. The reaction products are iodine oxides such as I₂O₅, I₄O₉, which will be abbreviated furtheron generally as IOₓ. These iodine oxides are non-volatile and either dissolve into aqueous droplets (formation of iodate, IO₃⁻) under condensing-steam conditions or settle down as aerosols (after condensation and agglomeration). In both cases, the volatile species I₂ is transformed into non-volatile iodine species.

In the severe accident iodine code IMPAIR (Günday 1992), the radiolytic oxidation of I₂ is represented by the reaction of I₂ with O₃. The modelling is based on experimental data in dry air, i.e. in the absence of steam (Vikis 1985, Vikis 1986). It is further assumed in IMPAIR that the I₂ concentration in the containment is much lower than the estimated concentration of O₃ (1 μl/l). The concentration of 1 μl O₃/l was estimated in (Vikis 1986) for containment
atmospheres during severe accidents. With this assumption, the original bi-molecular reaction kinetics in (Vikis 1985) reduces to a pseudo-first order kinetics:

\[ \frac{d[I_2]}{dt} = - k[I_2] \] (1)

Square brackets in Eq. 1 denote molar concentrations of I₂. The rate constant (k) corresponds to short half-lifes for the I₂ decrease: 125 min at 20°C, 22 min at 80°C and 8 min at 130°C. Consequently, IMPAIR predicts a fast conversion of gaseous I₂ into iodine oxides. IMPAIR further assumes instantaneous conversion of the iodine oxides into iodate which is modelled as an aerosol in the gas phase.

A theoretical analysis of the impact of radiolysis on I₂ in steam-containing atmospheres concluded that steam changes the reaction mechanism (e.g. formation of reactive OH radicals) and, subsequently, the rate of the I₂ oxidation should be enhanced (Sagert 1989).

Studying the effect of steam on the radiation-induced decrease of gaseous I₂ was therefore the main objective of the experiments in this report. It is aimed at generating a conclusive database and modelling for severe accident iodine codes.

2 EXPERIMENTAL

Batch-type experiments were performed by irradiating spherical glass flasks (Duran, volume 1 l) sealed with a septum and containing the I₂ vapour.

A ⁶⁰Co irradiation source was used with dose rates of 1.9 kGy/h and 20 kGy/h, selected by positioning the glass flasks at several distances to the source. Irradiation times were varied between 10 minutes and 72 hours.

For I₂ concentrations in the range of 1 mg/l (4·10⁻⁵ mol/l) to 5 mg/l (2·10⁻⁵ mol/l) small glass ampules were filled with weighed amounts (1-5 mg) of I₂ crystals. The sealed ampules were then destroyed in the flasks. Rapid vaporisation of the I₂ crystals and homogeneous distribution of gaseous I₂ in the flask follows at higher test temperatures. In tests at room temperature, slight local heating was necessary for I₂ vaporisation. I₂ concentrations of 0.15 mg/l were obtained through the Dushman reaction (5 I + IO₃⁻ + 6 H⁺ → 3 I⁺ + 3 H₂O), i.e. by introducing stochiometric amounts as aqueous iodide and iodate solutions.

Tests at 1.9 kGy/h were carried out at room temperature (about 20°C), at 80°C using water baths, and at 130°C using oil baths. Irradiations at 20 kGy/h were not temperature-controlled, but measurements indicated temperatures of about 40°C due to the high dose rate.

In the tests the amount of steam was varied. "Dry air" was obtained by flowing air over silica gel. For presence of steam in room temperature irradiations, air was saturated with steam at slightly lower than room temperature (± 0.02 mg steam/l). Tests at 80°C and at 130°C were carried out both in dry air and at a steam concentration of 200 mg/l, obtained by adding water during flask preparation. Prior to the irradiation, the flasks were shortly vented to avoid overpressure.

The post-test analysis was specific with respect to I₂. Following the irradiation, the flask inventory was washed by injecting defined amounts (typically 5 ml) of organic solvents
(CCl₄ or toluene) through the septum. This removed the remaining I₂ which was then determined photometrically by measuring the extinction at 506 nm and at 308 nm.

In a few tests, other iodine species were also analyzed. The flask inventory was then washed with a mixture of the organic solvent and water (pH 3). The aqueous phase was analysed by High Performance Ion Chromatography (HPIC) for iodide and iodate.

3 RESULTS AND DISCUSSION

3.1 Experimental Data

A pronounced scatter of the measured I₂ decreases was observed at the same test conditions. Therefore, a large number of irradiation tests were performed allowing averaging of the I₂ decreases at identical boundary conditions.

The I₂ concentrations decrease with time on irradiation at room temperature (Fig. 1). The error bars reflect the standard deviations upon averaging the test results. For a given irradiation time, lower I₂ fractions are found at the higher dose rate.

![Graph showing I₂ fraction (%) vs. time (h) for different dose rates with error bars.](image)

**Fig. 1** I₂ fractions as function of irradiation time at room temperature. For all data the initial I₂ concentrations are 4×10⁻⁶ mol/l (1 mg/l). The dashed-dotted line corresponds to the IMPAIR model.

The apparent dependency on dose rate in Fig. 1 vanishes upon re-scaling the I₂ fractions with the dose (Fig. 2). A remaining, slight difference of the I₂ fractions at 1.9 kGy/h and 20 kGy/h is attributed to the enhanced temperature at the higher dose rate as compared to room temperature valid for the 1.9 kGy/h data.

No significant effect of steam presence is identified in Fig. 2. A possible effect of steam on the I₂ fractions could be hidden by the limited accuracy of the data.
Fig. 2  I$_2$ fractions as function of dose at room temperature. For all data the initial I$_2$ concentrations are 4 x 10$^{-6}$ mol/l (1 mg/l).

Fig. 1 also reveals a more complex behaviour of the experimental data in comparison with the IMPAIR model. The IMPAIR model does not consider the effects of different dose rates or doses and only predicts a simple exponential decay of I$_2$ in the presence of radiation irrespective of the actual dose rate.

Figs. 3 and 4 show I$_2$ fractions at 80°C and at 130°C at a dose rate of 1.9 kGy/h. As with the lower temperature, there is no significant effect of steam. However, lowering the initial I$_2$ concentrations from 5 mg/l to 0.15 mg/l accelerates the rate of I$_2$ decrease significantly.

Iodine oxides as reaction products could be partially observed in the form of fine, bright deposits at the flask surface. Upon contacting these deposits with water, they were readily dissolved by hydrolyzing to iodate. This observation is consistent with the IMPAIR modelling where iodate is assumed to be the direct reaction product of the I$_2$/O$_3$ reaction.

Comparison of the Figs. 2, 3 and 4 reveals a slower I$_2$ decrease at higher temperature. At room temperature, the half-dose (50% I$_2$ decay) is 25 kGy, at 80°C it is 40 kGy and at 130°C it is 80 kGy. These values were obtained with the same initial I$_2$ concentration of 1 mg/l. This observation seems to contradict the simple picture of I$_2$ conversion to IO$_3$ by ozone put forward in (Vikis 1985) from which the reaction between I$_2$ and O$_3$ proceeds faster at higher temperatures and a more rapid I$_2$ decay should result. The apparent discrepancy will be discussed and resolved in Chapter 3.3.
Fig. 3  \( I_2 \) fractions as function of dose at 80°C and 1.9 kGy/h. Initial \( I_2 \) concentrations were at 2\( \times 10^{-5} \) mol/l (5 mg/l), 4\( \times 10^{-6} \) mol/l (1 mg/l) and 5.9\( \times 10^{-7} \) mol/l (0.15 mg/l).

Fig. 4  \( I_2 \) fractions as function of dose at 130°C and at 1.9 kGy/h. Initial \( I_2 \) concentrations were 2\( \times 10^{-5} \) mol/l (5 mg/l), 4\( \times 10^{-6} \) mol/l (1 mg/l) and 5.9\( \times 10^{-7} \) mol/l (0.15 mg/l). The lines are drawn to guide the eye.
3.2 Data Analysis

The experimental observations cannot be described by the simple exponential model in IMPAIR, cf. Eq. 1. A major reason is the assumption in IMPAIR of a large excess of O₃ over I₂ at all times, which is not fulfilled in the present tests since these start with zero O₃. Moreover, separate irradiated tests without I₂ show that the O₃ formation is not instantaneous. Consequently, O₃ formation has to be modelled for analysis of the present data. It is stressed that O₃ is considered in this work to represent all oxidation partners for I₂. Atomic oxygen being another product in the irradiated atmosphere could also participate in the oxidation of I₂.

The following model contains processes which formed the basis of the data analysis:

- Formation of O₃ by air or air/steam radiolysis (k₁)
- I₂/O₃ reaction with iodine oxides (IOₓ) as reaction products (k₂)
- Radiation-induced decomposition of O₃ (k₃)
- Radiation-induced decomposition of iodine oxides with I₂ as reaction product (k₆)

Rate constants k are denoted in the brackets.

The corresponding model equations are:

\[
\frac{d[I₂]}{dt} = -k₁D - k₂[O₃][I₂] + k₆D•0.5•[IOₓ] \quad (2)
\]

\[
\frac{d[O₃]}{dt} = k₁D - k₂[O₃][I₂]•F - k₃[O₃]•D+ k₆D•0.5•[IOₓ] \quad (3)
\]

Square brackets indicate molar concentrations (mol/l)

D Dose rate (kGy/h)

F Stoichiometric factor (F≈3.9 according to (Vikis 1985))

The rate constants for O₃ formation (k₁) and decomposition (k₃) were determined from separate tests without I₂, but under the same boundary conditions (Tab. 1).

Tab. 1   Rate constants for formation and decomposition of O₃ in steam/air mixture during irradiation in tests without I₂.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>k₁ (mol⁻¹•s⁻¹•(kGy/h)⁻¹)</th>
<th>k₃ (s⁻¹(kGy/h)⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>7.0•10⁻¹¹±1.0•10⁻¹¹</td>
<td>3.3•10⁻⁵±0.6•10⁻⁵</td>
</tr>
<tr>
<td>80</td>
<td>5.4•10⁻¹¹±0.8•10⁻¹¹</td>
<td>2.4•10⁻⁴±0.4•10⁻⁴</td>
</tr>
<tr>
<td>130</td>
<td>4.4•10⁻¹¹±0.6•10⁻¹¹</td>
<td>7.6•10⁻⁴±1.4•10⁻⁴</td>
</tr>
</tbody>
</table>

The analysis of the I₂ decrease data was performed by determination of two unknown parameters (k₂, k₆) and using two known parameters and considering their accuracy (k₁, k₃). Best fits of the model to data in steam/air atmospheres are shown in Fig. 5 (20°C), Fig. 6 (80°C) and Fig. 7 (130°C).
Fig. 5  Modelling of experimental $I_2$ fractions as function of the dose at $20^\circ$C and 1.9 kGy/h. The straight lines are best fits to the experimental data if all four processes represented by Eqs. (2) and (3) are taken into account. The dashed lines are obtained as best fits when the hypothetical radiation-induced IO$_x$ decomposition is excluded.

Parameters:
\[ k_1 = 7.10^{-11} \text{ mol}^{-1}\text{L}^{-1}\text{s}^{-1}\text{(kGy/h)}^{-1} \]
\[ k_2 = 2.10^{-5} \text{ s}^{-1}\text{(kGy/h)}^{-1} \]
\[ k_3 = 0 \text{ or } 4.10^{-6} \text{ s}^{-1}\text{(kGy/h)}^{-1} \]

Fig. 6  Modelling of experimental $I_2$ fractions as function of dose at $80^\circ$C and 1.9 kGy/h. The straight lines are best fits to the experimental data if all four processes represented by Eqs. (2) and (3) are taken into account. The dashed lines are obtained as best fits when the hypothetical radiation-induced IO$_x$ decomposition is excluded.

Parameters:
\[ k_1 = 5.4.10^{-11} \text{ mol}^{-1}\text{L}^{-1}\text{s}^{-1}\text{(kGy/h)}^{-1} \]
\[ k_2 = 9.9.10^3 \text{ l}\text{mol}^{-1}\text{s}^{-1} \]
\[ k_3 = 2.4.10^{-1} \text{ s}^{-1}\text{(kGy/h)}^{-1} \]
\[ k_4 = 0 \text{ or } 1.10^{-6} \text{ s}^{-1}\text{(kGy/h)}^{-1} \]
Fig. 7  Modelling of experimental I₂ fractions as function of dose at 130°C and 1.9 kGy/h. The straight lines are best fits to the experimental data if all four processes represented by Eqs. (2) and (3) are taken into account. The dashed lines are obtained as best fits when the hypothetical radiation-induced IOₓ decomposition is excluded.

Parameters:

\[ k₁ = 4.4 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \cdot (\text{kGy/h})^{-1} \]
\[ k₂ = 1.5 \times 10^{4} \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \]
\[ k₃ = 7.6 \times 10^{-4} \text{ s}^{-1} \cdot (\text{kGy/h})^{-1} \]
\[ k₄ = 0 \text{ or } 2 \times 10^{6} \text{ s}^{-1} \cdot (\text{kGy/h})^{-1} \]

It turns out from fitting the data, at the initial I₂ concentrations in the present experiments, that the O₃ formation rate \( k₁ \) is the most influential parameter. On the other side, the influence of the I₂/O₃ reaction rate constant \( k₂ \) is weak. This leads to a broad band of fitted \( k₂ \) values as shown in Tab. 2.

Tab. 2  Rate constants for the I₂/O₃ reaction obtained from the analysis of the present data, compared to values from (Vikis 1985).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( k₂ ) (this work) (l·mol⁻¹·s⁻¹)</th>
<th>( k₂ ) (Vikis 1985) (l·mol⁻¹·s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>100...10000</td>
<td>2250</td>
</tr>
<tr>
<td>80</td>
<td>300...3000</td>
<td>9900</td>
</tr>
<tr>
<td>130</td>
<td>500...15000</td>
<td>15000</td>
</tr>
</tbody>
</table>

Tab. 2 reveals a satisfactory overlap of the rate constants \( k₂ \) from this work and from (Vikis 1985). Since the Vikis data were determined with higher accuracy, it is concluded that they can be retained for future modelling of the I₂/O₃ reaction in IMPAIR.

By comparison of straight and dashed lines in Figs. 5-7, the importance of including the IOₓ decomposition in the model is obvious. This leads to remaining I₂ fractions even at
very large doses. The radiation-induced IO\textsubscript{x} decomposition producing I\textsubscript{2} (seen as a backward reaction to the I\textsubscript{2}/O\textsubscript{3} reaction) is considered in this study as a hypothetical reaction which leads to model predictions being consistent with the data also at high doses. Rate constants for the IO\textsubscript{x} decomposition (k\textsubscript{x}) were obtained from the above multi-parameter fits (see Figs. 5-7). However, future specific tests would be desirable for more precise determination of the corresponding rate constant k\textsubscript{x}.

3.3 Modelling in Severe Accident Iodine Codes

Effect of Steam

The analysis of the experimental data from this study showed that the presence of steam does not significantly change the rate of radiation-induced I\textsubscript{2} oxidation. The radiation-induced I\textsubscript{2} oxidation can be described by the sum of the processes given in the preceding section: O\textsubscript{3} formation and decomposition, I\textsubscript{2}/O\textsubscript{3} reaction and IO\textsubscript{x} decomposition. The already existing modelling of the I\textsubscript{2}/O\textsubscript{3} reaction has to be extended to include realistic O\textsubscript{3} concentrations. At the same time the rate constants from (Vikis 1985) in steam-free environment could be used also in steam atmospheres prevailing in severe accidents.

Effect of modelling Ozone

In the containment atmosphere during severe accidents, I\textsubscript{2} concentrations are expected to be much lower than in the current tests. This means that the O\textsubscript{3} concentration would be in large excess over the I\textsubscript{2} concentration, as assumed already in IMPAIR. The iodine chemistry would therefore not have a significant influence on the O\textsubscript{3} level. Consequently, O\textsubscript{3} formation and decomposition does not need to be modelled in iodine codes once its concentration is known with sufficient accuracy. On the other side, as turns out from the data analysis, the absolute O\textsubscript{3} concentration is a decisive factor for the overall process of the radiation-induced I\textsubscript{2} oxidation. Own tests on the build-up of O\textsubscript{3} show that an equilibrium is reached at high doses, given by the net effect of formation and decomposition of O\textsubscript{3}. The equilibrium concentration may be influenced by other reactions, e.g. the decomposition at surfaces such as painted containment walls, steel, and aerosols. These effects cannot be quantified at present.

The importance of knowing realistic O\textsubscript{3} concentrations is demonstrated exemplarily at 130°C and initial I\textsubscript{2} concentrations of 10\textsuperscript{-9} mol/l (severe accidents) in Fig. 8. A comparison is made between the current IMPAIR model, assuming three different O\textsubscript{3} concentrations, and the new model from this study. The parameter range of O\textsubscript{3} concentrations, 0.2-20 µg/l, corresponds to estimations in (Vikis 1986). Very different I\textsubscript{2} decay rates result showing a distinct sensitivity of the I\textsubscript{2} decrease on O\textsubscript{3} concentration. The new model, which considers radiolytical O\textsubscript{3} formation and decomposition as given in Eq. (3) is given as the straight line and does not coincide with any of the IMPAIR predictions. A half-life of about 30 minutes is obtained for the conversion of I\textsubscript{2} into IO\textsubscript{3}/iodate with the new model at 130°C. To compare, IMPAIR presently predicts a half-life of about 8 minutes at the same temperature.

Effect of Temperature

Further own tests in irradiated I\textsubscript{2}-free gas phases indicate that the O\textsubscript{3} concentration decreases with increasing temperature. This is the key to understand why the radiation-induced I\textsubscript{2} oxidation decreases with increasing temperature as stated in Section 3.1. The net production of O\textsubscript{3} as the reaction partner for I\textsubscript{2} slows down with increasing temperature. This
effect counteracts the higher I$_2$/O$_3$ reaction rate with increasing temperature (as modelled in IMPAIR). As a net effect, on the long term, the radiation-induced I$_2$ oxidation slows down with increasing temperature. This temperature effect is an important result of this study and needs to be included in the modelling.

![Graph](image)

**Fig. 8**  I$_2$ fractions as function of time at 130°C, predicted by the new model of this study with [I$_2$]$_{0}$=10$^{-9}$ mol/l and compared to the IMPAIR modelling with different O$_3$ concentrations.

**Effect of IO$_x$ Decomposition**

The experimental observation that a small level of I$_2$ remains even at very high doses means that the radiation-induced IO$_x$ decomposition as a so far hypothetical I$_2$-producing backward reaction could play a role, particularly at higher conversions of the I$_2$/O$_3$ reaction. Further studies are required on such I$_2$-producing reactions.

4 **CONCLUSION**

The kinetics of the radiation-induced I$_2$ oxidation in the gas phase was investigated experimentally at severe accident-relevant temperatures (20-130°C) and dose rates (2-20 kGy/h). Iodine oxides are the primary reaction products and these are readily converted into iodate upon contact with aqueous phases. Gaseous I$_2$ decreases with increasing dose. No significant effect of steam on the I$_2$ decrease was observed. The I$_2$ oxidation rate slows down with increasing temperature.

Analysis of the data reveals that O$_3$ plays an important role in the radiation-induced I$_2$ oxidation since it provides the necessary reaction partner for the I$_2$/O$_3$ reaction. O$_3$ is considered to represent all oxidants in the irradiated atmosphere that convert I$_2$ into IO$_x$. A new model was developed which contains the I$_2$/O$_3$ reaction, radiation-induced O$_3$ formation and decomposition reactions, and a hypothetical decomposition of the iodine oxides. This
model allows to analyse the experimental data correctly. This analysis also reveals the paramount importance of the O$_3$ concentration on the radiation-induced I$_2$ oxidation. Previous work on the I$_2$/O$_3$ reaction in steam-free environments can now be used also for steam-containing atmospheres.

The new model represents an important progress over the existing modelling in IMPAIR which only considers the I$_2$/O$_3$ reaction by assuming an estimated O$_3$ concentration. Despite some still missing data on ozone production and on decomposition of the iodine oxides, the new model describes the conversion of volatile I$_2$ into iodine oxides/iodate in a much more reliable way. Applying the new model to the containment atmosphere, and starting with no O$_3$ and an initial I$_2$ concentration of 10$^{-9}$ mol/l, half of the I$_2$ is converted into iodine oxides/iodate after about 30 minutes at 130°C. This change in iodine speciation influences the overall iodine chemistry in the containment, source term evaluations and accident management measures.

ACKNOWLEDGMENTS

The authors thank C. Hundebeck-Brinker for contributing data on ozone formation during radiolysis in air/steam mixtures. This project was funded by the Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (BMBF).

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CHLORINE RELEASE BY PYROLYSIS FROM HYPALON CABLE INSULATION MATERIAL AND ITS EFFECT ON IODINE SPECIATION IN THE CONTAINMENT

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ABSTRACT

In this work the dehydrochlorination of hypalon by pyrolysis was studied applying online activity measurements and neutron activation analysis. Temperature range studied varied from 200°C to 300°C. For comparison one experiment was conducted at 500°C. Object of the research was to determine the temperature, where the chlorine release takes place, as well as the chlorine release fraction. By comparing different experiments conclusions about the release mechanisms could be made. Based on the acquired data estimates of the amount of hydrochloric acid released to the containment building in a severe accident were also calculated. As a result it can be concluded, that the amount of chlorine release from the hypalon cable material is significant and will have an effect on iodine behaviour in a severe accident.

1. INTRODUCTION

In a severe nuclear accident iodine is one of the fission products that are most easily released from the reactor core. About one half of the iodine core inventory is estimated to be released to the reactor containment building, where it deposits mainly in the water pools (Beahm, 1992A). There is evidence that pH largely determines the extent of I₂ in aqueous solutions (Deane, 1986; Vikis, 1989). When pH levels fall below ~7, the formation of I₂ will take place in irradiated iodide solutions. In severe reactor accidents this will in turn increase the amount of I₂ in the containment atmosphere and consequently the iodine source term.

The acidity or basicity of the water pool in containment is determined by pH-control chemicals and by the materials that are released as a result of the accident. Most important of the released basic materials are fission product compounds such as cesium hydroxide or cesium borate and core-concrete aerosols. Most important acids in containment includes nitric acid (HNO₃), produced by irradiation of water and air, and hydrochloric acid (HCl), produced by heating or irradiation of electrical cable insulation (Beahm, 1992B).

Hypalon is a registered trademark of DuPont for chlorosulfonated polyethylene rubbers (C₈₅H₁₅₇Cl₁₃SO₂). It is widely used as cable insulation material in nuclear power stations due to its excellent flame and radiation resistance. As-fabricated material contains
approximately 17.5 wt-% chlorine. The chlorine content of hypalon is emphasised here, because it has been found that the vapour produced in the radiolysis or pyrolysis of hypalon is mostly HCl (Fridemo, 1988; Liljenzin, 1990). Pyrolysis has previously been described as a three-stage process with each successive stage occurring at a higher temperature (Smith, 1966):

- loss of SO₂ groups near 200°C
- loss of HCl near 300°C
- breakdown of the hydrocarbon chain near 400°C

Surveys of accident sequence calculations that employed the Source Term Code Package often predicted temperatures in excess of 300°C in a BWR containment (Gieseke, 1984; Denning, 1986).

Besides decreasing the pH of the water pool there are other unfavourable effects that result from the production of HCl in the containment. There is for example uncertainty in the formation of I₂ during irradiation of water pools that contain both chloride and iodide ions. There is also indication, that both capacity and retention of iodine species in charcoal filters will be degraded, when chlorine species are present (Beahm, 1992B).

2. EXPERIMENTAL APPARATUS AND METHODS

The samples of hypalon cable material were pyrolysed in a nitrogen flow using a programmable Entech ETF 30-12 tube furnace. The hot gas flowing from the furnace was cooled with pressurised air in a porous tube diluter. The objective of the design was to maintain stable flow conditions, while monitoring the release rate of chlorine from cable insulation material on-line with a gamma detector. In the on-line experiments the germanium detector was placed perpendicular to the sample 270 mm from the centre line of the furnace. The detector was shielded from down stream with 50 mm thick lead wall to avoid pulses coming from possible deposition to the walls. Since chlorine was expected to be mainly released in the form of hydrochloric acid, which has a boiling point at -84.9°C, condensation to the walls was not expected. Each measurement was 60 seconds long, so that good statistics could be achieved without compromising either time or temperature resolution. Schematic picture of the experimental apparatus is presented in figure 1.

2.1 Preparation of the samples

The samples used in the experiments were cut from an unused hypalon cable insulation obtained from a Finnish utility Teollisuuden Voima (TVO). For the first five on-line release experiments approximately 40 mm long (379...676 mg) strips were made. In addition, the sample used in the 6th experiment was cut into 135 pieces so that the effect of increased surface area could be verified. Samples were made as large as possible. Large sample size was thought to be more representative, when estimating the chlorine release in a reactor accident. Dimensions of all the samples are presented in the table 1. It should be noted, that the surface area for the sample in the sixth experiment is calculated by assuming that all 135 pieces are of uniform size. After the release experiments, all samples were cut into small pieces to minimise the geometric error, before their chlorine content were measured with neutron activation analysis.
Table 1. The dimensions of the samples used in the experiments.

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<td>=1990</td>
<td>=3.9</td>
</tr>
</tbody>
</table>

2.2 Neutron activation analysis

Neutron activation analysis (NAA) was applied to measure the initial chlorine content of the insulation material. The same method was applied again after the release experiments to determine the chlorine release fraction from the samples and to verify the on-line results. This method is much more accurate than the on-line measurements and it could be applied also in experiments of longer duration. However release rates cannot be obtained by NAA, if the vaporisation rate is time dependent.

To determine the chlorine content of the insulation with neutron activation analysis five samples with masses ranging from 414 mg to 604 mg were prepared. These samples were activated in the Triga Mark 2 reactor for 5 seconds in a neutron flux of $4 \times 10^{12}$ n/cm²s. After the activation the samples were left to decay for 10 minutes. During the 10 minute period
short lived aluminium isotope decomposed and therefore did not interfere with the measurements. The duration of the gamma measurements was 5 minutes and they were performed from the distance of 150 mm. To determine the amount of chlorine in the samples the activities were compared with a similarly activated 52.4 mg $^{38}$Cl-standard. The standard was prepared by mixing known KCl-solution with activated carbon. Also the activity of a 8.47 mg backup standard as well as three control samples and the background of the laboratory were measured.

The measured chlorine content of the samples varied between 15.6% and 16.1% (66.7...95.7 mg) the average being 15.82%. The result seems to agree well with the values found in the literature. The confident to the analysis was increased by the facts that the variance in the measurements were relatively small, difference from known chlorine content of the control samples was less than 2% and the chlorine background in the laboratory was below detection limit.

2.3 On-line chlorine release experiments

For the on-line gamma measurements, cable insulation samples were activated in a TRIGA Mk-2 nuclear reactor. During a short 1...2 minutes activation period some of the chlorine transformed into $\beta$-active $^{38}$Cl-isotope, which has a half-life of 37.3 minutes. In addition to $\beta$-particles, $^{38}$Cl-nuclide emits characteristic gamma radiation in 1642, 2167 and 3760 keV energies with relative intensities of 85%, 100% and 5% respectively. From the areas of these gamma peaks the concentration of chlorine in the samples could be determined.

In the experiments the release of chlorine from the cable insulation material was studied at temperatures between 200°C and 300°C. An activated sample was placed in a 50 mm long crucible made of glazed porcelain. The crucible was then injected into a tube furnace over the second heating element and temperature of the furnace was raised to the operating level. A thermocouple controlling the second zone of the furnace was in contact with the crucible. During the experiment nitrogen flow of 4.0 l/min (NTP) was directed through the processing tube. The decreasing intensity of the 1642 keV gamma peak was measured as the sample was heated in the flow reactor. The vaporisation of chlorine could be calculated from the difference between the measured values and the natural decay rate.

2.4 Experimental matrix

Altogether six experiments were conducted at different gas temperatures. In the first three tests the chlorine release was studied at 200°C, 250°C and 300°C. In the fourth experiment the sample was kept at 300°C for 24 hours after the on-line measurements, in order to examine the long term chlorine release from the material. In the fifth experiment the temperature of the furnace was raised up to 500°C, so that the effect of higher temperatures could be investigated. In the last experiment the effect of increased surface area was studied with a sample that was cut into pieces. The experimental matrix is presented in table 2.
Table 2. The experimental matrix of the on-line measurements.

<table>
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<td>5</td>
<td>173</td>
<td>120</td>
<td>Cut Sample</td>
</tr>
</tbody>
</table>

3. RESULTS

First in this chapter, as a result from the on-line experiments, the temperature and the duration of the chlorine release are presented. Then, as a result from the neutron activation analysis, the total amount of chlorine vaporised is calculated. After that, the relative importance of factors affecting the release is studied, by comparing results from these two methods. Finally, the release depth of chlorine from the samples is calculated, in order to estimate the chlorine release in a severe nuclear accident.

3.1 Duration and temperature of the chlorine release in the experiments

As an example the measured values from the sixth on-line experiment are presented in figure 2. In the figure the measured intensity is compared with the natural decay rate of radioactive chlorine and with the furnace temperature. The chlorine release from the sample is taking place, when the measured intensity is not following a parallel line with the natural decay rate.

It can be seen from the figure, that the release begins, when the temperature of the furnace increases above 220°C. In this experiment, the chlorine vaporisation lasts approximately 30 minutes and then seems to almost cease. In order to verify, if the release was stopped, the decay coefficient for the measured activity was calculated between 80 and 173 minutes. It was found, that the estimated value was very close to the natural decay coefficient ($\lambda_n = 0.0186 \text{ min}^{-1}$) of radioactive chlorine. Thus the vaporisation was assumed to be stopped.
Fig. 2  Measured intensity compared with the natural decay rate of Cl-38 isotope and the furnace temperature in the 6th experiment.

The estimated decay coefficients for all experiments as well as the duration and the rate of vaporisation are presented at table 3. As can be seen from the table, the vaporisation is virtually ended after approximately 30 minutes. The only exception to this was the second experiment, which was done at the lowest temperature.

Table 3. The duration and the rate of the chlorine release in the on-line experiments.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>$\lambda$ calculated between [min]</th>
<th>Decay coefficient $\lambda$ [min$^{-1}$]</th>
<th>Duration of the release [min]</th>
<th>Release rate [mg/s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>60...169</td>
<td>0.0186</td>
<td>24</td>
<td>5.0E-3</td>
</tr>
<tr>
<td>2.</td>
<td>80...162</td>
<td>0.0192</td>
<td>33</td>
<td>4.1E-3</td>
</tr>
<tr>
<td>3.</td>
<td>60...145</td>
<td>0.0186</td>
<td>29</td>
<td>5.0E-3</td>
</tr>
<tr>
<td>4.</td>
<td>70...160</td>
<td>0.0186</td>
<td>33</td>
<td>4.3E-3</td>
</tr>
<tr>
<td>5.</td>
<td>60...137</td>
<td>0.0184</td>
<td>31</td>
<td>6.8E-3</td>
</tr>
<tr>
<td>6.</td>
<td>80...173</td>
<td>0.0188</td>
<td>33</td>
<td>9.7E-3</td>
</tr>
</tbody>
</table>

3.2 Release fraction of chlorine from the samples

The release fraction of chlorine from the samples can be calculated from the difference between the measured intensities and the natural decay as follows:

$$M_{vap}(t) = \frac{I_{en}(t) - I(t)}{I_{en}(t)} \times 100$$  \hspace{1cm} (1)
where \( M_{\text{vol}}(t) \) is the release fraction in per cents at time \( t \), \( I_0 \) is the initial intensity of the sample corrected with natural decay rate and \( I(t) \) is the measured value. The cumulative release of chlorine can be evaluated by multiplying the release fraction with the initial chlorine mass of the sample. The cumulative release in the sixth experiment as a function of time is presented in figure 3. Since the statistical accuracy deteriorates towards the end of the experiment, an averaged value for the release is also presented.

![Cumulative release of chlorine from the sample in the sixth experiment.](image)

**Fig. 3** Cumulative release of chlorine from the sample in the sixth experiment.

Since the on-line measurements were done without a standard, total chlorine vaporisation was determined after the experiment applying neutron activation analysis (NAA). Results from the on-line measurements and NAA are compared in table 4. Also the mass of the samples, their chlorine content, mass loss during the experiment, chlorine concentration after the experiments and estimated chlorine release depths are presented in the same table.

From experiments 1 to 3 done at temperatures between 200°C and 300°C, the release fraction of chlorine was measured with NAA to be between 9.0% and 12%. Also the on-line measurements yielded similar results. Since vaporisation rate of chlorine dramatically decreased after 30 minutes although the release was not complete, it was assumed that the fast vaporisation took place only from the surface of the samples. This assumption was tested in the experiments 4 and 6.

In the fourth experiment the sample was kept at 300°C for 24 hours. From the on-line measurements the fast release fraction of chlorine at the beginning of the experiment could be estimated to be approximately 8.0%. From the difference between NAA and on-line measurements it was calculated that approximately 6% of the chlorine inventory had vaporised after this initial release.
Table 4. The release of chlorine from hypalon cable insulation material.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Sample Mass [mg]</th>
<th>Cl-mass [mg]</th>
<th>Mass loss [%]/[mg]</th>
<th>Chlorine release NAA/Online [%]</th>
<th>Chlorine release NAA/Online [mg]</th>
<th>Chlorine mass frac. at the end [%]</th>
<th>Release depth NAA Online [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>379</td>
<td>60</td>
<td>24 / 92</td>
<td>12 / 14</td>
<td>7.0 / 8.2</td>
<td>19</td>
<td>0.08</td>
</tr>
<tr>
<td>2.</td>
<td>559</td>
<td>88</td>
<td>7.5 / 42</td>
<td>9.0 / 7.9</td>
<td>8.0 / 6.9</td>
<td>16</td>
<td>0.06</td>
</tr>
<tr>
<td>3.</td>
<td>520</td>
<td>82</td>
<td>21 / 109</td>
<td>10 / 10</td>
<td>8.6 / 8.1</td>
<td>18</td>
<td>0.07</td>
</tr>
<tr>
<td>4.</td>
<td>661</td>
<td>105</td>
<td>23 / 155</td>
<td>14 / 8.0</td>
<td>14 / 8.4</td>
<td>18</td>
<td>0.10</td>
</tr>
<tr>
<td>5.</td>
<td>676</td>
<td>107</td>
<td>53 / 360</td>
<td>12 / 6.1</td>
<td>13 / 6.5</td>
<td>30</td>
<td>0.09</td>
</tr>
<tr>
<td>6.</td>
<td>647</td>
<td>102</td>
<td>26 / 167</td>
<td>19 / 18</td>
<td>19 / 18</td>
<td>17</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Since the chlorine vaporisation was assumed to take place from the surface of the sample, increasing the surface to volume fraction should also lead to a greater release. This was tested in experiment six by cutting the sample into 135 pieces. The duration of the vaporisation remained in approximately 30 minutes as in previous experiments, but the release fraction almost doubled to 19%. It was concluded that both experiments 4 and 6 strongly supported the hypothesis of fast chlorine vaporisation taking place from the surface.

In order to study the effect of elevated temperature to the vaporisation, experiment five was performed at 500°C. From the NAA results it can be seen, that higher temperature did not increase the chlorine release from the sample, even though the total mass loss during the experiment was significantly greater. Large difference between the on-line and the NAA results suggest though, that the release mechanism was not similar as before. Instead of vaporising as HCl, some of the chlorine release likely took place in a liquid form. Also an interesting result was, that exposure to higher temperatures increased significantly the chlorine mass fraction of the samples. In every experiment hydrocarbons seemed to be released at least as readily as chlorine. After the experiment done at 500°C the chlorine mass fraction of the sample had increased from initial 15.8% up to 30%.

3.3 Visual observation of the samples

The sample from the second experiment, in which the furnace was kept at 200°C, had retained its blue colour and most of its elasticity. In experiments one and three, which were performed at about 300°C, the blue colour of the samples was faded and their elasticity was
vanished. In experiment four, where the sample was kept at 300°C for 24 hours, the colour was bleached even more. Otherwise the sample seemed to resemble samples one and three. After experiment five, which was performed at 500°C, the sample had blackened and become fragile. In addition, there were droplets of sticky material on the surfaces of the sample. The pieces of the sliced sample, used in the sixth experiment, had adhered together. Its surface to volume fraction was still greater than that of the other samples. The colouring of the sample six resembled those used in experiments one, three and four.

3.4 Estimated release of chlorine to the containment building

In order to estimate the chlorine release from cables used in a power plant, the release depth of chlorine from the samples had to be calculated. It was assumed, that during an experiment sample loses all of its chlorine content down to a certain release depth. Vaporisation deeper than the release depth was assumed to be negligible. This simplification was thought to be reasonable, since the experiments indicated fast chlorine vaporisation taking place only from the sample surface. With this method, a release estimate that does not depend on sample geometry, could be calculated.

The depth of the chlorine release, that took place in approximately 30 minutes at moderate 200°C to 300°C temperatures, was varying between 0.05 to 0.09 mm. The variance in the estimates is primarily due to the uncertainties in the sample surface area. The lowest estimate came from the experiment six, in which there is the greatest uncertainty in the surface area. The release depths calculated from both NAA and on-line results are presented in table 4.

The fast vaporisation of chlorine is calculated assuming, that the mass of the rubber insulation inside the containment building is approximately 4400 kg (Liljenzín, 1990). The diameter of the cable is assumed to be 16.8 mm, which corresponds to the dimension of the sample material received from TVO. In the calculation the release depth was assumed to be the same as in our experiments. Thus the fractional release of chlorine in about 30 minutes at 200°C to 300°C temperatures is estimated to be between 1.2 % and 2.1 %. If all chlorine is released as hydrochloric acid, this would yield 240 - 410 moles of HCl to the containment. In a previous work it was estimated, that in pyrolysis of insulating materials at 400°C temperature, approximately 1600 moles of acidic compounds would be released to the containment (Liljenzín, 1990).

4. THE EFFECT OF CHLORINE RELEASE ON THE BEHAVIOUR OF IODINE

There is a general agreement that pH of the water pools is the key factor affecting iodine volatility (Weaver, 1996). Low pH conditions lead to the formation of I₂ in irradiated iodide solution, since the reduction of I₂ by H₂O₂ falls off with decreasing pH. In severe reactor accidents this will in turn increase the amount of I₂ in the containment atmosphere. The pH in the containment building during a severe accident was studied by Beahm (Beahm, 1992B). It was found that, in the absence of pH-control additives, strong acids, in amounts 500 to 1000 mol, would produce a pH of 7 in 24 hours in any of the accident sequence studied. It is thus highly probable, that the release of HCl by pyrolysis of the cable insulation material, would have a significant impact in the acidity of the water pools. Further more, the presence of chloride ions in the water pools may have an substantial effect on the iodine chemistry, since the elements are chemically very similar.
There is also evidence that gaseous chlorine species may degrade the capacity and retention of iodine species in filters (Beahm, 1992B). This might result an iodine release to the environment, if the containment building is vented during an accident. Containment filters usually have activated charcoal that may be impregnated with iodide such as KI or triethylenediamine (TEDA). The retention of I\textsubscript{2} by activated charcoal is described with reaction:

\[ I_2 + 2K^+ + 2OH^- \rightarrow 2K^+ + 2I^- + H_2O + \frac{1}{2}O_2 \]  \hspace{2cm} (2)

In the presence of HCl or Cl\textsubscript{2} this reaction could be superseded by:

\[ HCl + K^+ + OH^- \rightarrow K^+ + Cl^- + H_2O \]  \hspace{2cm} (3)

or

\[ Cl_2 + 2K^+ + 2OH^- \rightarrow 2K^+ + 2Cl^- + H_2O + \frac{1}{2}O_2 \]  \hspace{2cm} (4)

The result of the interactions of gaseous chlorine species would be to reduce the capacity of activated charcoal to absorb iodine.

Potassium iodide as an impregnant on charcoal removes radioiodine by isotopic exchange. If Cl\textsubscript{2} is introduced, the following reaction would take place:

\[ 2KI + Cl_2 \rightarrow 2KCl + I_2 \]  \hspace{2cm} (5)

The ability of this impregnant to remove iodine as I\textsubscript{2} would thus be degraded.

TEDA impregnant is applied to bind methyl iodide (CH\textsubscript{3}I) in a quaternary ammonium salt. However the basic TEDA would prefer to react with the strong acid HCl to form triethylenediamine hydrochloride. This would prevent the reaction of TEDA with CH\textsubscript{3}I.

5. CONCLUSIONS

In a severe nuclear accident chlorine is released to the reactor building mainly by pyrolysis and radiolysis of the electric cable insulation material. In this work only the pyrolysis was studied at moderate temperatures ranging from 200°C to 300°C. Surveys of accident sequence calculations that employed the Source Term Code Package often predicted temperatures in excess of 300°C in BWR containment (Gieseke, 1984; Denning 1986). In BWR containment large amount of cables are positioned in the immediate vicinity of the reactor pressure vessel, which increases the probability of pyrolysis even more.

In the experiments the release of chlorine from hypalon began as the temperature of the furnace was increased above 220°C. The rate of vaporisation decreased substantially after approximately 30 minutes, when about 10% of the chlorine inventory had been released. The decrease in the vaporisation rate can be verified from the table 3, where the decay coefficients at the end of experiments approach the natural decay coefficient of radioactive chlorine (λ\textsubscript{m} = 0.0186 min\textsuperscript{-1}). This kind of behaviour indicates that the release of chlorine takes place mainly from the surface of the material. In the experiment six this hypothesis was tested. The sample
was cut into small pieces, in order to increase the surface to volume fraction. In that experiment approximately 19% of the chlorine inventory vaporised almost doubling the release compared to earlier experiments. It was concluded, that after the initial fast vaporisation most probably changes in the material surface began to limit the release.

By applying a concept of release depth, the amount of fast chlorine vaporisation was estimated in a reactor accident. From the results of neutron activation analysis, it was calculated, that the chlorine release depth in hypalon varied between 0.05 and 0.09 mm. It would mean that 1.2 % to 2.1 % of the chlorine inventory would be released in 30 minutes from a 16.8 mm thick hypalon cable, once the temperature would increase above 220°C. If the amount of cable insulation is approximately 4400 kg, this would yield from 240 to 410 moles of hydrochloric acid to the containment building.

In a severe nuclear accident chlorine may have a significant impact on iodine behaviour in the containment. Since chlorine and iodine are both halogens, the presence of chlorine may influence the chemical form of iodine. Chlorine is most likely released to the containment in the form of hydrochloric acid. Any substantial release may lead to acidification of the water pools and thus increase the fraction of gaseous iodine in the containment atmosphere. Further more, iodine behaviour in the water pools containing chloride ions, has not been studied much. There is also indication, that chlorine compounds may seriously degrade the iodine removing efficiency of the active carbon filters (Beahm, 1992B). Especially, if the filters are scaled for the iodine inventory of the core (100...160 mol), they may be saturated easily with chlorine compounds. Chlorine inventory in the reactor building is approximately 2.0*10^4 moles.

In the experiments hydrocarbons were pyrolysing from the cable insulation at least at the same rate as chlorine. The mass fraction of chlorine in the samples was increased as a function of temperature. At 200°C the chlorine mass fraction was 15.6%. At 300°C it varied between 17.4% to 18.5%. After the experiment done at 500°C the chlorine mass fraction in the sample reached 29.9%. At temperatures between 200°C and 300°C hydrocarbons were most probably released in gaseous form similarly as chlorine, since neither cutting the sample nor longer duration of the experiment did have an effect on the final chlorine mass fraction. At higher temperature hydrocarbons were released at least partly in liquid form. After the experiment liquid droplets were clearly visible at the sample surface. Although the mass of the sample had decreased substantially, there was no detectable increase in the chlorine release at the higher temperature.

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IODINE VOLATILE SPECIES PRODUCTION FROM PAINTED SURFACES OF THE REACTOR CONTAINMENT, DURING A SEVERE ACCIDENT.

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ABSTRACT

Following a hypothetical severe reactor accident, volatile radioactive species such as molecular iodine (I₂) or organic iodides (RI) could be released in the environment. Therefore, it is important to know the quantity of volatile iodide species formed into containment. With this aim, the French Nuclear Safety and Protection Institute (IPSN) has performed a series of tests, under conditions relevant to a reactor accident, in order to provide quantitative information on volatile organic species production under radiation and in the presence of painted surfaces.

The effect of various parameters, such as temperature (90 to 130°C), solution pH (5 to 9) and initial iodide concentration (10⁻⁴ to 10⁻⁶ mol·dm⁻³), on volatile species production has been investigated. The tests consisted of irradiating glass flasks containing ¹³¹I-labelled iodide solutions and epoxy-painted coupons. Post-test measurements of I₂ and volatile RI were performed by means of Maypack filters.

From the overall results obtained, it appears that the greatest fractional yields of volatile organic iodides occurred under radiation, with painted coupons in the gas phase and for the less concentrated iodide solutions. High temperature and basic iodide solutions lead to a decrease of the volatile organic species production.

A possible approach to modelling the production of RI in the paint is briefly discussed.
1. INTRODUCTION

The radiological analysis of the consequences of severe accidents requires an understanding of iodine behaviour into the containment. In the event of a severe reactor accident leading to core melt, volatile species such as molecular iodine ($I_2$) or organic iodides (RI) could be released to the environment. However, the organic iodine chemistry is complex and consequently the RI formation mechanisms are uncertain. Possible processes include iodine interaction with painted surfaces, reaction with organic compounds dissolved in the sump or in the atmosphere, etc. Furthermore, although there seems to be consensus that the main volatile RI species are alkyl iodides, these species vary in their physicochemical properties, e.g., volatility, hydrolysis rates, thermal reactions, and stability under radiation. To help in understanding volatile RI formation, small-scale experiments have been performed to obtain quantitative information on volatile RI production under conditions representative of a reactor severe accident. This paper presents the results of these experiments, together with some preliminary interpretation.

2. EXPERIMENTAL

The experiments described in this paper consisted of irradiating 100 cm$^3$ sealed glass flasks containing 25 cm$^3$ of $^{131}$I-labelled iodide solution and a Ripolin epoxy-painted coupon. A series of scoping tests was performed in order to define radiation conditions to maximise the production of volatile RI species. Thus, the effects of the integrated dose and dose rate on RI formation were investigated (at pH 5, 90°C and with $10^{-4}$ mol·dm$^{-3}$ KI solutions). In the subsequent series of tests, the following parameters were varied systematically: the initial iodide concentration in solution (from $10^{-4}$ to $10^{-6}$ mol·dm$^{-3}$), the temperature (between 90°C and 130°C), the solution pH (from 5 to 9) and the location of the painted coupon (placed either in the solution or in the atmosphere of the experimental vessel). In addition, several blank tests were carried out without radiation, as well as one irradiated test without a painted coupon.

The Ripolin epoxy paint was chosen because it is representative of the containment lining of many French PWRs. The painted samples were prepared by the manufacturer, and stored for about two years before the experiments. They consisted of two primer coatings (Ripolin Centrepox N) and a water-repellent epoxy finishing coating (Ripolin Hydro-centrifugon) deposited on a carbon steel cylinder, $1.27 \times 10^{-2}$ m in diameter and $0.635 \times 10^{-2}$ m high.

The 100 cm$^3$ glass cells were designed so that painted coupons could be placed either in the aqueous phase or in the gaseous phase (Figure 1). Sealed glass vessels were used in order to minimise retention of iodine onto the vessel walls and avoid the formation of organic iodides from other organic sources such as grease or ground-glass joints.
The $10^{-4}$ mol·dm$^{-3}$ working solutions were prepared by dissolving the appropriate quantity of KI salt (R.P. Normanpur Prolabo) into a 0.2 mol·dm$^{-3}$ boric acid solution. The $10^{-5}$ and $10^{-6}$ mol·dm$^{-3}$ KI solutions were obtained by successive dilution of the $10^{-4}$ mol·dm$^{-3}$ solution with 0.2 mol·dm$^{-3}$ boric acid. The pH of the solutions was then adjusted to the desired value using potassium hydroxide or sulphuric acid. Finally, the 25 cm$^3$ working solutions were labelled with 74 to 185 kBq of $^{131}$I for cells subjected to radiation and with 185 to 370 kBq for the blank tests. The initial activity of the glass cells was then determined by gamma counting, using a NaI(Tl) detector calibrated for the geometry of the cells.

The cells were placed into a tightly closed aluminium heating device in order to maintain them at the desired temperature during the run. This device consisted of an electrical furnace and a container in which two glass cells could be placed simultaneously. For each test, the container was filled with water before placing the cells in it in order to avoid a pressure difference between the glass flasks and the environment during the heating period. The desired experimental temperature was generally reached in 20 minutes. The furnace temperature was continuously recorded so that a possible failure of the heating device could be detected. The tests under radiation were performed in a facility using a $^{60}$Co source providing various dose rates depending on the distance from the sample to the source (0.4 $< D < 1.8$ kGy/h for a sample-to-source distance ranging from 1.14 to 0.57 m).

After completion of the irradiation periods, the samples were cooled by immersing the container almost completely in cold water; the cooling period was between 60 and 90 minutes. The cell contents were then analysed at room temperature by a Maypack filter method in order to assess the yield of volatile organic iodides. Nitrogen was sparged into the cell and then drawn through the Maypack device containing selective absorbents, namely silver-coated copper filters (Knitmesh) for molecular iodine and 1% KI-impregnated charcoal for organic iodides (Figure 2). During this sampling, which typically lasted 20 to 30 minutes, the circuit was kept under slight negative pressure to prevent any loss of volatile iodine species. Thus, by measuring the $^{131}$I activity of each Maypack filter, the global quantity of I$_2$ and volatile RI present in both the liquid and gas phase was determined.
Solutions were then transferred into 60 cm$^3$ plastic flasks with a syringe in order to measure their final pH. The painted coupons were extracted from the glass cells, washed with distilled water, and their $^{131}$I activity was measured. The distilled water used to wash the coupons was added to the solution in the plastic flasks, prior to performing the gamma counting.

Finally, an iodine mass balance for each test was obtained by the assessment of iodine deposited onto the paint, the quantity of volatile iodine fixed by the Maypack filters and the amount of non-volatile iodine species remaining in the solution (I, IO$_3^-$, RI,...). The results were converted to percentages of iodine (Iw, Ipaint, ...) related to the initial quantity of iodide contained in the solution. The following discussion focuses on the RI data.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Presentation

Altogether, about 40 experiments were performed in order to study the influence of different parameters, such as integrated dose and dose rate for the scoping tests and initial iodide concentration, initial pH, temperature, and coupon location for the systematic tests.

The gamma counting results were analysed by assuming that the irradiation of iodide solutions leads to the formation of molecular iodine which is then trapped onto painted coupons and finally released as organic iodide species. Therefore, the total quantity of I$_2$ produced is estimated as the difference between the initial iodide concentration and the sum of the remaining non-volatile species measured in the aqueous phase and on the walls of the glass cells. We recognize that, in experiments with coupons immersed in the liquid phase, some I, as well as I$_2$, is likely to be absorbed by the paint.

The precision associated with the gamma counting method is generally very good. Furthermore, >99% of the measured RI and I$_2$ was typically recovered on the first of each of the specific filters (see Figure 2). However, considering the low amount of $^{131}$I initially introduced into the working solutions and, consequently, the low activity measured for each component, the accuracy of the RI measurements was evaluated to be ±10%.
3.2 Scoping test results

These preliminary tests were carried out in order to assess the effects of varying the integrated dose and the dose rate on the formation of volatile RI species, and hence to define experimental conditions to maximise their production. The results are represented in Figures 3 and 4.

**Figure 3**: Effect of the integrated dose on volatile organic iodide production ([KI] = 10^{-4} \text{ mol dm}^{-3} ; T = 90^\circ \text{C} ; \text{pH} = 5 ; D = 1.8 \text{ kGy/h})

**Figure 4**: Production of volatile organic iodides as a function of the dose rate ([KI] = 10^{-4} \text{ mol dm}^{-3} ; T = 90^\circ \text{C} ; \text{pH} = 5 ; \text{irradiation time} t_{irr} = 24 \text{ h})
As shown in Figure 3, the fraction of total volatile organic iodides measured after a 4-day exposure time was comparable to that in the tests performed without radiation (~0.05% of the initial iodide inventory). A greater RI production was obtained for a 1-day radiation period. In the same way, Figure 4 shows that the volatile RI yield was greatest at the intermediate dose rate studied (e.g. 0.8 kGy/h or 0.81 m from sample to \(^{60}\)Co source). Therefore, the systematic series of high-temperature irradiation experiments was performed with a fixed exposure time (\(t_{\text{in}}\)) of 24 h at a dose rate of 0.8 kGy/h.

### 3.3 Systematic test results

#### General observations

For all the experiments, most of the molecular iodine produced appears to be trapped by the paint, and only a small fraction is converted to volatile RI, as indicated by the relationship: \(0.8 < \frac{[\text{I}_{\text{paint}}]}{[\text{I}_{\text{volat}}]} < 1\). These results show that, under our experimental conditions, the epoxy paint is very efficient in trapping molecular iodine and behaves as a sink.

Without radiation and at room temperature, the iodine fractions fixed to the immersed painted coupons are consistent with those obtained by AEAT experiments (Baston, 1998) and by previous IPSN studies (Verdier, 1997): I\(_2\) retention ranging from 30 to 60% on 20x140 mm painted coupons for AEAT and about 50% on 20 x 150 mm samples for IPSN. For similar experiments undertaken with coupons immersed into iodide solutions (Verdier, 1997), a significant decrease in the iodine retention rate has been observed. This is in agreement with the results of the blank tests and with experiments performed in basic solutions. Furthermore, from the blank test results, it appears that gamma radiation enhanced the production of volatile organic iodides by a factor of 3 to 5 (or higher for some tests with dilute iodide solutions; see below).

In general, the painted coupons showed good resistance to the test conditions. They presented a more or less yellowish coloration, which appeared to vary with the quantity of molecular iodine deposited on the surfaces. Nevertheless, some blisters appeared on paint after the tests, but no detachment of the paint was observed.

#### pH effect

The pH effect on volatile RI production at \(T = 90^\circ \text{C}\) and \([\text{KI}] = 10^{-4}\ \text{mol}\cdot\text{dm}^{-3}\) is illustrated in Figure 5. The results obtained with painted coupons in the gaseous phase showed a significant decrease in the RI formation with increasing pH. This is probably directly linked to the pH effect on the molecular iodine formation rate, which strongly decreases when pH increases.
The experiments with coupons in the aqueous phase showed a less pronounced pH effect, both on the quantity of iodine deposited on painted surfaces and on the free I\(_2\) concentration. The RI production seemed unaffected by a pH increase from 5 to 7. However, at higher pH, a reduction of the RI fraction was observed. This reduction may be due to a change in the reaction rate for RI hydrolysis, which is faster in the basic medium (0.15 dm\(^3\)/mol\cdot s at 100°C for CH\(_3\)I; Bathgate et al., 1959) than in the acidic or neutral solution (5 \(10^{-4}\) dm\(^3\)/mol\cdot s at 100°C for CH\(_3\)I; Parsley 1971).

Furthermore, from these results, it appears that significant quantities of volatile RI might be generated in the containment sump, even under neutral or basic conditions. Specifically, the experimental points in Figure 5 show that at pH higher than 7, the volatile RI fraction is significant when the painted coupons are immersed in the liquid phase. Further investigations might be performed at basic pH and at various temperatures in order to confirm this trend.

Finally, in all the irradiated tests conducted at pH \(-5\), a significant decrease in pH was observed, varying from 0.3 to 1 unit and depending on temperature and initial iodide concentration. A similar effect has been noticed in the Canadian bench scale tests performed with the French paint in support of the Phoebus FP programme (Ball et al., 1994). This could be due to the oxidation of the Ripolin epoxy paint to release CO\(_2\) during the organic iodides formation phase, as demonstrated by Marchand (1997). The pH change is likely due to organic acid intermediates in the oxidation process (see Section 4).

**Temperature and iodide concentration effects**

The effects of varying temperature and iodide concentration are represented in Figures 6 and 7, which show results for RI formation obtained with the painted coupons in the gas phase and the liquid phase, respectively.
Figure 6: Production of volatile organic iodide as a function of temperature and initial iodide concentration (Paint in gas phase; pH = 5; D = 0.8 kGy/h; irradiation time t_{irr} = 24 h)

Figure 7: Production of volatile organic iodide as a function of temperature and initial iodide concentration (Paint in liquid phase; pH = 5; D = 0.8 kGy/h; irradiation time t_{irr} = 24 h)

These two figures show that the percentage yield of volatile RI generally represented less than 3% of the initial iodine inventory, and tended to be greater for the lower initial iodide concentrations.

In addition, the results show that under radiation, the amount of volatile organic iodides produced is generally greater when the painted coupons are placed in the gas phase (except at high pH, as noted above). This difference could be explained by the fact that radiolytic RI decomposition seems to be practically inhibited in moist atmosphere whereas
this reaction is probably not negligible in the liquid phase (Tang, 1968; Marchand, 1997). Other possible interpretations are discussed in Section 4.

Overall, these results indicate that volatile organic iodides in a reactor containment could originate principally from the painted surfaces exposed to the gas phase, if slightly acidic conditions exist in solution.

Based on the preceding discussion, the net average RI formation rates have been estimated from experiments with paints in the gas phase by assuming that the volatile organic iodides were only generated by the iodine trapped onto the painted coupons. The calculated values, representing the net amount of volatile organic iodides produced and decomposed during a test, range from 2 to $6 \times 10^3$ h$^{-1}$. They show that the organic iodide release from the painted surfaces in the gas phase is favoured at 90°C and decreases significantly at 130°C.

Furthermore, Figures 6 and 7 show that the RI fractions decrease with temperature for the more concentrated solutions ($10^{-4}$ and $10^{-5}$ mol dm$^{-3}$), but with a less pronounced effect for the coupons in the aqueous phase. Several competitive processes in this system are temperature-dependent, e.g., molecular iodine formation in a radiolytic field, RI hydrolysis reaction rate and I$_2$ formation by thermal reaction. The first two reactions contribute to a reduction of the volatile RI production and could explain the results obtained in both the liquid and gas phases. Perhaps the "peak" at 110°C for the less concentrated solutions reflects a stronger temperature dependence for destruction processes than for RI production.

Overall, the results of these tests indicate that the conditions relevant to a reactor accident may favour the formation of volatile organic iodides. To confirm this observation, further research is needed with lower initial iodide concentrations.

4. INTERPRETATION

The interpretation of the results raised some difficulties because under the test conditions, many phenomena are taking place concurrently, for example:

- molecular iodine production under radiation;
- mass transfer of volatile iodine species between the gas and liquid phases;
- mass transport, physical and chemical sorption, and chemical reaction of iodine within the paint;
- release of iodine (including RI) from the paint, into either the gas or liquid phases;
- destruction of RI by oxidation and/or radiolysis in the aqueous phase;
- other reactions influencing pH and hence affecting the processes above.

In addition to investigating separate effects, as discussed above, it is useful to detect trends within the data set as a whole. Figure 8 shows the data from all the experiments for both RI yield and iodine uptake by the paint (as percentages of the total amount of iodine). Although there is a lot of scatter in the data, because of changes in the different experimental variables, there is a clear discrimination between results for experiments with the coupon either immersed in the liquid phase or suspended in the gas phase, as well as a rough correlation between the RI yield and the iodine uptake in each case. Overall, the RI yields are about four times higher for coupons in the gas phase than the liquid phase, for a given iodine loading in the paint.
As noted above, this difference may be related to RI hydrolysis kinetics in the gas and liquid phases. It is also possible that it is related to uptake of elemental iodine alone in the gas phase, but a mixture of iodine and iodide in the liquid phase. In contrast with the trends in Figure 8, we observed negative correlation (not illustrated) between the RI yield and the quantity of iodine remaining in solution. Thus, there appears to be good evidence that the generation of RI took place primarily within the paint phase, with subsequent release to the gas or liquid phase, rather than being formed directly in solution. Alternatively, one might argue that both RI generation and I₂ uptake are controlled by a third process in solution.

All of the unirradiated tests yielded very low quantities of RI (open symbols in Figure 8), indicating that radiolytic processes were the primary source of RI, and also indicating that the overall detection limit for RI in the experiments (as opposed to counting error alone) is probably in the neighbourhood of 0.05% yield. Because similar quantities of tracers were used in all tests, the detection limit is not strongly dependent on the initial iodide concentration.

![Graph showing iodine on paint percentage vs organic iodide yield percentage (RI) with markers for coupon in gas phase, coupon in liquid phase, gas phase unirradiated, and liquid phase unirradiated.]

**Figure 8:** Organic iodide data (% RI) from current experiments, plotted as a function of the quantity of iodine retained by the paint and labelled according to coupon location.

It is interesting to compare the results from the current experiments with those from previous, similar tests that were run at higher doses (~100-140 kGy) in the same laboratories (Ventre and Albioi, 1995). Figure 9 shows a compilation of data (RI yield) from current and previous tests, plotted as a function of integrated dose, with data points identified according to the dose rate. Note that the origin has been shifted to clarify the unirradiated test data. Two key points that emerge from this plot are:

- an apparent peak in RI yield at doses near 20 kGy (and dose rates near 0.8 kGy/h);
no obvious discrimination between data obtained at different dose rates (1 - 7 kGy/h) at higher integrated doses (>100 kGy) and in unirradiated tests. However, many of these data may be near or below the detection limit.

Other trends (with pH, iodide concentration and temperature) are essentially as described in Section 3.

Figure 9: Organic iodide data (% RI) from current and previous experiments, plotted as a function of integrated gamma radiation dose and labelled according to dose rate.

Figure 10 shows a similar plot to Figure 9, but with the data limited to experiments run at 90°C and an initial pH of 5, and labelled according to initial iodide concentration and coupon location. This figure shows more clearly the peak in RI production (as a percentage of total iodine) at doses near 20 kGy, especially for the more dilute iodide solutions.
**Figure 10:** Organic iodide data (% RI) from experiments at 90°C and pH(initial) = 5, including earlier experiments. Data points are labelled according to the initial KI concentration and the coupon location.

As noted above, the measured final pH values for the current tests were typically lower than the starting value of 5. Figure 11 shows a plot of RI yields versus final pH values for all of the tests depicted in Figure 10 (i.e., 90°C and initial pH ~5). Clearly, the high RI yields are correlated with low pH values (~4), as well as with intermediate doses (~20 kGy). In unirradiated tests, the pH generally remained near 5 (4.6-5.3) and in the high-dose tests (>100 kGy), the pH varied between 4.2 and 6.6, with most values being ≥5.8.

To achieve a pH of 4 from a starting value of 5 (unbuffered), it would be necessary to add $1-2 \times 10^{-4}$ mol/dm$^3$ of a relatively strong organic acid (e.g., oxalic, formic, iodoacetic), but $\sim 10^{-3}$ mol/dm$^3$ of a weaker acid (acetic, propionic, etc.), or a much larger quantity of CO$_2$. Thus, it seems that the observed pH change is more likely due to organic acids than to CO$_2$. Such acids could originate from oxidation/radiolysis of the paint itself or from leached solvent residues (Wren et al. 1999b). Eventual decomposition of organic acids to CO$_2$ will allow the pH to rise again, even allowing for the formation of several CO$_2$ molecules per organic precursor molecule. This is consistent with some intermediate-scale test results obtained at the Canadian Radioiodine Test Facility (Wren et al. 1999a, and references therein). It should be noted, however, that “transient” behaviour in the present discussion has been deduced from a series of separate tests, as opposed to sequential analyses in a single test. Note also that O$_2$ and CO$_2$ analyses, comparable to those conducted by Marchand (1997), were not feasible in these tests.

Another possible cause for the apparent transient pH reduction is nitric acid formation from air hydrolysis, but if this is important it is more difficult to rationalise the return to
higher pH values at higher doses. Furthermore, no reduction in pH was observed in the blank, irradiated test without a painted coupon.

![Graph](image.png)

**Figure 11**: Plot of RI yield as a function of final measured pH, for all IPSN experiments at 90°C and an initial pH of ~5.

5. APPROACH TO MODELLING

As a starting point for modelling the formation of RI, let us assume that all of the RI measured in the IPSN experiments is formed in the paint, rather than the solution or gas phases. We recognize that this is consistent with, but not proven by the experimental findings presented here. It is reasonable to expect that the reaction to form RI in the paint obeys a kinetic expression of the type:

\[
\frac{d[R]}{dt} = D \sum_{i,j} (k_{ij}[I]^a[R]^b) \tag{1}
\]

where \( D = \) Dose rate, \([I] = \) concentrations of \( i \) specific iodine species and \( j \) specific organic precursor groups in the paint. This expression simply recognizes the complexity of both the paint structure and the speciation of absorbed iodine in the paint. This preliminary approach does not include the RI production at zero dose rate: this point has to be improved in future developments.

*If one reaction predominates, and if it displays first-order kinetics*, this expression may reduce to a form as simple as:

\[
\frac{d[R]}{dt} = D \cdot k' \cdot f[I] \tag{2}
\]
where $f$ is the fraction of the total absorbed iodine that is in a reactive form, and $k'$ is a composite term of several factors that are assumed to be constant.

If diffusion of RI to the paint surface and release to the gas or solution phase is fast, then the rate of release of RI from the paint, per unit of surface area, can be expressed as:

$$\frac{d(N'_{RI})}{dt} = D \cdot k'f[I_S]$$

where $N'_{RI}$ is the number of moles of RI released per unit surface area, and $I_S$ is the surface concentration of iodine. In many situations, however (especially at low temperature and/or low humidity), the RI release kinetics are likely to be complicated by slow diffusion processes in the paint. This is especially difficult to model, on account of the variability of the diffusion coefficient with humidity, temperature, and likely also with iodine loading and the drying history of the paint (Perera et al. 1971, Frisch and Stern, 1983). It is also likely that the speciation of iodine between various physisorbed and chemisorbed forms in the paint, and hence the value of $f$, varies with time, temperature and radiation history.

The lower limit for the term $D \cdot k'f$ during the early stages of RI formation, as estimated from the IPSN experimental data (assuming that the only mechanism for producing RI is a radiolytic process involving the iodine in the paint), is in the neighbourhood of $10^3 \text{h}^{-1}$. Simple consideration of the paint radiolysis process suggests an upper limit for the term $D \cdot k'f[I_S]$ of $\sim 10^9 \text{mol} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$. This is based on the assumption that hydrogen-generating radiolytic processes are strongly favoured over organic fragmentation processes in the paint radiolysis, as found by Burnay et al.(1980) for model epoxy resins.

This approach to modelling will be presented in more detail elsewhere (Taylor, 1999).

6. CONCLUSION

About 40 experiments have been carried out on the high-temperature radiolysis of iodide solutions in the presence of painted surfaces, in order to provide information on the production of volatile organic iodides under conditions relevant to a reactor severe accident. The influence of the initial iodide concentration, the temperature and initial pH has been studied. From the overall results obtained, the following general trends can be observed:

- An enhancement of the organic iodides formation for the samples submitted to a gamma radiation field ($D = 0.8 \text{ kGy/h}$ for 24 hours) has been noticed, in comparison with unirradiated tests.

- In an acidic medium, at all temperatures and initial iodide concentrations, the RI production was favoured for the samples with the painted surfaces in the gas phase.

- A reverse trend was observed in the only two experiments performed at initial pH values higher than 5, i.e. the RI release was greater from painted coupons in the aqueous phase than in the gas phase.

- The greatest percentage yield of volatile organic iodide species ($<3 \%$ of the initial iodide inventory) was obtained for the less concentrated iodide solutions ([KI] = $10^{-5}$ and $10^{-6} \text{ mol} \cdot \text{dm}^{-3}$).
With the painted coupons in the gas phase, a temperature increase resulted in decreased RI production.

In conclusion, the results show that significant RI production is possible under conditions relevant to a reactor accident. The greatest percentage yield of RI occurred for a combination of intermediate temperature (110°C) and low iodide concentration in solution (10^{-6} mol.dm^{-3}), with the paint specimen in contact with the gas phase. To complement this study it should be interesting to confirm the observation made at pH > 5 by conducting additional investigations involving a basic medium, and especially by performing experiments in which the kinetics of I_2 and RI production could be measured.

Thus, in order to improve the knowledge and understanding of RI formation under conditions relevant to a reactor accident, IPSN is designing a new facility named EPICUR (Experimental Program on Jodine Chemistry Under Radiation), which will allow on-line measurement of the volatile inorganic and organic species produced by radiolysis with a dose rate close to that expected in a reactor containment during a hypothetical accident, i.e. ~10 kGy/h. First results should be available early in 2001.

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EXPERIMENTAL STUDIES OF ORGANIC IODIDE PRODUCTION

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ABSTRACT

An experimental programme has been carried out to quantify the production of volatile organic iodides from dissolved organic material in irradiated iodine solutions, and from iodine absorbed onto painted surfaces.

In the first series of tests, the volatile organic and inorganic iodide evolved from sparged, irradiated iodide solutions was measured before and after the addition of an organic materials. The rate of evolution of organic iodine was shown to be dependent on the ratio of organic to iodide concentrations, and the duration of its production was dependent on the concentration of organic. The rate of evolution of organic iodide was always less than that of I₂, and the rate of I₂ production following the addition of the organic solute appeared to be dependent on the type and concentration of the material. It is not possible to draw firm conclusions on the formation mechanism, but it probably involves the reaction of I₂ either with an organic radical in competition with O₂, or with a stable radiolysis intermediate.

In the second set of tests, painted coupons were immersed in I₂ or I⁻ solutions for several days to allow iodine to be absorbed onto the surface. The coupons were then heated and/or irradiated under a variety of conditions, and the released organic iodide measured as a function of time. In the tests without irradiation, the released RI species were analysed by gas chromatography and found to consist almost exclusively of CH₃I.

The organic iodine release rate in the absence of irradiation increased strongly with temperature over the range studied (90 to 150°C). The production rate was much less than for the irradiated tests; only at 150°C did the CH₃I production rate approach that observed at room temperature under irradiation (~ 10⁻⁴ hr⁻¹). The effect of temperature on the production rate under irradiation was much less pronounced, increasing by a factor of 2 to 5 on heating from 25 to 80°C.

The absolute rate of CH₃I production in the absence of irradiation appeared the same at 90°C regardless of whether I₂ or I⁻ was the absorbed. However, much less I⁻ was absorbed so the fractional release rate was higher. Under irradiation, the fractional release rate was smaller from I⁻ - loaded coupons than from those treated with I₂.

The rate of release of volatile organic iodide was unchanged when the coupon was immersed in acidic solution. Aging of the coupons did not appear to have a significant effect on the release.
1 INTRODUCTION

If iodine is released from fuel into the containment of a PWR as a result of a loss of coolant accident, it is assumed initially to be mainly in the form of CsI. This would be either associated with blowdown aerosol suspended in the containment atmosphere, or deposited in the sump. However, it is well known that iodide can be oxidised to the volatile form I$_2$ by radiolytic reactions and can also form volatile organic iodine by processes that are not understood. It is important to understand the mechanisms which lead to the formation of volatile forms of iodine in order to quantify the consequences of such an accident and to ensure that mitigation procedures are adequate or consequences are acceptable.

There has been a large amount of work on the radiation chemistry of I$^-$ both from fundamental or academic studies and for reactor safety applications, and the situation is generally reasonably well understood although there are aspects of the mechanisms which are still debatable. There have been rather fewer studies of organic iodine production which adds an extra degree of complexity to the iodine chemical system and there is no agreement as to the major production route for volatile organic iodides. Some workers have proposed a gas phase process, whilst others proposed solution mechanisms and others surface mechanisms.

This paper describes experimental studies aimed at quantifying the rate of organic iodide production under irradiation by both surface and solution reactions. This work formed part of a shared cost action undertaken as part of the EC Fourth Framework Programme on Nuclear Fission Safety. Other parts of this programme are reported elsewhere at this workshop (Belval-Haltier, 1999; Funke, 1999; Karjunen, 1999).

2 EXPERIMENTAL

The apparatus used for this work, which is shown schematically in Figure 1, is similar to that used in previous studies (Ashmore, 1996), except that a TEDA impregnated charcoal trap was added after the alkaline inorganic iodide trap to trap organic iodine. Samples labelled with $^{131}$I were contained in a glass irradiation vessel of about 100 cm$^3$ volume, and irradiated at a dose-rate of 1.12 kGy hr$^{-1}$ as measured by the Fricke (1966) method. Air was drawn through traps to remove CO$_2$ and to prehumidify it before passing through the irradiation vessel, the inorganic and organic iodine traps (both of which were counted to determine the iodine activity on-line throughout the tests) and a final back-up charcoal trap. The irradiation temperature was maintained at about 25 °C. At the end of each experiment the activities remaining in the sample, collected in the NaOH/I$^-$ and activated charcoal traps, and washed from the delivery lines (with 10% HCl) were measured to allow the activity balance to be calculated.

In order to confirm that the inorganic trap did not trap the CH$_3$I, some initial experiments were carried out using CH$_3^{131}$I prepared by exchange labelling of CH$_3^{127}$I with $^{131}$I in aqueous solution. The solution was then sparged with air which passed through the two traps, and the CH$_3$I was found to pass through the NaOH solution onto the charcoal trap.

Two types of experiments were done, to study organic iodine production from solutions and painted surfaces respectively. In the solution tests, the irradiation vessel contained ~20cm$^2$ of iodide solution buffered to pH 7 with phosphate (0.1 mol dm$^{-3}$) and boric acid (0.2 mol dm$^{-3}$). Solutions were made up using high purity water (Millipore milli-RO/milli-Q). The test solutions were irradiated until a consistent rate of inorganic iodine production was established, and an aliquot of organic liquid was then added and the irradiation continued.
Figure 1. Schematic diagram of irradiation apparatus

In the surface tests, stainless steel coupons painted with Epoxy paint (Epigrip M253 in most tests) were loaded with iodine by immersion in ~10^{-4} or 10^{-3} mol dm^{-3} I_{2} solution in 0.2 mol dm^{-3} boric acid. The coupon was then transferred to the sample vessel and irradiated in a flow of moist (saturated at room temperature) air. The coupon was not dried before transferring to the irradiation vessel. In one test, the coupon was loaded "dry" by supporting it above a small volume (~1 cm³) of 10^{-4} mol dm^{-3} I_{2} in boric acid.

The coupons used in most of the tests were cured at 60°C for one week after air-drying, then aged for a further 12 months at room temperature. A small number of tests were done using uncured coupons, some of which had been aged for 5 years. Painted coupons supplied by IPSN (France) and STUK (Finland) were used in a limited number of irradiated tests.

A series of tests was done without radiation to measure the release of organic iodine from painted surfaces at temperatures up to 150°C. These tests used a similar experimental arrangement, though on a slightly larger scale. The vessel containing the loaded coupon was immersed in a thermostatically controlled, stirred oil bath and heated to the required temperature for up to 100 hours. The gas was sampled at intervals by drawing air through the vessel onto an activated charcoal sorbent tube. The charcoal was then extracted with toluene and the extract analysed by gas chromatography with an electron capture detector. No measurements were made of the inorganic iodine release in the non-irradiated tests.

3 RESULTS

3.1 Solution Tests

A total of 18 irradiated tests involving addition of organic material were carried out. A summary of the test conditions and results is given in Table 1.
3.1.1 Effect of iodide concentration (Experiments 1, 2, 3, 5 and 7)

In these tests, 10³ mol dm⁻³ of MEK was added to solutions of 10⁴, 10⁻³ and 10⁻⁶ mol dm⁻³ I⁻. Virtually no organic iodine was observed with 10⁻⁴ mol dm⁻³ I⁻, although the rate of inorganic iodine transfer fell following the organic addition. With an I⁻ concentration of 10⁻⁴ mol dm⁻³, about 0.15% of the total iodine was transferred to the organic trap in the few hours following the addition of MEK. (Figure 2) This equates to a fractional rate of production of 4×10⁻⁴ h⁻¹, which is about one-tenth of the inorganic production rate. After about 8 hours, the organic iodine production stopped, presumably due to depletion of the organic solute by a combination of radiolysis and volatilisation. In the experiment with 10⁻⁶ mol dm⁻³ I⁻, both the rate of transfer and the total transferred were increased by a factor of ~2.

![Graph showing fraction in organic trap vs time](image)

Figure 2. 10³ M MEK added to 10⁻⁴ M iodide solution at pH 7

3.1.2 Effect of steel surface (Experiment 4)

The addition of a steel coupon previously cleaned with methyl ethyl ketone did not affect the organic production rate but did appear to reduce temporarily the inorganic rate. The subsequent addition of methyl ethyl ketone caused a pulse of organic iodine of similar magnitude to that in Experiment 3, and again the inorganic production rate appeared to be temporarily lowered.
### Table 1. Summary of solution experiments

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<td>1.0E-04</td>
<td>butyrate</td>
<td>1.0E-03</td>
<td>4.20E-05</td>
<td>8.4E-11</td>
<td>0.15%</td>
<td>3.0E-03</td>
</tr>
<tr>
<td>18b</td>
<td>1.0E-04</td>
<td>butyrate</td>
<td>1.0E-02</td>
<td>1.40E-04</td>
<td>2.8E-10</td>
<td>0.80%</td>
<td></td>
</tr>
</tbody>
</table>
3.1.3 Effect of organic solute

No organic iodine was observed with acetate or acetone, (Experiments 8, 9 and 11) but the rate of production of inorganic iodine was reduced following the organic addition in all cases (Figure 3). The results with $10^3$ mol dm$^{-3}$ propionic or butyric acid (Experiments 12 to 18) were similar to those with methyl ethyl ketone.

![Graph showing fraction in organic trap and inorganic trap over time](image)

**Figure 3**  $10^3$ M Acetate added to $10^{-4}$ M iodide solution at pH 7

3.1.4 Effect of organic concentration

Very little organic iodine was observed with $10^4$ mol dm$^{-3}$ organic, $10^5$ mol dm$^{-3}$ I$^-$ (Experiments 16a and 17a). Generally the organic iodide release rate increased with increasing solute concentration. In experiments 12 and 14, the multiple closely-spaced additions of propionic acid appeared to cause a significant increase in the organic iodine release rate compared with experiments 10 and 16. However the pH of the inorganic trap fell to ~7 in experiment 14, which was presumably due to an air leak and the CO$_2$ produced by the radiolysis of the organic material. The fraction in the inorganic trap appeared to fall following the organic addition and so some of the increase in activity in the organic trap could have been due to inorganic iodine carry-over.

These results are consistent with the effect of iodide concentration and indicate that the fractional organic iodide production increases with the ratio of organic to iodide concentrations.

3.2 Tests with painted surfaces

3.2.1 Non-irradiated tests

The results of the non-irradiated tests are summarised in Table 2. There was no evidence for significant production of any volatile iodine species except CH$_3$I in any of the tests.
Table 2. Summary of non-irradiated test conditions and results

<table>
<thead>
<tr>
<th>Test ref</th>
<th>Coupon preparation</th>
<th>CH$_3$I release test</th>
</tr>
</thead>
<tbody>
<tr>
<td>t hr</td>
<td>Vol cm$^3$</td>
<td>$[I]_{init}$ mol dm$^3$</td>
</tr>
<tr>
<td>C1r</td>
<td>67</td>
<td>56</td>
</tr>
<tr>
<td>C2r</td>
<td>162</td>
<td>56</td>
</tr>
<tr>
<td>C5</td>
<td>21</td>
<td>60</td>
</tr>
<tr>
<td>C6</td>
<td>71</td>
<td>60</td>
</tr>
<tr>
<td>C7</td>
<td>89</td>
<td>60</td>
</tr>
<tr>
<td>C8</td>
<td>92</td>
<td>60</td>
</tr>
<tr>
<td>C10</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>C11</td>
<td>70</td>
<td>60</td>
</tr>
<tr>
<td>C12</td>
<td>138</td>
<td>100</td>
</tr>
<tr>
<td>C13</td>
<td>no pre-treatment: coupon immersed in I$^-$_solution</td>
<td>90</td>
</tr>
<tr>
<td>C14</td>
<td>132</td>
<td>100</td>
</tr>
<tr>
<td>C15</td>
<td>64</td>
<td>60</td>
</tr>
<tr>
<td>C16</td>
<td>64</td>
<td>60</td>
</tr>
<tr>
<td>C17</td>
<td>75</td>
<td>60</td>
</tr>
<tr>
<td>C18</td>
<td>132</td>
<td>100</td>
</tr>
<tr>
<td>C19</td>
<td>100</td>
<td>3</td>
</tr>
</tbody>
</table>

*CH$_3$I release rate with respect to absorbed iodine.

$t$ assuming 1% of iodide absorbed on the coupon
3.2.1.1 *Iodine absorbed as I\textsubscript{2}*

The results show that the production of CH\textsubscript{3}I increases substantially with temperature over the range 90 to 150°C (Figure 4). The production rates appear generally constant with time, at least at the lower temperatures. The rates were independent of the time between samples, indicating that the gaseous CH\textsubscript{3}I concentration did not reach an equilibrium with the surface.

*Figure 4*  Effect of temperature on CH3I production from painted coupons without irradiation

The results at 90°C are subject to substantial uncertainty as the measured CH\textsubscript{3}I concentrations are close to the limit of detection. The release rate from the “standard” coupon was about 5×10\textsuperscript{-7} hr\textsuperscript{-1} in tests C2r and C8. Test C6 gave an apparently anomalous result, with about ten times as much CH\textsubscript{3}I being released than in any other test at this temperature. This may have been linked to the lower iodine concentration on the surface of this coupon, as the absolute amount of CH\textsubscript{3}I released from C2r and C6 were similar. The rates from the both uncured coupon (C10) and long-aged coupon (C11) was at least a factor of four lower; all of the measurements in this case were below the detection limit in both cases.

The production of CH\textsubscript{3}I from a treated coupon submerged in 0.2 M H\textsubscript{3}BO\textsubscript{3} (C7) was also below the detection limit. However, when a small amount of water was added to a “dry” test, there was no apparent in the release rate.

The release rates at 120°C were generally in the range 1 to 6×10\textsuperscript{-4} hr\textsuperscript{-1} based on the individual sample measurements, and the averaged rates for each test were in the range 2 to 5×10\textsuperscript{-4} hr\textsuperscript{-1}. The release rates do not appear to have been significantly affected by the paint pretreatment, with the two tests with “standard” coupons spanning the overall range of the results. In the test at 150°C (C5), the release rate was initially very rapid (3×10\textsuperscript{-4} hr\textsuperscript{-1} in the
first sample) but decreased by an order of magnitude after the first few hours. It should be noted that only at 150°C did the CH₃I production rate approach those observed at room temperature under irradiation (~10⁴ hr⁻¹).

3.2.1.2 Iodine absorbed as I

The amount of iodide absorbed on the coupon was too low to be measured by a change in concentration of the absorbing solution. In the irradiated test F5, about 4% of the iodide was absorbed from the solution in 44 hours (measured by radiolabelling). Deane (1989) formulated an expression for the absorption of I⁻ onto this paint type; according to this relationship, about 1% of the I⁻ would be expected to be absorbed onto the coupon. This value was assumed in the current work to allow the scale of the fractional production rates to be compared with the I₂ tests, but the rather large uncertainty should be noted.

The two “dry” iodide tests at 90°C produced very different results, with C12 showing significant CH₃I production whereas C14 only gave a measurable quantity in one sample taken after 60 hours’ continuous heating. Furthermore, the release rate in C12 was very close to that measured 120°C in C18, suggesting that this result was anomalously high. In the test in which I⁻ was deposited as an aqueous aerosol (C19), the fractional release rate at 120°C was similar to that for the solution-absorbed case at 90°C.

The absolute amounts of CH₃I released from the iodide-treated coupons were similar to those observed in the I₂ tests; however, because the amounts of I⁻ absorbed on the surfaces were much smaller, the corresponding release rates are substantially higher. If it is assumed that the C12 result is spuriously high, then the molar release rates are about a factor of 10 lower than the I₂ rates from the “standard” coupons, but the fractional rates are about a factor of 10 higher.

3.2.2 Irradiated tests

The results of the irradiated tests are summarised in Table 3. In the initial tests, air was passed over the samples and into the traps for 24 hours before starting the irradiation. No iodine was detected in the charcoal trap during this period, confirming that organic iodine production is predominantly a radiolytic process, at least at low temperature. A typical result is shown in Figure 5.

A small amount of inorganic transfer was observed in Tests F1 to F7 both before and after the source was lowered; the increase in the inorganic trap activity correlates closely with the small fluctuations in the sample temperature, suggesting that some very loosely-bound I₂ was released. A total of 6 to 12% of the iodine activity was found on the two traps at the end of the tests, the majority of which (80 - 90%) was on the inorganic trap. In runs H1 and H3, very little activity was observed on the inorganic trap before the sample was heated to 80°C. The reason for this different behaviour is unknown, but it may have been due to slight differences in the source temperature.
<table>
<thead>
<tr>
<th>Ref.</th>
<th>[I]</th>
<th>I ads</th>
<th>RI release rate</th>
<th>RI formation rate</th>
<th>Inorg release rate</th>
<th>notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mol dm⁻³</td>
<td>mol cm²</td>
<td>hr⁻¹</td>
<td>25°C</td>
<td>80°C</td>
<td>25°C</td>
</tr>
<tr>
<td>F1</td>
<td>I₂</td>
<td>10⁻⁴</td>
<td>8.3E-08</td>
<td>1.3E-04</td>
<td>7.2E-11</td>
<td>8.2E-04</td>
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<tr>
<td>F2</td>
<td>I₂</td>
<td>10⁻⁴</td>
<td>6.2E-08</td>
<td>1.6E-04</td>
<td>6.7E-11</td>
<td>2.5E-03</td>
</tr>
<tr>
<td>F3</td>
<td>I₂</td>
<td>10⁻³</td>
<td>5.9E-09</td>
<td>3.8E-04</td>
<td>1.4E-11</td>
<td>1.8E-03</td>
</tr>
<tr>
<td>F4</td>
<td>I₂</td>
<td>10⁻³</td>
<td>6.8E-09</td>
<td>4.0E-05</td>
<td>1.8E-12</td>
<td>6.1E-04</td>
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<tr>
<td>F5</td>
<td>I</td>
<td>10⁻⁵</td>
<td>5.1E-10</td>
<td>7.0E-05</td>
<td>2.3E-13</td>
<td>1.3E-03</td>
</tr>
<tr>
<td>F6</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>5.7E-09</td>
<td>2.0E-03</td>
<td>3.7E-11</td>
<td>3.8E-03</td>
</tr>
<tr>
<td>F7</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>2.4E-09</td>
<td>1.0E-03</td>
<td>1.0E-04</td>
<td>1.6E-11</td>
</tr>
<tr>
<td>H1</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>1.8E-09</td>
<td>2.6E-03</td>
<td>2.0E-02</td>
<td>3.0E-11</td>
</tr>
<tr>
<td>H3</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>1.9E-09</td>
<td>1.5E-04</td>
<td>6.4E-03</td>
<td>1.9E-12</td>
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<tr>
<td>H4</td>
<td>I₂</td>
<td>10⁻⁵</td>
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<td>(1.0E-05</td>
<td>1.1E-12</td>
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<tr>
<td>H5</td>
<td>I₂</td>
<td>10⁻⁵</td>
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<td>1.6E-11</td>
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<tr>
<td>H6</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>1.8E-08</td>
<td>2.9E-05</td>
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<td>2.7E-12</td>
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<tr>
<td>H10</td>
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<td>10⁻⁴</td>
<td>3.1E-09</td>
<td>2.2E-05</td>
<td>4.3E-13</td>
<td>2.1E-04</td>
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<tr>
<td>H11</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>4.6E-09</td>
<td>1.6E-04</td>
<td>8.0E-04</td>
<td>3.1E-12</td>
</tr>
<tr>
<td>H12</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>3.9E-09</td>
<td>4.6E-04</td>
<td>1.1E-11</td>
<td>9.0E-03</td>
</tr>
<tr>
<td>H13</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>2.1E-09</td>
<td>4.0E-04</td>
<td>3.8E-04</td>
<td>5.3E-12</td>
</tr>
<tr>
<td>H14</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>2.8E-09</td>
<td>6.6E-04</td>
<td>6.2E-04</td>
<td>1.2E-11</td>
</tr>
<tr>
<td>H15</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>3.0E-09</td>
<td>3.5E-04</td>
<td>1.4E-04</td>
<td>6.6E-12</td>
</tr>
<tr>
<td>H16</td>
<td>I₂</td>
<td>10⁻⁵</td>
<td>2.4E-10</td>
<td>9.3E-06</td>
<td>9.3E-06</td>
<td>1.4E-14</td>
</tr>
</tbody>
</table>

* 25°C, solution added  ** 25°C, after immersion in pH 7 solution  † 25°C, coupon added to I solution
† final value  ‡ maximum value at the start of the test  ‡ total release on heating, assumed to occur over 1 hour
Figure 5. Transfer of iodine to organic trap in Experiment F2

3.2.2.1 Effect of surface loading

The two runs with the higher iodine loading (F1 and F2) gave release rates of 1.3 and 1.6×10^4 hr^-1. A decrease in the surface loading by a factor of ~10 led to an increase in the volatile organic formation rate by a factor of 3-10 in runs F3, F6 and F7. However the scatter is further increased with initial rates from runs H1 and H3 varying between 2.6×10^3 hr^-1 and 1.6×10^4 hr^-1. The rate from the aged coupon in run F6 was within the scatter for the other low surface loading coupons and it was not possible to discern any effect of ageing.

3.2.2.2 Effect of bulk solution and pH

Coupons were loaded at pH 4.6 in order to ensure sufficient iodine absorption onto the surface; at higher pH the I₂ in solution would have hydrolysed and disproportionated. In some tests, the coupon was submerged in pH 7 solution during irradiation in order more closely to simulate the conditions expected in a containment. In run F4, a coupon with a similar loading to run F3 was submerged in a buffered solution at pH 7. The release rate was a factor of 10 lower than previous runs where coupons were not submerged. A similar effect was observed in run F7 where solution was added part way through the run and again the release rate fell by a factor of 10. The rate of production from a CEA coupon was also a factor of 5 lower when the coupon was immersed in pH 7 solution.

To show whether this was an effect of pH or the presence of bulk solution, in test H15 the paint coupon was irradiated “dry” for about 24 hours. The irradiation was then stopped, and the coupon immersed in solution at pH 7 for about 15 minutes with occasional agitation. Finally the coupon was removed from the pH 7 solution and replaced in the irradiation vessel, and the irradiation restarted. The rate of organic iodine production fell by a factor of ~3, which is less than observed previously, but examination of the F7 results shows that it took several hours to decrease to the low rate, presumably because of the time to re-equilibrate the pH.
Initially it was thought that the pH effect was due to the effect of the presence of bulk solution, as a result further runs were carried out, tests H12 and H13, where a sample was loaded at pH 4.6, irradiated, then submerged at pH 4.6. The organic iodine continued to be released at the same rate after immersion, confirming that the previously observed effect was due to the pH increase. The inorganic iodine production rate was slower from the submerged coupons.

3.2.2.3 Iodide as adsorbed species

In run F5, a coupon treated with I showed no organic iodine release but in this case the loading was so low that it was probably below the limit of detection. Counting of the organic iodine trap at the end of the test showed that about 0.7% of the iodine was released as organic, corresponding to a release rate of \( \sim 10^4 \text{ hr}^{-1} \).

3.2.2.4 Effect of heating

In the first two tests in which the coupons were heated to 80°C, H1 and H3, it appears that a short burst of organic iodine was produced and then no further organic was formed. The release rates shown in Table 3 for these tests were estimated by assuming that the “step” release occurred over a period of \( \sim 1 \) hour, as indicated by examination of the data. A third test, H14, was carried out with a painted coupon with a thicker paint coating and in this case there was very little effect of temperature. However, heating the coupon supplied by IPSN led to an increase in rate by a factor of 2 on heating to 80°C and the production rate from a coupon supplied by STUK increased by a factor of 5 (Figure 6).

![Figure 6. Effect of heating on organic iodine release from painted coupons](image)

3.2.2.5 Coupon suspended over aqueous solution

In this test the coupon was suspended above bulk solution (pH 7) to try to ensure that it did not dry out during the heating process. The production rate at room temperature was

130
low, $9 \times 10^5\text{ hr}^{-1}$, consistent with results from bulk solution, and fell on heating. The coupon would have had a film of solution covering it as a result of splashing.

3.2.2.6 Coupon loaded from gas phase

In run H10 a coupon loaded from the gas phase was tested. This coupon gave a very low organic iodine production rate, lower than that from coupons immersed during irradiation. The rate did not increase after immersion in boric acid solution and re-irradiation.

3.2.2.7 Paint leachate

In one experiment, an aliquot of solution prepared by leaching a painted coupon was added to the CsI solution during irradiation. No organic iodide release was observed after this addition.

3.2.2.8 Addition of coupon to irradiated iodide

In run H16, CsI solution was irradiated at pH 7, 25°C, after 24 hours a coupon was added to the irradiated solution and the irradiation was restarted. There was no observable change in the organic iodine production rate which continued at a very low rate. Only 0.25% of the iodine was found on the coupon at the end of the test.

3.2.2.9 Other paint types

The production rate in run H5, using a Ripolin-painted coupon supplied by IPSN (France), was similar to that from the UK paint when comparing similar surface concentrations, although the uptake from solution was somewhat greater. The effect of heating to 80°C was to increase the production rate of organic iodine by a factor of ~2 (Figure 6). The effect of bulk solution was similar to the test with UK paint, and the production rate was reduced by a factor of 5, but heating then caused a factor of 5 increase.

The first coupon supplied by STUK (Finland) had bare cut metal sides which corroded in the labelling solution leaving a precipitate of iron oxides, which appeared to decrease the uptake of iodine on the coupon probably because of reduction of $I_2$ to $I^-$, and a low organic iodine production rate was observed. The second coupon with a different substrate (H11) gave similar results to previous work and the effect of heating was to increase the organic iodine production rate by a factor of 5 (Figure 6).

4 DISCUSSION AND CONCLUSION

The production of volatile organic iodine has been shown to occur both in solution and at painted surfaces in the presence of a radiation field; the mechanisms are not known, but are probably similar in both cases with the surface being a source of organic material and capable of locally concentrating iodine. Furthermore, thermal production at painted surfaces can also be a significant mechanism at high temperature.

Production in solution appears to depend on the ratio of the concentrations of organic solute and iodide, which is probably a result of the need to form $I_2$ and a reactive organic species; too much $I^-$ will suppress organic radiolysis, whereas the limited results suggest the converse is not true. The results also imply that a CH$_3$CH$_2$ (or longer) group on the organic solute is necessary for the production of volatile organic iodide.
Organic iodide formation at painted surfaces is assumed to involve similar mechanisms to the solution phase process, the effect of radiolysis was to release I\textsubscript{2}, and organic iodine and the effect of increasing pH was to decrease the organic production rate. The presence of bulk solution made little difference to the volatilisation rate because the residence time of the organic iodine in the solution would have been very short, this would be more important at higher temperatures where hydrolysis is fast. The effect of temperature was to increase the production rate for a limited time, possibly due to faster diffusion and release of the product. A final feature of note is that in most cases the surface production rate decreased with time/dose probably because of removal of a reactant. It is possible that the organic component could be depleted on this timescale if there is only a small quantity available; the iodine certainly was not depleted as more than 60\% of the initial concentration remained at the coupon at the end of all the tests. The most likely explanation is that a substantial fraction of the iodine on the surface reacted with the paint to form a non-labile product.

From the work reported here it has so far not been possible to identify the predominant process. The rate of production in solution will depend on the rate of dissolution of organic materials and their nature which are likely to be different to those used in these experiments, whereas the rates of production from surfaces should not be too dissimilar from the rates measured in this work. However, it can be noted that the production rates in solution at pH 7 were of the same order as those obtained from painted surfaces which were loaded with iodine at pH 4.6. The production rates from surfaces immersed in pH 7 solution were rather lower. Furthermore, the deposition of I\textsubscript{2} onto painted surfaces in either the solution or the gas phase would be lower under neutral/high pH conditions (Belval-Haltier, 1999), which suggests that production in solution could become more important under such conditions. It should also be emphasised that the measurements reported here are production rates and not equilibrium levels. Organic iodine destruction can occur as a result of (i) gas phase radiolysis, (ii) solution phase radiolysis and (iii) solution phase hydrolysis, the latter would be expected to be significant at the elevated temperatures of a LOCA, the rates of the first two processes need confirmation.

Empirical models for the thermal and radiolytic production rates from painted surfaces have been formulated by Funke (1999) based on the data reported here and from the earlier studies of Hellmann (1996) and Marchand (1997). This work indicates that the radiolytic production will be dominant under most conditions of interest, with thermal production only being significant at very high temperatures (>150°C) and low dose rate. However, there appear to be inconsistencies between this model and the expressions derived by Belval-Haltier (1999) based on studies at IPSN, with the latter showing higher production rates particularly at the lower end of the temperature range studied (90°C). These differences are likely to be linked to the different ways in which the iodine was loaded onto the painted surfaces in the two sets of tests. For example, pre-loading from an I\textsubscript{2} solution over a period of days at low temperature and in the absence of a radiation field (as in the tests assessed by Funke (1999)) could lead to increased formation of non-labile forms of iodine within the paint, compared with the IPSN case in which the I\textsubscript{2} production, surface reaction and RI release processes all occurred simultaneously, at high temperature and in a radiation field.

The next stage in this work is to assess the importance of the different production routes, and to make experimental measurements of the decomposition processes to allow the equilibrium formation levels to be predicted and an improved comparison to be made with other work, leading hopefully to the production of a consistent empirical model.
ACKNOWLEDGEMENTS

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SMALL SCALE EXPERIMENTS ON ORGANIC IODIDE PRODUCTION FROM IODINE - PAINTED SURFACE INTERACTION

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ABSTRACT

In case of a severe accident with a core melt occurring in a Pressurized Water Reactor (PWR), iodine is released to the containment. As iodine is a volatile fission product, it is assumed that most, if not all, of the initial inventory enters the containment.

Complex physical and chemical phenomena take place in the containment, depending on conditions such as temperature, dose rate and sump pH. In particular, depending on the nature of paints used in the containment, several processes may lead to the production of organic iodides. In this paper, results for a specific route for organic iodide production are presented.

Separate effect experiments have been carried out to determine the formation of organic iodides from iodine adsorbed on painted surfaces. The studied parameters include temperature (60-140°C), dose rate (0.05-5kGy/h), species adsorbed (I₂, I⁻), and pH (3, 9). These parameters were chosen to be as representative as possible.

For measurements of the gas phase composition, the main analytical methods used were: gas phase chromatography with electron capture detector, gas phase chromatography coupled with mass spectrometry and mass spectrometry.

In a first step, some experiments have been conducted at relatively high concentrations in order to maximize the organic iodide production. Then, concentrations have been lowered in order to make the experiments more representative of nuclear power plant accident.

Dose rate and temperature effects were first studied separately and then in combination. To compare the different effects, an experiment plan method has been used. This method allowed the important parameters in the production of organic iodides to be determined while minimizing the number of experiments to be carried out.

The separate effects of temperature and dose rate appeared to be different from joint effects. For the separate effects, at relatively high iodine surface concentrations, increased
temperature led to higher organic iodide production than irradiation. This was not the case for combined effects at the same surface iodine concentration.

Effects were shown to be dependant on iodine surface concentration, showing that a representative surface iodine concentration is needed to study organic iodide production.

1. INTRODUCTION

During a hypothetical severe reactor accident, iodine is released from the core into the containment. Iodine is an important fission product because it conveys a large fraction of the core activity and it causes serious radiological consequences.

To determine the source term, it is necessary to know the quantity and the chemical forms of iodine present in the gas phase. Partitioning of iodine in the containment will occur between the sump (aqueous phase), the atmosphere and painted surfaces. Volatile iodine I₂ has a great affinity for painted surfaces. Such surfaces will thus play a significant role in the trapping of this species.

Organic iodides are of particular importance because they are not easily trapped on filters. For these species, several mechanisms of production have been identified: homogeneous or heterogeneous reactions, in aqueous phase or gas phase (Parsly, 1971). Among these mechanisms, PHEBUS-FP experiments showed that one of the most significant is the interaction of molecular iodine with paintings in gas phase (Jacquemain et al., 1997, 1999).

The small scale experiments described below make it possible to improve knowledge on the production of organic iodides from the iodine – paint interaction. The paint chosen for these experiments is the Ripolin Freitag hydrocentrifugon, which is the most commonly used in the containment of French PWRs. The studied parameters are temperature (60-140°C), dose rate (0.05 - 5kGy/h), adsorbed species (I₂ and I) and pH (3 and 9).

Initially, feasibility experiments were carried out. They were performed without coupling of the dose rate and the temperature, at identical concentrations of I and I₂ which are much higher than those estimated in reactors. An experiment plan method was used in order to minimize the number of experiments while deducing the relative influence of the various studied parameters. Following these preliminary experiments, a study for more representative conditions was carried out, taking into account the dose rate - temperature coupling. The concentrations were decreased gradually as much as possible to approach the conditions expected in reactors.

A short description of the procedure and methods of analysis used are given below, followed by the experiment plans and associated results.

2. PROCEDURE

The procedure includes the following stages. Initially, the adsorption of iodine on the 150 mm x 20 mm two side painted plates is carried out in aqueous phase, during 72 h at 25°C in 1.5 l of solution. The plates containing iodine are then withdrawn from the aqueous phase, washed, and placed in 100 cc glass flasks containing a synthetic air medium. They are finally exposed either to elevated temperature, irradiation or both during one week in order to allow
equilibrium to be reached. It must be noted that moisture was present in the gas phase because plates were introduced in the cells with remaining water droplets from the washing. The two principal stages of this procedure are schematized in figure 1.

![Diagram of the experimental procedure](image)

**Figure 1:** The two stages of the experimental procedure

The gaseous atmosphere and plates are then analyzed by various methods, chosen for their high sensitivity:
- gas chromatography coupled with mass spectrometry, for the identification of gaseous compounds,
- gas chromatography with electron capture detector, for the quantification of organic iodides (RI),
- mass spectrometry, for the quantification of gases $O_2$, $N_2$, $CO_2$... and for the organic iodides in quantities higher than 1ppm,
- a catalysis - colorimetry association, for the analysis of total iodine forms ($I_2$ and RI),
- infra-red spectrometry, for the analysis of painted plates.

3. **PRELIMINARY STUDIES WITHOUT TEMPERATURE – DOSE RATE COUPLING**

The preliminary studies have demonstrated the feasibility of such experiments and shown the relative influence of various parameters: the chemical form of iodine, the temperature, the dose rate and the pH. In this first series of experiments, organic iodides formation was intentionally maximized by using high surface concentrations and a surface/volume ratio (6 dm$^{-1}$) larger than in the reactor.
3.1 First series

The first series of experiments have made it possible to estimate the effect of temperature, dose rate, species adsorbed and pH in the intervals specified in the table 1. The concentration of I or I₂ in solution is always equal to 10⁻³ mol/l in the first series.

Table 1: Parameter ranges for the first series

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>T0 = 25, T1 = 60, T2 = 80, T3 = 100</td>
</tr>
<tr>
<td>Dose rate (kGy/h)</td>
<td>DD0 = 0, DD1 = 5, DD2 = 0.5, DD3 = 0.05</td>
</tr>
<tr>
<td>Adsorbed species</td>
<td>I, I⁻</td>
</tr>
<tr>
<td>pH</td>
<td>pH1 = 3, pH2 = 9</td>
</tr>
</tbody>
</table>

Table 2 summarizes the conditions and results of the 20 experiments conducted.

Table 2: Conditions and results for the first series

<table>
<thead>
<tr>
<th>Cell number</th>
<th>Adsorbed species</th>
<th>pH</th>
<th>Dose rate (kGy/h)</th>
<th>Temperature (°C)</th>
<th>ICH₃ concentration (mol/l)</th>
<th>IC₃H₅ concentration (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I, I₂</td>
<td>3</td>
<td>0</td>
<td>60</td>
<td>6.32 10⁻⁸</td>
<td>1.49 10⁻⁸</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>3</td>
<td>0</td>
<td>60</td>
<td>1.12 10⁻⁹</td>
<td>3.35 10⁻⁹</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>4.37 10⁻¹⁰</td>
<td>6.25 10⁻¹⁰</td>
</tr>
<tr>
<td>4</td>
<td>I₂</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>1.68 10⁻⁹</td>
<td>6.70 10⁻⁹</td>
</tr>
<tr>
<td>5</td>
<td>I, I₂</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>1.38 10⁻⁶</td>
<td>6.06 10⁻⁷</td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>3</td>
<td>0</td>
<td>100</td>
<td>2.34 10⁻⁷</td>
<td>3.35 10⁻⁷</td>
</tr>
<tr>
<td>7</td>
<td>I</td>
<td>3</td>
<td>0</td>
<td>80</td>
<td>1.81 10⁻⁹</td>
<td>1.0 10⁻⁹</td>
</tr>
<tr>
<td>8</td>
<td>I₂</td>
<td>3</td>
<td>0</td>
<td>80</td>
<td>9.06 10⁻⁷</td>
<td>3.98 10⁻⁷</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>3</td>
<td>0.05</td>
<td>25</td>
<td>3.76 10⁻¹⁰</td>
<td>6.76 10⁻¹⁰</td>
</tr>
<tr>
<td>10</td>
<td>I₂</td>
<td>3</td>
<td>0.05</td>
<td>25</td>
<td>2.31 10⁻⁸</td>
<td>3.73 10⁻⁹</td>
</tr>
<tr>
<td>11</td>
<td>I</td>
<td>3</td>
<td>0.05</td>
<td>25</td>
<td>8.57 10⁻⁹</td>
<td>3.35 10⁻⁹</td>
</tr>
<tr>
<td>12</td>
<td>I, I₂</td>
<td>3</td>
<td>0.05</td>
<td>25</td>
<td>1.27 10⁻⁸</td>
<td>2.61 10⁻⁹</td>
</tr>
<tr>
<td>13</td>
<td>-</td>
<td>9</td>
<td>0.05</td>
<td>25</td>
<td>2.27 10⁻¹⁰</td>
<td>3.03 10⁻¹⁰</td>
</tr>
<tr>
<td>14</td>
<td>I₂</td>
<td>3</td>
<td>0.5</td>
<td>25</td>
<td>3.49 10⁻⁸</td>
<td>7.75 10⁻⁹</td>
</tr>
<tr>
<td>15</td>
<td>I</td>
<td>3</td>
<td>0.5</td>
<td>25</td>
<td>6.73 10⁻⁹</td>
<td>3.74 10⁻⁹</td>
</tr>
<tr>
<td>16</td>
<td>I₂, I</td>
<td>3</td>
<td>0.5</td>
<td>25</td>
<td>2.61 10⁻⁸</td>
<td>7.47 10⁻⁹</td>
</tr>
<tr>
<td>17</td>
<td>-</td>
<td>9</td>
<td>0.5</td>
<td>25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>-</td>
<td>3</td>
<td>5</td>
<td>25</td>
<td>2.18 10⁻⁹</td>
<td>1.09 10⁻⁹</td>
</tr>
<tr>
<td>19</td>
<td>I, I₂</td>
<td>3</td>
<td>5</td>
<td>25</td>
<td>3.61 10⁻⁷</td>
<td>4.51 10⁻⁸</td>
</tr>
<tr>
<td>20</td>
<td>I</td>
<td>9</td>
<td>5</td>
<td>25</td>
<td>9.77 10⁻⁹</td>
<td>6.15 10⁻⁹</td>
</tr>
</tbody>
</table>

For this study, an experiment plan was used. The assumption of independence of parameters with respect to the production of organic iodides was made. With this assumption, the development of the experiment plan relies on the use of Hadamard’s matrices (Vigier, 1988). This method allows a quantitative evaluation to be made of the influence of a great number of parameters (presumably independent) while minimizing the number of experiments to be realized.

The absorption of the species I₂ imposes the use of an acid solution (dismutation of I₂ at high pH). Moreover, when the dose rate is non-zero, the temperature is equal to T0. This
led to the use of a set of matrices of order 4. In the set of experiments carried out, ICH₃ is the species mainly formed but IC₂H₅ is also present and was quantified.

One of the advantages of this method is that it allows a comparison to be made between the relative influence (called effect) of the various parameters on the production of organic iodides. If the effect is positive, then the parameter enhances the production; it is the opposite when the effect is negative. The parameters being able to take a high value or a low value, for the matrices chosen, the effect of a parameter is simply calculated in the following way:

\[ E_f = \frac{\sum R(+) - \sum R(-)}{4} \quad (1) \]

R(+) being the result of the experiments for a high value of the parameter, R(-) that of the experiments for a low value of the parameter. In the case of the preliminary experiments, the result is the amount of organic iodides formed in the cell expressed in vpm.

For example, the effect of dose rate in the range 0.5-5 kGy/h is determined as follows. The experiments are defined by:

\[
\begin{align*}
\text{exp 1} & : (1 \quad -1 \quad -1 \quad 1) \quad DD \\
\text{exp 2} & : (-1 \quad 1 \quad -1 \quad 1) \quad I_2 \\
\text{exp 3} & : (-1 \quad -1 \quad 1 \quad 1) \quad I' \\
\text{exp 4} & : (1 \quad 1 \quad 1 \quad 1) \quad T
\end{align*}
\]

With the conventions that -1 refers to 0.5 kGy/h, with I' and with I₂, and that +1 refers to 5 kGy/h, without I' and without I₂, then the rows of the matrix define the experiments number 19, 15, 14 and 18. According to equation 1, the effect is then calculated as:

\[ E_f = (R(19) + R(18) - R(14) - R(15)) / 4. \quad (2) \]

The results obtained in terms of effect on the production of ICH₃ and IC₂H₅ are presented hereafter.
Effects of temperature, I₂ and I⁻

These effects are presented in figures 2 and 3.

**Figure 2:** Effects of parameters without radiation at pH = 3 in the 60 - 80°C temperature range

**Figure 3:** Effects of parameters without radiation at pH = 3 in the 80 - 100°C temperature range

Whatever the temperature range, the effects of the various parameters on the production of IC₂H₅ are proportional to those on the production of ICH₃. The production of ICH₃ is thus related to that of IC₂H₅, probably by the same mechanism.

The effect of the species I₂ very largely increases when the temperature increases (comparison of the intervals 60-80°C and 80-100°C). In temperature, the effect of I⁻ is negligible. The site on which iodine is fixed (according to its chemical form) is thus of primary importance for the later organic iodide formation.
The effect of the temperature remains the same in the two considered intervals.

**Effects of dose rate, I₂ and I⁻**

These effects are presented in figures 4 and 5.

![Figure 4: Effects of parameters at 25°C and pH = 3 in the 0.5 – 5 kGy/h dose rate range](image)

![Figure 5: Effects of parameters at 25°C and pH = 3 in the 0.05 – 0.5 kGy/h dose rate range](image)

The effects are all equivalent at large dose rates. They are definitely weaker than those of high temperatures. This difference can be attributed either to a production of organic iodides weaker for an exposure under radiation than for an exposure in temperature, or to a destruction of organic iodides by the radiation more significant than by the temperature.
Effects of pH, dose rate and I⁻

These effects are presented in figures 6 and 7.

![Graph](image)

**Figure 6:** Effects of parameters without I₂ at 25°C in the 0.5 – 5 kGy/h dose rate range

![Graph](image)

**Figure 7:** Effects of parameters without I₂ at 25°C in the 0.05 – 5 kGy/h dose rate range

The effect of the pH, in a range in which the effects are weak can be regarded as negligible. One can explain its limited influence either by the fact that the species I⁻ is fixed on an identical site and in equal quantity independent of the pH, or by the fact that under radiation the production of organic iodides is not influenced by the site on which iodine is fixed. One cannot thus highlight the action of the pH in the considered intervals.

Moreover the effect of the pH cannot be studied on the species I₂, this species not being stable in solution at pH higher than 4. The interest in the study of the influence of the pH on the production of organic iodides is thus limited. However, the knowledge of the pH is essential because it determines the initial species which will be adsorbed on the paint.
3.2 Complementary study for the 120°C-140°C temperature range

The analysis of the results of the first series shows that the parameters having the largest influence are the adsorbed species and the temperature. The study was thus continued at higher temperature to confirm the expected evolutions for species I⁺ and I₂.

The results show that the quantities of organic iodides formed from species I⁺ remain negligible. Furthermore, by comparing the results of experiments at identical temperature or dose rate with I₂ or (I₂ + I⁺), then one concludes that the interaction between the parameter I₂ and I⁺ is negligible.

The evolution of the production of ICH₃ and IC₂H₅ from the species I₂ with respect to temperature is illustrated in figure 8.

![Figure 8: Formation of organic iodides from species I₂ without radiation as a function of temperature](image)

This study confirms that in absence of radiation, the temperature has a great influence on the production of organic iodides.

3.3 Comparison of temperature and dose rate effects

Under the conditions of the preliminary experiments, the temperature has a much more significant effect on organic iodide formation than the dose rate. The thermal reactions of destruction of ICH₃ in the gas phase are very slow and thus negligible, but it can be different for radiolytic destruction. Although radiolysis of organic iodides is not likely to be important in presence of moisture, this hypothesis is not firmly established. It is then interesting to assess the possible impact of organic iodides destruction on the results.

The destruction of ICH₃ by irradiation in dry air at 15°C was studied by Tang and Castleman (1968). The following relation was given:

\[
[CH₃I] = [CH₃I]₀ e^{-0.59D}
\]  (3)
with \( D \) being the dose in kGy and \([\text{CH}_3\text{I}]_0\) the initial \( \text{ICH}_3 \) concentration. This integrated form comes from the kinetic equation:

\[
\frac{d([\text{CH}_3\text{I}])}{dt} = -0.59DD[\text{CH}_3\text{I}]
\]  \hspace{1cm} (4)

with \( DD \) the dose rate in kGy/s.

If one assumes that after one week equilibrium is reached, then the rate of formation of \( \text{ICH}_3 \) is equal to its destruction rate. Furthermore, if one makes the assumption that the formation of \( \text{ICH}_3 \) is constant with time, it is possible to estimate the quantity of \( \text{ICH}_3 \) that would have been accumulated in the cell if there were no radiolytic destruction. This result can then be compared with the production at high temperature. The calculation for a cell (\( I_1 \), \( I_2 \), maximum dose rate) gives a \( \text{ICH}_3 \) production rate equal to \( 1.4 \times 10^4 \) mol/l/h, leading to a final concentration of \( 2.3 \times 10^4 \) mol/l. This is a maximum value as the radiolytic decomposition rate is expected to be lower in the moist atmosphere in this test. The production of organic iodides would then have been very largely higher under radiation than in temperature.

It is also important to note that, according to the mechanism proposed by Tang and Castleman, the iodine released by destruction of \( \text{ICH}_3 \) would be in the form of \( I_1 \). For these experiments, the analysis by catalysis-colorimetry showed that no significant amount of iodine was present in the cells except under organic form. However, released molecular iodine could in turn have been adsorbed on paint, or further reacted with air radiolysis products, thus not being detectable during gas analysis.

Although we favor the hypothesis that radiolytic organic iodides destruction did not play an important role in these experiments, the previous elements show that it is difficult to conclude on this point which may have important implications with respect to the analysis of the results.

4. EXPERIMENTS WITH TEMPERATURE – DOSE RATE COUPLING

Scoping experiments carried out under dose rate and temperature coupling showed that there is actually interaction between the two parameters. The study was then pursued in this direction, once again using an experiment plan to estimate the relative effects of the various parameters (adsorbed iodine quantity, temperature, dose rate) and to determine a simplified model of organic iodides formation.

For this series of experiments, the effects of temperature, dose rate and surface concentration were studied for intervals of variation specified in table 3.

**Table 3:** Parameter ranges for the experiments with temperature – dose rate coupling

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>T1 = 80, T2 = 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose Rate (kGy/h)</td>
<td>DD1 = 5, DD2 = 0.5</td>
</tr>
<tr>
<td>I surface concentration (mol/cm²)</td>
<td>CS1 = 2.5 ( \times 10^5 ), CS2 = 2.5 ( \times 10^6 ), CS3 = 2.5 ( \times 10^7 )</td>
</tr>
</tbody>
</table>

The study was limited to species \( I_2 \) because it is more reactive with respect to the production of iodide organic and its affinity with the painting is clearly greater than that of \( I_1 \). In addition, these experiment were intended to be representative of the containment atmospheric surfaces on which \( I_2 \) is the species likely to adsorb.
The surface concentration was estimated by supposing that 50% of iodine $I_2$ present in solution is adsorbed on the painted plate. This percentage was established during adsorption experiments for a high initial concentration (Verdier, 1997). The experiments were not carried out yet for smaller concentrations in $I_2$ but it will be supposed that the percentage of adsorbed iodine remains equal to 50. This assumption is supported by the following observations:

- the adsorption of $I_2$ leads to the release of $I$ in solution, and therefore 50% of adsorption is the maximum that can be obtained,
- as no saturation of the paint with large concentration in $I_2$ was noticed, this is all the more true with small concentration,
- the time of adsorption (72 h) was sufficiently long to allow the complete adsorption of $I_2$.

In order to determine the effects of each parameter but also the effects of the coupled parameters, a complete factorial experiment plan was implemented (Vigier, 1988).

With $Y$ being the response and $X_1$, $X_2$ and $X_3$ being the normalized parameters, the following relation is written:

$$\{Y\} = E \{X_1, X_2, X_3\}$$

with $E$ the matrix of experiments defined as follows:

$$E = \begin{pmatrix} 
-1 & -1 & -1 \\
1 & -1 & -1 \\
-1 & 1 & -1 \\
1 & 1 & -1 \\
-1 & -1 & 1 \\
1 & -1 & 1 \\
-1 & 1 & 1 \\
1 & 1 & 1 
\end{pmatrix}$$

Parameters $X_1$, $X_2$ and $X_3$ are arbitrarily chosen to be the dose rate, the temperature and the surface concentration.

The response $Y$ studied in this case is different to that in the experiments without coupling because in this series of experiments, the surface concentrations are variable and it is necessary to be able to compare the results and the effects between them. $Y$ is thus defined as the percentage of conversion of the number of moles of adsorbed $I$ into ICH$_2$. The calculated effects will then not be directly comparable with those of the preliminary experiments.

If we denote $B = \{b_0, b_1, b_2, b_3, b_{12}, b_{13}, b_{23}, b_{123}\}$ the effects, then we have:

$$B = 1/8 \ M' \ Y$$

with $M$ the matrix of effects defined as:
\[
M = \begin{pmatrix}
1 & -1 & -1 & -1 & 1 & 1 & 1 & -1 \\
1 & 1 & -1 & -1 & -1 & 1 & 1 & 1 \\
1 & -1 & 1 & -1 & 1 & -1 & 1 & 1 \\
1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 \\
1 & -1 & -1 & 1 & 1 & -1 & 1 & 1 \\
1 & 1 & -1 & 1 & -1 & 1 & -1 & -1 \\
1 & -1 & 1 & 1 & -1 & -1 & 1 & -1 \\
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\end{pmatrix}
\]

From this formulation, one can deduce an empirical model, valid only in the parameter ranges defined by the experiments, of the following form:

\[
R = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3
\]

(7)

with \( R \) the percentage of conversion.

Ranges \( DD = 0.5 - 5 \text{ kGy/h}, T = 80 - 100\text{°C}, [I_{surf}] = 2.5 \times 10^{-6} - 2.5 \times 10^{-5} \text{ mol/cm}^2 \)

The results which allow the calculation are gathered in table 4.

**Table 4: Conversion percentage**

<table>
<thead>
<tr>
<th>Yi</th>
<th>cell number</th>
<th>DD kGy/h</th>
<th>T °C</th>
<th>([I_{surf}] ) mol/cm²</th>
<th>mean conversion percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>y1</td>
<td>c62</td>
<td>0.5</td>
<td>80</td>
<td>2.5 \times 10^{-4}</td>
<td>4.9 \times 10^{-3}</td>
</tr>
<tr>
<td>y2</td>
<td>c76, c77</td>
<td>5</td>
<td>80</td>
<td>2.5 \times 10^{-4}</td>
<td>3.5 \times 10^{-3}</td>
</tr>
<tr>
<td>y3</td>
<td>c63, c64</td>
<td>0.5</td>
<td>100</td>
<td>2.5 \times 10^{-4}</td>
<td>5.3 \times 10^{-3}</td>
</tr>
<tr>
<td>y4</td>
<td>c66, c67</td>
<td>5</td>
<td>100</td>
<td>2.5 \times 10^{-4}</td>
<td>5.75 \times 10^{-3}</td>
</tr>
<tr>
<td>y5</td>
<td>c68</td>
<td>0.5</td>
<td>80</td>
<td>2.5 \times 10^{-5}</td>
<td>7.2 \times 10^{-3}</td>
</tr>
<tr>
<td>y6</td>
<td>c44, c45</td>
<td>5</td>
<td>80</td>
<td>2.5 \times 10^{-5}</td>
<td>1.35 \times 10^{-3}</td>
</tr>
<tr>
<td>y7</td>
<td>c69</td>
<td>0.5</td>
<td>100</td>
<td>2.5 \times 10^{-5}</td>
<td>7.2 \times 10^{-2}</td>
</tr>
<tr>
<td>y8</td>
<td>c52, c53</td>
<td>5</td>
<td>100</td>
<td>2.5 \times 10^{-5}</td>
<td>3.35 \times 10^{-3}</td>
</tr>
</tbody>
</table>

Note that the value for cell number c69 is substantially higher than those for the other cells. This experiment was unfortunately not doubled. There is no particular reason to think that this value is wrong. Furthermore, the trends exhibited by the gas analysis were qualitatively consistent with the other experiments. This result is then used in the subsequent analysis. However, it would be valuable to check this value in a new experiment.

The calculated effects are represented in figure 9.
Figure 9: Effects of parameters in the $0.5 - 5$ kGy/h dose rate, $80 - 100^\circ$C temperature and $2.5 \times 10^{-6} - 2.5 \times 10^{-5}$ surface concentration ranges

The results show that the effects are all equivalent in the studied intervals. All the parameters have an equivalent weight on the result. It is noted that the effect of the dose rate (b1) is negative, therefore when the dose rate increases, the percentage of conversion decreases. The couplings dose rate - temperature, dose rate - surface concentration and dose rate - temperature - surface concentration are also negative. Any effect including the dose rate parameter (with coupling or not of other parameters) is negative.

Ranges DD $= 0.5 - 5$ kGy/h, $T = 80 - 100^\circ$C, $[I_{surf}] = 2.5 \times 10^{-7} - 2.5 \times 10^{-6}$ mol/cm$^2$

The results which allow the calculation are gathered in table 5.

Table 5: Conversion percentage

<table>
<thead>
<tr>
<th>$Y_i$</th>
<th>cell number</th>
<th>DD kGy/h</th>
<th>T $^\circ$C</th>
<th>$[I_{surf}]$ mol/cm$^2$</th>
<th>mean conversion percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y_1$</td>
<td>c70</td>
<td>0.5</td>
<td>80</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>$y_2$</td>
<td>c73</td>
<td>5</td>
<td>80</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$y_3$</td>
<td>c71, c72</td>
<td>0.5</td>
<td>100</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$3.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$y_4$</td>
<td>c74, c75</td>
<td>5</td>
<td>100</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$7.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>$y_5$</td>
<td>c62</td>
<td>0.5</td>
<td>80</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$4.9 \times 10^{-3}$</td>
</tr>
<tr>
<td>$y_6$</td>
<td>c76, c77</td>
<td>5</td>
<td>80</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$3.45 \times 10^{-3}$</td>
</tr>
<tr>
<td>$y_7$</td>
<td>c63, c64</td>
<td>0.5</td>
<td>100</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$5.3 \times 10^{-3}$</td>
</tr>
<tr>
<td>$y_8$</td>
<td>c66, c67</td>
<td>5</td>
<td>100</td>
<td>$2.5 \times 10^{-6}$</td>
<td>$5.7 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

The calculated effects are represented in figure 10.
Figure 10: Effects of parameters in the 0.5 – 5 kGy/h dose rate, 80 – 100°C temperature and 2.5 \(10^7 – 2.5 \times 10^8\) surface concentration ranges

In this case, the parameters having the greatest influence are the dose rate (b1) and the surface concentration (b3). The effects of the single parameters are all negative, whereas the couplings are positive. The dose rate - temperature coupling (b12) has almost no effect. The effects are very inhomogeneous in contrast to those of the 2.5\(10^8\) - 2.5\(10^5\) mol/cm² surface concentration range.

It is therefore concluded that it is important to carry out experiment under representative conditions because it is not possible to extrapolate a model of organic iodides formation out of the experimental conditions explored.

5. OXYGEN UPTAKE

The exposure of the painted plates to increased temperature and irradiation causes an oxygen uptake in the cell and the formation of CO₂. Table 6 presents an example of the results for elevated temperature without irradiation. This oxygen uptake seems to play an important role in these experiments and to be related to the production of CO₂. It is an increasing function of the temperature and is less pronounced when the plate is exposed to the radiation.
Table 6: Oxygen uptake and carbon dioxide formation (experiments without irradiation)

<table>
<thead>
<tr>
<th>cell number</th>
<th>temperature (°C)</th>
<th>initial amount of oxygen (mol)</th>
<th>final amount of oxygen (mol)</th>
<th>oxygen uptake percentage</th>
<th>final amount of carbon dioxide (mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>80</td>
<td>7.44 10^-4</td>
<td>5.48 10^-4</td>
<td>26.3</td>
<td>8.40 10^-5</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>7.44 10^-4</td>
<td>1.87 10^-4</td>
<td>74.9</td>
<td>1.78 10^-4</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>7.44 10^-4</td>
<td>2.16 10^-4</td>
<td>71.0</td>
<td>1.68 10^-4</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>7.44 10^-4</td>
<td>1.72 10^-4</td>
<td>76.9</td>
<td>1.96 10^-4</td>
</tr>
<tr>
<td>21</td>
<td>120</td>
<td>7.06 10^-4</td>
<td>1.68 10^-4</td>
<td>76.2</td>
<td>1.55 10^-4</td>
</tr>
<tr>
<td>22</td>
<td>120</td>
<td>7.06 10^-4</td>
<td>1.03 10^-4</td>
<td>85.4</td>
<td>1.79 10^-4</td>
</tr>
<tr>
<td>23</td>
<td>140</td>
<td>7.06 10^-4</td>
<td>-</td>
<td>100</td>
<td>2.53 10^-4</td>
</tr>
<tr>
<td>24</td>
<td>140</td>
<td>7.06 10^-4</td>
<td>3.31 10^-7</td>
<td>100</td>
<td>2.61 10^-4</td>
</tr>
<tr>
<td>25</td>
<td>140</td>
<td>7.06 10^-4</td>
<td>-</td>
<td>100</td>
<td>2.54 10^-4</td>
</tr>
</tbody>
</table>

The oxygen consumption at 60°C is negligible. At 140°C, the oxygen uptake is such that there is no more oxygen present in the cell at the end of the test. Complementary experiments were carried out in order to determine the oxygen uptake at this temperature. They were carried out in absence of iodine with a larger cell volume and duration of 1 and 2 weeks. They were performed with a different paint batch and showed some differences in oxidation. However, a clear relation between oxygen uptake and carbon dioxide can be derived, with one mole of CO₂ produced for three moles of O₂ consumed as shown in figure 11.

![Graph showing the relationship between carbon monoxide formation and oxygen uptake](image)

**Figure 11:** Carbon dioxide formation as a function of oxygen uptake

It was also noted that the presence of iodine on the surface affected the oxidation of the paint. Oxidation decreases when the surface iodine concentration increases. However, visually, painted coupons with high iodine concentrations seems definitely more degraded than those with small concentrations.
6. CONCLUSION

The organic iodides formation from iodine – painted surface interaction was studied with respect to the species, temperature and dose rate parameters. Experiment plans were used in order to limit the number of tests and estimate the relative effects of the parameters.

Experiments without dose rate - temperature coupling lead to the following conclusions: the temperature has an effect definitely more important than the dose rate, the species I₂ is more reactive than species I with respect to the adsorption and of the organic iodide formation.

Experiments at various I₂ concentrations, with dose rate – temperature coupling, lead to completely different results. Moreover, the results depend on the concentration ranges. In the range 2,5.10⁻⁶ - 2,5.10⁻⁴ mol/cm², the effects of the concentration, dose rate and temperature are quite homogeneous. This is not the case for range 2,5.10⁻⁷ - 2,5.10⁻⁴ mol/cm².

These experiments highlight the fact that it is very important to use representative surface concentrations in order to establish empirical models of organic iodides formation.

The formation of organic iodide from painted surfaces is likely to be a complicated process, and these experiments do not provide any direct information about the mechanism. The results show that organic iodide production is favored under conditions which also lead to extensive oxidation of the paint surface, but further experiments would be required to determine whether there is a connection between the two processes.

7. REFERENCES


ACKNOWLEDGEMENTS

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DATA ANALYSIS AND MODELLING OF ORGANIC IODIDE PRODUCTION AT PAINTED SURFACES

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ABSTRACT

Painted surfaces in the containment during severe accidents are a source of production of volatile organic iodide which contributes to the fraction of gaseous iodine in the containment atmosphere. Experimental studies on the release of organic iodide from painted surfaces pre-loaded with iodine are analyzed with the aim of deriving rate constants suitable for modelling in current severe accident iodine codes. Major influencing parameters are dose rate, temperature, and iodine deposition (DEP) on the painted surface. Rate constants from tests with and without radiation obey the same empirical relationship $k = A \cdot \text{DEP}^B$, but with different model parameters $A$ and $B$. The same model is valid for different Epoxy-type paints as used in British, Finnish, French and German containments. Without radiation, RI release is much higher after I$_2$ deposition than after I$^-$ deposition. There is no difference in the presence of radiation. The models for RI release with and without presence of radiation predict rate constants within one order of magnitude. Within this accuracy, the model is recommended for use either in dry atmospheres or in condensing-steam atmospheres, and also for RI release from painted surfaces immersed in the sump.

1 INTRODUCTION

Iodine is one of the most important fission products which would be released in the event of a severe reactor accident. Plant assessments have shown that it contributes significantly to the source term for a range of accident scenarios. However, the considerable differences between the iodine behaviour observed in PHEBUS test FPT0 and that predicted by containment chemistry calculations indicate that the current models do not correctly treat all of the phenomena that could be important in a reactor accident.

In particular, formation of volatile organic iodide represents an important uncertainty in source term calculations. Organic iodide is, compared with other volatile iodine forms, less susceptible to accident management measures designed to reduce the iodine concentration in the gas phase (sprays) and in the vent gas (filters). Variations in the estimated organic iodide concentrations are therefore reflected more or less directly in source term predictions, irrespective of the accident sequence under consideration.

Volatile organic iodide is produced by organic material dissolved in aqueous solutions (sumps) or in the containment atmosphere, and it is produced at the painted surfaces of the containment walls and structures, either exposed to the gas phase or immersed in sumps. The
formation of organic iodide at painted surfaces, also called the heterogeneous formation of organic iodide, is of particular interest in this report due to the large surface area of painted walls.

Recent experimental studies provided data on heterogeneous organic iodide formation at high temperatures and under irradiation which are appropriate for model development. These data are analyzed with the aim of understanding the mechanism of organic iodide formation and to derive a model suitable for severe accident iodine codes such as IMPAIR (Güntay 1992).

In the following, the expression organic iodide is abbreviated as RI. It includes the whole class of volatile organic iodides with e.g. methyl iodide (CH$_3$I), ethyl iodide (C$_2$H$_5$I) and propyl iodide (C$_3$H$_7$I) as a few prominent, exemplary members.

2 DATA ANALYSIS

Experimental data under sufficiently defined boundary conditions are selected to derive rate constants for the production of volatile RI at painted surfaces. This set of rate constants serves as a basis for further model development.

It is distinguished formally between thermal and radiation-induced RI production, based on the experimental boundary conditions (presence or absence of radiation). The strategy in this paper is to consider these two boundary conditions as separate reaction paths with own, separate modeling. Phenomenologically, radiation-induced RI production should be an additional mechanism to the thermal RI production. Nevertheless, radiation-induced RI production could itself also depend on temperature.

2.1 Marchand Data

Experimental Conditions

The radiation-induced and thermal RI production at painted surfaces exposed to a steam-free gas phase was recently studied in a French thesis (Marchand 1997). The objective was to study parameter influences on the extent of RI formation. However, no kinetic evaluation of the obtained data had been performed.

Painted coupons were loaded with I$_2$, I or I$_2$/I mixtures from solution. The pre-loaded coupons were placed in closed glass flasks with defined atmospheres and kept for one week. During this time, the flasks were either irradiated at 20°C, or the flasks were heated up to 140°C without irradiation. At test end the gas phase was analyzed by gas chromatography and mass spectrometry. Methyl and ethyl iodide were identified, with methyl iodide mostly but not always dominating.

Painted Coupons were of 2 cm x 15 cm, representative of French PWR's, and inserted into glass flasks of 100 ml volume. The volumes were conditioned with air/Kr mixtures, but without steam. Iodine loadings were between 9·10$^{-3}$ mol I/m$^2$ and 2·10$^{-1}$ mol I/m$^2$, dose rates were zero or between 0.05 kGy/h and 5 kGy/h.

The resulting volatile RI fraction was based on the sum of methyl iodide and ethyl iodide, related to the total iodine inventory. Appreciable destruction of the painted coupons was observed after the tests which is an important source for scattering results.
Thermal RI Production (Tests without Radiation)

The well-known first-order kinetics is applied to derive rate constants from the experimental RI fractions:

\[
d[RI]/dt = k_T \cdot [DEP] \cdot S/V
\]  \hspace{1cm} (1)

- [RI] RI concentration in the gas phase \(\text{(mol/m}^3\text{)}\)
- \(k_T\) rate constant for thermal RI formation \(\text{(s}^{-1}\text{)}\)
- [DEP] iodine deposition on paint \(\text{(mol/m}^2\text{)}\)
- \(S\) painted surface area \(\text{(m}^2\text{)}\)
- \(V\) gaseous volume \(\text{(m}^3\text{)}\)

During the Marchand tests, the quantity [DEP] remained practically constant, and Eq. 1 is therefore readily integrated:

\[
k_T = \%RI / (\Delta t \cdot S/V)  \hspace{1cm} (2)
\]

- \(\%RI = [RI]/[DEP]\cdot 100\%\), the fractional RI release \(\text{(\%)}\), given in (Marchand 1997)
- \(\Delta t\) test duration (= 1 week) \(\text{(s)}\)

The Marchand tests had shown that RI production after I\(_2\)-loading was much higher than after I-loading. The following analysis therefore concentrates on data with I\(_2\)-loading. Nevertheless, data with common I\(_2\)/I-loading were included, too, in this analysis, considering the additional effect of I on RI production as negligibly small.

Rate constants on thermal RI production at painted surfaces were calculated from data in (Marchand 1997) using Eq. 2. Fig. 1 shows the temperature dependency of these rate constants. From the fit to the data according to the Arrhenius model, \(k_T(25\,^{\circ}\text{C}) = 7.59 \cdot 10^{-13}\, \text{s}^{-1}\) and an activation energy of 71700 J/mol is derived. This model is valid under the conditions 60\(^\circ\text{C}-140\,^{\circ}\text{C}, no radiation, steam-free atmosphere (air/inert gas), and for French PWR paint loaded with I\(_2\). The iodine deposition is not yet considered as a model parameter at this stage as will turn out to be necessary in the modelling Chapter.

Radiation-induced RI Production (Tests with Radiation)

A first-order kinetics similar to Eq. 1 was used to describe production of volatile RI in the presence of radiation:

\[
d[RI]/dt = k_r \cdot [DEP] \cdot S/V \cdot D
\]  \hspace{1cm} (3)

- \(k_r\) rate constant for radiation-induced RI formation \(\text{(s}^{-1}\cdot\text{kGy/h})^{-1}\)
- \(D\) Dose rate \(\text{(kGy/h)}\)

However, during the tests, RI is also decomposed by radiation and I\(_2\) is formed. The corresponding equation is:

\[
d[RI]/dt = - k_{doc} \cdot [RI] \cdot D
\]  \hspace{1cm} (4)
Fig. 1 Arrhenius plot of rate constants for thermal RI production at painted surfaces, based on evaluation of data from (Marchand 1997). The straight line is a least-squares fit to the data according to the Arrhenius model.

According to (Tang 1970) the rate constant is $k_{\text{dec}}=1.64\cdot10^{-4}$ s$^{-1}$ (kGy/h)$^{-1}$. For solving both differential equations simultaneously and deriving rate constants for RI production ($k_\ell$), IMPAIR (Güntay 1992) was used. The immediate output from the so far existing model in IMPAIR corresponds to a rate constant $k'=k \cdot D$. Dividing this value by the dose rate provides the rate constant $k_\ell$.

Rate constants for radiation-induced RI production ($k_\ell$) at 20°C are shown in Fig. 2. The scatter of data is partly thought to reflect the restricted experimental accuracy, considering e.g. partial destruction of paint surfaces during irradiations. Fig. 2 shows that, although the dose rates differed by two orders of magnitude (between 0.05 and 5 kGy/h), similar rate constants are obtained.
Fig. 2. Rate constants for radiation-induced RI production at painted surfaces, based on evaluation of data from (Marchand 1997). The dashed line averages all data points.

2.2 Siemens and AEA Data

Introduction

Examples of experimental fractional RI releases \(f\) for thermal RI production at iodine-loaded painted surfaces exposed to a gas phase, measured at Siemens (Hellmann 1996) and at AEA (Baston 1998), are displayed in Fig. 3. The different lines correspond to Eq. 5 with different exemplary values for the rate constant \(k_T\). Eq. 5 is obtained from Eq. 1 by integration which also considers a decrease of the iodine deposition with time:

\[
f = 1 - \exp(-k_T t)
\]

The quantity \(f\) (fractional RI release) is dimensionless and defined as \(f = ([RI]-V)/([DEP]-S)\).

Fig. 3 shows that the model is not satisfactory: in the early test stage, calculated RI releases are too low. Moreover, in later test stages the model does not reproduce the leveling-off of the RI releases. Therefore, a re-analysis of these data is performed, with the additional objective to arrive at a consistent model for both datasets, the AEA tests and the Siemens tests. A consistent evaluation of rate constants is even more desirable since the Siemens and the AEA tests were performed under quite similar boundary conditions.
Fig. 3  Fractional thermal RI releases at painted surfaces, based on data from Siemens (Hellmann 1996) and AEA (Baston 1998). The lines correspond to Eq. 5 with several exemplary rate constants $k_T$ as indicated.

**Influence of Diffusion**

In the Siemens tests the fractional $I_2$ releases had also been measured (Hellmann 1996). They show the same behaviour with time as the RI releases in Fig. 3. Therefore, since the simple release model (Eq. 5) fails independent of the chemical nature of the released iodine species (RI and $I_2$), it was studied whether mass transfer of iodine from the interior of the paint to the surface, e.g. delay of releases by diffusion, produces the observed release behaviour. On the other side, even inclusion of a simple diffusion model does not reproduce the observed leveling-off up to saturation of the fractional RI releases, it only slows down the increase of the fractional releases. It is concluded that super-imposing a diffusion model on the above RI release model does not explain the experimental observation. No further attempt was therefore made on modelling diffusion, although this study does not necessarily exclude a small effect of diffusion.

**Re-Analysis of Initial-Stage-Data**

As stated above, the leveling-off of the fractional RI releases in the long term is not represented by Eq. 5. On the other side, this leveling-off could also be an experimental artefact which is not prototypical of the containment situation: in the containment there are no separate iodine adsorption and (RI/$I_2$)-desorption phases as in the experimental procedures. Instead, adsorption of iodine and desorption of RI can take place simultaneously or shortly after each other. Therefore, RI formation and desorption could concern essentially only the outer layers of the paint near to the neighbouring gas phase. This picture is thought to be better represented by the initial stage of the experimental tests. Consequently, only the
fractional releases in the first 3-5 hours of each test were re-analyzed. In this case, Eq. 5 should still be applicable. Moreover, since $k_{\text{des}} t << 1$ in the initial stage, Eq. 5 simplifies to the linear relation:

$$f = k_T t$$

Eq. 6 was used to analyze Siemens tests (Hellmann 1996) and AEA tests (Baston 1998) with RI release into dry atmospheres. Fig. 5 displays all short-term rate constants $k_T$ for analyses according to the Arrhenius model. Three different fit curves are shown. The separate fits of Siemens and AEA data show similar slopes, but the rate constants generally differ by an order of magnitude. The common fit to all data remains unsatisfactory. From Fig. 5 alone, the difference in rate constants between Siemens and AEA data could be attributed to different paint types used in the Siemens and in the AEA tests. However, this conclusion does not yet consider the parameter iodine deposition, and this will be studied in the next Chapter.

Fig. 4 shows exemplary analyses of the experimental data from the same Siemens and AEA tests as in Fig.3, applying Eq. 6 to the initial stage data.
Fig. 5  Arrhenius plot of rate constants for thermal RI releases from painted surfaces, derived from Siemens (Hellmann 1996) and from AEA (Baston 1998) data. The lines are least-squares fits to the data according to the Arrhenius model.

3 MODELLING OF RATE CONSTANTS

3.1 Radiation-induced Production of Organic Iodide

Data at 20°C-25°C

Rate constants for radiation-induced RI release from painted surfaces exposed to a dry gas phase at room temperature (20°C-25°C) were assembled from AEA tests (Baston 1998) and from the evaluation of the French tests (Marchand 1997) described in Chapter 2. Fig. 6 shows all rate constants as a function of the iodine deposition. Since the iodine deposition remained practically constant in all experiments, it therefore serves tentatively as a suitable scaling parameter.

Fig. 6 shows that a potential relation between rate constants and iodine deposition as indicated by the straight line is fulfilled over many orders of magnitude for both, iodine deposition and rate constants for radiation-induced RI release:

\[ k = A \cdot \text{DEP}^B \]  \hspace{1cm} (7)

The obtained parameters of Eq. 7 at 25°C are indicated in Fig. 6 and correspond to A=5.2 \cdot 10^{-10} \text{s}^{-1} (\text{kGy/h})^{-1} and B=-0.574.

Since both, steam-containing data (Baston 1998) and steam-free data (Marchand 1997) fit into the same model, presence of steam is no influencing parameter.
Fig. 6  Radiation-induced RI release rates at room temperature as function of the iodine deposition. Data are from AEA (Baston 1998) and from the data analysis of (Marchand 1997) in Chapter 2. The straight line is a least-squares fit to the data according a potential relationship (k=A·DEP^B).

Fig. 6 includes data for several Epoxy-type paints typical for British, French and Finnish containments. All these paints are obviously represented by the same model. Since German containment paints are also on an Epoxy-basis, it can therefore be expected that they are also represented by the model in Fig. 6.

Temperature Dependency

Analysis of rate constants at higher temperatures is less straightforward since data are scarce and only available at 80°C. A common plot of data at room temperature (20°C-25°C) and at 80°C in the same way as in Fig. 6 is shown as Fig. 7.

Rate constants at 80°C are at most slightly above the 25°C data, indicating at most a very small temperature dependency. The small set of 80°C data taken from (Baston 1998) does not show a clear trend with iodine deposition. Nevertheless, a least-squares fit to the 80°C data according to Eq. 7 was performed keeping the parameter B=0.574 fixed. The resulting model curve is shown as the dashed line in Fig. 7 with the parameter A(80°C)=1.8·10^-9 (kGy/h)^-1.

An Arrhenius analysis of the A parameters at 25°C and at 80°C yields an activation energy of 19700 J/mol. This is a comparatively small value, i.e. the temperature dependency is weak. It is noted that the activation energy determination is associated with appreciable uncertainty due to data scattering. Extrapolations of rate constants from more than 80°C up to 160°C according to Eq. 7 as performed with the dashed-dotted and the dotted lines in Fig. 7.
are therefore associated with appreciable uncertainties. The restricted accuracy of the model is visualized in Fig. 7 where the highest experimental 80°C rate constant seems to be consistent even with the model at 160°C. On the other side, the model fits the existing data within less than one order of magnitude. Very recently further rate constants at 80°C were provided by AEA which are consistent with those at 20°C data. This indicates a zero activation energy at least between 20°C and 80°C.

![Graph showing radiation-induced RI release rates](image)

**Fig. 7** Radiation-induced RI release rates at 25°C and at 80°C as function of the iodine deposition. Data are from AEA (Baston 1998) and from the data analysis of (Marchand 1997) in Chapter 2. The straight line is the same as in Fig. 6. The other lines are explained in the text.

**Influence of adsorbed Iodine Species**

The above analysis is based on data with loading from I_2_ solution as well as from I solution. Data from (Marchand 1997) do not provide any evidence for a different radiation-induced RI production after I_2_ or I loading. Therefore, the modelling includes data with both loading of I_2_ and I.

The RI release rate from AEA test F5 (k=1.8·10^{-8} s^{-1}(kGy/h)^{-1}), taken from (Baston 1998), deviates more strongly from the new model. In this test, loading was with I (5.1·10^{-6} mol/m^2). This data point was omitted in the analysis with Eq. 7. On the other side, this deviation is observed only at 25°C, and no experimental information is available at higher temperatures being more relevant to containment conditions. The deviation could also be caused by detection limit problems according to (Baston 1998). From this single observation alone it is not possible to identify a different impact of I_2_ or I on radiation-induced RI release.
3.2 Thermal Production of Organic Iodide

Experimental data on thermal RI production at painted surfaces exposed to a dry gas phase as evaluated in Chapter 2 represent the database for modelling. A simple scaling with temperature is unsatisfactory as already demonstrated in Fig. 5, and this holds even more if the rate constants derived from (Marchand 1997) are added. Moreover, such a simple model would not yet take into account the major result from the preceding modelling of the radiation-induced RI production rates which clearly depend on the iodine deposition.

An analysis analogous to the analysis performed with the radiation-induced RI production rate constants is not straightforward with the present thermal RI production rate constants because there are on a first sight not enough data at constant temperature with sufficiently different iodine depositions. However, this problem is overcome by re-grouping data into pre-defined narrow temperature ranges. This pre-definition is somewhat arbitrary but considers the conditions of narrow temperature ranges and of "sufficient" amount of data in each data group. The four data groups are shown in Fig. 8.

![Graph showing thermal RI production rates vs. iodine deposition]

**Fig. 8** Thermal RI release rates between 60°C and 160°C as function of the iodine deposition. Data are from AEA (Baston 1998), Siemens (Hellmann 1996) and from the data analysis of data in (Marchand 1997). The lines are model curves according to Eq. 7 and explained in more detail in the text.

The experimental rate constants in Fig. 8 indicate a decreasing trend with increasing deposition as in the case of the radiation-induced RI production rate constants. However, there is a large data scattering of up to one order of magnitude. Nevertheless, a potential approach according to Eq. 7 was applied to fit the data. The determination of the model parameters A and B of Eq. 7, applied here to thermal RI production, is complex.
The parameter B was determined at first. Given the scarce data points in each group, only a rough determination is possible and yields \( B = -0.5 \). This value was fixed for each data group, i.e. B was considered to be independent of temperature. The poor accuracy in determining B is accepted here since \( B = -0.5 \) for thermal RI release nearly coincides with B for the radiation-induced RI production (\( B = -0.574 \)). Using the fixed parameter \( B = -0.5 \), the parameter A was then determined for each group, i.e. for each temperature. The Arrhenius analysis of the resulting values for A at different temperatures is shown in Fig. 9. The corresponding Arrhenius model parameters are \( A(25^\circ C) = 2.2 \times 10^{-13} \text{ s}^{-1} \), and the activation energy is 78400 J/mol. Inserting these parameters A and B into the model expression \( k = A \cdot \text{DEP}^B \) (Eq. 7) provides the predictions at the four different temperatures as shown in Fig. 8. Within the data scattering, the accuracy of the model predictions appear to be acceptable since deviations are less than one order of magnitude for the thermal RI production rate constants.

![Arrhenius analysis diagram]

\[
\ln(A) = -9435.1/T + 2.5188
\]

**Fig. 9** Arrhenius analysis of the parameter A derived at four different temperatures as shown in Fig. 8.

**Influence of adsorbed Iodine Species**

The model for thermal RI release relies on a database with adsorption of aqueous \( I_2 \). Only two tests of this database were performed with adsorption of a mixture of \( I_2 \) and \( \Gamma \) where the RI release was dominated by the effect of \( I_2 \) adsorption (Marchand 1997). In the same sense, data from (Hellmann 1996) show a lower release after \( \Gamma \) loading by a factor of 3 between 90°C and 160°C. The same trend is qualitatively obtained from data in (Baston 1998) at 90°C and at 120°C. As a conclusion, thermal RI release after \( I_2 \) loading is higher than after \( \Gamma \) loading. This can be explained by the higher extent of RI formation with \( I_2 \) (compared to \( \Gamma \)).
For painted surfaces exposed to the containment atmosphere, there may be less significance of RI release after \( \Gamma \) deposition since \( I_2 \) deposition could dominate the iodine deposition. However, in the containment sump with typically dominating \( \Gamma \) fraction (unless not trapped by silver to form unsoluble AgI), the \( \Gamma \) deposition could significantly influence the RI release. Assuming that deposition of \( \Gamma \) produces the same RI release as deposition of \( I_2 \) would therefore mean to conservatively overestimate the RI release rate in case of \( \Gamma \) deposition in the sump when applying the model.

### 3.3 Modelling in Severe Accident Iodine Codes

#### Role of Paint

According to the previous Sections, radiation-induced and thermal RI production are no longer described within simple first-order release models with respect to the iodine deposition. Instead, the release depends in a more complex way on the iodine deposition. This indicates that RI formation within the paint prior to the RI release is a complex mechanism leading usually to non-integer reaction orders. The very similar values of the reaction orders (see model parameters B) for radiation-induced and thermal RI production is interesting because it indicates that the reaction mechanism, or at least the rate-determining step, is in both cases similar.

The decrease of RI production rates with increasing iodine deposition can be interpreted based on the ratio of iodine and organic molecules (R) concentrations in the paint. If the iodine deposition is low, the ratio iodine/R is low, i.e. a large fraction of the deposited iodine can be converted into volatile RI (parts of the iodine can also produce non-volatile RI but this is not relevant here). A high fraction of the produced volatile RI means a high production rate constant. To conclude, a low iodine deposition leads to a high RI production rate constant, and this is consistent with the experimental observation.

Paint ageing was in all individual experimental studies consistently found to have no significant influence on thermal RI release rates (Hellmann 1996, Baston 1998).

All experimental data used in this work are based on several Epoxy-type organic paints. For radiation-induced RI releases, British, French and Finnish paints fitted into the same model. For thermal RI releases, British, French and German paints fitted into the same model. It is therefore concluded that the model is generally applicable to Epoxy-type British, French, Finnish and German containment paints.

#### Influence of Paint Location during Iodine Adsorption

Except one single test with \( I_2 \) loading from the gas phase, all other irradiated tests in (Baston 1998) were done with pre-loading from an aqueous \( I_2 \) solution. The RI release rate to the gas phase with loading from solution is higher by a factor of 24 compared to loading from the gas phase, based on the same iodine deposition. If it is assumed that this ratio is constant with iodine deposition and with temperature, the radiation-induced model would have to be scaled down by a factor of 24 when applying it to dry loading conditions at the large painted walls exposed to the containment atmosphere. However, this conclusion would be based on only one single test result, and on RI release data only at 25°C (not relevant to most containment conditions).
Influence of Paint Location during RI Release

There are only a few irradiated tests in (Baston 1998) that allow to assess whether there is a difference between RI release from painted surfaces exposed to the gas phase or immersed in aqueous solution. These tests show lower RI release rates from paints immersed in solution at 25°C by factors of 5-10 compared with RI releases from paints exposed to the gas phase. However, the AEA tests also show that this effect is at least partially due to hydrolysis of RI, destroying RI after its release into the aqueous solution. Given the restricted accuracy of the new model, it is therefore recommended to use it with the same rate constants also for modelling of the RI release from painted surfaces immersed in the sump. Concerning IMPAIR, such a modelling has the additional advantage that it is at the same time compatible with the already modelled, subsequent step of RI hydrolysis.

Influence of condensing Steam

The only experimental study investigating the effect of condensing steam on RI releases was from (Hellmann 1996), however without radiation. Thermal RI release rates under condensing-steam conditions are higher than under dry steam conditions except at 160°C where they are close to each other. On the other side, from the same work, thermal RI releases under condensing-steam conditions are essentially similar to RI releases in aqueous solution. Since it was concluded above to use the new model also for modelling RI releases from immersed paints, it would be consistent to recommend the same for paints exposed to the containment atmosphere under condensing-steam conditions.

There is no experiment on the influence of condensing steam in the presence of radiation. Therefore, there appears to be no argument for a different conclusion than for thermal RI release.

Comparison of old and new Models

Comparisons between old and new models on RI release rates from painted surfaces exposed to the containment atmosphere are made using Fig. 10. The new models in Fig. 10 refer to the radiation-induced model and the thermal model described in the previous Sections. The old model (Hellmann 1996) is only valid for thermal releases but distinguishes between dry and condensing-steam conditions (the new model does not!). Dose rates between 0.1 kGy/h and 10 kGy/h were chosen covering the containment-relevant dose rates, at least those in the long term. The iodine deposition of $10^{-5}$ mol/m² was estimated for an equilibrium between the I₂ deposition and the I₂ desorption from painted surfaces (Hellmann 1996), and an assumed I₂ concentration of $10^{-8}$ mol/m³.

Thermal RI release rates depend on the iodine deposition in the new model whereas they do not in the old model (see also Fig. 10). The old model in dry atmosphere is very similar to the new model for the estimated iodine deposition of $10^{-5}$ mol/m². The very similar temperature dependency is due to the very similar activation energies. The old model for condensing-steam conditions is much faster than the new model except for temperatures approaching 160°C. The old model in condensing-steam is based on data between 100°C and 160°C (Hellmann 1996) and cannot be extrapolated to temperatures lower than 100°C.

The new model for thermal RI production is much slower than the new model for radiation-induced RI release (Fig. 10). This is consistent with the experimental observation in
(Baston 1998) where release of volatile RI at 25°C was only detected after switching on the radiation. The new thermal model approaches the radiation-induced model only at very high temperatures and at the same time very low dose rates.

In principle, the thermal release rates should represent a "baseline" with the radiation-induced release rates as an effective offset. Fig. 10 shows that this asymptotic behaviour is fulfilled only qualitatively due to the simplified procedure for parameter determination. It is however questionable, given the restricted amounts of data and their restricted accuracy, whether a more sophisticated multi-parameter analysis reflecting the above asymptotic condition would be successful.

Although the old model does not include the effect of radiation, it produces similar rate constants under condensing-steam conditions as the new model for radiation-induced RI release. However, this overlap is purely by chance.

Fig. 10  Comparison of RI release rates for the new models (thermal and radiation-induced, described in this paper) and for old models from (Hellmann 1996), which distinguish between dry and condensing-steam atmosphere. The estimated iodine deposition of $10^{-5}$ mol/m$^2$ is only relevant for the new models.
CONCLUSION

The kinetics of the release of organic iodide from painted surfaces, with and without radiation, is studied theoretically.

In a first step, experimental data are analyzed with the objective of deriving rate constants suitable for severe accident iodine codes. Based on the experimental procedure, it is distinguished between radiation-induced RI release (tests in the presence of radiation) and thermal RI release (tests in the absence of radiation). Both, thermal and radiation-induced RI production, are considered in this study as separate mechanisms with subsequent separate modelling. Experimental studies at Siemens, AEA and at the University of Paris form the database with RI production rate constants under closely defined boundary conditions. Besides derivation of so far not available rate constants especially at higher temperatures, important results are (i) that the rate constants do not only depend on temperature but also depend on the iodine deposition, and (ii) that the rate constants for the radiation-induced RI production can be scaled linearly with dose rate.

The model development shows, separately for thermal and for radiation-induced RI release from painted surfaces exposed to a dry gas phase (no condensing steam), that rate constants derived from different experimental studies (essentially: different Epoxy-paints) fit into the same model if the iodine deposition is taken into account. The rate constants follow the empirical relationship \( k = A \cdot \exp(B) \) with the model parameters A and B.

For radiation-induced RI release, \( A(25^\circ C) = 5.2 \times 10^{-10} \text{s}^{-1}(\text{kGy/h})^{-1} \) with an activation energy according to the Arrhenius model of 19700 J/mol. Based on further, very recent AEA data, the activation energy is zero between 20°C and 80°C. The dimensionless parameter B = 0.574 is modelled as independent of temperature. The parameters A and B are valid for iodine depositions between 1 mol/m² and 10⁻⁵ mol/m², dose rates between 0.05 kGy/h and 5 kGy/h, and, Epoxy-type paints as used in British, French and Finnish containments. Within the experimentally studied parameter ranges the model predicts the experimental rate constants within less than one order of magnitude. A significant influence of the deposited iodine species, \( \text{I}_2 \) or \( \Gamma \), prior to RI release is not found.

For thermal RI production, \( A(25^\circ C) = 2.2 \times 10^{-13} \text{s}^{-1} \) with an activation energy of 78400 J/mol, and B = -0.5. These parameters are valid for \( \text{I}_2 \) depositions between 1 mol/m² and 10⁻⁴ mol/m², temperatures between 60°C and 160°C, and Epoxy-type paints as used in German, British and French containments. Within the experimentally studied parameter ranges the model predicts all RI production rate constants within one order of magnitude. Thermal RI release rates after deposition of \( \Gamma \) are lower than after \( \text{I}_2 \) deposition but should be covered in a conservative sense by using the model also in case of \( \Gamma \) loading.

The rate constants from the new models fit into the same global modeling of RI release as already contained in severe accident iodine codes such as IMPAIR. Except for very high temperatures and at the same time very low dose rates, the model predicts that the radiation-induced RI production is clearly dominating.

It is concluded that the new models can be used for prediction of RI releases from painted surfaces exposed to a dry or a condensing-steam atmosphere, as well as for painted surfaces immersed in the sump. This conclusion considers the restricted accuracy of the
model. None of the various analyzed experimental works detected any effect of ageing of the paint, thus this parameter is not modelled.

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ORGANIC IODIDE FORMATION IN BWR ACCIDENTS

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ABSTRACT

This paper describes the results from an experimental study, in which the reactions between iodine with hydrocarbon gases were investigated in conditions simulating BWR containment during a severe accident.

In the first set of experiments glass vessels containing iodine, nitrogen, hydrogen, methane, ether, noble gases and in some cases also oxygen, steam and chlorine were irradiated. After irradiation the vessels were purged and the gaseous organic and non-organic compounds were separated using selective filters. The fraction of organic iodide was determined using gamma counting. Very high organic iodide yields (up to 30 - 70 % of all iodine) were obtained in dry conditions and in humid conditions without oxygen or with chlorine. When the samples contained both steam and oxygen, but no chlorine the organic iodide fractions varied between 1 and 13 %. The results indicate that organic iodide formation in the BWR containment gas phase is more efficient than previously assumed, particular when the effect of chlorine is taken into account.

In the second set of experiments a gas mixture of nitrogen, hydrogen, oxygen, noble gases and methane was vented through an iodine solution, after which the organic and non-organic gaseous iodine compounds in the gas flow were trapped using selective filters. The efficiency at which iodine and methane reacted was found to be affected by iodine concentration and water pH and temperature. The results imply that systems such as suppression pools and scrubber filters not only retain iodine in elemental and aerosol form, but also act as a organic iodide sources. The magnitude of these sources can be quantified by scaling the results into plant scale.

1. INTRODUCTION

The formation of organic iodides in containment gas phase was suspected already in some of the very first studies on iodine behaviour in the late 1950’s (Megaw, 1962). The reactions between iodine and organic compounds were later verified in experiments, in which
irradiated fuel samples were heated in air or in gas mixtures containing large proportion of carbon dioxide (Eggleton, 1962). The organic iodide compounds were identified with gas chromatography as methyl and ethyl iodides. It was suggested that the compounds were produced in a reaction between iodine and free radicals formed by the pyrolysis of traces of organic matter. This hypothesis was later supported by the analysis of the effluents from a fuel processing plant, which indicated that as much as 10 - 60 % of iodine in the effluent gases was in organic form (Haller, 1967). Again, a reaction between iodine and free radicals, this time produced in paraffin compound radiolysis, was suggested as a plausible formation mechanism.

Once it had been demonstrated that organic iodides can be produced in reactor accident conditions, a serious effort to quantify organic iodide yield was initiated. The results have been reviewed by Parsley (1971) and by Postma and Zadowski (1972), who also derived a correlation for organic iodide yield as a function of iodine concentration. Later Beahm et al. (1985) reanalysed the data and derived new correlations taking into account only the experiments in which irradiation was used. According to all these correlations, organic iodide yield decrease with increasing iodine concentration, but the absolute magnitudes vary widely. According to the correlation by Postma and Zadowski, organic iodide yields decrease from 1 % at 0.001 mg/m³ to 0.1 % at about 10 mg/m³, while the results from the irradiation experiments indicate that the yields may larger by a factor of 100. These estimates cover only reactions in the gas phase, no attempts to quantify organic iodide formation in water pools during venting were made.

Although the early studies left considerable uncertainty in the organic iodide yield estimates, only relatively few more recent studies have been carried out. The reactions between iodine and gaseous hydrocarbons have been studied by Bartonicek and Habersbergerova (1980, 1986, 1987) and Lutz and Kelly (1987).

The formation of organic iodides occurs most likely as a results of a reaction between iodine and a methyl radical, and thus the amount of competing components, such as oxygen, in the gas may have a large impact on the results. Yet all recent experiments, and probably also most of the early tests, have been carried out using air as a major component in the test gas mixture. The test results and the correlations derived on the basis of them are therefore most applicable to PWRs and Candu-reactors, while their applicability to inerted (oxygen concentration less than 5 vol-%) BWRs is questionable.

BWRs have also the unique feature (in addition most RBMKs) that the accident mitigation systems include suppression pools and scrubber filters, through which all non-condensable containment gases are likely to be vented. As above, very little BWR relevant data is available. Beahm et al. (1985, 1987) did carry out experiments, in which methane-argon gas was vented through an iodine solution. The tests demonstrated that the reactions between organic gases bubbled through an iodine solution may yield considerably quantities of organic iodides in most favourable conditions, i.e. with acidic or neutral iodine solution and with radiation. However, only pure or borated water was used, so the data does not cover situations in which for example HCl is released due cable insulation pyrolysis or radiolysis. In the scrubber filters the elimination of organic iodides formation is striven for by keeping high pH in the filter water and by adding sodium thiosulfate (Na₂S₂O₃). No requirements for organic iodide retention capability has been set for these filters.
Since the data applicable to BWR accidents was judged insufficient, an experimental study was initiated by STUK in 1996. The study was not limited to iodine reactions, but included also analysis of the most likely source of gaseous hydrocarbons, i.e. boron carbide oxidation and cable insulation pyrolysis. However, the scope of this paper is limited to iodine work.

2. GAS SAMPLE EXPERIMENTS

2.1 Experimental

The formation of organic iodine from elemental iodine was studied by irradiating glass containers filled with iodine (initially in ether solution), carrier gas and in some cases also with water and chlorine using a $^{60}$Co gamma source. Two different carrier gas mixtures were used, see Table 1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Carrier gas compositions.</th>
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<td></td>
<td>N$_2$ %</td>
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<td>Mixture A</td>
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</tr>
<tr>
<td>Mixture B</td>
<td>44.7</td>
</tr>
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</table>

The carrier gas mixture A was chosen to represent a situation, in which the nominal oxygen concentration in the containment is 1 vol-% and about 40 % of the zircaloy is the reactor core has oxidised producing hydrogen, which is released into containment.

The amount of methane in the carrier gas was selected to be about 100 times that of the maximum iodine amount. In a plant scale this concentration would correspond to about 600 mole of methane evenly distributed in a BWR containment. The amount was judged to be physically reasonable, since it can be produced by pyrolysing about 750 kg of cable insulation material at sufficiently high (800°C) temperature or by oxidising few percents of boron carbide in reducing conditions, in which methane is the likely to be the main reaction product. Assuming that ether (CH$_3$-CH$_2$-O-CH$_2$-CH$_3$) is twice as likely source of methyl radicals as methane, the maximum methane radical concentration with ether is about 20 larger than with methane alone. It can be assumed that the addition of ether corresponds roughly to the increase of methane concentration from 0.1 % to about 2 %.

The samples were prepared in a nitrogen atmosphere in a glove box. The containers (volume 1 l) were filled with the carrier gas, after which iodine was added in an ether solution. The amount of ether pipetted into the containers was 50 µl. In some tests also 20 µl hydrochloric acid or 15 µl water was added.

The iodine solutions used for the sample preparation were made by extracting carrier free $^{131}$I into ether and dissolving elemental iodine into this solution. The amount of iodine added into samples was 0.01 or 0.1 mg/l. The amount of iodine used in the tests was calculated to represent a situation in which 0.5 – 5 % of the iodine core inventory is released into a BWR containment atmosphere, where the concentration is about 10 – 100 mg/m$^3$. Iodine activity was 250 kBq/sample at the beginning of the experiments. The radioactive tracer used in the tests was $^{131}$I.
After preparation the samples contained hydrogen (2.2·10⁻² mol/l), nitrogen (1.8·10⁻² mol/l), oxygen (0 - 1.8·10⁻⁴ mol/l), methane (4.1·10⁻⁵ mol/l), ether (4.8·10⁻⁴ mol/l), steam (0 - 8·10⁻⁴ mol/l), chlorine (0 - 1·10⁻⁴ mol/l), argon (9·10⁻⁶ mol/l), xenon (7·10⁻⁵ mol/l) and iodine (I) (8·10⁻⁸ - 8·10⁻⁷ mol/l).

The irradiation of samples at 25 °C was made by using a ⁶⁰Co source. Sixteen samples were irradiated simultaneously with a dose rate of 1 kGy/h. The dose rate was calibrated using Fricke dosimetry.

The separation of different forms of iodine was performed after irradiation by leading nitrogen through the sample bottles, and then first through a NaOH-solution (2g/l) to absorb inorganic iodine, and then through ethanol to absorb organic iodine. The iodine left in the bottles was rinsed into NaOH-solution. The amount of iodine in the filters and the rinse was analysed by gamma counting using 364.5 keV energy in the measurements. The standards for these measurements were prepared simultaneously with and using the same solution as in the sample preparation. The amount of iodine in the standards was determined by ICP-MS in the first experiments to control the preparation of iodine solution.

2.2 Results

The main test parameters were the concentrations of iodine, oxygen, steam and chlorine. All tests were made with high and low iodine concentrations (0.1 mg/l and 0.01 mg/l), and for other parameters five different combinations were used. The results are given in Figures 1 – 5 showing the fraction of organic iodides of all iodine detected in the filters and the rinse after irradiation.

It was initially assumed that oxygen would have a major impact on the efficiency at which iodine reacts with hydrocarbons. When the samples contain steam, this hypothesis appears to be true with low (up to 100 kGy) doses, but at high doses the effect of oxygen seems to disappear, see Figures 1 and 2. When both steam and oxygen are present, organic iodine yields are initially very low, but increase then slowly to about 4 % with higher and to 12 % with lower iodine concentration at about 200 kGy dose. Without oxygen the yields are initially very high (15 – 30 %), but they decrease with dose reaching finally the same levels as in the tests with oxygen. When chlorine was added into samples, the organic iodide yields increased substantially at low doses with the maximum yield reaching nearly 70 %. The enhancement was not limited to low doses, as the yields measured at about 240 kGy dose were considerably higher than in the similar tests without chlorine.
Fig. 1 Organic iodide yields, when the samples contain steam and oxygen but no chlorine.

Fig. 2 Organic iodide yields, when the samples contain steam but no oxygen nor chlorine.

Fig. 3 Organic iodide yields, when the samples contain steam, oxygen and chlorine.
Fig. 4 Organic iodide yields, when the samples contain oxygen but no steam nor chlorine.

Fig. 5 The formation of organic iodides during irradiation, when the samples contain no steam, oxygen nor chlorine.

The effect of oxygen appears to be connected to the presence of steam, as in the absence of steam the results from tests with and without oxygen are nearly identical. In both cases the yields are between 5 – 50 % at doses up to 100 kGy, while at large doses the conversion is limited to about 10 – 20 %, as shown in Figures 4 and 5.

Although the tests were made using glass containers, some surface effects were clearly apparent in the results. In the tests with steam, a considerable portion of iodine, in some cases 60 – 80 %, was found in the NaOH-solution, with which the containers were rinsed after each test. At high doses the fraction of iodine retained in the rinse decreased being 20 – 30 % in the tests with steam and oxygen, but without chlorine. Without oxygen or with chlorine, this fraction was less, typically below 10 %. A clear difference was seen in the tests without steam, in which the fraction of iodine retained in the rinse did not depend on dose and was in nearly all cases below 10 %.

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2.3 Discussion

The measured organic iodide yields can be compared to the earlier results by Bartonicek and Habersbergerova (1980, 1986, 1987), although the conditions in their experiments were designed to simulate mainly PWR-conditions. For example, they did experiments irradiating samples which contained air (2.4-10^{-2} mol/l), steam (1.2-10^{-3} mol/l), methane (5.4-10^{-7} mol/l) and elemental iodine (3-10^{8} mol/l) at room temperature. In these tests the methane concentration was only about 1% of the concentration used in our tests, while the oxygen concentration was more than 20 times larger. However, the results from these tests are quite similar to the results show in Fig. 1 for the lower iodine concentration. In both cases the methyl iodide concentration increased with dose reaching a maximum of about 12 - 15% of all iodine at about 200 kGy dose. Bartonicek and Habersbergerova did also tests with higher doses and noted that the organic iodide yields started to decrease after 500 kGy and went down to few percent at 1000 kGy.

Bartonicek and Habersbergerova also tested the effect of temperature irradiating samples at 60, 80 and 100°C. In all cases the maximum conversion was between 20 – 30%, but for tests at 80 and 100°C the decrease to a few percent occurred already at 10 – 20 kGy dose, while at 60°C the organic iodide yields remained unchanged up to 70 kGy, which was the highest dose used in these tests.

In order to see whether the same trend would be repeated in other conditions, a few tests with samples that contained steam, oxygen and a 0.1 mg/l of iodine (same concentrations as in the tests, which gave the results shown in Figure 1) were repeated at 80°C temperature. Organic iodide yields in these tests were 2% at 20 kGy, 10% at 35 kGy and 1% at 120 kGy, while at room temperature the yields varied between 1 and 4%. The results are in full agreement with the earlier ones, except in the earlier tests at the same elevated temperature a steep reduction in yield was observed already at about 15 kGy dose. The difference may be due to lower hydrocarbon and iodine concentrations used in the earlier tests.

Also tests with two phase systems have been carried out using gaseous hydrocarbons. Lutz and Kelly did their tests using a vessel filled with water and carrier gas (air or a mixture of air and methane). Iodine was introduced into the vessel in water solution, which had pH of 5 and an initial iodine concentration of 10 mg/l. The methyl iodide concentration in the vessel was found to increase as a function of methane concentration from 5-10^{-9} mol/l with 0.04 vol%- of methane to about 4-10^{-7} mol/l with 8 vol-% of methane. Assuming that low pH would yield relatively high iodine concentration and the reactions in the liquid phase can be disregarded, the results of Lutz and Kelly can be compared to those shown in Figure 1 for the higher iodine concentration. In these tests the maximum organic iodide concentration was about 3-10^{-6} mol/l, i.e. between the values measured for the high and the low methane concentrations in the earlier tests. The increase in the maximum organic iodide yield from the earlier tests with the lower methane concentration may be explained by the decrease in the oxygen concentration and by the addition of ether.

The results can be compared also to those obtained without any extra methane. Probably the best comparison point in this respect are the ACE/RTF tests, where both liquid and gaseous phases were present. In most tests iodine was fed into the test chamber both in liquid solution and as methyl iodide gas, and the gaseous iodine concentration was measured as a function of time. In the test with initially low water pH the methyl iodide concentration
decreased soon after the injection below $10^{-8}$ mol/l, after which it continued to decrease at slow rate (Kupferschmidt et al., 1992). The organic iodide concentration did no change significantly after the water pH was increased to nine. The fact that the organic iodide concentration in these tests was lower than the concentrations observed in our tests may be explained by the higher oxygen level and lower gaseous hydrocarbon concentrations used in the ACE/RTF tests. Also temperature may have affected the results, as the ACE/RTF test three was conducted at 60°C, although our tests seem to indicate that organic iodide formation is enhanced by elevated temperatures at least at low doses.

3. EXPERIMENTS WITH A SPARGING APPARATUS

3.1 Experimental

The apparatus used in these experiments consisted of a Gammacell irradiation facility, in which the sample solution was irradiated at a dose rate of 0.8 kGy/h. The solution was sparged with gas mixture A simulating BWR containment atmosphere during a severe accident (see Table 1). The gas was vented from a bottle through a control valve, a flow meter, a sample solution, an NaOH-trap for non-organic iodine and ethanol traps for organic iodides. The gas flow rate used in the tests was 5.8 or 6 l/h and the amount of water was 500 ml. The sample solutions were bubbled with a nitrogen-oxygen mixture (99% and 1%) at least three hours before each test.

Iodine was added into the water as CsI-solution and $^{131}\text{I}$ was used as a radioactive tracer. The tracer of the sample solution amounted to 15 kBq/ml. When chlorine also was used, it was added to the sample solutions as HCl so that the chlorine concentration of $1\times10^{-4}$ M was obtained.

In the tests with pure water no pH control was applied. In other tests pH was adjusted by using NaOH-solution. In one test also 0.2 w-% sodiumthiosulfate (Na$_2$S$_2$O$_3$) was added.

Inorganic iodine was trapped by a 2g/l solution of NaOH. The amount of solution in each trap was 200 ml. The efficiency of the traps was validated by calculating the activity balance in each experiment. The activity of the first ethanol trap was followed by on-line gamma measurement. The amount of radioactive tracer used in these experiments was sufficient for detection of $<0.0005\%$ of total iodine in traps.

3.2 Test conditions and results

Initial scoping tests were run with varying water pH (4,7 and 9), sparging gas composition (pure methane or a lean methane mixture) and iodine and chlorine concentrations at room and elevated temperature. These tests indicated that although less organic iodides are formed with lean methane gas mixture than with pure methane, the methane reaction efficiency is larger with a lean methane mixture. Therefore it was decided to carry out the main tests with only the lean methane mixture. The scoping tests also showed that organic iodides are formed more readily in acidic solution, as was expected. However, the goal of accident management is to minimise iodine volatilisation by keeping containment water pH sufficiently high. As the number of tests had to be limited, the main tests were decided to be run only with two initial water pH values, 7 and 9.
The scoping tests implied that organic iodide formation is enhanced at high temperature. Therefore most of the main tests were run at elevated (80 °C) temperature. However, as the number of scoping tests was small, some tests were repeated also at room temperature (32 °C).

The iodine concentration in the experiments was selected to represent a situation, in which 10 - 100% of iodine inventory is released into suppression pool. The corresponding iodide concentrations were 4.5·10^{-6} and 4.5·10^{-5} mol/l. A single experiment was performed simulating the conditions in a scrubber filter, which is a filter design often used in containment filtered venting systems. In this test the iodine concentration was increased by a factor of 100.

Since it was anticipated that chlorine may also be released in containment during a severe accident, the tests at high temperature were repeated with and without chlorine. The chlorine concentration used in the tests was selected to be larger that the corresponding iodine concentration at least by a factor of two. The chlorine concentration corresponds to a situation, in which about 1% of chlorine present in the containment cables is released into containment water pools. The results from the tests with a sparging apparatus are shown in Table 2.

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<th>T °C</th>
<th>C&lt;sub&gt;HCl&lt;/sub&gt; (Mol/l)</th>
<th>Non-organic iodine (%/h)</th>
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<td>3.7·10^{-5}</td>
</tr>
<tr>
<td>12</td>
<td>9</td>
<td>4.5·10^{-6}</td>
<td>80</td>
<td>1.0·10^{-4}</td>
<td>0.0072</td>
<td>0.0071</td>
<td>6.2·10^{-5}</td>
</tr>
<tr>
<td>13</td>
<td>12.8</td>
<td>4.5·10^{-3}</td>
<td>80</td>
<td>-</td>
<td>0.0005</td>
<td>0.0027</td>
<td>2.3·10^{-2}</td>
</tr>
</tbody>
</table>

In all cases studied high temperature enhanced organic iodide formation roughly by a factor two, while the trend for non-organic iodide was in most cases just the opposite. At elevated temperature organic iodides formed more readily in pure than alkaline water, as was expected. The methane reaction efficiency with high iodine concentration with pure water was about 20 times higher than at pH 9. However, with lower iodine concentration the difference nearly disappeared. The effect of chlorine was twofold: in neutral water the presence of chlorine lead to reduction in organic iodide yields, while at pH 9 chlorine enhanced organic iodide production. This may be explained by different pH evolution during irradiation in tests with and without chlorine.
Most important factor affecting the methane reaction efficiency appears to be iodine concentration. Tests similar with respect to water pH and temperature gave consistently higher efficiencies with higher iodine concentration. Furthermore, the highest efficiency of all tests was measured in a test with the highest iodine concentration. This was quite unexpected, since the test simulated conditions in a scrubber filter, which is designed in particular for iodine retention. This is striving for by adding 0.2 w-% Na$_2$S$_2$O$_3$, which is supposed to react with elemental iodine according to the following reaction

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}.$$ 

Although the addition of sodiumthiosulfate did limit the release of elemental iodide, as non-organic volatile iodine release rate (in relative terms) was the smallest of all tests, this was not enough to result a similar reduction in organic iodide yield, which was of the same order as with lower iodine concentration at pH 9 and without thiosulfate.

3.2 Discussion

The results from the tests can be compared to those obtained by Beahm and co-workers (1991). They also used a sparger apparatus, but with a smaller water pool (0.15 l) and flow (1 l/h) and higher dose rate (6.8 kGy/h) and iodine concentration (2·10$^{-4}$ mol/l). They did tests varying water pH, but unfortunately only the results from the tests with pure water (pH 7) are comparable to ours. According to their results, the methane reaction efficiency with a mixture of methane (15 %) and argon in pure water is 2.4 – 5.3·10$^{-4}$ %, while according to our results the reaction efficiency in pure water is 1.4·10$^{-3}$ %. The increase in reaction efficiency may be caused by the use of lean gas mixture (methane concentration 0.1 vol-%), as compared tests with pure methane and an iodine concentration of 7·10$^{-5}$ mol/l gave a reaction efficiency very close to the values given by Beahm et al.

Although the values obtained in the study and by Beahm and co-workers are nearly in full agreement, care should be taken when the results are extrapolated into plant scale. It is likely that the reaction efficiency does not depend only on test parameters, such as water temperature, pH, iodine concentration and methane concentration in the sparging gas, but also other parameters, such as pool geometry, flow rate and pressure are probably important, as they determine the gas retention time in the pool.

4. CONCLUSIONS

The experiments presented here simulated the conditions in a BWR containment during a severe accident. BWR containments are characterised by small gas and water volumes, low oxygen concentration in containment atmosphere and the use of organic materials as neutron absorbers and cable insulation. Consequently, should an accident proceed into severe core damage and/or pressure vessel rupture, iodine released from the fuel may contact also hydrocarbon gases produced either in boron carbide oxidation or by cable insulation pyrolysis. Since the containment is inerted, these hydrocarbons may not be oxidised into carbon monoxide and dioxide, as would be the case in PWR plants.

Preliminary tests with boron carbide pellets indicate that in atmosphere consisting of both steam and hydrogen in equal volume fractions as much as 14 % of carbon reacts forming methane already at moderate (1000°C) temperature. There are about 1200 kg of boron carbide
in a typical BWR core, which thus provides significant source of gaseous hydrocarbons. Some boron carbide is likely to be consumed in the formation of eutectic melts, but as the stainless steel-boron carbide mass ratio is at least in some designs below six, some boron carbide may be left to oxidise. Another potential source of gaseous hydrocarbons are the cables located in the vicinity of the vessel, which are likely to become partly pyrolysed, should the vessel fail.

In these experiments the formation of organic iodides was assumed to be limited by gas phase reactions alone, i.e. iodine was added into samples in a volatile form and no water phase was included in the test samples. In these conditions the efficiency at which gaseous iodine is converted into organic compounds appears to vary greatly according to the atmosphere composition. When the atmosphere is inerted with nitrogen and hydrogen and saturated by steam, the conversion is limited to 4 – 12 % of total iodine up to doses of 200 kGy. However, with also chlorine present the organic iodide yields can be much larger, several tens of percents of total iodine. In this case organic iodide concentration may be as high as \(3 \times 10^7\) mol/l of gaseous iodine. This concentration is considerably larger than those observed in the tests simulating Candu and PWR conditions.

The maximum concentration observed, \(3 \times 10^7\) mol/l of gaseous iodine, corresponds roughly to 2 % of iodine inventory in a typical BWR. Should such high organic iodide loading be present in the containment at the time of the containment venting, the results would be detrimental, since the current filters designed for severe accidents have typically very low retention factors for organic iodides. However, the risk of large iodine releases due to the formation of organic iodides in the containment gas phase can be limited by eliminating iodine volatilisation in the containment by effective control of containment water pH. Unfortunately the current systems used for pH control in many BWRs are not designed to cope with large quantities of acids that could be produced during a severe accident as a result of the degradation of paints or cables, for example.

Organic iodides are also formed when hydrocarbon gases are vented through a water pool containing iodine. The efficiency at which the gases react with iodine depends on iodine concentration and water pH and temperature. When geometrical and thermohydraulic effects are not taken into account, the reaction efficiency for a suppression pool with no buffering at 80°C and with high iodine loading may be taken to be \(2,3 \times 10^{-3}\) %. In real case the sparging gases may be transported through water pools many meters deep and under a pressure of several bars, which is likely to result in significant increase in reaction efficiencies.

The releases caused by containment venting may be limited by efficient control of the containment water pH, which prevents iodine volatilisation at least in the long term. However, if iodine is volatilised already before the pH control is activated or if the iodine released from the core is carried straight into the filtered venting system without passing through the suppression pool, a substantial amount of iodine may still be transported into the filter. In this case the threat of large iodine releases can be eliminated only by new filter designs with an enhanced capability to retain the iodine in the filter permanently, irrespectively of hydrocarbons, chlorine and other impurities which the venting gases may contain.

**ACKNOWLEDGMENTS**

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STUDIES ON THE EFFECTS OF ORGANIC-PAINTED SURFACES ON pH AND ORGANIC IODIDE FORMATION

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ABSTRACT

The effects of organic-painted structural surfaces on iodine behaviour under reactor accident conditions have been studied. Organic impurities in containment water derived from these painted surfaces could have a significant impact on iodine volatility following an accident. This impact has been evaluated by experimental and modelling studies on (1) the radiolysis of organic compounds in the aqueous phase, (2) thermal and radiolytic formation and decomposition of organic iodides, (3) dissolution of organic solvents from various painted surfaces into the aqueous phase, and (4) hydrolysis and aqueous-gas phase partitioning of organic iodides. The experimental studies consist of intermediate-scale “integrated effects” tests in the Radioiodine Test Facility (RTF) and bench-scale “separate effects” tests. This paper summarizes recent findings from these studies and discusses their significance for managing iodine behaviour in a reactor containment following a severe accident.

1. INTRODUCTION

Organic impurities in the containment sump water could have a significant impact on iodine volatility following an accident. Organic compounds dissolved in the sump water will undergo radiolytic decomposition to form organic acids and eventually CO₂, lowering the pH of the sump water. Since iodine volatility in containment following an accident will depend strongly on the pH of the sump water, the control of the sump water pH at a high value is, considered to be one of the most practical and promising methods of controlling iodine behaviour. Organic impurities in the aqueous phase will also form organic radicals which can react with iodine species to form organic iodides. In contrast to molecular iodine (I₂), organic iodides in the gas phase are more difficult to remove by engineered systems, such as spray or filters, and are considered to be more of a safety issue. From the perspective of severe accident management therefore, the effect of organic impurities on aqueous pH and organic iodide formation are of great interest.

To identify the sources of organic impurities in the sump water and to quantify their effects on iodine volatility, pH and organic iodide formation, we have performed extensive experimental and modelling studies. A comprehensive review of these studies has been published elsewhere (Wren, 1999-1). This paper summarizes recent findings from these studies and discusses their significance for managing post-accident iodine behaviour in a reactor containment.
2. IODINE CHEMICAL AND TRANSPORT BEHAVIOUR WITHIN CONTAINMENT

2.1 Homogeneous Aqueous Phase Reactions of Iodine

Thermodynamic calculations and various experiments have established that under most accident conditions, the iodine released from fuel into containment would be primarily in its reduced state as cesium iodide. Cesium iodide is highly soluble in water and would readily dissolve in the water originating from the discharged coolant and safety spray systems. Subsequently, in the presence of dissolved oxygen in the water (from the containment atmosphere) and high radiation fields from released fission products, non-volatile I⁻ dissolved in the containment sump water would react to form volatile iodine species (mainly I₂ and some organic iodides). A fraction of the volatile iodine species formed in the aqueous phase would be transferred to the gas phase to form airborne iodine. Regardless of the accident sequence, or the initial speciation of iodine released from fuel, the net conversion of non-volatile iodine to volatile iodine in the sump water is the major source of airborne iodine.

Iodine chemistry in containment is a dynamic equilibrium involving reactions that lead to the oxidation of non-volatile I⁻ to volatile I₂ and organic iodides, and reactions which convert these volatile species back to I⁻:

\[
\begin{align*}
\text{Non-Volatile Iodine} & \rightarrow \text{Volatile Iodine} \\
\text{Volatile Iodine} & \rightarrow \text{Non-Volatile Iodine}
\end{align*}
\]

The net production of volatile iodine is determined by the overall rates of Processes (1) and (2). Except for unusual circumstances, not likely to be encountered in containment, iodine will quickly make its way to the aqueous phase during the earliest stages of an accident. Therefore, processes that generate volatile iodine in the aqueous phase will be the major source of iodine in the gas phase and control of iodine concentrations in the gas phase will be dependent upon controlling the production of volatile iodine in the aqueous phase. Although there are some areas of iodine behaviour where large uncertainties still exist, a relatively clear picture of aqueous phase iodine chemistry has emerged. The current understanding of the chemistry of iodine in the aqueous phase under accident conditions is summarized below.

**Aqueous Phase Conversion of Non-Volatile Iodine to Volatile Iodine**

In the presence of high radiation field following an accident, non-volatile I⁻ initially dissolved in the containment sump water will be oxidized by the following reaction sequence to form volatile molecular iodine (I₂) (Wren, 1999-2):

\[
\begin{align*}
\text{I}^- + \text{OH} & \rightarrow \text{I}^- + \text{OH}^- \\
\text{I}^- + \text{I}^- & \rightarrow \text{I}_2(\text{aq})^1
\end{align*}
\]

¹ Note that the designation (aq) is assigned only to volatile species (e.g., molecular iodine, organic iodide, and organic compounds, see below) to differentiate them from the same species in the gas phase, e.g., I₂(g).
where hydroxyl radical (·OH) is formed by water radiolysis\(^2\) (Buxton, 1988). Under accident conditions the rate of thermal oxidation of I\(^-\) to I\(_2\), known to be catalyzed by light and impurities in water, is negligible compared to the radiolytic oxidation described above.

Organic iodides may also be formed through the reaction of I\(_2\)(aq) and organic impurities present in the sump water. Organic impurities in the presence of radiation undergo the following reaction (Wren 1999-1, Driver, 1999).

\[
\text{RH(aq)} + \cdot \text{OH} \rightarrow \text{R}^- + \text{H}_2\text{O} \quad (5)
\]

where RH is the organic compound (impurity) in the aqueous phase. The organic radical (R·) produced from this reaction eventually forms either an organic acid, thereby decreasing the pH of the sump water, or an organic iodide.

\[
\cdot \text{R} + \text{O}_2\text{(aq)} \rightarrow \text{RO}_2\cdot \rightarrow \cdot \text{R}^-' \text{, alcohols, aldehydes, acids and CO}_2 \quad (6)
\]

\[
\cdot \text{R} + \text{I}_2\text{(aq)} \rightarrow \text{RI(aq)} + \text{I}^- \quad (7)
\]

Reactions (3) to (7) result in the conversion of non-volatile iodine to volatile iodine in the aqueous phase. They are fast free radical reactions with relatively low activation energies (i.e. they are not strongly dependent on temperature). The production rate of the key reactant ·OH (and therefore that of volatile iodine species) increases with an increase in the radiation dose rate. Reaction (6) produces acids that can lower the sump water pH (its importance is discussed below) and promote the formation of volatile iodine species.

**Aqueous Phase Conversion of Volatile Iodine to Non-Volatile Iodine**

Volatile iodine in the aqueous phase, I\(_2\)(aq), can follow two chemical paths. It can be oxidized further to non-volatile iodine oxides (\(\text{IO}_3^-\)), or it can be reduced back to non-volatile I\(^-\). The second of these two is the major path (Wren 1999-1,2) with the key reactions being:

\[
\text{I}_2\text{(aq)} + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{I}^- + \text{H}^+ \quad (8)
\]

\[
\text{I}_2\text{(aq)} + \text{O}_2^- \rightarrow \text{I}_2^- + \text{O}_2\text{(aq)} \quad (9)
\]

\[
\text{I}_2\text{(aq)} + \text{H}_2\text{O}_2 \rightarrow 2\text{I}^- + 2\text{H}^+ + \text{O}_2\text{(aq)} \quad (10)
\]

where \(\text{O}_2^-\) and \(\text{H}_2\text{O}_2\) are products of water radiolysis (\(\text{O}_2^-\) from the reaction of \(\text{e}_\text{aq}^-\) and dissolved oxygen), and HOI and I\(_2^-\) are in equilibrium with I\(_2\).

Volatile organic iodides, RI(aq), can also be decomposed radiolytically to release iodide and organic radicals, or hydrolyze to form non-volatile I\(^-\) and a corresponding alcohol (Wren, 1999-1):

\[
\text{RI(aq)} + \text{H}_2\text{O} \rightarrow \text{I}^- + \text{H}^+ + \text{ROH(aq)} \quad (11)
\]

\[
\text{RI(aq)} + \text{OH}^- \rightarrow \text{I}^- + \text{ROH(aq)} \quad (12)
\]

\(^2\) 4.1 H\(_2\text{O} = 2.6 \text{ e}_\text{aq}^- + 0.6 \cdot \text{H} + 2.7 \cdot \text{OH} + 0.7 \text{H}_2\text{O}_2 + 2.6 \text{ H}^+ + 0.45 \text{ H}_2\). Coefficients in this equation are the G-values for primary radiolysis products from \(\gamma\)-radiolysis of water (units of molecules produced per 100 eV absorbed dose).
Reactions (8) to (12) are the key reactions that are involved in the conversion of volatile iodine species to non-volatile iodine in the aqueous phase. Their rates, except for the electron transfer reaction (9), are a strong function of temperature (Burns, 1990) increasing with an increase in temperature. Although increasing temperature also increases the partitioning of volatile iodine species into the gas phase, the strong temperature dependence of the iodine reduction reactions result in iodine volatility decreasing with increasing temperature.

The rates of all of the iodine reduction reactions increase with increasing pH (Burns, 1990, Schwarz, 1986, Ball, 1997-2). The overall pH dependence of iodine reduction is complex, however over a pH range of 5 to 10, it results in the aqueous concentration of volatile\(^3\) iodine species increasing by approximately by an order of magnitude with a decrease in pH by one unit. Therefore, maintaining the pH of the reactor sump at a high value following an accident may be one of the practical mitigation methods that can be considered.

2.2. Heterogeneous Surface Reactions of Aqueous Iodine Species

In addition to the homogeneous reactions shown in Reactions (3) - (12), aqueous iodine species can undergo heterogeneous surface reactions. Irreversible chemical adsorption of iodine species on surfaces has the potential to reduce the overall iodine inventory in the aqueous phase, thereby resulting in the reduction of the net volatile iodine production. Although many painted surfaces or clean steel surfaces in contact with water are not very good iodine adsorbers (Wren, 1999-3, Ball 1997-1), inorganic zinc primer coated surfaces in contact with water at high pH (9 - 10) have been shown to retain iodine effectively (Kupferschmidt, 1992). Another metal surface which has a great affinity for iodine is silver. Discussion on iodine behaviour on these surfaces can be found elsewhere and is not presented here.

Direct chemical reaction of aqueous iodine species on surfaces has been invoked as a route for formation of organic iodides (Deane, 1990). There are numerous ways in which substituents on painted surfaces could react with iodine species to form organic iodides. It is difficult however, to formulate any radiolytic or thermal reaction that would cleave organic iodides from a polymer backbone at a rate sufficient to release large quantities of organic iodides. By analogy to polyvinyl chloride, which contains organic chloride substituents, painted surfaces containing organic iodide substituents would be far more likely to release iodine atoms than organic iodides upon exposure to radiation (Dole, 1973). The experiments described by Deane do not present unequivocal evidence that organic iodides observed in the gas phase originated directly from iodine reactions on surfaces in contact with the aqueous phase. Deane’s observations could also be attributed to homogeneous reactions between iodine species and organic compounds dissolved in residual water on the surfaces or in pores and channels within the coating.

2.3 Iodine Transfer between the Gas and Aqueous Phases

Volatile iodine species are continually transported between the aqueous and gas phases, (and to and from surfaces), eventually achieving a state of dynamic equilibrium. The relative

\(^3\) Note that iodine species other than I\(_2\)(aq) and RI(aq) are soluble in water, i.e., non-volatile. There is speculation that HOI and I\(_\bullet\) may contribute to iodine volatility, but their presence in the gas phase over water containing these species has not been observed unambiguously.
concentrations of a species in the aqueous and gas phases at equilibrium, referred to as the partition coefficient, depends on temperature, whereas the speed at which the system reaches equilibrium depends on the gas-aqueous interfacial mass transfer rate and mixing rates within both the aqueous and gas phases. These rates depend on fluid flow conditions and also on temperature.

It is essentially impossible to establish unambiguously the gas-aqueous interfacial mass transfer rate under accident conditions. Nevertheless, under accident conditions in which there is an ample supply of hot water, evaporation and condensation on surfaces will occur, and the gas-aqueous interfacial mass transfer rate can be assumed to be very fast. Under these conditions the equilibrium partition coefficients of the volatile iodine species will be the factors controlling the relative amounts of iodine in the gas phase. These partition coefficients vary considerably from one compound to another (e.g. the partition coefficient at 25°C is 4 for CH₃I, 88 for I₂, 725 for 2-iodophenol (Wren, 1999-1)). They also depend strongly on temperature. For significant volatile iodine species the partition coefficient decreases with an increase in temperature (i.e., they become more volatile).

2.4 Iodine Behaviour in Gas Phase

Gaseous iodine species, whether released initially from fuel or formed in the aqueous phase and subsequently transferred into the gas phase, will undergo homogeneous and heterogeneous (surface) reactions during the course of an accident. Among the homogeneous gas phase reactions, the most important are those of I₂ with volatile organic compounds to form organic iodides, and of organic radicals with oxygen to form organic acids. These have the same mechanisms as do the aqueous phase processes, (Reactions (5)-(7)). The reaction of I₂ with ozone and •OH to form non-volatile solid iodine oxides (Sagert, 1989) also occurs in the gas phase. Finally, organic iodides formed in the gas phase or transferred there from the aqueous phase are subject to radiolytic decomposition. In general, homogeneous reactions of iodine species in the gas phase are not as important as aqueous and surface reactions of I₂. The gas phase reactions are much slower than their counterpart aqueous phase reactions because the less dense containment atmosphere does not absorb as much ionizing radiation to produce reactive radicals (including •OH and •R). In addition, the concentrations of iodine species in the aqueous phase are higher than those in the gas phase.

2.5 Heterogeneous Surface Reactions of Gas Phase Iodine Species

The interaction of iodine with painted surfaces in the gas phase have been studied by numerous groups, and the results of these studies are crucial to interpreting and modelling iodine behaviour. One of the most important features regarding iodine deposition is that molecular iodine is readily adsorbed on many surfaces, whereas organic iodides are much less likely to be retained. In RTF experiments (Ball 1997-1, Kupferschmidt, 1992), this adsorption results in the attenuation of observed gaseous I₂ fractions relative to the fractions of organic iodides. It also results in a large portion of the iodine inventory in many experiments being retained on gas phase surfaces.
Deposition studies performed on relatively dry surfaces are of limited applicability to the problem of predicting iodine behaviour during a severe accident. High temperatures and the large amount of hot water present in containment can be expected to result in extensive production of water vapour and condensation on all containment surfaces. The resulting water films, are not in hydraulic contact with the large water inventory in the containment building sump and will be continually removed and replenished (by draining and condensation). Although the iodine content, the organic and inorganic impurity content and the pH of these films will differ from that of the sump water, they will still act as an aqueous phase from the perspective of dissolution of organic materials from paints, and as a medium for homogeneous aqueous phase reactions of iodine.

The rate constant for adsorption of molecular iodine in condensing water films, as observed in the PHEBUS RTF4 tests is smaller than that observed for iodine adsorption on dry surfaces (Wren, 1999-4). Desorption of iodine from the wet surfaces can be ignored because iodine, once absorbed in a condensing water film, will be quickly hydrolyzed to form non-volatile I^- or transferred from the wall by drainage into the sump water. At this point, there is insufficient information to determine whether the deposition process involves iodine absorption into water aerosol droplets that are carried with the steam to walls by processes such as thermophoresis, or whether gas-phase molecular iodine adsorption occurs directly onto the wet wall surfaces.

Heterogeneous processes on gas phase surfaces have been used to explain organic iodide formation in the gas phase from painted surfaces previously exposed to molecular iodine (I2) (Deane, 1989, Bennett, 1970). However, as is the case for heterogeneous aqueous phase reactions, the evidence that organic iodide formation occurs on the surface is ambiguous. In the experiments reported by Bennett, the small amounts of organic iodide formed could also be explained by invoking homogeneous gas phase reactions between molecular iodine which was reversibly adsorbed on the surface, and released to react with organic species in the gas phase.

3. EFFECTS OF ORGANIC COMPOUNDS

Organic compounds can influence iodine volatility by changing the pH of aqueous solutions, and by promoting the formation of organic iodides. From previous discussion on iodine behaviour, it can be summarised that the pH change is the most important of these effects, and that it controls the amount of organic iodide formation. Radiolysis of organic materials in water decreases the aqueous pH, thereby increasing the amount of I2 in the aqueous phase. Organic iodide production is most likely to occur by homogeneous aqueous phase reactions of organic radicals with I2 because the largest portion of the iodine inventory in an accident is initially in the aqueous phase, and homogeneous aqueous phase reactions are the most efficient way of producing free organic radicals. Therefore, the net rate of production of organic iodides will always be only a fraction of the net rate of production of I2, and therefore dependent upon pH. Various intermediate- and bench-scale experimental studies are presented below to support and/or confirm the importance of these effects.

4 vessel wall temperature of 75-80°C and water temperature of 90°C
Figure 1 Log of concentration of iodine in the gas phase, and aqueous pH as a function of time observed from irradiated (1.5 kGy-h⁻¹) solutions of CsI in organic painted vessels.

Figure 1 shows pH changes and gas phase iodine concentrations as a function of time observed in intermediate-scale tests performed in organic painted vessels in the Radioiodine Test Facility (RTF). All three organic painted vessels showed similar results: the pH decreased with time, and an increase in the gas phase iodine concentration closely followed the decrease in the pH.

Both nitric acid production by the radiolysis of air, and hydrochloric acid (HCl) production from chloride substituents in the paint have been ruled out as the cause for these pH changes, the former because large pH changes were not observed in RTF tests performed in the absence of painted surfaces, and the latter because painted surfaces without chlorine substituents have the same effect on aqueous pH. The most likely cause of the pH decrease in painted vessels is the radiolytic oxidation of organic impurities in the aqueous phase to form organic acids and CO₂, which reduces the pH of the solutions (Reaction 7). This assumption was tested by adding MEK (methyl ethyl ketone), one of the common organic solvents used for paints, into the water phase during an RTF test performed in a zinc-primed vessel.

Figure 2 Concentration of iodine in the gas phase, aqueous pH and dissolved oxygen from an irradiated solution of CsI in a zinc-primer coated vessel. The increase in iodine concentration coincides with the addition of MEK to produce a 1 x 10⁻³ mol·dm⁻³ solution.

Tests were performed at 25°C, initial I⁻ concentration of ~1 x 10⁻³ mol·dm⁻³, initial pH of 10, dose rate of ~1.5 kGy-h⁻¹. The volume of the gas phase was 315 dm³ and that of the aqueous phase, 25 dm³.
The addition of MEK resulted in significant decreases in pH (from ~ 10 to ~6) and dissolved oxygen concentration, and an increase in the gas phase iodine concentration (Figure 2).

3.1 Organic Radiolysis

The decomposition of aqueous organic compounds under radiolytic conditions has been examined extensively by experimental and modelling studies. Studies performed on the radiolytic decomposition of MEK have established that, in aerated aqueous solutions, MEK decomposes into 3-hydroxy-2-butanone and 2,3-butanedione which further decompose to acetaldehyde and acetic acid, formaldehyde and formic acids, and eventually to CO₂ (Driver, 1999, Glowa, 1999). The formation of carboxylic acids and CO₂ lowers the pH of the solutions. The decomposition of MEK, formation of the radiolysis products, and the associated pH changes have been successfully modelled using recently developed kinetic models for MEK (Glowa, 1999, Wren, 1999-1). Work on a generic organic decomposition model, which incorporates experimental studies on other common paint solvents such as MIBK (methyl isobutyl ketone), xylene and toluene, is on-going, and is therefore not discussed in detail here. Nevertheless it has been established that there is a predictable relationship between the type and quantity of organic compound in aqueous solution, the dose-rate at which it is decomposed, and the final pH of the solution.

The key conclusions from organic radiolysis studies that are relevant to iodine chemistry are that organic impurities will be decomposed to organic acids and CO₂, lowering the pH of the sump water (Reaction (6)), and that radiolytic decomposition of organic compounds is a very fast process: Approximately 90% of 1 × 10⁻³ mol·dm⁻³ MEK would decompose in 4 h at a dose rate of 1 kGy·h⁻¹, with a minimum pH being attained within about 1 h. Therefore, the effects of organic impurities must be considered not only because of the potential for them to form organic iodides, but because of their direct impact on net molecular iodine production (see Reactions (3) to (12)).

3.2 Organic Dissolution Studies

There are many potential sources of organic impurities in containment. These include surface coatings (organic paints), cable sheathing (polymers), lubricants (grease and oils), etc. Beaum (1986) has estimated that the radiolysis of many of these sources could produce organic compounds in the gas phase at a rate of 1 × 10⁻³ mol·dm⁻³·h⁻¹. Many of these, being small alkanes would not be water soluble. The most important organic impurities in terms of iodine behaviour are those that have the highest solubility in water because the homogeneous aqueous phase reaction (Reaction (6)) to form organic acids involves the solvated water radiolysis product •OH. Long chain organic molecules (components of oil), and non-polar alkyl-organic compounds (such as methane, ethane, etc.) that may be formed from the pyrolysis of organic polymers, are not very soluble in water, and will not be as likely to produce organic acids as will the more soluble organic compounds like ketones and alcohols.

Studies on the dissolution kinetics of organic solvents from various containment paint surfaces, including vinyl-, polyurethane-, and epoxy-coatings, have established that solvents from these paints will be a large source of organic impurities in the aqueous phase in containment under accident conditions (Wren 1999-1). These studies show that the concentration of an organic solvent in aqueous solution [ORG(aq)] at time t follows first order kinetics, i.e.
\[ \text{[ORG(aq)]}_t = \text{[ORG(ab)]}_0 \cdot (1 - \exp(-kt)) \]  \hspace{1cm} (13)

where:

aq, and ab represent aqueous, and absorbed phase, respectively, \( k \) (s\(^{-1}\)) is the dissolution rate constant and \([\text{ORG(ab)}]_0\) (mol dm\(^{-3}\)) is the maximum concentration of solvent in the paint polymer phase at the start of dissolution available to be released into water.

The dissolution kinetics of many common solvents found in paint applications (e.g. toluene, xylene, MIBK and MEK), from polyurethane, vinyl and epoxy paints followed the same mechanism, with approximately the same dissolution rate constant \( k \). This rate constant was found to be independent of the age of the paint (although \([\text{ORG(ab)}]_0\) was a function of paint age), pH and radiation exposure, but dependent upon temperature, with an activation energy ranging between 80 and 100 kJ mol\(^{-1}\) for the three paint types studied. (Wren, 1999-1). These studies also showed that the effect of radiation on the rate of dissolution of the organic compounds from painted surfaces was negligible, although radiation rapidly decomposed the organic compounds once they had been released into the aqueous phase.

The concentration of organics available to be released into the aqueous phase in dissolution studies \([\text{ORG(ab)}]_0\) was found to decrease with the age of the coating, implying the organic content in the coating decreases because of evaporative losses. Even after several years, however, there are significant quantities of organic solvents which are available to be released by dissolution. For example, studies on Ripolin epoxy paint have shown that for an aqueous surface area to volume ratio of 0.13 cm\(^{-1}\), as much as 5 x 10\(^{-5}\) mol dm\(^{-3}\) MIBK was released from paint aged for four years. Numerous other organic solvents, such as xylene, toluene and acetone were also detected.

3.3 Rates of Decomposition vs. Dissolution of Organic Compounds

Decomposition studies of MEK have established that 90\% of a 1 x 10\(^{-3}\) mol dm\(^{-3}\) solution of MEK would decompose in 4 hours when irradiated at 1 kGy h\(^{-1}\), with the minimum pH value being reached within the first hour (Driver, 1999). Consequently, the pH changes observed in Figure 1 are slower than expected if the radiolytic decomposition of organic impurities is rate determining (e.g. for the fastest pH decrease, a minimum is reached only after 4 h), implying that another process is controlling the rate of the pH change. Dissolution studies described in the previous discussion have established that the rate of dissolution of these organic solvents from containment paints at room temperature is slow relative to the rate at which these solvents undergo radiolytic decomposition.

\[
\begin{align*}
\text{organic solvent in the paint matrix} & \rightarrow \text{organic impurities in water: slow} \hspace{1cm} (14) \\
\text{organic impurities in water} & \rightarrow \text{acids and CO}_2: \hspace{1cm} \text{fast} \hspace{1cm} (15)
\end{align*}
\]

A number of examples are available to illustrate Equations (14) and (15). In Figure 2 for example, an immediate decrease in pH and dissolved oxygen concentration (accompanying the decomposition of MEK) was observed when MEK was intentionally added to an irradiated solution of CSI to give a concentration of 1 x 10\(^{-3}\) mol dm\(^{-3}\). Recovery of the dissolved oxygen concentration, which implies that radiolytic degradation to acids and CO\(_2\) is essentially complete,
requires only about 20 h. In contrast, dissolution of MIBK from vinyl paint to reach concentrations of $1 \times 10^3 \text{mol-dm}^{-3}$ in the same water volume required almost 100 h (Figure 3). The relative rates of dissolution vs. decomposition of organic solvents has also been demonstrated in numerous intermediate-scale studies where, for a given paint surface, observed concentrations of paint solvents such as toluene and xylene were orders of magnitude higher in tests performed in the absence of radiation than in the presence of radiation. The much higher concentrations observed in the absence of radiation imply that radiation rapidly decomposes these solvents in the aqueous phase (Wren, 1999-1).

![Graph showing MIBK Additions](image)

**Figure 3** Dissolution of MIBK observed in an RTF test performed in a vinyl painted vessel in the absence of radiation. The sharp increase in MIBK concentration coincides with an intentional addition of the ketone.

The relative rates of radiolysis and dissolution dictate that the dissolution rate will control the rate at which organic compounds decompose, and acid is formed in the aqueous phase. The rate constant for dissolution of solvents from organic paints appears to be independent of solvent or paint type, and the final pH of solution is controlled by the amount of solvent in the paint. These findings greatly simplify development of models to predict the effects of organic compounds on iodine volatility. Because iodine volatility is mainly due to $I_2$, it will be controlled primarily by the time-dependent aqueous phase pH evolution, which will in turn be controlled by solvent dissolution kinetics, it is not necessary to construct detailed models for the decomposition of organic compounds in order to predict iodine behaviour. An assessment of the effects of organic compounds on aqueous pH and iodine volatility, requires only an estimate of the amount and type of solvent in the paint.

### 3.4 Organic Iodide Formation

Discussions in Section 2 have suggested that aqueous phase homogeneous processes will be of primary significance in determining the rate of organic iodide formation under accident conditions. As a result, the findings of the dissolution and radiolysis studies discussed in Sections 3.1 to 3.3 also have implications for organic iodine behaviour. The fact that dissolution from paints results in concentrations of organic compounds which are sufficient to alter the pH of the aqueous phase via Reaction (6), implies that there will be a variety organic radicals in solution, all of which will also be available to react with molecular iodine ($I_2$) (Reaction (7)). Furthermore, if organic iodides are formed primarily from homogeneous aqueous reaction of $I_2$...
with organic radicals, their rate of formation will be very dependent upon the concentration of $I_2$ in the aqueous phase, and therefore also sensitive to pH changes induced by organic radiolysis.

Confirmation that, in the presence of painted surfaces, organic iodide formation is primarily by aqueous phase homogeneous processes (Reaction (7)) has been obtained from several RTF experiments. In experiments with epoxy, polyurethane and vinyl painted vessels, it was observed that the temporal behaviour of organic iodides in the gas phase and aqueous phases were closely related to the behaviour of the aqueous pH, implying the participation of $I_2$ in the primary formation process ($I_2$ concentrations would be pH dependent (Reaction (9)-(12)). The quantities of organic iodides formed were much too large to be accounted for by homogeneous gas phase processes involving $I_2$, therefore the experiments demonstrate that organic iodide formation is occurring primarily in the aqueous phase. Furthermore, in all of these experiments, a large portion of the organic iodides formed from the paint impurities in the aqueous phase are much less volatile than $\text{CH}_3I$. Based on a partition coefficient of 3 for $\text{CH}_3I$ at room temperature, if $\text{CH}_3I$ were the predominant organic iodide in the aqueous phase, the gas phase concentration, would be expected to be only three times less than the aqueous phase. In most experiments, the concentration of organic iodides in the gas phase was an order of magnitude lower than that observed in the aqueous phase indicating that in the presence of organic compounds derived from containment paints, formation of many organic iodides which are less volatile than $I_2$ (e.g. highly soluble iodo-ketones, alcohols, phenols, and acids) compensate for the effects of forming a few organic iodides which are more volatile than $I_2$.

Because it would be extremely difficult to identify all of the organic iodides which could form, and to assign partition coefficients to each of them, developing an organic iodide model for predictions of iodine volatility will probably have to rely on obtaining an estimate for an overall partition coefficient for organic iodides. Detailed studies on organic iodide formation from several solvents found in paints will provide data on the distribution of organic iodides likely to be found. From this data, a weighted average for the partition coefficient for organic iodides can be obtained.

### 3.5 An Integrated Test on Dissolution vs. Radiolysis

From analysis of the dissolution, radiolysis and intermediate-scale studies described in the previous sections, a number of hypotheses have been formulated. These are:

1) Organic impurities which will have the greatest effect on iodine volatility are those which can change the aqueous pH, and promote organic iodide formation, i.e. water soluble organic compounds. A significant source of these impurities will be containment paints from which organic compounds can be leached.

2) Radiolysis of organic materials to form organic radicals is a faster process than dissolution of organic compounds from containment paints. Consequently the latter process will be the rate determining step in formation of organic acids and organic iodides.

3) Many organic iodides that are more soluble, and less volatile than $I_2$ will be formed as a result of radiolysis of iodide solutions in contact with containment paints.
These hypothesis have been tested in an RTF experiment designed to examine the effect of rate of dissolution of containment paint solvents on an irradiated solution of CsI. The test was performed in a stainless steel vessel at a dose-rate of about 0.7 kGy·h⁻¹. Dissolution of the solvent from a painted surface was simulated by adding the solvent slowly (via syringe pump) to the aqueous phase in the RTF main vessel. In the first 24 hours of the experiment, the pH was controlled at 10, and there was no introduction of organics. Then, pH control was removed and MIBK was added at a rate similar to its rate of dissolution from vinyl paint at 25°C. After several days, the organic addition was stopped and the pH was controlled at pH 8 for 24 hours. Finally, pH control was removed, and a second addition of MIBK was initiated at a rate 5 times faster than the first. Selected results from the experiment are shown in Figures 4 to 6.

![Graph showing concentration vs. time profiles](image)

**Figure 4** Iodine speciation measurements and pH in an irradiated solution (0.7 kGy·h⁻¹) of CsI in a stainless steel vessel. Iodine volatility and pH changes are associated with the addition of solutions of MIBK.

Figure 4 clearly shows that the concentration vs. time profiles of organic iodides in the aqueous phase and in the gas phase are closely related to each other, and to the aqueous pH, indicating that homogeneous aqueous phase processes are responsible for the production of both. Furthermore, the aqueous phase concentrations are two orders of magnitude greater than the gas phase concentrations confirming that the overall partition coefficient for organic iodides is much greater than that of CH₃I.

Figure 5 shows the measured dissolved oxygen concentration in the aqueous phase, as compared with the concentration expected for air saturated water. The lower oxygen concentration during MIBK addition arises as a result of oxygen consumption by organic radicals, and as one would expect, when MIBK addition is faster, there are more organic radicals formed, and more oxygen consumed. The fact that the oxygen concentration reaches a steady-state has important implications regarding the reactions of organic compounds in the aqueous phase:

\[ \cdot R + O_2(g) \rightarrow O_2(aq) \]  \hspace{1cm} (16)

\[ O_2(aq) \rightarrow \cdot RO_2 \]  \hspace{1cm} (17)
Figure 5  Dissolved oxygen concentration resulting from addition of MIBK into an irradiated solution (0.7 kGy h\(^{-1}\)) of CsI in a stainless steel.

A steady-state concentration of oxygen in the aqueous phase implies that the concentration of organic radicals (-R) in the aqueous phase is relatively constant, or at steady-state. The fact that [-R] is at steady-state is supported by the organic iodide concentration in Figure 4, which remains constant during addition of MIBK. A steady-state concentration of -R requires in turn that the concentration of the precursor (RH) is also at steady-state. In short, the steady-state concentration achieved by the dissolved oxygen confirms that introduction of organic compounds (RH) is the rate-determining step for the formation of organic radicals, and therefore for subsequent reactions of the radical with \(O_2\) to produce organic acid, and with \(I_2\) to produce organic iodides.

Figure 6 presents the most convincing data regarding the influence of “dissolution rate” on pH changes. The addition of MIBK, beginning at 50 h in the experiment resulted in formation of acid at a rate of about \(6 \times 10^{-10}\) mol dm\(^{-3}\) h\(^{-1}\). Increasing the rate of addition of MIBK by a factor of five resulted in a five-fold increase in the rate of acid production.

Figure 6  Aqueous [H\(^+\)] concentrations resulting from addition of MIBK into an irradiated solution of CsI
The observation that the organic compounds (RH) and organic radicals (·R) attain steady state concentrations in irradiated solutions in contact with containment paints greatly simplifies modelling both pH changes and organic iodide formation. As mentioned previously, since dissolution is the rate determining step for acid and organic iodide it is not necessary to model radiolytic decomposition of organic compounds in detail in order to accurately predict the rates of these processes. Both of these phenomena will be solely dependent upon the quantities, and types of organic material present in the paint, the temperature, and the dose-rate (because I\textsubscript{2} and -OH concentration will be dependent upon dose-rate). A semi-empirical model, to predict the phenomena of pH change and organic iodide formation can be easily constructed utilizing steady-state approximations for [RH] and [·R]. A model developed using this approach is near completion.

3.6 Mitigation Strategies

Based on experimental observations\textsuperscript{6}, we have concluded that the main driver for changing the pH of the sump water during the course of a severe accident (after the effects of chemical additives contained in all water sources have been considered) will be the radiolytic degradation of organic impurities in the sump water. Aqueous pH dictates the net rate of formation of molecular iodine (I\textsubscript{2}) and organic iodides in the aqueous phase, therefore pH control is the most effective way to minimize the production of volatile iodine species.

Experiments have also shown that, under radiolytic conditions, the pH of the sump will be directly related to the amount of the dissolved organic impurities. Consequently, reliable information on the inventory of soluble organic material in containment paints is expected to be important in determining the amount of buffering agent needed to control the pH of the sump water following an accident.

4. CONCLUSIONS

Studies on the influence of the chemistry of painted surfaces on iodine volatility under postulated reactor accident conditions have shown that:

1) One of the major sources of organic impurities found in containment water will be the organic compounds dissolved from various surface paints.
2) The main impact of organic compounds on iodine behaviour will be through aqueous-phase reactions of these organic compounds to reduce solution pH, and promote higher steady-state concentrations of I\textsubscript{2}.
3) The rates of the processes described in 2 are likely to be controlled by the dissolution kinetics of the organic compounds from the surface coatings.

---

\textsuperscript{6} Under RTF conditions (gas/aqueous volume ratios of \( \approx 10 \), dose-rate of 2 kGy·h\(^{-1}\), and aqueous surface/volume ratios of 20 m\(^{-1}\)), the theoretical rate of production of nitric acid, (a G-value of 3.19 was reported by Sagert), could induce pH changes at a rate comparable to the changes produced by dissolution and radiolysis of organic solvents from containment paints. Nevertheless, in several intermediate-scale studies performed at similar dose-rates in the absence of organic materials, the pH changes expected due to formation of nitric acid in the gas phase were not observed.
4) aqueous phase reactions will be primarily responsible for formation of organic iodides, but organic iodide formation does not necessarily lead to increased iodine volatility.

The identification of aqueous phase reactions as being of primary importance in determining iodine volatility, and of solvent dissolution as being a rate-controlling process for the pH evolution, have implications for both modelling and mitigating iodine volatility. Iodine volatility will be controlled primarily by pH changes in the aqueous phase, which in turn will be dependent upon solvent dissolution kinetics. Control of the pH in the aqueous phase will therefore be essential for mitigation, and predicting pH changes will be required for modelling iodine behaviour. Ensuring pH control will rely upon knowledge of the quantities and types of soluble organic material in containment paints. This information will also be required for predicting iodine volatility, since the net rate of production of I\(_2\) and organic iodides will depend upon the rate of dissolution of these materials into the aqueous phase.

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REFERENCES


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CALCULATIONS ON IODINE SPECIATION IN GAS AND LIQUID PHASES

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The possible release of radioactive material to the environment during and after a severe reactor accident in a modern light water reactor (LWR) depends to a considerable degree on the amount of radioactive species in the gas phase within the containment at the time of the release regardless if the release is due to a filtered venting or a diffuse leakage. After an initial period it is often argued that various species of iodine would dominate the activity of the containment atmosphere for many weeks. Other possible radioactive substances having long residence times in the containment atmosphere are those which may contain tritium and $^{14}$C, e.g. water vapour, CH$_4$, CO and CO$_2$.

The volatility of iodine is strongly dependent on the redox potential and to some degree also on the pH of the water present in the containment. Furthermore, the chemical composition of aqueous solutions also affects the chemical speciation of iodine, and hence its volatility. In general, low pH values in the waters lead to a higher amount of volatile iodine than high pH-values. It is therefore of interest to be able to compute the expected pH-values and composition of all aqueous solutions present at any time within the containment once the accident has begun to develop [1].

There are several well tested and widely used general computer codes (with the corresponding data bases) for calculation of the equilibrium chemistry of any aqueous solution in contact with gases and solids at any temperature, e.g., PHREEQE [2], EQ3/6 [3], and SOLGAS-WATER from the SOLGAS family of codes [4].

The limitation of these codes and the uncertainty in their results are mostly due to possible deficiencies in their data base, i.e. incomplete or faulty knowledge derived erroneously from correct measurements, derived correctly from erroneous measurements, or caused by theoretical interpolations/extrapolations in place of actual measurements. The effects of such uncertainties are not discussed here but it naturally constitutes a problem which ought to be looked into more deeply. An important limitation is that equilibrium codes cannot describe non-equilibrium situations where limited reaction and mass transfer rates leads to transient phenomena.

The present paper aims at a determination of the speciation of iodine in the water in the containment of a reactor during and after a severe accident and to estimate the partial equilibrium pressures of various iodine species in the gas phase. Our calculations are based on the masses, temperatures and pressures in the containment
calculated by MAAP-4 for a hypothetical TB-sequence in a large Swedish BWR. The gas phase content from our calculations has then been used to calculate the approximate isotopic composition and total radioactivity of iodine in the gas phase.

As a "by-product" a wealth of chemical composition and speciation data for other elements in the water are obtained. Furthermore, some information is also obtained with regard to likely solid phases present on submerged surfaces in the system.

PROGRAM DESCRIPTION
A previously developed user interface and management program, AUTOPHREEQE [5], has been modified and extended to handle the problem of water chemistry in connection with a core melt. The program creates input data files for PHREEQE and extracts the useful part of the results from the result files of PHREEQE. The AUTOPHREEQE program is able to handle creation of an initial water, change the temperature (which also changes the equilibria involved), equilibrate with several solids and external reactions and finally to mix two solutions with different initial temperatures. Examples of reactions are dissolution of aerosols and HCl which may be formed by pyrolysis of cable isolation.

AUTOPHREEQE is able to handle groups of related calculations. Such a group is named a project. The related calculations could be different steps in a series of events. New projects are created by making a copy of another project. In this way, modifications of a calculation are easily performed without the need to rewrite such input data which do not change. Often a project requires hundreds of values to be entered, a task which would be very time consuming without the project manager.

Similarly, the individual steps are handled by a step manager, which makes use of data already present and gives the opportunity to modify those data whenever necessary.

pH DEVELOPMENT IN THE SYSTEM
Inside a nuclear reactor containment almost all elements of the periodic table are present. Handling such a complex chemical system is still outside the possible range for programs like PHREEQE. Thus, elements which could be expected to have a small influence on the pH, the redox potential, or iodine speciation have to be excluded from the model system in order to make calculations possible. The following set of elements have been chosen to be present in the model system: Cl, Cs, Cu, H, I, Mo, N, O, Sr, Ru, U, and Zr.

In most cases, MAAP does not give enough information concerning the chemical states of the elements entering the containment. In our calculations the following initial oxidation states have been assumed to be dominant: Cl(-I), Cs(+I),
Cu(0), H(+I) and (0), I(-I), Mo(0), N(-III), O(-II), Sr(+II), Ru(0), U(+IV), and Zr(+IV). At the temperatures of interest (<100 °C), Zr(0) and H(0) have been treated as inert.

As discussed above, the same substance is able to drive the system towards either a higher or a lower pH value. The direction depends upon the initial pH value and what other species are present in the system. Considering pH = 7 as a standard value, two classes of pH controlling substances can be found.

Substances tending to decrease the pH value are mainly products from pyrolysis of cables, HCl, H₂SO₃ and CO₂ [6]. Besides, some fission products (e.g. iodine) and their oxides may act in the same direction. The effect of all pH lowering substances is small compared to HCl, and thus only this substance has been considered.

With the species tending to increase the pH value, the situation is quite different. Most metal oxides and hydroxides have this property and several of them have to be considered. In particular, UO₂ and cement (approximated as Ca(OH)₂) are present in quantities large enough to increase the pH value considerably if they could react rapidly enough and did not have limited solubilities. The ZrO₂ formed during the meltdown process also has a potential for increasing the pH of the solution.

The dissolution of cement is slow, and probably the cement will have a small influence on the pH value of the system. UO₂, on the other hand, could be expected to react rapidly enough. It has been assumed that the UO₂ formed by the melting and subsequent rapid solidification is essentially amorphous. Unfortunately, the solubility at the temperatures reached is too small to restore the pH value. Some fission products, like Cs and Sr, are at least partly present as oxides, have high solubilities and thus are able to increase the pH value considerably. The quantities present are, however, too small and thus they are not able to increase the pH value up to the desired range (10.5 - 11). The high pH is desired for three reasons, i) it limits the amount of gaseous iodine species, which is important on a short time scale, ii) it keeps both zinc and aluminum corrosion products in solution, which emanate from the large amounts of these metals present in a BWR containment (typically more than 10 metric tons of Zn and several tons of Al, both with very large surface areas), and iii) it reduces corrosion of steel, which is important on a long time scale.
CALCULATION SET-UP
The calculations have been performed for an average of the relevant compartments because these are connected together with possible circulation of gases and liquids after the first couple of hours, see Figure 1. The water content, temperature, gas volume and amount of different elements in the various compartments are therefore estimated from MAAP output and summed or averaged. The variation of gas and water volumes with time is shown in Figure 2. To minimise the risk for numerical problems in the equilibrium program, the following set of elements has been chosen to represent the system in the PHREEQE calculations: Cl, Cs, Cu, H, I, Mo, N, O, Sr, Ru, U, and Zr.
Figure 2, Variation of water and gas volumes in the reactor

For each element, the quantity needed to form a saturated solution has been calculated in order to determine whether the available quantity may be totally dissolved or not. It has been found that most elements are able to dissolve totally (in available quantities). The following solid phases were used as model substances for the core-melt: ZrO$_2$(am), U(OH)$_4$, Mo, Cu and Ru.

The rest of the elements have been assumed to enter the solution by dissolution of the total available quantity. In the case of a decreasing concentration, it has been assumed that the cause is dilution with pure water. In order to simulate dilution, the proper negative amounts of the elements already present in the solution have then been added to the solution in oxidation states corresponding to the dominant species of the undiluted solution.

The water in the compartments is assumed to be well mixed, i.e. there exist no gradients neither in concentration nor in temperature. Since MAAP produces results in discrete time steps, it is assumed that the reaction paths may be represented by the time steps used.

The conceptual model
The conceptual model is based on a sequence of events described below. For each sequence calculations have been made to follow the evolution of the chemistry of the system.

Hours 0-2
The initial state when the TB-sequence is initiated is shown in Figure 1. In this Figure, the original water levels and connections between compartments are shown in the

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upper left part. Flooding of the lower drywell was initiated 0.8 hours into the accident and battery power was lost at about 2 hours.

**Hours 2-6**
The initial state of the water is supposed to be pure water at a temperature of 25 °C. The pH of such water is 7.0 and the pE value is supposed to be zero. The first event taken into account is an increase in temperature up to 50.4 °C and simultaneous dissolution of the material released during the first two hours of the accident.

During the following hours, the quantity of water in each compartment is not constant. The upper right part of Figure 1 shows the water levels and connections between compartments at 6.1 hours into the accident, a time when melt through of the pressure vessel is imminent. Decreases in the amount of water are assumed to occur as a result of evaporation and flow between compartments, especially from compartment 6 into compartment 1 through the open flooding valve. Increases in the amount of water are for simplicity assumed to be due to pure water entering the compartment, either by condensation of steam, flow between compartments or injection through the upper drywell spray system.

An increase in the water quantity results in a lower concentration which is technically handled in PHREEQE by a quasi reaction in which negative quantities are added to the solution. Aerosols dissolving in the water are treated as reactions adding positive quantities of the corresponding elements. Most of the elements are in oxide states and in quantities far below the solubility limit. Thus, they are assumed to dissolve which causes the pH to increase.

**Hours 6-8**
During this period, the core melts through the reactor tank. This results in pyrolysis of cables causing HCl to form. Since this gas is highly soluble in water, it is assumed to dissolve rapidly and thus the pH drops to low values. A rubble bed is formed from core melt at the bottom of compartment 1. The valve to the filtered venting system opened at 7 hours and stayed open until about 9 hours, permitting a decrease of the containment pressure to about 1.5 bar.

**Hours 8 - 24**
Water is being pumped into the containment through the drywell spray system, beginning at about 8 hours. This causes a slow increase of the water volumes. The filtered venting system is in operation up to 9 hours after initiation of the accident in order to release pressure and to permit the filling up of the containment with water. The lower left part of Figure 1 shows the water levels 13.9 hours into the accident.
Vigorous boiling is caused by the debris bed formed at the bottom of compartment 1 and rises the water level in this compartment above the water level in compartment 6. The boiling forces a flow of gases out of compartment 1 - mainly into compartments 2 and 4. Water is also transferred into compartment 2 from which it drains down into compartment 6, thereby causing a mixing of the liquids. As a result of the boiling, almost all of the gases initially present in compartment 1 are replaced by steam rising as bubbles through the water.

The addition of water causes compartment 1 to be filled-up with water at about 17 hours. After that time the gas phase present in this compartment is in the form of steam bubbles rising in hot water.

The molten core consists essentially of UO$_2$, ZrO$_2$, Zr, fission products and actinides formed by neutron capture. Together with this material, there is Zr from the cladding, Cu from the cables and Fe from the steel container. The quantities of these elements released after vessel melt-through are far too great for a total dissolution. Thus, the solution is assumed to be saturated with respect to a selection of the corresponding solids. In some cases, the dissolution has been assumed to be too slow for saturation to occur. Then the corresponding elements have been assumed to dissolve in the same oxidation state as they have in the core melt.

In some cases, one or more elements have been excluded from the calculations or added in reduced quantities to make PHREEQE able to converge. In those cases, approximate calculations have confirmed that the influence of the approximation upon the results are less than half a unit on the pH scale.

Sporadic venting of the containment through the filter system occurs from 22 hours and onwards. The lower right part of Figure 1 shows the end condition reached 24 hours into the accident, which was the termination time for the MAAP run on which we based our calculations. At this stage the core is covered with water again.

Case set-up
There are several factors for which it is difficult to make a prediction. Examples are the quantity of concrete available to reaction with water, the extent to which the cable material will be pyrolysed and whether the molten fuel will be in equilibrium with the water. To address those cases a factorial design has been used, in which a high and a low value has been chosen for each parameter, see Table 1.
Table 1, $2^3$ factorial design

<table>
<thead>
<tr>
<th>Case</th>
<th>Cable pyrolysis</th>
<th>Cement equilibration</th>
<th>Fuel equilibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 %</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>2</td>
<td>20 %</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>3</td>
<td>20 %</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>20 %</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>5</td>
<td>50 %</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>50 %</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>7</td>
<td>50 %</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>50 %</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The evaluation of a factorial design is rather straightforward. The effect (E) of for example, cement equilibrium is calculated according to Equation 1.

$$E_{\text{cement}} = -Y_1 - Y_2 + Y_3 + Y_4 - Y_5 - Y_6 + Y_7 + Y_8 \quad (1)$$

where $Y_i$ are the results of calculation case $i$, i.e. pH.

$E$ may be a good representation of the partial derivative of the system function with respect to the selected variable. As seen in Table 1, the cement and fuel equilibrium is a binary process, i.e. either the water is in equilibrium with the solid phase or no dissolution occurs. There are naturally other parameters that may be argued to be uncertain, for example the thermodynamic data used for the equilibrium calculations. However, in these calculations it is assumed that the values in the data base [7] are correct.

The cases given in Table 1 have, when possible, been calculated throughout the time span concerned, i.e. 1-24 hours. This gives the opportunity to see when the changes in pH occur. However, the results used for the evaluation of the factorial design are the ones obtained after 24 hours, see Figure 3.

![Figure 3](image-url)  
Figure 3, Final pH values for the cases in the factorial design
The results from the simple sensitivity analysis of the factorial experiment is shown in Table 2. As can be seen, equilibration with cement has a large effect by increasing the final pH, whereas the degree of cable pyrolysis has a smaller and opposite effect. Equilibration with the quenched core melt has only a small effect, but tends to decrease the final pH, which may seems surprising at a first look. From the cases presented here only one of the most acidic cases, i.e. case 5, has been used for the iodine calculations. This is due to the very small amounts of iodine present in the gas phase for the cases with a high pH.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>cement equilibration</td>
<td>8.89</td>
</tr>
<tr>
<td>cable burnup</td>
<td>-0.69</td>
</tr>
<tr>
<td>fuel equilibrium</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

**RESULTS**

The results of the calculations may be divided into two parts: one dealing with the pH in the water and the other with the iodine speciation. In the first case the behaviour pH as a function of time was calculated for the different cases of the factorial design. The results are given in Table 2. The development of pH as function of time is shown in Figure 4.

![Figure 4, pH as function of time for case 5](image)

As can be seen from Table 2 and Figure 3, case 5 and 6 yields the lowest pH-value. The difference between cases 5 and 6 is marginal. Hence, data from case 5 was used in our calculations of iodine speciation in the aqueous and gas phases and of the total iodine concentration in the gas phase.

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Table 3, Iodine in aqueous solution and in the gas phase. Main species are I− in aqueous solution, HI in the gas phase and CSI in the aerosol.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>P_H2 = 1.3 bar</th>
<th>P_H2 = 3.16E-10 bar</th>
<th>CSI aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P_HI (Pa)</td>
<td>[I_{tot}(aq)] (M)</td>
<td>P_HI (Pa)</td>
</tr>
<tr>
<td>2</td>
<td>3.2E-18</td>
<td>1.7E-05</td>
<td>3.2E-18</td>
</tr>
<tr>
<td>3</td>
<td>2.5E-17</td>
<td>3.3E-05</td>
<td>2.5E-17</td>
</tr>
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<td>5</td>
<td>2.5E-16</td>
<td>3.6E-05</td>
<td>3.2E-16</td>
</tr>
<tr>
<td>6</td>
<td>2.5E-16</td>
<td>3.6E-05</td>
<td>2.5E-16</td>
</tr>
<tr>
<td>8</td>
<td>1.0E-09</td>
<td>7.9E-10</td>
<td>3.5E-05</td>
</tr>
<tr>
<td>11</td>
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<td>2.9E-05</td>
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Table 3, summarizes the results from the iodine speciation calculations at times from 2 hours up to 24 hours. The reason for omission of times below 2 hours is that there was only a small amount of cesium iodide released before this time according to MAAP output. Figure 5 shows the total gaseous iodine radioactivity as function of time. This graph was calculated from the iodine concentration in the gas phase and the estimated specific activity of iodine assuming a 28 MWd/kg average burnup of the fuel.

![Gaseous Iodine (HI)](image)

Figure 5, Iodine-activity and conc in gas vs. time

These data show that a rather complete equilibrium calculations of the iodine speciation result in an extremely low total iodine content in the gas phase, in
contradiction to experience. However, an important - but not new - conclusion is that the gas borne iodine observed in many experiments is due to a transient equilibrium. The thermodynamic driving force is thus towards a low gaseous iodine concentration, especially in moderate pH, low oxygen and high hydrogen conditions. Could we find ways to improve mass transfer and catalyse the reactions, we should expect a reduction in gaseous iodine, at least for cases where little, or no, oxygen is present. On the other hand, the activity from aerosols will then be the dominating source of activity in the gas phase.

Is the total iodine concentration in the gas phase a significant factor from an accident management point of view in cases where the containment remains intact and filtered venting is available? The answer is probably yes. This is due to the unavoidable diffuse leakage of a small fraction of the containment atmosphere to the environment in all cases where the containment pressure is above ambient. Our speciation and pH calculations indicate the relative importance of concrete dissolution, cable pyrolysis, and core melt dissolution in water for the development of the pH of water in the containment. Even if the equilibrium calculations of the iodine speciations does not reflect important kinetic factors, the aqueous pH is still of importance in dynamic iodine speciation models. Here, calculations of the type described can contribute.

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KINETICS OF THE UPTAKE OF AQUEOUS IODINE ON SILVER SURFACES

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ABSTRACT

A shared-cost action on Iodine Chemistry has been undertaken as part of the CEC 4th Framework programme on Nuclear Fission Safety. Organisations from six EC countries have been involved in an integrated programme of experiments and analysis to clarify the phenomenology, and to increase confidence in the modelling of iodine behaviour in containment. The project was focused on understanding and quantifying the effects of silver on iodine behaviour, providing new experimental data, which have been used to validate and improve the existing models and to stimulate code development. The main conclusions of the work are as follows:

The reaction of I₂ with Ag surfaces is very rapid and is probably mass transfer limited under the conditions of these experiments. The experimental results fit well to a pseudo-first-
order kinetic law. No effect of chloride or nitrate ions at concentrations of 0.01 mol dm$^{-3}$ is detectable.

The $\Gamma$ - Ag reaction is much less rapid, at least for un-oxidised silver surfaces, and the reaction appears to follow zero-order kinetics with respect to $\Gamma$. If an oxide layer is present on the silver surface, the reaction is initially mass transfer limited resulting in much faster uptake of $\Gamma$.

The radiolytic formation of nitric acid in air-water mixtures is predominantly a gas-phase process. The G-value is approximately $2 \mu$100 eV, and this is not influenced by the temperature.

Iodine volatility from irradiated iodine solutions is substantially reduced in the presence of excess silver. The reduction in volatility in the current studies is consistent with the rate constant for the $\text{I}_2$ - Ag reaction determined from non-irradiated studies.

Silver iodide, either on silver surfaces or formed from reaction with colloidal silver, is very largely stable to radiation at the dose rates and temperatures used in this work.

Based on the experimental data generated in this programme, models have been formulated to describe the kinetics of reaction of $\text{I}_2$ and $\Gamma$ with silver surfaces. These models have been applied in plant calculations to assess the sensitivity of predicted iodine releases to the silver - iodine modelling for three different accident sequences. The effect is highly sequence-dependent and varies to some extent between the different models used.

The most important remaining uncertainties for modelling the silver - iodine reaction are the aerosol size and degree of surface oxidation. A good knowledge of the aqueous mass transfer rates is also required if the uptake rates are to be predicted with confidence.

In summary, this programme has provided extensive experimental kinetic data on the reaction of aqueous iodine with silver surfaces. Experiments have shown that the volatility of iodine from irradiated iodide solutions is greatly reduced in the presence of excess silver, and that this can be understood in terms of the thermal reactions of $\text{I}_2$ with the silver surface. Moreover, the AgI product appears stable to irradiation at the dose rates studied.

The source term evaluation has shown that this reaction has significant potential to reduce the formation of volatile iodine under some severe reactor accident conditions. The effect of this reduction on the predicted release of iodine to the environment depends strongly on the sequence being considered. The presence of silver has the greatest potential impact under conditions of low pool pH and high Ag/I ratio.

1 INTRODUCTION

Iodine is one of the most important fission products that would be released in the event of a severe reactor accident. Plant assessments have shown that it contributes significantly to the source term for a range of accident scenarios. However, the considerable differences between the iodine behaviour observed in Phoebus Test FPT0 and that predicted by containment chemistry calculations indicate that the current models do not correctly treat all of the phenomena that could be important in a reactor accident (Jacquemain, 1999; Chuaqui,
In particular, the presence of a large quantity of silver aerosol appears to influence very strongly the volatility of iodine from solution.

It is assumed that iodine released from the fuel in a severe accident would be transported to the containment primarily in the form of iodide. This would dissolve in containment water pools to give involatile I\textsubscript{3}, which could then be oxidised under irradiation to volatile I\textsubscript{2}. Reaction of either I\textsubscript{3} or I\textsubscript{2} with silver to form insoluble AgI would substantially lower the amount of I\textsubscript{2} formation, which could have important consequences for active and passive safety measures and for accident management strategies.

A programme of experimental and analytical work to study the reaction of aqueous iodine with silver surfaces was carried out as a shared-cost action under the EC fourth framework programme. The project was focused on understanding and quantifying the effects of silver on iodine behaviour, and providing new experimental data that can be used to validate and improve the existing models and to stimulate code development.

The work was divided into three activities: Experimental Studies; Analysis and Model Development; and Source Term Evaluation. This paper concentrates mainly on the results of the experimental work and the source term evaluation; the analysis and modelling is described in more detail in a separate paper.

2 EXPERIMENTAL STUDIES

This activity comprised three experimental programmes whose objective was to provide new data on the reaction of aqueous iodine with silver under accident-relevant conditions. The two main questions being addressed in this work were:

How quickly are I\textsubscript{3} and I\textsubscript{2} removed from solution by reaction with silver surfaces? and

Is the AgI formed in these reactions stable under irradiation?

This activity was divided into the three tasks described below.

Task 1.1: Non-irradiated experiments to measure the rate of uptake of aqueous iodine (I\textsubscript{2} or I\textsubscript{3}) onto silver surfaces in the absence of radiation, in order to provide detailed kinetic data to supplement and extend the existing database and to clarify anomalies in previous work. The main focus of this work was initially to investigate the effects of impurities on the reaction rates. As the work progressed the different behaviour of different types of surface became evident and additional tests were performed to clarify these observations.

Task 1.2: Experimental studies on the possible effects of irradiation on the silver - iodine reaction. The radiolytic formation of nitric acid in irradiated air-water mixtures could lead to the production of Ag\textsuperscript{+}, which could react directly with I ions in solution. One of the objectives of this task was therefore to provide experimental data on the rate of HNO\textsubscript{3} production at elevated temperature. The other objective was to quantify the effect of silver on the volatility of iodine from irradiated solution, and in particular to assess whether the AgI formed is stable to irradiation.

Task 1.3: High-temperature radiolysis experiments. Results from Phebus test FPT0 indicated that silver could be partially present in the sump as a colloidal suspension together
with soluble silver. In this task, therefore, the stability of colloidal AgI species is studied under conditions relevant to a severe accident, to quantify the effects of temperature, radiation and Ag⁺ concentration on the decomposition of silver iodide.

2.1 Non-Irradiated Studies

2.1.1 I₂ - Silver Reaction Kinetics

These experiments were performed to study the kinetics of reaction of I₂ in solution with silver surfaces, and in particular to study the effects of representative impurities (NO₃⁻, Cl⁻). In these experiments, silver mesh (surface area ~0.008 m² g⁻¹) was added to solutions of I₂ (10⁻⁴ mole dm⁻³) in 0.2M H₃BO₃. The decrease in the I₂ concentration due to uptake on the silver was then followed colorimetrically. The rate constant k was calculated assuming first order kinetics:

\[
\frac{[I₂]_t}{[I₂]₀} = e^{-(kt)}
\]

(1)

If Aₜ is the measured absorbance of the solution at time t, which is proportional to the I₂ concentration, then

\[
\ln(Aₜ) = \ln(A₀) - kt
\]

(2)

k was therefore determined for each experiment by linear regression of ln(Aₜ) on t. Correlation coefficients of ≥0.98 were obtained in almost all cases.

Tests were performed at 20 and 50°C, with an initial iodine concentration of ~10⁻⁴ mol dm⁻³ and silver surface concentrations in the range 20 to 300 m⁻¹. The effects of adding 0.01 mol dm⁻³ of Cl⁻ and NO₃⁻ impurities was studied.

Initial experiments were carried out using the spectrophotometric cell as the reaction vessel, allowing the I₂ concentration to be monitored continuously. The experiments showed a rapid fall in the I₂ concentration in the first 10 - 20 seconds, after which the system appeared to follow first-order kinetics. The same behaviour was observed when fresh I₂ solution was added to silver which had already been used in an experiment, indicating that the change in rate was not due to the surface initially being free of iodine. It was therefore concluded that the reaction was mass transfer limited, and that the initially rapid rate reflected the greater turbulence in the solution when it was injected into the reaction cell. Subsequent tests were therefore performed in a stirred reaction vessel, and samples removed periodically for measurement. In these tests, the decreased in the measured concentration I₂ with time was in good agreement with the expected first-order behaviour.

The first order rate constants are plotted against the silver surface / liquid volume ratio [Ag] in Figure 1. This also shows the best-fit lines for the unstirred and fast-stirred experiments at 25 and 50°C.
Figure 1  I₂ - Ag Reaction Kinetics

The gradient of the regression line gives the pseudo-first order rate constant, or deposition velocity, \( k_d \), which is defined by

\[
-\frac{d[I_2]}{dt} = k_d [I_2] [Ag]
\]  \( (3) \)

The figure shows a strong effect of stirring on the reaction rate, implying that the reaction is mass-transfer limited, at least in the unstirred or less rapidly-stirred experiments. The difference between the rate constant at 25 and 50°C is quite small; the higher rate of iodine loss from the solution at the higher temperature is mainly due to evaporation, as shown by the experiments with no silver present. The closed diamonds represent tests with various additives; these do not differ significantly from the other fast-stirred results.

2.1.2  I - Silver Reaction Kinetics

A second set of experiments was performed to study the kinetics of the Ag - I reaction. These conditions of these experiments were similar to the I₂ studies described above, with Ag mesh being added to 10⁻⁴ M CsI solutions and the iodide concentration monitored by ion chromatography. In some tests, silver powder was used for comparison with earlier work by Funke (1996).

The results of these experiments show that the reaction of I with silver mesh is considerably slower than that of I₂, with pseudo-first order rate constants of 10⁻⁸ to 10⁻⁶ m s⁻¹ being observed at 25°C. The reaction rate was slightly higher at 90°C and showed a weak dependence on pH. The rate was not affected by the presence of 0.01 M concentrations of chloride or nitrate ions at 90°C and pH ~ 5. However, a significant effect of nitrate was observed at low pH. This difference may be due to the oxidation of the silver by the nitric acid; however, oxidation of I to I₂ would also increase the reaction rate.
The decrease in I⁻ concentration with time measured in these tests could be fitted equally well by a linear (zero-order rate law) or exponential (first-order rate law) correlation. It is therefore difficult to determine, on the basis of the results of the individual experiments, which rate law gives a better fit. However, the rate constant was found to be dependent on the initial I⁻ concentration indicating that a zero order rate law is more appropriate. This could be explained by a two stage reaction involving, for example, an initial, rate-limiting, surface oxidation step followed by rapid reaction of iodide with the product.

The tests using silver powders showed an initially rapid reaction when the silver was added to the iodide solutions, which was not observed in the tests with silver mesh, as shown in Figure 2.

![Graph showing I⁻ uptake onto Ag surfaces - comparison of mesh and powder results](image)

**Figure 2. I⁻ uptake onto Ag surfaces - comparison of mesh and powder results**

This different behaviour was attributed to different degrees of surface oxidation of the silver powders. Further evidence for the role of surface oxidation is provided by the tests in which silver mesh was immersed in a boric acid solution for 1 or 2 days before adding the iodide; the observed behaviour then resembled the powder tests with an initially rapid removal of I⁻ from the solution. Furthermore, in some high-temperature experiments in which the silver was not fully submerged in the solution, unexpectedly fast reaction rates were observed. This is thought to have been due to enhanced oxidation of the exposed silver in the steam-air above the solution.

Earlier work by Funke (1996) has already established the importance of oxygen to the Ag-I⁻ reaction, and the differences between the two sets of tests are probably due to the differing degrees of surface oxidation on the different types of silver used. In the one case where the same type of silver was used in the two programmes, the results were almost identical.
2.2 Radiation Effects

2.2.1 Nitric Acid Formation

It is well known that the irradiation of moist air leads to the formation of nitric acid. This phenomenon has been investigated by a number of groups for various reasons mainly associated with corrosion of plant or storage vessels used for radioactive fuel or waste. It is generally accepted that the formation of $\text{HNO}_3$ is a gas phase phenomenon (although some groups maintain that it occurs in the solution phase), and that the yield is about 2 molecules/100 eV energy absorbed in the gas phase, although reported yields range from 1-6 molecules/100 eV.

Nitric acid formation may have important consequences in the containment of a light water reactor in the event of a LOCA involving release of fission products from fuel. The formation of nitric acid would tend to cause a decrease in pH of the sump and suspended aqueous aerosol; it could also lead to dissolution of silver particles which may be present from vaporised control rods. These factors are likely to be important for iodine behaviour in containment.

The temperature and humidity in the containment during a LOCA would be somewhat higher than used in most studies of radiolytic formation of $\text{HNO}_3$ and no systematic measurement of the effect of temperature on nitric acid formation in air in contact with liquid water has been reported. This could be an important factor when trying to simulate iodine behaviour in a fault. A number of experiments were therefore carried out to study the effects of temperature on nitric acid production.

Vials containing air and water were irradiated in a Gamma Irradiation Facility at a dose rate of 1.6 kGy hr$^{-1}$. The volume of the vial was ca. 48 ml and the diameter of the irradiated section was 2.2 cm. The vials were made from Pyrex and washed by soaking in high purity water (Millipore milli-RO/milli-Q). High purity water was then added to the vial and the amount measured by weight, the vials were then flame sealed. The samples were placed inside a resistance furnace tube in the $^{60}\text{Co}$ source cavity and thermocouples in the thermocouple pocket provided a continuous record of the temperature. Irradiations were carried out from room temperature up to 88°C. Nitrite and nitrate analyses were carried out using a Dionex ion chromatography system.

The programme of irradiations was carried out with four objectives:

1. To measure the radiation chemical yield of $\text{HNO}_3$ from a system with a fixed gas to liquid ratio, ca. 43 cm$^3$ air in contact with 5 cm$^3$ water, as a function of dose.

2. To measure the effect of reducing the gas to liquid ratio (but with the same geometry) on the yield of $\text{HNO}_3$.

3. To measure the effect of temperature on the yield of $\text{HNO}_3$.

4. To measure the effect of silver surface on the yield of nitric acid, and the resulting dissolution of silver.

The yield vs. dose is shown in Figure 3.
Figure 3 Nitric Acid Production in Irradiated Air-Water Mixtures

The solid line shows the yield for a G value of 2.2 molecules HNO₃/100 eV. There was no observable effect of increasing temperature from 25°C to 90°C on the yield of HNO₃. The total amount of nitrate formed in the solution was proportional to the volume of gas in the vial, and independent of the liquid volume, showing that it was formed predominantly by a gas-phase process.

A sample with 0.66 g silver in contact with the solution phase (Ag₁) at 90°C gave a yield of 2.2 molecules/100 eV, the same as in the absence of silver. In a sample with 0.5 g silver in contact with the gas phase (Ag₂) at 90°C the yield was 2.7 molecules/100 eV, a little higher than in the absence of silver. Both solutions had a dissolved silver concentration of about $4 \times 10^{-5}$ mol dm$^{-3}$ after irradiation, similar to the nitrate concentration. It should be noted that in Ag₂, although the silver was in the gas phase during irradiation, it became immersed in the solution when the vessel was inverted after the irradiation. It is likely, therefore, that the oxidation / dissolution of the silver occurred during the period between irradiation and analysis.

2.2.2 Iodine Volatility from Irradiated Solutions

AgI is unstable to visible light in the photographic process, and it has therefore been suggested that this instability should also occur in an ionising radiation field. Previous studies have failed to demonstrate any decomposition but it has often been difficult to quantify the results because of experimental difficulties associated with the use of powdered silver or post irradiation reactions. Further tests to study the effect of silver on the volatility of iodine from irradiated solutions were therefore carried out using a well-defined silver surface.

Sample solutions were prepared by dilution of appropriate quantities of caesium iodide in boric acid (0.2 mol dm$^{-3}$) and, for solutions of pH >4.6, sodium phosphate (0.1 mol dm$^{-3}$) spiked with a small quantity of $^{131}$I, typically 10 to 50 kBq. Silver wool (surface area
79.5 cm\(^2\) g\(^{-1}\) was added to the sample solutions which were then irradiated at a dose rate of 1.5 kGy hr\(^{-1}\). The solutions were sparged with air which was drawn through the irradiation circuit into an iodine trap consisting of 0.05 dm\(^3\) sodium hydroxide (2.5 \times 10\(^{-2}\) mol dm\(^{-3}\)) and iodide (2 \times 10\(^{-3}\) mol dm\(^{-3}\)) solution. On exiting the NaOH/T trap the gas passed through a small charcoal trap for measurement of organic iodine compounds. At the end of each experiment the \(^{131}\)I activities remaining in the sample solution, collected in the NaOH/T trap, collected in the small charcoal trap, deposited on the silver and washed from the delivery lines (with 10% HCl) were measured and the activity balance calculated.

In the absence of silver, 60-70% of the iodine from a solution of 10\(^{-4}\) mol dm\(^{-3}\) CsI at pH 4.6 was transferred to the trap in 3-4 hours. With the highest mass of Ag (200 mg) at 25°C and pH 4.6, only ~10% of the iodine was released after 24 hours with 5% remaining in solution. At 70°C the amount of iodine released was very similar, though the rate of release might have been higher. The data from this experiment were difficult to interpret since the sample dried out. At an intermediate mass of Ag (40 mg) at 25°C and pH 4.6, ~25% of the iodine was released after 24 hours. At the lowest mass of Ag (9 mg) at 25°C and pH 4.6, the results appeared similar to those with no silver except that the rate of production was slightly less and about 20% of the iodine was on the silver at the end of the experiment.

At pH 7 the solution was irradiated in the absence of silver for several hours in order to show that the rate of production of I\(_2\) was the same as that expected from previous work at this pH, and to eliminate run-to-run variations. Silver mesh was then added to the solution and the irradiation continued. The rate of production of iodine was initially unaffected by the presence of the silver, but after several days continued irradiation the rate of transfer fell to zero (Figure 4). It was concluded that at this time, all of the iodine had either transferred or reacted with the silver to form silver iodide. The time at which this occurred, and the final fraction of iodine in the trap compared with the amount on the silver, was dependent on the amount of silver present.

![Figure 4. Effect of silver on iodine volatility under irradiation at pH 7](image-url)
It was concluded from these tests that the AgI formed on the silver surface was stable to irradiation, since no further iodine volatilisation was observed after a certain time. This was confirmed by placing a sample of silver with a surface coating of AgI in a fresh solution of boric acid. When this sample was irradiated and sparged, less than 3% of the absorbed iodine was released in 64 hours (total dose 96 kGy). This is consistent with the trace solubility of AgI and indicates that there was no significant radiolytic decomposition of AgI under these conditions.

The results from irradiation of sparged solutions of CsI in contact with Ag can be considered to be the result of a competition between volatilisation of I₂ into the gas stream and reaction with the silver to remove I₂ from solution. A pseudo first order reaction rate constant for I₂ with Ag, \( k_{\text{react}} \), is given by,

\[
k_{\text{react}} / \text{s}^{-1} = k_d \frac{A}{V}
\]

where \( k_d \) is the I₂ deposition velocity (m s\(^{-1}\)), \( A \) is the area of the silver (m\(^2\)) and \( V \) the volume of solution (m\(^3\)). The rate constant for removal by sparging of I₂, \( k_{\text{vol}} \), is given by,

\[
k_{\text{vol}} = \frac{\text{flow rate}}{\text{aq. volume} \times \text{volume partition coefficient}}.
\]

For the conditions of these experiments, \( k_{\text{vol}} \) is 1.06×10\(^{-3}\) s\(^{-1}\). The fraction of iodine reacting with the silver should then be given by:

\[
f = \frac{k_{\text{react}}}{k_{\text{vol}} + k_{\text{react}}}
\]

The deposition velocities calculated from the fraction of I bound to the silver at the end of the tests are in the range 4×10\(^{-5}\) to 10\(^{-4}\) m s\(^{-1}\), which in reasonable agreement with the value of 1.3×10\(^{-4}\) m s\(^{-1}\) obtained in the non-irradiated studies. The difference is likely to be due to mass transfer effects in the two types of experiment. The results imply that treating the system as a competition between I₂ volatilisation and reaction is appropriate for these solutions.

Radiolytic nitric acid formation can lead to dissolution of silver, as discussed above. The removal of iodine by direct reaction between I and Ag\(^+\) therefore also needs to be considered. With a G value of 2.2 /100 eV, the nitrate production rate would be about 2×10\(^{-6}\) mol dm\(^{-3}\) hr\(^{-1}\). If NO₃\(^-\) instantly produced Ag\(^+\), which then instantly reacted with I, the rate of removal of iodine would be 5×10\(^{-6}\) s\(^{-1}\) (for 10\(^{-4}\) mol dm\(^{-3}\) I). This is insignificant even compared with the 9 mg silver case (\( k_{\text{react}} = 4\times10^{-4} \text{ s}^{-1} \)). This route for I removal is therefore not important in the current studies. However, the nitrate concentration is inversely proportional to the liquid/gas volume ratio which is rather high (0.2) in these experiments.

Simulation of these tests with the INSPECT model showed that the results were consistent with the radiolytically-produced I₂ reacting with the silver surface at a mass-transfer controlled rate (Figure 4). The effect of including the I reaction was minimal, even at pH 7.

The conclusions from this work are that AgI does not decompose radiolytically under the conditions used in these experiments. The only factor which is likely to cause instability
would be an increased dose-rate; this is considered elsewhere in this Workshop (Cripps et al., 1999).

2.3 High-Temperature Radiolysis

This series of experiments were performed in order to study the stability of colloidal AgI species in solution under conditions relevant to a severe reactor accident. Experiments were performed in sealed glass flasks containing colloidal silver iodide solutions, labelled with $^{131}$I. Painted coupons, located in the gaseous phase of the cells, were used to trap the volatile iodine which could be formed by silver iodide decomposition.

The colloidal silver iodine solutions were prepared by adding colloidal silver to labelled I or I$_2$ solutions. In some cases, Ag$^+$ cation was also added to the test solution. The sealed cells were placed in a temperature-controlled oven and irradiated for 24 or 168 hours at a dose rate of about 1.9 kGy/h. At the end of each test, vessels were removed from the oven and the AgI decomposition was evaluated by gamma counting of the painted coupon.

In initial tests at 80°C without radiation practically all the paint activities were below the detection limit of the gamma counting method. So in these experimental conditions, the AgI colloids can be considered as stable species in solution.

The irradiated tests showed that the amount of AgI decomposition increased with temperature, from ~ 0.3% at 60°C to ~ 3% at 110°C. There appears to be no effect of the initial form of the iodine (I or I$_2$) in solution or of the addition of Ag$^+$, as shown in Figure 5.

![Graph showing the stability of AgI Colloid under Irradiation](image)

**Figure 5.** Stability of AgI Colloid under Irradiation

3 DATA ANALYSIS AND MODEL DEVELOPMENT

The kinetic data obtained in the experiments described in Section 2, together with data from Funke (1996), have been analysed with the objective of establishing an appropriate model and rate constants for the reactions of I$_2$ and I with silver surfaces. This work is described fully elsewhere in this Workshop (Krausmann, 1999). The results indicate that the
reaction of I₂ with silver surfaces is limited by the rate of mass transfer of I₂ in the liquid phase. Slower rates observed in the earlier tests of Funke (1996) can be attributed to different mass transfer conditions in the early phase, and to agglomeration and/or colloidal AgI production in the later phase. This reaction can thus be described by

$$\frac{d[I_2]}{dt} = -k_1[I_2]_aq \frac{S_Ag}{V_i} \quad \text{where} \quad \frac{1}{k_1} = \left( \frac{1}{k_m} + \frac{1}{k_r[Ag]} \right) \quad (7)$$

in which $k_m$ is the mass transfer coefficient, $k_r = 2 \times 10^{-4}$ m$^4$ mol$^{-1}$ s$^{-1}$ and [Ag] is the silver concentration in mol m$^{-3}$. Since under almost all conditions the reaction with Ag will be very rapid, $k_r [Ag] > k_m$, so (7) becomes:

$$\frac{d[I_2]}{dt} = -k_m[I_2]_aq \frac{S_Ag}{V_i} \quad (3)$$

The importance of O₂ on the reaction of I with silver was demonstrated by the Siemens tests (Funke 1996), and differences between the results of the two programmes can be attributed to differing degrees of oxidation of the starting materials. If an oxide layer is initially present on the surface, the uptake of I is limited by the I mass transfer in the liquid phase. Once the oxide layer has been consumed, the reaction proceeds much more slowly, probably via a rate-determining oxidation step. This can be expressed simplistically as

$$\text{Ag} + \text{O}_2 \rightarrow \text{Ag}_\text{ox} \quad \text{(slow)}$$

$$\text{Ag}_\text{ox} + \text{I}^- + \text{H}^+ \rightarrow \text{AgI} + \text{H}_2\text{O} \quad \text{(fast)}$$

The rate of I- uptake can thus be described by:

$$\frac{d[I^-]}{dt} = -k_1 \frac{S_Ag}{V_i} [I^-] \quad \text{where} \quad \frac{1}{k_1} = \left( \frac{1}{k_m} + \frac{1}{k_o[Ag_\text{ox}]} \right) \quad (8)$$

in which $k_m$ is the mass transfer coefficient, and $k_o$ has a value of about $2 \times 10^3$ m$^4$ mol$^{-1}$ s$^{-1}$. The oxide concentration [Ag$_{ox}$] is given by

$$\frac{d[Ag_{ox}]}{dt} = k_s \times [Ag] - \frac{d[AgI]}{dt} \quad \text{where} \quad k_s = k_s \times S_m \quad (9)$$

In the above equations, $k_s$ is the rate of oxidation per unit surface area (eg in mol dm$^{-2}$ s$^{-1}$), and $S_m$ is the specific surface of the silver (in dm$^2$ mol$^{-1}$). The value of $k_s$ in these tests was $(9 \pm 4) \times 10^{-11}$ mol dm$^{-2}$ s$^{-1}$ at room temperature, with no clear pH dependence. At 90°C $k_s$ increased to $(2.4 \pm 0.7) \times 10^{-10}$ mol dm$^{-2}$ s$^{-1}$ at pH 4.6 and $(6 \pm 1) \times 10^{-11}$ mol dm$^{-2}$ s$^{-1}$ at pH 7. This reaction can be neglected at pH > 7 and under conditions where the dissolved O₂ concentration is close to zero.

This model gives reasonable agreement with the experimental data for a range of I and Ag concentrations. However it should be noted that the rate of iodine uptake is very sensitive to the initial degree of oxidation of the silver surface, and to the value of $k_{ox}$, both of which are largely unknown under containment conditions.
4 SOURCE TERM EVALUATION

The objective of this part of the work was to assess the importance of the Ag – I reactions in terms of those accident sequences which are important in the overall risk assessment of a nuclear plant. This involved generic plant calculations to determine the impact of the model developments on the calculated reactor source term for risk-dominant sequences identified in probabilistic safety assessment studies for commercial reactor plants, similar to those described previously by Dutton (1996). Calculations were performed using the INSPECT, IMPAIR and ACT-WATCH codes.

Calculations were made for three severe accident sequences: (i) a large break LOCA into the reactor building, (ii) a large break in the residual heat removal system (RHRS) at intermediate shutdown, and (iii) a steam generator tube rupture (SGTR). The input data included design details for the reactor plant and descriptions of the fault progression, thermal-hydraulic and fission product behaviour as predicted by MAAP 3.0B.

The main parameters of the work were the Ag particle size, and the inclusion (or not) of the reaction I with Ag in addition to the I reaction. In cases where the I reaction was important, the degree of oxidation assumed for the silver particles was an important parameter.

The results showed that the impact of silver - iodine reaction modelling on the predicted iodine releases to the environment is very sequence-dependent. In the LOCA cases, the predicted releases are low and dominated by aerosol, so although the inclusion of a silver model can strongly influence the chemical behaviour of the iodine, the resulting changes in volatile iodine production do not substantially change the overall release. In contrast, the predicted releases from the auxiliary building and SGTR faults are dominated by gaseous species due to the relatively low pHs and high gas flow rates through the water pools. In these cases there is more sensitivity to the modelling used, both in terms of differences between the models and of the assumptions made in the silver - iodine modelling (particularly the mass transfer rates and particle sizes). However, silver was generally found to have little effect on the iodine release in the SGTR case, largely because of the fairly low Ag / I ratio (~ 1, compared with ~40 in the auxiliary building sequence).

5 CONCLUSIONS

The rates of reaction of I and I with silver surfaces have been measured in the absence of irradiation. The I reaction is very fast and can be treated as mass-transfer limited. The I reaction with silver mesh surfaces is much slower and follows pseudo-zero-order kinetics under the conditions of these studies. Tests with silver powders showed much higher initial reaction rates and this is attributed to differences in the extent of surface oxidation of the starting materials. The presence of chloride and nitrate impurities has little or no effect on the reaction rates.

The G-value for nitric acid production in air-water mixtures has been measured over the temperature range 25 to 90°C and confirmed to be in the order of 2, with no effect of temperature or steam pressure. These tests have demonstrated that the formation occurs principally by a gas phase process. The G value appears slightly higher when silver is present in contact with the gas phase.
The volatility of iodine from irradiated CsI solutions is greatly reduced when a silver surface is present. Good agreement is obtained between these test results and INSPECT simulations using rate constants derived from the non-irradiated studies. Very little volatile iodine is produced after reaction with the silver surface, consistent with the trace solubility of AgI. There is no evidence for radiolytic decomposition of the AgI under the dose rates used in this work.

Colloidal AgI species in solution are also found to be largely stable under irradiation. The amount of volatile iodine production increases slightly with temperature, but no effect of pH or Ag$^+$ are observed.

On the basis of these experimental results, models have been developed to describe the uptake of $I_2$ and I onto silver surfaces. The effect of this modelling on the calculated source term for three representative accident sequences has been investigated using the INSPECT, IMPAIR and ACT-WATCH codes. This evaluation has shown that the reaction has significant potential to reduce the formation of volatile iodine under some severe reactor accident conditions. The effect of this reduction on the predicted release of iodine to the environment depends strongly on the sequence being considered. The presence of silver has the greatest potential impact under conditions of low pool pH and high Ag / I ratio.

6 ACKNOWLEDGMENTS

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A model of heterogeneous silver–iodine reactions in the liquid phase

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Abstract

In a severe accident the control rods usually employed in a LWR would fail due to the prevailing high temperatures, causing the release of silver and to a lesser extent of indium and cadmium. Results of the first two tests FPT0 and FPT1 of the Phebus–FP test programme as well as separate–effects studies on the effect of silver on iodine volatility suggest that the presence of a large amount of silver has a major impact on the volatility of iodine from solution and hence on the source term to the environment. It was found that the reaction of silver with water–soluble iodide or dissolved molecular iodine leads to the formation of silver iodide which is non–volatile and has a very low solubility in water. Provided that silver iodide withstands radiolytic decomposition it represents a permanent iodine sink, inhibiting volatilisation of iodine from the sump.

We have developed a model to describe the reaction of iodine with silver surfaces. This model incorporates transport phenomena, i.e. mass transport in the liquid and solid phase, as well as the chemical reaction at the reaction interface, considering these processes as 'resistances in series'. The resistance–in–series models were successfully validated against separate–effects tests performed by AEA Technology and Siemens.

The developed models have been implemented into the iodine chemistry code IMPAIR3, which has been applied to the integral tests Phebus RTF3 and FPT0. The results suggest that in the presence of oxidised silver, Ag–I reactions have a pronounced impact on the sump chemistry, reducing the formation of volatile iodine. A reasonable agreement between model predictions and available experimental data is obtained.

1 Introduction

Results of the Phebus FPT0 test [Hanniet, 1999] and recent studies on the effect of silver on iodine volatility suggest that the presence of a large amount of silver considerably

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influences iodine volatility from solution [Cake and Dickinson, 1997, Funke et al., 1996a]. Reaction of silver (Ag) with either water–soluble iodide (I⁻) or dissolved molecular iodine (I₂) in solution leads to the formation of non–volatile silver iodide (AgI) which acts as an iodine sink, thus reducing the amount of volatile iodine transferred to the containment atmosphere.

A shared–cost action on iodine chemistry, carried out under the CEC 4th Framework Programme, aimed at understanding the effect of excess silver on the behaviour of iodine in the containment sump and to improve the poor agreement between the iodine behaviour observed in Phebus FPT0 and containment chemistry simulations [Dickinson et al., 1999]. Within the scope of this project we have developed models to describe the reaction of silver with iodine and its consequences on iodine volatility [Krausmann and Drossinos, 1999a, Krausmann and Drossinos, 1999b]. We have implemented these models into the iodine chemistry code IMPAIR3, which was originally developed by the Paul Scherrer Institut in Switzerland [Güntay and Cripps, 1992]. The extended code has been successfully validated against separate–effects tests performed by AEAT [Cake and Dickinson, 1997] and Siemens [Funke et al., 1996a] and has been applied to the integral tests Phebus RTF3 and Phebus FPT0.

2 Model description

Under accident conditions AgI is thought to be formed by the heterogeneous reaction of I⁻ or I₂ with Ag on the surface of a metallic Ag sample in solution. The net chemical reactions are formulated as

\[ 2 \text{Ag} + \text{I}_2 \rightarrow 2 \text{AgI} \]

\[ \text{Ag} + \text{I}^- \rightarrow \text{AgI} + \text{e}^- . \]

With advancing reaction an immobile AgI layer builds up at the first point of contact between the reactants (solid–liquid interface). This non–porous layer, whose molar volume is bigger than that of the metal consumed, separates the reactants in the course of the reaction, thus constituting a barrier which impedes further reaction. Diffusion processes of one or both of the reactants in the interior of the product layer have to occur to sustain the reaction [Hannay, 1967]. In a Frenkel disordered crystal like AgI the disordered fraction of silver ions (Ag⁺) and electron holes are the diffusing species [Hannay, 1967]. The tarnishing reaction proceeds as long as the concentration gradient required for the diffusion of Ag⁺ is maintained, slowly consuming the Ag sample.

The overall conversion rate is derived by investigating the interplay between the physical transport processes (transport of iodine to the surface of the Ag sample and solid–state diffusion of Ag⁺ through the AgI product layer) and the chemical reaction rate. Each of the contributing processes is characterised by a corresponding resistance, defined as the reciprocal of the velocity of the respective process. These resistances are combined
in a resistance–in-series (RIS) model, where the largest resistance and hence the slowest process controls the overall rate [Clark, 1996, Westerterp et al., 1987].

2.1 The reaction of I₂ with Ag

The 3-RIS model describing the reaction between I₂ and Ag incorporates diffusion of I₂ (A) and the diffusing Ag species (B) to the reaction interface

\[ R_{A1} = k_m a_p (c_{Ab} - c_{As}) \]
\[ R_{A2} = k_s a_p (c_{Bb} - c_{Bs}) \]

and the chemical reaction of I₂ with Ag

\[ R_{A3} = k_r a_p c_{As} c_{Rs} \]

where \( k_r \) is the surface reaction rate constant. The quantities \( R_{Ai} \), \( i = 1, 2, 3 \) are the rates of change of A in mol/m²·s and \( a_p \) denotes the total surface area of solid per unit volume of liquid, accounting also for surface roughness effects.

An estimation of the characteristic times of the respective processes shows that establishment of steady state is fast. It is therefore justified to assume that the rates of the contributing processes are equal, which allows us to eliminate the unknown surface concentrations and which yields an expression for the rate of disappearance of A [Doraiswamy and Sharma, 1984]

\[ R_A = \frac{a_p}{2 k_r} \left( \left[ k_s (k_r c_{Bb} + k_m) + k_m k_r c_{Ab} \right] - \left[ k_s (k_r c_{Bb} + k_m) + k_m k_r c_{Ab} \right]^2 - 4 k_r^2 k_m k_r c_{As} c_{Bs} \right)^{1/2} \]  

On the other hand, \( R_A \) is equal to the rate of disappearance of B, which for spherical particles is given by [Castellan, 1983]

\[ R_{B,sph} = \frac{1}{\nu_B} \frac{dC_B}{dt} = \frac{1}{\nu_B} \frac{4\pi}{3} n_p \rho_B \frac{dr_{c,sph}^3}{dt}, \]

where \( \nu_B \) is the stoichiometric coefficient of B, \( n_p \) the number of particles per unit volume of liquid, and \( \rho_B \) and \( M_B \) are the density and molar weight of Ag, respectively. Eq. (6) together with Eq. (7) yields an expression for the change of \( r_c \) with time

\[ \frac{dr_{c,sph}}{dt} = a \left( \frac{r_s}{r_c} \right)^2 \left( \left[ \frac{b c r_c}{(r_s - r_c)} + d \right] - \left[ \frac{b c r_c}{(r_s - r_c)} + d \right]^2 - \frac{e b r_c}{(r_s - r_c)} \right)^{1/2} \]  

with

\[ a = -\frac{M_B f}{k_r \rho_B}, \quad b = \frac{D_s}{r_s}, \quad c = k_r c_{Bb} + k_m \]
\[ d = k_m k_r c_{Ab}, \quad e = 4 k_r^2 k_m c_{Ab} c_{Bb}. \]
After integration of Eq. (8) the fractional conversion $X_{B,sph}(t) = 1 - (r_c/r_s)^3$ is calculated, which is a measure of how much product C (AgI) has been formed by the reaction. The mass of C is given by

$$m_{C,sph}(t) = \rho_C \frac{4\pi}{3} r_s^3 X_B \Delta V_M n.$$

(10)

The number of particles is denoted by $n$ and $\Delta V_M = (\nu_C/\nu_B) M_C \rho_B / (\rho_C M_B)$ is the difference of molar volumes between Ag and AgI. The concentration of AgI can be calculated easily from Eq. (10).

As the bulk concentrations of A and B are gradually depleted with advancing reaction, $c_{AB}$ and $c_{BB}$ are recalculated at every time-step making use of the advancement of reaction [Castellan, 1983]. This procedure makes the model quasi-steady state.

Model equations for cylindrical geometry are derived in analogy to Eqs. (8) and (10) [Krausmann and Drossinos, 1999a].

2.2 The reaction of I⁻ with Ag

Experimental evidence indicates that the reaction of Ag with I⁻ proceeds via a two-step process where an initial, rapid step precedes a long-term, slow one [Funke et al., 1996a, Cake and Dickinson, 1997]. These experiments also suggest that the degree of oxidation of the Ag surface plays an important role, where a significant conversion of I⁻ and Ag to AgI is only observed under oxidising conditions.

A thin layer of silver(I) oxide forms on top of metallic Ag in air at room temperature [Gmelin, 1971]. The hypothetical reaction of this oxide layer with I⁻ according to

$$\text{Ag}_2\text{O} + 2\text{I}^- + 2\text{H}^+ \rightarrow 2\text{AgI} + \text{H}_2\text{O}$$

(11)

could explain the initial, rapid step observed for Ag–I⁻ reactions.

Eq. (11) is modelled by means of a 2–RIS model which incorporates diffusion of iodine to the particle surface

$$R_{A1} = k_m a_p' (c_{AB} - c_{A_S})$$

(12)

and subsequent reaction with silver oxide

$$R_{A2} = k_{ox} a_p' c_{A_S} c_{DB}.$$  

(13)

Diffusion processes within the solid AgI layer have been neglected in this analysis, assuming that the product layer does not inhibit further diffusion of iodine to the reaction interface. The surface reaction rate constant is denoted by $k_{ox}$, $c_{DB}$ is the bulk silver oxide concentration and $a_p'$ is the total surface area of solid per unit volume of liquid. The overall reaction rate is determined by employing the same procedure as described in section 2.1.
The transition to the subsequent, slow reaction occurs when the initially present silver oxide has been consumed. The long-term process is modelled by means of a 3–RIS model, where we use Eqs. (3), (4) and

\[ R_{A3} = k'_t \alpha_p \frac{c_{A2} c_{B2}}{c_{A0} c_{B0}} \]  

(14)

instead of Eq. (5). The quantities \( c_{A0} \) and \( c_{B0} \) are \( I^- \) and Ag concentrations at the beginning of the second, slow step.

An exhaustive description of the model development and determination of model parameters can be found in [Krausmann and Drossinos, 1999a].

3 Phebus RTF3

The models discussed in the previous sections have been implemented into the iodine chemistry code IMPAIR3, which was originally developed by the Paul Scherrer Institut in Switzerland. In the following, validation of the extended code against Phebus RTF3 and FPT0 will be discussed. Validation of the Ag–I models against separate–effects tests performed by AEAT and Siemens can be found in [Krausmann and Drossinos, 1999a]. Phebus RTF3 was the third in a series of six tests performed in the Radioiodine Test Facility (RTF) at Whiteshell Laboratories (Canada), whose scope was to help interpret the Phebus FP experiments. RTF3 was performed in an electropolished stainless steel vessel, investigating iodine volatility from an irradiated solution at \( pH=5 \). The gas and sump temperature was \( 110^\circ \text{C} \) and \( 90^\circ \text{C} \), respectively. Silver wool was placed in the aqueous phase to assess its effect on iodine volatility. Painted coupons were suspended in the gas and aqueous phase to study organic iodide formation [Ball et al., 1995].

3.1 Input parameters

The RTF vessel initially contained \( 10^{-5} \) mol/l \( I^- \) and 32.15 g Ag, yielding \( \text{Ag/}I = 990/1 \). Further addition of \( I^- \) to the test solution after 21 hours resulted in a new \( I^- \) concentration of \( 7.5 \cdot 10^{-5} \) mol/l, decreasing \( \text{Ag/}I \) to 116/1.

No organic impurities were assumed to be initially present in the sump. However, radiolytic decomposition of organic iodides formed by heterogeneous processes produces organic residues, thus rendering possible the homogeneous production of organic iodides.

The processes we consider for simulation of RTF3 and their respective rate constants are listed in the appendix. Our aim was to reproduce the volatile iodine concentrations observed (\( I_2 \), CH\(_3\)I and high molecular weight organic iodides HMWI) and the concentration of \( I^- \) in the aqueous phase. Whenever possible we used rate constants that have been determined experimentally, else recommended values from the IMPAIR3 handbook have been used [Güntay and Cripps, 1992, Cripps, 1999]. In some cases the rate constants were fitted to reproduce the experimental data.
The water–side mass transfer coefficient $k_w$ has been found to lie in the range $10^{-5}$ to $10^{-6}$ m/s for a weakly mixed containment pool [Evans et al., 1997]. Given the shallow nature of the RTF pool a value closer to $10^{-5}$ m/s is expected. Estimation of the gas–side mass transfer coefficient $k_g$ is associated with considerable uncertainty as $k_g$ depends on the extent of mixing of the air above the pool. Assuming weakly mixed conditions we use $k_g = 10^{-3}$ m/s. The interfacial mass transfer coefficient $k_{if}$ is then calculated according to $1/k_{if} = P_v/k_g + 1/k_w$ in IMPAIR3. At 90°C the volume partition coefficient $P_v \simeq 10$ for I₂, yielding $k_{if} \simeq 10^{-5}$ m/s. This value is also used for phase transfer of CH₃I, HMWI and HOI.

Modelling of iodine–steel interactions is based on experiments performed by Siemens. A deposition velocity of $6.3 \times 10^{-5}$ m/s was determined for I₂ adsorption on steel that had not undergone any previous surface treatment [Funke et al., 1996b]. However, we expect the deposition velocity to be lower for the electropolished RTF vessel. Rate constants for the interaction of iodine with epoxy paint are taken from [Hellmann et al., 1996]. The deposition of I⁻ on paint will, however, be modelled with $k(37) = 3.5 \times 10^{-7}$ m/s instead of the experimentally determined mean value of $7 \times 10^{-7}$ m/s to improve the agreement with the experimental data.

The rate constant $k(20)$ determines the overall radiolytic oxidation of I⁻ to I₂. With the given set of parameters and the recommended value of $k(20)$ from the IMPAIR3 handbook we do not obtain a satisfactory agreement between model predictions and experimental data. In accordance with recent studies [Jacquemain and Tirini, 1998] we increased $k(20)$, obtaining the best agreement with the observed volatile iodine concentrations for $k(20) = 1.5 \times 10^{-3}$ M⁻¹s⁻¹Gy⁻¹.

Organic iodine modelling in IMPAIR3 is basically unvalidated due to a lack of experimental data. It should not go unnoticed that despite a recent assessment with promising results [Cripps and Güntay, 1996] the organic iodine modelling needs to be completely reassessed upon availability of new experimental data.

### 3.2 Discussion

Silver iodide is predicted to be the main iodine species in the sump at the end of the test, accounting for 96% of the total iodine inventory. A comparison with the experimental data seems to suggest that the code overpredicts the amount of AgI formed in the sump. However, the measurements yielding 50% of AgI in the sump are based on samples taken three weeks after test initiation and may therefore be too low due to a loss of iodine. An extrapolation of the available data backwards in time to the test termination indicates that over 80% of iodine was actually trapped on silver. Deposition of iodine on painted surfaces in the gas and liquid phases is underpredicted (Table 1). Moreover, the modelling of the interaction of iodine with aqueous steel surfaces is based on Siemens experiments where no net iodine deposition was observed [Funke et al., 1996b].

A comparison of the extended IMPAIR3 model predictions with the experimental RTF3 data is shown in Fig. 1. The observed I⁻–concentration in the aqueous phase is
Figure 1: A comparison of extended IMPAIR3 model predictions (without Ag–I reaction (dotted line), with Ag–I2 reaction only (dashed line), with all implemented Ag–I models (solid line)) and RTF3 experimental data (solid dots). For CH3I and HMWI the gas phase concentrations are shown.
Table 1: Comparison between RTF3 data and IMPAIR3 model predictions at $t = 72h$ (*see text). The total iodine inventory is $2.55 \times 10^{-3}$ mol/l [Ball et al., 1995].

<table>
<thead>
<tr>
<th></th>
<th>RTF3</th>
<th>IMPAIR3</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>% of total iodine inventory</td>
<td>% of total iodine inventory</td>
</tr>
<tr>
<td>Final aqueous phase</td>
<td>2.2 ± 0.1</td>
<td>0.23</td>
</tr>
<tr>
<td>Painted aqueous coupons</td>
<td>0.8 ± 0.08</td>
<td>0.22</td>
</tr>
<tr>
<td>Aqueous steel surfaces</td>
<td>3 ± 1</td>
<td>0</td>
</tr>
<tr>
<td>Silver</td>
<td>50 (80*)</td>
<td>96.1</td>
</tr>
<tr>
<td>Final gas phase</td>
<td>0.02 ± 0.002</td>
<td>0.033</td>
</tr>
<tr>
<td>Painted gas coupons</td>
<td>5 ± 0.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Gas steel surfaces</td>
<td>1-10</td>
<td>1.2</td>
</tr>
<tr>
<td>Washes</td>
<td>19 ± 2</td>
<td>-</td>
</tr>
<tr>
<td>Aqueous lines</td>
<td>3 ± 1</td>
<td>-</td>
</tr>
<tr>
<td>Mesh holders</td>
<td>1.8 ± 0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

found to be reproduced reasonably well even without considering the reaction of iodine with silver. This is due to other fast $I^{-}$ removal mechanisms like radiolytic oxidation of $I^{-}$ to $I_{2}$ or deposition of $I^{-}$ on the painted coupons in the aqueous phase. A better agreement is obtained by taking into account the reaction of Ag with $I_{2}$ which competes with $I_{2}$ deposition on paint and subsequent dissolution as $I^{-}$, thus decreasing the concentration of free $I^{-}$. Test runs including all the presented Ag–I models in the aqueous phase yield the best agreement between model predictions and experimental data, assuming that Ag is slightly oxidised (0.07% by weight). The $Ag_{2}O–I^{-}$ reaction is one of the processes dominating the behaviour of $I^{-}$ for the first 21 hours of the test apart from radiolytic oxidation of $I^{-}$ to $I_{2}$, as well as $I^{-}$ deposition on paint with subsequent dissolution of $I^{-}$. For times greater than about 21 hours no silver oxide is found to be left with the given set of parameters.

The $I_{2}$ concentration in the gas phase is largely overpredicted in the absence of the reaction between Ag and I. The concentration of molecular iodine in the gas phase is caused by radiolytic oxidation of $I^{-}$ to $I_{2}$ in the aqueous phase and subsequent phase transfer to the gas phase. Inclusion of the Ag–$I_{2}$ reaction improves the agreement between model predictions and experimental data since it competes with interfacial mass transfer for $I_{2}$, thus decreasing the rate of $I_{2}$ transfer to the gas phase. On the other hand, the $Ag_{2}O–I^{-}$ reaction reduces the amount of $I^{-}$, which in turn leads to a decreased production of $I_{2}$ by radiolytic oxidation of $I^{-}$. Deposition of $I_{2}$ on paint and steel surfaces in the gas phase is found to play an important role in depleting the concentration of volatile molecular iodine.

In the absence of Ag–I reactions the concentration of CH$_{3}$I and HMWI is largely over-
predicted as already observed for I₂. A significant improvement is obtained by considering the Ag—I₂ reaction, as the desorption of CH₃I or HMWI from painted gas phase surfaces depends strongly on the I₂ concentration. Taking into account the reaction between (oxidised) Ag and I⁻ improves the model predictions especially for the first 21 hours of the RTF3 test. The dominant production mechanism of CH₃I in the aqueous phase appears to be desorption of methyl iodide from paint subsequent to adsorption of I⁻. Homogeneous formation of CH₃I in the aqueous phase does not seem to be of importance. The heterogeneous production of CH₃I in the gas phase, i.e. desorption of methyl iodide from the painted coupon subsequent to I₂ deposition, appears to be a non-negligible process. Nevertheless, the amount of CH₃I found in the gas phase results from interfacial mass transfer of methyl iodide from the aqueous phase.

The agreement between model predictions and experimental data for HMWI is not satisfactory for the second part of the RTF3 test. Heterogeneous formation of HMWI in the gas phase is found to be the dominant production mechanism, contrary to what is observed for CH₃I. Due to the lack of well established rate constants for both the gas and aqueous phases the uncertainty associated with the model predictions is, however, considerable.

The model predictions underline the importance of including models for both the Ag—I₂ and Ag—I⁻ reactions into iodine chemistry codes. Moreover, radiolytic oxidation of I⁻ to I₂ and ad/desorption processes both in the gas and aqueous phases are found to contribute significantly to the overall rate.

4 Phebus FPT0

Phebus FPT0 was the first test of the Phebus–FP programme, aimed at investigating the main phenomena occurring during a severe accident in a light water reactor [Schwarz et al., 1999]. The release, transport and retention of fission products and structural materials were studied in an in–pile test facility under representative severe accident conditions. The test was conducted in four main stages, starting with the degradation phase, whose objective was to study fission product and structural material release from the bundle and its transport through the experimental circuit during the first five hours of the test. The following aerosol phase lasted for about 20 hours and analysed the settling of aerosols in the containment atmosphere. The washing phase, with a duration of 15 minutes, aimed at draining the aerosols deposited on the containment elliptic bottom into the sump to initiate the radiolytic processes. The final stage, the so–called chemistry phase, lasted for four days and was devoted to the study of fission product chemistry in the sump and containment atmosphere. The last two phases were preceded by preparatory phases to change the containment thermalhydraulic conditions according to the requirements of the test protocol [Hanniet, 1999].
4.1 Input parameters

Test origin for our calculations is $t_0 = 16800$ s, i.e. roughly 20 minutes before shutdown of the Phebus driver core, when the highest aerosol concentration was detected in the containment atmosphere. The amount of $I^-$ and Ag entering the sump by aerosol settling during the degradation and aerosol phases was 2.6 mg (7.2% b.i.) for $I^-$ and 4.9 g (1.03% b.i.) for Ag. The corresponding increase of the $I^-$ and Ag concentrations in the sump was approximated by $I^-(t) = 1.6 \cdot 10^{-7}[1 - \exp(-k_{sett} t)]$ mol/l and $Ag(t) = 3.5 \cdot 10^{-4}[1 - \exp(-k_{sett} t)]$ mol/l. The settling constant $k_{sett}$ was estimated from the iodine activity decrease in the containment atmosphere and is given by $k_{sett} = 3 \cdot 10^{-4}$ s$^{-1}$, yielding a time constant of 1.1 hours. In addition, 4% (b.i.) of molecular iodine have been assumed to be initially present in the containment atmosphere.

The $I^-$ and Ag input during the washing phase is given by 7.2 mg (20% b.i.) and 29.1 g (6.1% b.i.), respectively. It has been modelled assuming a constant rate. During the degradation phase and the first part of the aerosol phase the thermal-hydraulic conditions were such that steam condensation on the wet part of the condensers would occur, leading to enhanced deposition of gaseous I$_2$ with subsequent washdown of $I^-$ into the sump [Güntay and Cripps, 1992]. This phase coincides with the maximum concentration of iodine in the gas phase and will therefore be of importance for the first few hours of the test. On the other hand, the major part of FPT0 was performed under non-condensing conditions. To obtain the correct long-term behaviour, rate constants for non-condensing conditions will be used throughout the test.

The FPT0 test will be modelled using the same rate constants that have been optimised for Phebus RTF3 and which are listed in the appendix. Deposition of $I^-$ is, however, now given by the experimentally determined mean value $k(37) = 7 \cdot 10^{-7}$ m/s.
Figure 3: A comparison of model predictions for the total iodine concentration in the gas phase with FPT0 data (assuming 10% of Ag by weight oxidised).

4.2 Discussion

To assess the importance of the reaction between silver oxide and I⁻ we performed simulations with 1%, 10% and 20% of Ag oxidised. A comparison of IMPAIR3 predictions for different degrees of oxidation and a test run with the Ag–I₂ reaction only clearly demonstrates the impact of the presence of silver oxide on the concentration of I⁻ in the sump (Fig. 2). Silver iodide is predicted to be the dominant iodine species in the aqueous phase, constituting about 80% of the iodine entering the sump (Table 2). However, due to a lack of experimental data on sump speciation no comparison with the model predictions was possible.

The Ag–I reactions affect the formation of volatile molecular iodine in two ways: The fast Ag₂O–I⁻ reaction rapidly decreases the I⁻ concentration in the sump, thus decreasing the rate of radiolytic production of I₂. Moreover, any I₂ that will eventually be produced has to escape the Ag–I₂ reaction before it can be transferred to the gas phase. Due to the impact of the Ag–I models on the sump chemistry, the liquid phase I₂ concentration remains low throughout the test (apart from the washing phase) and I₂ transfer from the gas to the aqueous phase is observed. Only little change of the gas phase I₂ concentration was found for different degrees of Ag oxidation.

The total iodine concentration in the gas phase is found to depend sensitively on the amount of gaseous iodine initially injected into the containment (Fig. 3). The concentration of gaseous iodine quickly decreases at the beginning of the test due to reaction with surfaces and I₂ phase transfer to the aqueous phase. The long-term behaviour is characterised by the establishment of a steady state with organic iodides constituting the dominant species.
Table 2: Comparison of IMPAIR3 model predictions for different degrees of Ag oxidation at \( t = 400000 \) s in % of the total amount of iodine entering the sump.

<table>
<thead>
<tr>
<th></th>
<th>1%</th>
<th>10%</th>
<th>20%</th>
<th>only Ag–I(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>aqueous phase:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( I_2 )</td>
<td>3.4 ( \times ) 10(^{-5} )</td>
<td>3.8 ( \times ) 10(^{-6} )</td>
<td>2 ( \times ) 10(^{-6} )</td>
<td>5.8 ( \times ) 10(^{-5} )</td>
</tr>
<tr>
<td>( I^- )</td>
<td>2.5 ( \times ) 10(^{-4} )</td>
<td>5.3 ( \times ) 10(^{-5} )</td>
<td>4.1 ( \times ) 10(^{-5} )</td>
<td>3.1 ( \times ) 10(^{-3} )</td>
</tr>
<tr>
<td>( IO_3^- )</td>
<td>6.1 ( \times ) 10(^{-2} )</td>
<td>9.3 ( \times ) 10(^{-3} )</td>
<td>3.8 ( \times ) 10(^{-3} )</td>
<td>8.8 ( \times ) 10(^{-2} )</td>
</tr>
<tr>
<td>( RI )</td>
<td>3.9 ( \times ) 10(^{-5} )</td>
<td>3.8 ( \times ) 10(^{-5} )</td>
<td>3.8 ( \times ) 10(^{-5} )</td>
<td>4 ( \times ) 10(^{-5} )</td>
</tr>
<tr>
<td>( I_2 ) dep. paint</td>
<td>1.3 ( \times ) 10(^{-5} )</td>
<td>1.5 ( \times ) 10(^{-6} )</td>
<td>7.9 ( \times ) 10(^{-7} )</td>
<td>3.8 ( \times ) 10(^{-5} )</td>
</tr>
<tr>
<td>( AgI )</td>
<td>74.4</td>
<td>78.9</td>
<td>80.5</td>
<td>80.9</td>
</tr>
<tr>
<td>( HOI )</td>
<td>8.6</td>
<td>4.6</td>
<td>3.1</td>
<td>1.2</td>
</tr>
<tr>
<td>( I^- ) dep. paint</td>
<td>1.3 ( \times ) 10(^{-5} )</td>
<td>2.9 ( \times ) 10(^{-6} )</td>
<td>2.2 ( \times ) 10(^{-6} )</td>
<td>1.8 ( \times ) 10(^{-4} )</td>
</tr>
<tr>
<td><strong>gas phase:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( I_2 )</td>
<td>5.4 ( \times ) 10(^{-2} )</td>
<td>5.3 ( \times ) 10(^{-2} )</td>
<td>5.2 ( \times ) 10(^{-2} )</td>
<td>5.7 ( \times ) 10(^{-2} )</td>
</tr>
<tr>
<td>( RI )</td>
<td>6.2 ( \times ) 10(^{-2} )</td>
<td>6.1 ( \times ) 10(^{-2} )</td>
<td>6.1 ( \times ) 10(^{-2} )</td>
<td>6.5 ( \times ) 10(^{-2} )</td>
</tr>
<tr>
<td>( I_2 ) dep. paint</td>
<td>12.7</td>
<td>12.4</td>
<td>12.4</td>
<td>13.3</td>
</tr>
<tr>
<td>( I_2 ) dep. steel</td>
<td>4</td>
<td>3.9</td>
<td>3.9</td>
<td>4.4</td>
</tr>
</tbody>
</table>

IMPAIR3 models phase transfer of HOI which makes HOI the dominant iodine species in the gas phase with the given set of parameters. Since dissociation of HOI into \( IO^- \) and \( H^+ \) is not modelled in the code and estimation of the partition coefficient is associated with considerable uncertainty, interfacial transfer of HOI has not been taken into account, although there is evidence in the literature that under certain conditions (low \( I^- \) concentration, high temperature and pH) HOI is predominantly volatilised from solution instead of \( I_2 \) [Tani, 1995].

The interaction of aerosols with surfaces is not modelled in IMPAIR3. Moreover, our simulation is based only on the amount of \( I^- \) and Ag entering the sump and not on what was released into the containment. Hence, we cannot make any conclusive statement about gas phase deposits. The predicted amount of iodine deposited on the sump walls and bottom agrees with the experimental results if we assume that the data also comprise AgI deposition, which is strongly supported by experimental evidence.

Radiolytic oxidation of \( I^- \) is found to play only a secondary role since the Ag–I reactions dominate the sump chemistry. This is, however, not surprising considering that Ag/I \( \sim \) 3600 in the FPT0 sump.
5 Conclusions

The reaction of iodine with silver in a light water reactor containment sump has a major impact on iodine volatility from solution. To improve agreement between experimental data and containment chemistry simulations we have developed resistance-in-series models for the reaction of silver with iodine, incorporating physical transport processes and a chemical reaction. After successful validation of the models against separate-effects tests these models have been implemented into the iodine chemistry code IMPAIR3, leading to a considerable improvement between code predictions and experimental data. Application of the modified code to integral tests like Phebus RTF3 and FPT0 suggests that in the presence of oxidised silver, Ag–I reactions have a pronounced impact on the sump chemistry. For the given dose rates the fast reaction of silver oxide with $I^-$ deprives the radiolytic processes of $I^-$, resulting in a very low airborne iodine concentration. The model predictions also indicate that the Ag–I$_2$ reaction alone is powerful but not sufficient to explain the observed low volatile iodine concentrations. In general, a reasonable, overall agreement of the model predictions with the available experimental data was obtained.

References


### Appendix: Processes considered for the simulation of Phebus RTF3.

<table>
<thead>
<tr>
<th>Process</th>
<th>Rate Constant $k$ Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>I$_2$(g) $\rightarrow$ paint</td>
<td>$k(4) = 5 \times 10^{-4}$ m/s</td>
</tr>
<tr>
<td>paint $\rightarrow$ I$_2$(g)</td>
<td>$k(62) = 6.6 \times 10^{-8}$ s$^{-1}$</td>
</tr>
<tr>
<td>I$_2$(g) $\rightarrow$ steel</td>
<td>$k(51) = 2 \times 10^{-5}$ m/s</td>
</tr>
<tr>
<td>steel $\rightarrow$ I$_2$(g)</td>
<td>$k(63) = 6 \times 10^{-6}$ s$^{-1}$</td>
</tr>
<tr>
<td>I$_2$ interfacial mass transfer coefficient</td>
<td>$k(35) = 10^{-5}$ m/s</td>
</tr>
<tr>
<td>I$_2$ + H$_2$O $\xrightarrow{k(11)}$ HOI + I$^-$ + H$^+$</td>
<td>$k(11) = 506.6$ s$^{-1}$</td>
</tr>
<tr>
<td>I$_2$(l) $\rightarrow$ paint</td>
<td>$k(12) = 1.9 \times 10^{13}$ M$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>I$_2$ dissolution from paint after I$_2$ deposition</td>
<td>$k(17) = 4 \times 10^{-6}$ m/s</td>
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<tr>
<td></td>
<td>$k(38) = 2 \times 10^{-6}$ s$^{-1}$</td>
</tr>
<tr>
<td>Radiolytic oxidation of I$^-$ to I$_2$</td>
<td>$k(20) = 1.5 \times 10^{-3}$ M$^{-0.35}$ kGy$^{-1}$</td>
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<tr>
<td>reverse reaction</td>
<td>$k(21) = 10^{-6}$ s$^{-1}$</td>
</tr>
<tr>
<td>I$^-$ dissolution from paint after I$_2$ deposition</td>
<td>$k(69) = 3.4 \times 10^{-5}$ s$^{-1}$</td>
</tr>
<tr>
<td>I$^-$ dissolution from steel after I$_2$ deposition</td>
<td>$k(55) = 7.9 \times 10^{-7}$ m/s</td>
</tr>
<tr>
<td>I$^-$ $\rightarrow$ paint</td>
<td>$k(37) = 3.5 \times 10^{-5}$ m/s</td>
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<tr>
<td>I$^-$ dissolution from paint after I$^-$ deposition</td>
<td>$k(19) = 4 \times 10^{-5}$ s$^{-1}$</td>
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<tr>
<td>Radiolytic decomposition of CH$_3$I(g)</td>
<td>$k(65) = 10^{-4}$ kGy$^{-1}$</td>
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<tr>
<td>reverse reaction</td>
<td>$k(67) = 10^{-15}$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>paint $\rightarrow$ CH$_3$I(g)</td>
<td>$k(7) = 4.3 \times 10^{-8}$ s$^{-1}$</td>
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<tr>
<td>CH$_3$I interfacial mass transfer coefficient</td>
<td>$k(36) = 10^{-8}$ m/s</td>
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<td>radiolytic decomposition of CH$_3$I(l)</td>
<td>$k(24) = 3 \times 10^{-4}$ kGy$^{-1}$</td>
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<tr>
<td>reverse reaction</td>
<td>$k(25) = 10^{-15}$ M$^{-1}$ s$^{-1}$</td>
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<tr>
<td>CH$_3$I dissolution from paint after I$_2$ deposition</td>
<td>$k(18) = 10^{-6}$ s$^{-1}$</td>
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<td>CH$_3$I dissolution from paint after I$^-$ deposition</td>
<td>$k(39) = 3.5 \times 10^{-7}$ s$^{-1}$</td>
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<tr>
<td>HOI + CH$_3$ $\xrightarrow{k(40) \rightarrow k(41)}$ CH$_3$I + OH$^.$</td>
<td>$k(40) = 0.4$ M$^{-1}$ s$^{-1}$</td>
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<tr>
<td>CH$_3$I hydrolysis with H$_2$O</td>
<td>$k(41) = 4.2 \times 10^{-15}$ s$^{-1}$</td>
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<tr>
<td>reverse reaction</td>
<td>$k(30) = 2.1 \times 10^{-4}$ s$^{-1}$</td>
</tr>
<tr>
<td>CH$_3$I hydrolysis with OH$^-$</td>
<td>$k(31) = 5.8 \times 10^{-12}$ M$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>reverse reaction</td>
<td>$k(32) = 6.2 \times 10^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>$3$ HOI $\xrightarrow{k(13) \rightarrow k(15)}$ IO$_3^-$ + $2I^-$ + $3H^+$</td>
<td>$k(13) = 1.5$ M$^{-1}$ s$^{-1}$</td>
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<tr>
<td>HOI partition coefficient</td>
<td>$k(15) = 10^6$ M$^{-3}$ s$^{-1}$</td>
</tr>
<tr>
<td>HOI interfacial mass transfer coefficient</td>
<td>$k(72) = 2.4 \times 10^2$</td>
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<tr>
<td>radiolytic reduction of IO$_3^-$</td>
<td>$k(71) = 10^{-5}$ m/s</td>
</tr>
<tr>
<td></td>
<td>$k(29) = 2 \times 10^{-4}$ M$^{-0.3}$ kGy$^{-1}$</td>
</tr>
<tr>
<td>Reaction</td>
<td>Rate Constant $k$</td>
</tr>
<tr>
<td>-------------------------------------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>paint $\rightarrow$ HMWI(g)</td>
<td>$k(3) = 5.2 \cdot 10^{-7} s^{-1}$</td>
</tr>
<tr>
<td>radiolytic decomposition of HMWI(g)</td>
<td>$k(66) = 10^{-4} kGy^{-1}$</td>
</tr>
<tr>
<td>reverse reaction</td>
<td>$k(68) = 10^{-15} M^{-1} s^{-1}$</td>
</tr>
<tr>
<td>paint $\rightarrow$ HMWI(l)</td>
<td>$k(70) = 10^{-7} s^{-1}$</td>
</tr>
<tr>
<td>HMWI partition coefficient</td>
<td>$k(44) = 2$</td>
</tr>
<tr>
<td>HMWI interfacial mass transfer coefficient</td>
<td>$k(43) = 10^{-5} m/s$</td>
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<td>radiolytic decomposition of HMWI(l)</td>
<td>$k(59) = 5 \cdot 10^{-5} kGy^{-1}$</td>
</tr>
<tr>
<td>reverse reaction</td>
<td>$k(60) = 10^{-15} M^{-1} s^{-1}$</td>
</tr>
<tr>
<td>$CH_3R + HOI \xrightleftharpoons[k(45)]{k(42)}$ HMWI</td>
<td>$k(42) = 0.4 M^{-1} s^{-1}$</td>
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<tr>
<td>HMWI hydrolysis with OH$^-$</td>
<td>$k(45) = 4.6 \cdot 10^{-15} s^{-1}$</td>
</tr>
<tr>
<td>reverse reaction</td>
<td>$k(48) = 6.2 \cdot 10^{-2} s^{-1}$</td>
</tr>
<tr>
<td>HMWI hydrolysis with H$_2$O</td>
<td>$k(61) = 7.7 \cdot 10^{-13} s^{-1}$</td>
</tr>
<tr>
<td>reverse reaction</td>
<td>$k(49) = 2.1 \cdot 10^{-3} s^{-1}$</td>
</tr>
<tr>
<td>rate constant $k_r$ for Ag–I$_2$ reaction</td>
<td>$k(50) = 5.8 \cdot 10^{-12} M^{-1} s^{-1}$</td>
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<tr>
<td>I$_2$ mass transfer coefficient in the aqueous phase</td>
<td>$k(77) = 2 \cdot 10^{-4} m^4/(mol s)$</td>
</tr>
<tr>
<td>rate constant $k_{ox}$ for Ag$_2$O–I$^-$ reaction</td>
<td>$k(78) = 3 \cdot 10^{-4} m/s$</td>
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<tr>
<td>I$^-$ mass transfer coefficient in the aqueous phase</td>
<td>$k(79) = 2 \cdot 10^{-3} m^4/(mol s)$</td>
</tr>
<tr>
<td>rate constant $k_r'$ for Ag–I$^-$ reaction</td>
<td>$k(80) = 10^{-4} m/s$</td>
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<tr>
<td>Ag$^+$ diffusion coefficient in AgI</td>
<td>$k(81) = 2 \cdot 10^{-8} mol/(m^2 s)$</td>
</tr>
<tr>
<td></td>
<td>$k(83) = 10^{-14} m^2/s$</td>
</tr>
</tbody>
</table>
STABILITY OF AGI COLLOIDS IN THE PRESENCE OF A DISSOLVED HIGH DOSE-RATE β-EMITTING RADIONUCLIDE

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ABSTRACT

Silver is released from melting control rods during a postulated core-melt accident in a pressurised water reactor (PWR) and can form non-volatile and insoluble silver iodide (AgI) with fission product iodine. It is postulated that silver is an effective sink for volatile molecular iodine and consequently leading to a potential reduction of the volatile iodine fraction.

The reaction of iodine with silver forming silver iodide in aqueous phase has been reasonably well understood and the kinetics of the reaction under various conditions (pure or oxidised silver) have been determined. The reverse reaction causing liberation of iodine, especially under irradiation due to the radiolytic stability of silver iodide in a PWR sump, has generated less international interest. Few experimental studies on silver iodide in aqueous suspension were previously performed. Experiments were carried out elsewhere within the CEC 4th Framework Programme using γ-radiation at a dose-rate of about 0.4 Gy/s on AgI-coated silver wool. The low yield of volatile iodine obtained was reasoned to be due to the solubility of AgI and hence AgI was considered radiolytically stable under these conditions.

PSI has concentrated effort to study the AgI stability under β-radiation to establish if the above conclusion can be extended to this type of radiation and to other relevant conditions which might enhance the liberation of iodine. Some scoping experiments were also performed by PSI, whilst associated to the CEC 4th Framework Programme on Nuclear Safety, on AgI aqueous colloids in the presence of impurities (nitrate, chloride and boric acid) using an external 2.5 MeV electron beam at a higher dose-rate (4.4 Gy/s). During the initial exposure, volatile iodine was rapidly released, which was due to the oxidation of excess iodide ions used to stabilise the AgI colloid. Later, a much lower iodine release rate was then detected. It was, however, greater than the rate, which could only be obtained from oxidation of the iodide concentration (about 10^7 mol.dm^-3) due to the solubility of AgI at the temperature of the AgI suspension.

It is conceivable that when radionuclides are in close range or they are adsorbed on the surface of the silver iodide particles, as may be the case in an accident sump, then a
greater proportion of the emitted electrons will interact directly with the particle than via hydroxyl radicals generated from radiolysis of water.

The results of the Phebus Test FPT1 have indicated an unexpectedly higher iodine concentration in the containment atmosphere than in FPT0. Exact source of this additional volatile iodine has not been identified yet. Radiolytic decomposition of AgI, which could provide additional iodine source in the sump, could not be clearly excluded based on the current measurements and available information. Therefore, a further experimental programme has been established as a part of the Swiss contribution to the Phebus programme in order to assess this impact on AgI stability under extended β-exposure by performing experiments on AgI aqueous colloids in the presence of a dissolved β-emitting radionuclide (Re-188). The investigation of the effects of relevant dissolved impurities (e.g. nitrate, nitrite, chloride etc.) is a part of the experimental programme.

The primary objective of the experimental programme is to establish a sound data basis to be used to determine the rate constant for the liberation as a function of relevant PWR sump parameters. Additional experiments under Phebus sump conditions are also planned. Although the work is in an early stage to draw a firm conclusion, the Helsinki workshop is a convenient forum to disclose the provisional findings. This paper presents the experimental programme and provides the results to date.

1. INTRODUCTION

Silver is released from melting control rods during a postulated core-melt accident in a pressurised water reactor (PWR) and can form non-volatile and insoluble silver iodide (AgI) with iodine and iodide. It has been established that silver is an effective sink for iodine. Although silver-iodine reactions have been explored very intensively the radiolytic stability of silver iodide precipitate in an LWR containment sump has generated much less international interest, and few studies have been performed to date, while research was done mainly on the effects of γ-radiation. The experiments indicated the release iodine is ascribed to the solubility of AgI under the used experimental conditions and hence it is generally perceived that AgI is stable under irradiation. However, self-radiolysis by β-decay as well as β-irradiation from sump debris may have a greater effect on silver iodide stability since the cross-section for β-absorption by silver iodide, water and other sump components is larger than for γ-absorption.

1.1 Previous studies

Previous investigations on the radiation stability of dry AgI crystals have shown that AgI decomposes by the direct interaction of electrons or γ-photons (Malm et al, 1991; Ostwald and Weil, 1969; Cubicciotti and Davis, 1976). Decomposition can take place even by using only low energy electrons in the high vacuum of an electron microscope. The high vacuum acts as an excellent iodine sink and hence recombination is presumably negligible.

The radiolytic stability of AgI as a layer on silver wool in boric acid solution using γ-rays has been investigated (Dickinson, 1999). The experiments indicated a total release of
about 3% of the iodine after receiving a dose of 96 kGy at a dose-rate of 0.42 Gy/s. It was concluded that the low volatile release was due to the oxidation of part of the free iodide determined by the solubility of AgI at the irradiation temperature. Hence it was reasoned that AgI was radiolytically stable under the conditions used and that the only parameters which might enhance iodine liberation are higher dose-rates and the presence of a large excess of impurities suppressing Ag and I₂ recombination.

Irradiations were performed at Leeds University on AgI suspensions using a 2.5 MeV electron beam from a Van de Graaf generator at a higher dose-rate (4.4 Gy/s) for a maximum of 9 hours (142 kGy). This work formed a project in which PSI was associated to the CEC 4th Framework Programme on Nuclear Fissinon Safety (Cripps et al, 1998). Conditions were chosen to favour iodine release rather than to simulate anticipated accident sump conditions, by using nitrous oxide carrier gas to scavenge the solvated electrons and increase the -OH concentration and at pH2-3. A higher iodine volatility was observed, under enhanced oxidising conditions than could be ascribed to either the excess iodide used to stabilise the AgI colloid, or that which can be deduced from the solubility of AgI. The consistent trends obtained, however, require verification and further experiments under anticipated accident-summ conditions.

1.2 Investigation of AgI in colloidal form

In contrast to other studies using AgI-layered silver wool, it was decided to perform irradiations on colloidal AgI, which was based on the interpretation of the PHEBUS FPT0 and FPT1 results (Jacquemain D. et. al. 1997), namely that silver behaviour in the sump was consistent with colloidal Ag/AgI formation as well as for the reasons set out in section 1.3.1 below. The technique (Woodridge, 1962) chosen to prepare the AgI colloids is just one of a set of established methods and provides AgI colloids with well defined characteristics and with fairly good reproducibility.

1.3 Interaction processes of radiation with AgI

The interaction mechanisms of radiation with AgI in aqueous suspension are simply defined here in two groups:

1. Direct interaction by electrons emitted from ion-radionuclides, which are either adsorbed on the AgI particle surface or are concentrated in the electrical double-layer solution surrounding the colloid particle of AgI.

2. Generation of water radiolysis species by dissolved or particulate ion-radionuclides, followed by their interaction with the AgI particle surface.

The iodine release from an AgI-containing sump is likely to be due to a combination of both.

1.3.1 Direct interaction of radiation with AgI

Much research has been done by the photographic industry on the direct interaction of radiation (mainly with light-photons) with dry emulsions of silver halides. A detailed study
and investigation of the mechanistic processes, under the conditions used here, is outside the scope of this project. However, for the purposes of discussion, the following simplified mechanism is given below.

According to a modified theory (Mitchell, 1958) based on the original photolysis theory of Gurney and Mott, conduction electrons and positive holes are formed by the absorption of the light photons or by deposition of kinetic energy from charged particles. They do not recombine, but diffuse to the external surfaces or to internal sub-boundaries (dislocation lines). The positive holes are trapped before the electrons by iodide ions on surface sites or edge dislocation lines, by added chemical sensitizers, such as Ag₂S molecules, NO₃⁻ ions or dissolved Ag₂O. When a positive hole is trapped by an iodide ion, iodine atoms are formed which remain adsorbed to the adjacent iodide ion (I₂⁻) after the interstitial silver ion has diffused away. The I₂⁻ molecular-ion then provides a deeper trap for positive holes than an iodide ion at a kink site. A second positive hole is, therefore, likely to be adsorbed at the same site with the liberation of a second interstitial silver ion. If an iodine molecule is formed on an external surface, it could then diffuse away. Once I₂⁻ is formed, it does not act as a recombination centre. The photoelectrons reduce silver ions to silver atoms in a reversible process, which form stable clusters (latent image centres) once they contain three or four Ag atoms.

Hence additives are important to increase the light sensitivity of silver halide sols for their use in the photographic industry (Mitchell, 1958 and Tani, 1995). It is feasible that these and other chemically similar species used to increase light sensitivity may be present in a containment accident sump and could enhance AgI decomposition under irradiation. For example, a telluride may be formed on AgI particles. In addition, it could be an additional source of irradiation. However, although in the substantial research literature on photographic science much data and theory on the mechanisms of the silver ions and image formation in the silver halide lattice under light irradiation are given, little information on the fate of the halogen ions or atoms seems to be available.

Iodine release from AgI will depend on conditions determining the balance between decomposition and recombination. The large surface area presented to the solution by small colloidal AgI particles in aqueous suspension may favour release compared with the smaller surface of AgI-coated silver wool, as used in experiments elsewhere (Dickinson, 1999) under otherwise identical conditions of pH, temperature and ionic concentration. AgI particles in water with no other potential-determining ions are normally negatively charged, because the iodide ions are preferentially adsorbed on the particle surface. The electrical double-layer surrounding the particle, which is required to maintain electrical neutrality, will contain a higher concentration of cations and a lower concentration of anions immediately above the particle surface than in the bulk solution. Hence it is reasonable to assume that the particle would experience a high dose-rate from both the adsorbed anions and the double-layer surrounding the particle, if the counter-cations are also radioactive. If the Ag⁺ concentration in solution is higher than 3.2 x 10⁻⁸ M, that is, if pAg <5.5 (point of zero charge), then the polarity of the charges on the particle and in the double layer will reverse. In such a case, a high localised dose-rate may still result depending on the ion-radionuclides present.

Although the β-dose-rate estimation from the cesium and iodine inventories core-melt accident only about 15% (1 Gy/s) of the γ-contribution (7 Gy/s) to the total sump radiation
field, 6h after meltdown, according to a Siemens estimate for a 1300 MWe PWR (Neeb, 1997), the effective dose received by Agl-coated Ag particles or Agl colloids could be higher due to possibility that β-emitting ion-radioisotopes could be adsorbed on Agl particle surfaces as described above. In addition the dose from other adsorbed radionuclides may be significant, such as, tellurium-radionuclides (e.g. Ag$_2$Te) to form a local and high dose-rate source. It is reasonable then to speculate that Agl decomposition from such sources may make a significant contribution in addition to the interactions of water radiolysis products.

1.3.2 Initial rapid release of volatile iodine from the Agl colloid under radiation

An -OH can, of course, oxidise either an iodide ion chemically bound or adsorbed on a Agl particle surface or a free iodide ion in solution to molecular iodine.

The rate constant for the reaction of -OH with iodide ions as well as their diffusion constant are known. It can be shown that, after making some assumptions, which are based on dose-rates and initial iodide concentrations used in the PSI experiments, the fractional oxidation rate of -OH with the iodide ions on the Agl particle surface is much slower than their reaction with dissolved iodide ions at the initial bulk concentration, since only those radicals, which are able to diffuse to the Agl particle surface within their half life, calculated for the initial iodide concentration, will survive to react with the adsorbed or bound iodide ions. Thus most of the radiolytic iodide oxidation will first take place with free iodide ions in solution resulting in a rapid release of iodine at the beginning of the irradiation. The results of the PSI-experiments using an excess of iodide to stabilise the Agl colloids support this explanation.

2. PROGRAMME OBJECTIVES

The objective of the programme is to investigate the stability of Agl colloids in aqueous phase subjected to in-situ β-irradiation by performing separate-effect tests. The primary objective of the experiments is to demonstrate the effect and to establish a sound data base to be used to determine the rate constant for the liberation as a function of relevant PWR sump parameters. The later can be introduced into silver-iodine interaction models. Specially designed experiments will consider Phbus sump conditions to provide an insight into the iodine behaviour under Phbus conditions, some of which (e.g., dose rate) may vary from the large-scale PWR plants. It is not intended to perform integral experiments to explore the iodine volatility from the sump.

3. EXPERIMENTAL PROGRAMME

The experimental programme consists of five stages as follows:

1a) to characterise and commission the irradiation facility using CsI solutions under conditions of enhanced iodine oxidation (low-pH, N$_2$O and He as sparging gas) in order
1.b) to perform scoping irradiations on the AgI colloid under enhanced oxidation conditions to determine the effect of dose. Pre-humidified (to reduce evaporation) and dry gas-flows were used.

2. to repeat the above programme using air as the sparging gas and to irradiate AgI colloids containing an excess of silver ions under enhanced conditions. Higher doses will be achieved by further addition of rhenium activity to compensate for decay.

3. to investigate the effect of impurities on the radiolytic decomposition of AgI, e.g. Ag₃O. The investigation of the effect of impurities was restricted to cesium, chloride, nitrate and sulphate ions at the concentrations used for the preparation of the AgI colloid. One experiment was carried out using 0.2M boric acid in addition to the above ions (excepting sulphate).

4. to perform irradiations on AgI colloids containing chloride or nitrite ions on iodine release

5. to perform irradiations under near-Phebus specific sump conditions (additives). On the basis of the Phebus results, silver/iodine ratios of up to 1000:1 were reported. Hence AgI colloids are envisaged containing an excess of Ag⁺ ions. Irradiations of AgI-layered silver surfaces are also planned.

Furthermore AgI particle sizes and colloid concentrations will be varied. A limited number of scoping experiments from the Phases 1, 2, and 4 have been currently performed and will be presented in this paper. The initial conditions used in the performed experiments are shown in Table 1.

4. EXPERIMENTAL DETAILS

4.1 Choice of irradiation source

To carry out a programme of irradiations, the radionuclide ¹⁸⁶Re, in the form of the ReO₄⁻ dissolved in a saline solution (0.85% NaCl in water), was used and has a half-life of 17 hours, a maximum β-energy of 2.1 MeV and an average electron energy of 0.762 MeV. The radionuclide is eluted from a ¹⁸⁶Re/¹⁸⁸W-generator of 3Ci initial activity (see section 4.3). The generator was the best choice with respect to safety and cost considerations.

No data have yet been found which contradicts the improbability that ReO₄⁻ ions are adsorbed on AgI particle surfaces to any great extent, but it is reasonable to assume that the small AgI particles produced (see below) will be subjected to more irradiation due to the large interfacial area between them and the ReO₄⁻ ions in solution.
4.2 Dose-rates used in the PSI-investigations

In-situ β-dose-rates, up to about 0.4 Gy/s were available. Since the generator decays and the eluted volumes are not identical, the initial dose-rates, shown in Table 1, are different for each experiment. No compensation by replenishment for activity decay was made in these first experiments, but it is foreseen for later experiments to achieve higher doses. A beta dose-rate, corresponding to Phebus FPT0/FPT1 sump conditions, will be used for the experiments to be conducted in the last phase of the experimental programme.

4.3 $^{188}$Re radionuclide generation facility

The Facility for Experimental Nuclear Research with In-Situ Irradiated Samples (FENRIS) was developed to enable efficient elution of $^{188}$Re activity from the $^{188}$Re/$^{188}$W-generator (Figure 1). A saline solution at a pressure of 0.25 MPa is pushed through plastic tubing (0.8 mm diameter). The activity, transport and location in the system are monitored by detectors. To ensure maximum generator yield, three elutions are performed which give a total volume of 30-40 cm$^3$. This activity is then concentrated by temporary storage in in-line cationic and anionic exchangers so that a small final volume of about 2 cm$^3$ is achieved. This volume can be freed of chloride ions, to achieve a carrier-free $^{188}$Re activity of about 40 GBq/cm$^3$. The active solution is transferred into the reaction vessel containing the AgI colloid.

4.4 Preparation of AgI colloids

Due to their obvious importance in the photographic industry, much literature on the preparation and characteristics of silver halide colloids is available (Ottewill and Woodbridge, 1961). Since the surface area of an AgI particle is likely to influence decomposition, experiments are also foreseen to use particles of different average diameters. For the purposes of these initial irradiation experiments, the preparation method used was restricted to one published method for AgI particles of small average diameter (literature value about 40 nm) to present a large surface area to the in-situ radiation (Woodbridge, 1962). This technique was adapted to produce a stable AgI colloid at low pH (sulphuric acid). The negatively charged colloid was prepared by slowly adding an equal volume (100 cm$^3$) of AgNO$_3$ solution (1.25 x 10$^{-3}$ mol.dm$^{-3}$), tagged with $^{110m}$Ag, to a rapidly-stirred CsI solution (1.38 x 10$^{-3}$ mol.dm$^{-3}$), tagged with $^{131}$I, at room temperature. The resulting colloid was allowed to stir over 24 hours at room temperature.

4.5 Experimental facility

A view and schematic diagram of the facility are shown in Figures 2 and 3 respectively. It consists of a glass reaction vessel (15 cm$^3$) equipped with a central gas tube with frit to purge the active AgI colloid free of volatile iodine and a heated water jacket to control temperature. The reaction vessel is situated in a lead container, which together with a lead wall provides sufficient shielding to conform to safety regulations. A heated vent tube carries the sparging gas to a water-cooled trap. The gas then passes through an active charcoal column, impregnated with TEDA, to trap possible traces of organoiodine. The
active perrenenate solution (2 – 3 cm³) is pushed by gas pressure through the central sparging tube into the AgI colloid (8 cm³). Further equipment is used to control gas flow rates and detection of leaks.

5. ANALYSIS

5.1 In-situ dose-rate determinations

Estimations of the bulk dose-rate in the reaction solution or colloid were obtained by direct addition of a small measured volume of radioactive solution from the 186Re-generator to a Fricke solution, which was first placed in the reaction vessel. The radionuclide solution was allowed to decay to an activity level to within the dose range for the Fricke method and to allow safe handling before its addition to the Fricke solution. The dose-rate was then calculated from the measured extinction of the mixture in the cell of a UV-spectrophotometer as a function of time. The activity of the mixture was also measured for the same reference time. At the end of each irradiation, the initial dose-rate in an AgI colloid was determined by backwards extrapolation of the post-irradiation activity value. This procedure attained a 75% estimate of the theoretical dose-rate, which was simply estimated by converting the emitted β-rate to joules/sec deposited in water using the average electron energy of 762 keV for 186Re and ignoring irradiation lost to and from the reaction vessel.

Table 1. Experimental conditions for the radiolysis of CsI solutions and AgI colloids

<table>
<thead>
<tr>
<th>Experiment no.</th>
<th>Sparging gas type</th>
<th>type</th>
<th>L/min.</th>
<th>*Chloride present</th>
<th>Temp. °C</th>
<th>Volume cm³</th>
<th>pH</th>
<th>Iodide conc.</th>
<th>Dose rate Gy/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re9-04</td>
<td>CsI</td>
<td>N₂O</td>
<td>0.25</td>
<td>Yes</td>
<td>50</td>
<td>10</td>
<td>2.2</td>
<td>n/a</td>
<td>0.42</td>
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<tr>
<td>Re9-08</td>
<td>CsI</td>
<td>He</td>
<td>0.25</td>
<td>No</td>
<td>60</td>
<td>10</td>
<td>4.6</td>
<td>2.9</td>
<td>0.35</td>
</tr>
<tr>
<td>Re9-09</td>
<td>CsI</td>
<td>N₂O</td>
<td>0.25</td>
<td>No</td>
<td>68</td>
<td>10</td>
<td>2.2</td>
<td>2.9</td>
<td>0.31</td>
</tr>
<tr>
<td>Re9-03</td>
<td>AgI</td>
<td>N₂O</td>
<td>0.25</td>
<td>Yes</td>
<td>50</td>
<td>10</td>
<td>2.2</td>
<td>n/a</td>
<td>0.28</td>
</tr>
<tr>
<td>Re9-05</td>
<td>AgI</td>
<td>N₂O</td>
<td>0.25</td>
<td>Yes</td>
<td>50</td>
<td>10</td>
<td>2.2</td>
<td>n/a</td>
<td>0.29</td>
</tr>
<tr>
<td>Re9-06</td>
<td>AgI</td>
<td>N₂O</td>
<td>0.25</td>
<td>Yes</td>
<td>60</td>
<td>10</td>
<td>2.2</td>
<td>4.0</td>
<td>0.30</td>
</tr>
<tr>
<td>Re9-07</td>
<td>AgI</td>
<td>N₂O</td>
<td>0.25</td>
<td>No</td>
<td>60</td>
<td>10</td>
<td>2.2</td>
<td>4.0</td>
<td>0.14</td>
</tr>
<tr>
<td>Re9-10</td>
<td>AgI</td>
<td>Air</td>
<td>0.25</td>
<td>No</td>
<td>68</td>
<td>12</td>
<td>2.2</td>
<td>4.0</td>
<td>0.19</td>
</tr>
<tr>
<td>Re9-11</td>
<td>AgI</td>
<td>N₂O</td>
<td>0.25</td>
<td>No</td>
<td>68</td>
<td>10</td>
<td>2.2</td>
<td>4.0</td>
<td>0.27</td>
</tr>
<tr>
<td>Re9-12</td>
<td>AgI</td>
<td>Air</td>
<td>0.25</td>
<td>Yes</td>
<td>68</td>
<td>10</td>
<td>2.2</td>
<td>4.0</td>
<td>0.26</td>
</tr>
<tr>
<td>Re9-13</td>
<td>AgI</td>
<td>Air</td>
<td>0.25</td>
<td>Yes</td>
<td>68</td>
<td>10</td>
<td>4.6</td>
<td>4.0</td>
<td>0.24</td>
</tr>
<tr>
<td>Re9-14</td>
<td>AgI</td>
<td>Air</td>
<td>0.25</td>
<td>No</td>
<td>68</td>
<td>10</td>
<td>4.6</td>
<td>4.0</td>
<td>0.23</td>
</tr>
</tbody>
</table>

n/a = not available; *Chloride concentration: 2.9 x 10⁸ mol.dm⁻³
5.2 Measurement of the free iodide concentration in a AgI colloid

An Orion iodide ion-selective electrode was used in AgI colloidal suspensions to determine iodide concentrations. The excess iodide concentrations in the AgI colloid were measured before and after flocculation. Results have shown that about 87% of the iodide is bound as AgI, about 3% adsorbed on or in the AgI particles and 10% in solution before flocculation. After flocculation, the measured iodide concentration rose to within 2% of the weighed (mol) excess of iodide. With immediate electrode calibration before sample measurement, direct electrode measurements reproducible to ±2% can be obtained with the acidified CsI solutions. It was suspected that iodide measurements may be affected by the presence of AgI colloids. However, the results obtained and the mass balance done indicate that unacceptably large measurement errors through the use of an ion-selective-electrode in AgI colloids did not occur.

6. DISCUSSION AND RESULTS

The doses (in kGy) have been corrected for both decay and loss of reaction solution due to evaporation. Activity measurements show, that carry-over of $^{188}$Re with droplets or colloids to the iodine trap is extremely small (activity fraction: $10^{-1} - 10^{-5}$) and hence the transport of tagged non-volatile iodine species can be discounted, since the $^{131}$I-activity is several orders of magnitude lower than the $^{188}$Re activity. This outcome proved that the flow rate of the sparging gas does not cause any droplet or aerosol entrainment but is still high enough for efficient transport of gaseous iodine out of the reaction vessel.

6.1 Radiolysis of cesium iodide solutions

Three experiments were performed to characterise the yield (fraction of the initial iodine inventory which is transported out of the reaction vessel) where the effect of pH, sparging gas type, flow rate and possibly radiolytically generated chlorine at various doses were studied. The results are presented in Table 2 and in Figure 4.

An almost quantitative release was obtained from CsI solutions ($1.38 \times 10^3 \text{ mol.dm}^{-3}$) after a dose of 20 kGy under the same enhanced oxidative conditions with and without the presence of chloride ions (experiments Re9-04 and Re9-09 respectively). Using an integral measurement error estimate of 10%, the scatter of the data points seem to indicate that there is little or no difference in volatile iodine release due to the presence of chloride ions. Further experiments are necessary for confirmation.

The purpose of these experiments was to establish optimum conditions to provide a 100% yield of volatile iodine such that its removal from the solution is fast enough for reduction reactions and processes to be considered negligible. Experiments with lower CsI concentrations ($\leq 1.0 \times 10^5 \text{ mol.dm}^{-3}$) are also planned in anticipation of iodide concentrations resulting from AgI solubility.
<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Type</th>
<th>( I_1 ) released to trap(%) after dose:</th>
<th>Final conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 kGy</td>
<td>10 kGy</td>
</tr>
<tr>
<td>Re9-04</td>
<td>Csl</td>
<td>53</td>
<td>78</td>
</tr>
<tr>
<td>Re9-08</td>
<td>Csl</td>
<td>13</td>
<td>24</td>
</tr>
<tr>
<td>Re9-09</td>
<td>Csl</td>
<td>77</td>
<td>95</td>
</tr>
<tr>
<td>Re9-03</td>
<td>Agl</td>
<td>51</td>
<td>76</td>
</tr>
<tr>
<td>Re9-05</td>
<td>Agl</td>
<td>42</td>
<td>66</td>
</tr>
<tr>
<td>Re9-06</td>
<td>Agl</td>
<td>39</td>
<td>63</td>
</tr>
<tr>
<td>Re9-07</td>
<td>Agl</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>Re9-10</td>
<td>Agl</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>Re9-11</td>
<td>Agl</td>
<td>26</td>
<td>29</td>
</tr>
<tr>
<td>Re9-12</td>
<td>Agl</td>
<td>32</td>
<td>39</td>
</tr>
<tr>
<td>Re9-13</td>
<td>Agl</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Re9-14</td>
<td>Agl</td>
<td>0.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

% I: iodine species remaining in reaction vessel; speciation analysis is in progress; *) extrapolated from a lower dose to the one selected for this column; **) mass balance is to be further verified.

### 6.2 Scoping experiments: Radiolysis of Agl colloids

The data showing released iodine as a function of dose are given in Table 2 and Figure 5. In later experiments, the sparging gas was pre-humidified, which compensated for reaction vessel volume losses. However, in all experiments, the reaction water level dropped below the level of the frit which drastically reduced the transport efficiency of the sparging gas flow. Work is underway to quantify this effect.

Since the in-situ dose-rate is dependent on the \(^{185}\text{Re}\) activity concentration eluted from the generator, a dose of 14 kGy was attained in experiments Re9-07 and Re9-10 compared with a dose of 36 kGy obtained with an evaporating reaction solution in experiment Re9-06.

A release of about 20% and 15% of the iodine in the Agl colloid solution was obtained after 14 kGy at the same pH and temperature for nitrous oxide and air respectively. The former result is about twice the iodide excess (10.4 mol%) used to stabilise the Agl colloid.

In the experiments Re9-03 and Re9-05, Csl with tracer was added to the Agl colloid to exchange with inactive iodide ions of Agl whereas in experiment, Re9-06, tagged Csl was directly used to prepare the Agl colloid. In these three experiments, a volatile iodine release approaching 90% was obtained. Figure 6 shows these releases with the release obtained by irradiating a Csl solution (1.38 x 10⁻⁶ mol dm⁻³) under otherwise the same conditions. Considering measurement errors of up to 10%, the curves show that no significant difference of release iodine could be seen between the Csl solution and Agl colloids, although some plots have been extrapolated.
A plausible explanation is that radiolytically generated chlorine might have enhanced the iodide oxidation, although the irradiation of a CsI solution where Cl⁻ was used (experiment Re9-04) did not seem to support this trend given the measurement uncertainties. However, in the chloride-ion free AgI experiments, iodine volatility was considerably reduced, reaching about 20% release after a dose of 14 kGy. At this stage one can only assume that the chloride ions had reacted with the AgI colloid by a number of processes and achieved a higher release of iodine. This effect will be investigated.

If further experiments confirm enhanced liberation due to the presence of chlorine then experiments (Phase 4) are planned to quantify the sensitivity. In addition, irradiations using air sparging gas, and at pH 4.6 (2.0 x 10⁻¹⁰ mol dm⁻³ boric acid) for comparison are also planned.

The lower release observed in experiments without chloride ions as well as a fraction of the release observed during the high release experiment can be explained by the dissociation of AgI at 60 °C (K ≈ 1 x 10⁻⁸). Assuming that AgI dissociation is fast, iodide ions are rapidly oxidised and removed, then an iodine release of about 1.5%/h can be roughly estimated based on the mass of AgI present. This would lead to a 100% release in two days. However, an increasing free silver ion concentration would reduce the iodide concentration to maintain the solubility product.

7. CONCLUSIONS

The CsI solution irradiations confirm an almost quantitative iodine release after a dose of 10-20 kGy depending on the presence of chloride ions at pH 2.2 and using nitrous oxide sparging gas. About 42% and a 67% iodine release after 20 kGy and 40 kGy dose were obtained respectively with He sparging gas and at pH 4.6 (boric acid). Using the specified gas flow rate, negligible amounts of droplets or colloid were carried out of the reaction vessel. A larger droplet transport could have made sample activity measurements meaningless.

Notwithstanding the few unconfirmed results, the enhanced iodine release obtained is greater than the iodide excess used to stabilise the AgI colloid. Chloride ions have significantly enhanced iodine release, although the responsible mechanism is presently unclear. Further experiments to confirm these first findings and also under Phebus-relevant conditions are planned in order to provide a reliable data base to derive a model for the radiolytic decomposition of AgI as well as to compare with earlier data under similar conditions.

8. ACKNOWLEDGEMENTS

The authors would like to thank Professor R. H. Ottewill, University of Bristol, UK for the very useful discussions on the preparation and characteristics of silver halide colloids. In addition, the authors are indebted to Dr. G. Bart, PSI Laboratory for Material Behaviour, for providing the laboratory facilities as well as to Mr. H.P. Linder for his continued support by performing the γ-analysis of the samples.

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9. LITERATURE

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Figure 1: AgI radiolysis experiments: schematic diagram of the activity transport and control

G: W-188/Re-188 Generator
G': Security Vessel for Generator
AS1-AS8: Activity Sensors
V1-V6: Multiple Valves
R: Reaction Vessel
R': Security Vessel for Reaction Vessel
R'": 2. Security Vessel for Reaction Vessel
T: Iodine Trap
S: Storage Vessel
1-3: Elution Vessels
C: Cation Exchanger
A: Anion Exchanger
P: Pressure Device

Waste

Air

inactive Fluid

active Fluid

Syringe (press)
Figure 2: A View to the Irradiation facility
Remote medium pressure elution of $^{188}$Re from a W/Re-generator and study of AgI stability under beta-radiation (schematic set-up)
Figure 4: Release of iodine from CsI-Solution

- pH 2.2 (sulphuric acid, Cl₂ / N₂O), (Re9-04)
- pH 4.6 (boric acid / He), (Re9-09)
- pH 2.2 (sulphuric acid / N₂O), (Re9-08)
Figure 5: Release of Iodine from AgI-Colloid Suspension

- ●: pH 2.2 (sulphuric acid, Cl⁻ / N₂O), (Re9-03)
- ■: pH 2.2 (sulphuric acid, Cl⁻ / N₂O), (Re9-05)
- □: pH 2.2 (sulphuric acid / N₂O), (Re9-06)
- ◇: pH 2.2 (sulphuric acid / N₂O), (Re9-07)
- ▲: pH 2.2 (sulphuric acid / Air), (Re9-10)

Release [%]

Dose [kGray]
Figure 6: Comparison of Iodine Release from Irradiation of Csl and Agl under the same Conditions
MODELING OF IODINE AND NITROGEN OXIDES TRAPPING BY ACIDIC HYDROXYLAMINE IN NUCLEAR SPENT FUEL REPROCESSING – CONSIDERATION OF APPLICABILITY TO REACTOR SEVERE ACCIDENT MANAGEMENT

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ABSTRACT

This paper introduces the proposal to replace soda by hydroxylamine in reactor containment spraying during severe accident management. This new approach to trap iodine was based on the similarities between the physicochemical system met in such conditions and the one corresponding to dissolution off-gas scrubbing in nuclear spent fuel reprocessing.

In the reprocessing framework, laboratory experiments have shown that, in acidic medium, hydroxylamine reduces both iodine into non-volatile iodide and nitrous acid into inert dinitrogen monoxide; moreover, the reactions are fast enough to be compatible with the gas residence time in a counter-current column. The rate controlling parameters were optimized by modeling of the I₂/T/HNO₂/NH₃OH⁺ reactive system using the Methodology of the Experimental Research.

In the field of nuclear reactor safety, hydroxylamine could help to keep iodine in the sump as iodide, even if it becomes acidic (pH as little as 1). The chemical parameters optimization used in the case of fuel reprocessing could be transposed to spraying without any particular difference compared to soda regarding hydrodynamics; additional supply of hydroxylamine directly in the sump could be also considered. The compatibility of hydroxylamine with the structures in the containment and with the physicochemical properties which are met there, are outlined. The available data are rather promising as for applicability of hydroxylamine in severe accident management.
1. INTRODUCTION

The new management of the low and medium activity effluents, which was currently set up in COGEMA La Hague reprocessing plants, consists in vitrifying these effluents, instead of bituminizing them, so as to produce more compact wastes. This change in the process requires a significant decrease in their saline load. In particular, sodium amounts must be reduced so as to ensure a low leachability of the glass.

To achieve this aim in the first step of the process (spent fuel dissolution), investigations have been carried out to find a substitute to sodium hydroxide which was currently used to trap into solution iodine and nitrogen oxides by counter-current scrubbing of the off-gas.

Hydroxylamine (in the form of nitrate) has been selected as a potential candidate for the following reasons: (i) this reactant was sodium- and sulfur-free (sulfur is prohibited because it leads to severe corrosion at high temperature), (ii) it is already used in other steps of reprocessing (when partitioning uranium from plutonium).

As far as nuclear reactor safety is concerned, such a reducing reagent, instead of soda, could be of interest for iodine removal and NOx reduction by containment sprays in severe accident management. Indeed, there are similarities between the physicochemical system met in such conditions and the one corresponding to dissolution off-gas scrubbing in nuclear spent fuel reprocessing. Together with silver in an acidic solution, hydroxylamine could help to keep iodine in the sump in the form of iodide ion with pH as little as 1 and to prevent formation of higher oxidation degree species and volatile compounds.

The first part of the paper deals with reactions in solution likely to occur during dissolution off-gas scrubbing in spent fuel reprocessing. In a previous work (Cau-dit-coumes, 1996, 1998, 1999), were studied separately. First of all, a synthesis of the results obtained previously through a comprehensive study are provided and, after a brief discussion about the possible reactions, three of them which play a major role in the rate control of the process in solution were identified. Then an attempted modeling of the reaction system is reported. After a phenomenological approach based on extensive kinetics studies, an empirical one, considering the reaction system as a whole, was carried out in order to widen the range of validity of the model. The latter was then used to determine the effect of each operating parameter on the reduction rate of iodine and nitrous acid and the optimal values corresponding to the shortest reaction duration; indeed, the use hydroxylamine as a scrubbing reagent can only be conceivable if the involved reactions are fast enough (residence time of the gases in the scrubber estimated to be 8 seconds).

In a second part, the applicability of these results to severe nuclear reactor accident conditions is discussed in terms of compatibility of hydroxylamine with the structures in the containment and with the physicochemical properties of the liquid and gaseous phases which are met inside, stressing on the established knowledge and those which must be enhanced.
2. REVIEW OF THE MOST IMPORTANT FEATURES OF THE REACTION SYSTEM

An extensive study of the reaction system I\textsubscript{2} - I\textsuperscript{−} - HNO\textsubscript{2} - NH\textsubscript{3}OH\textsuperscript{+} - H\textsuperscript{+} was carried out between 1995 and 1998 in our laboratory (stoichiometry, kinetics, mechanisms); it should be remembered that the first results were presented in similar circumstances during the last workshop (Cau-dit-coumes, 1996). The most important features of the system, required for modeling, are reviewed hereafter. Calculations from general literature data have shown that gas-liquid transfer was not the rate limiting step in gas scrubbing, investigations were restricted to reactions in solution.

The reduction of iodine by hydroxylamine, which is extremely fast in basic medium, also takes place in acid medium but is inhibited by the protons and the iodide ions. The oxidation of hydroxylamine by nitrous acid takes place only in acid medium and, contrary to the former, is catalyzed by the protons and iodide ions. Only an acidic hydroxylamine solution makes it possible to reduce the totality of the nitrous acid formed during the absorption of nitrogen oxides. Under these conditions, the reaction between NO and hydroxylamine is negligible because excessively slow. NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{4} and N\textsubscript{2}O\textsubscript{3} were absorbed in solution where they undergo fast hydrolysis in nitric and/or nitrous acid. The latter is then reduced into nitrous oxide by hydroxylamine (rate limiting step). The reactions of direct nitrosation of hydroxylamine by N\textsubscript{2}O\textsubscript{3} and N\textsubscript{2}O\textsubscript{4} were not observed (figure 1).

![Chemical reactions involved in the absorption of a gaseous mixture of nitrogen monoxide and dioxide by a soda or hydroxylamine solution.](image)

The reactions of oxidation of the iodide ions or hydroxylamine by nitric acid which would be used to acidify the scrubbing solution can be neglected in H\textsuperscript{+} diluted medium since, to be fast enough, the reduction of iodine by hydroxylamine requires a pH higher than 1. Lastly, the reduction of iodine by nitrous acid can be neglected; it takes place only in solution close to neutrality (pH ~ 6-7), incompatible conditions with a fast reduction of the nitrous acid by hydroxylamine (pH < 4).

Regarding organic iodine compounds (a few percent of total iodine), it must be noticed that the dissolution off-gas scrubbing with acidic hydroxylamine would be ineffective to trap

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iodoalkanes (Cau-dit-coumes, 1998). Indeed, a study of the reaction with CH₃I (classical model of organic iodine in reprocessing), showed that the reaction was all the more rapid as hydroxylamine was in a more nucleophilic form (ranked by increasing nucleophilicity: NH₃OH⁺<NH₂OH<NH₂O); these forms correspond to the amphoteric properties of hydroxylamine so that the reaction rate increased with pH; indeed, the pKₐ of the acid-base couples NH₃OH⁺/NH₂OH and NH₂OH /NH₂O are respectively about 6 and 13.7 at 25°C. In concrete terms, there would be no improvement compared to the current process with sodium hydroxide. In neutral hydroxylamine solutions, a reaction would occur, but with a slow kinetics at ambient temperature. With a molar solution of hydroxylamine and a temperature of 25°C, the methyl iodide half life (initial concentration: about 10⁻⁴ mol.L⁻¹) would be 101 min at pH 8, 20 min at pH 12 and 3 min at pH 13 (at 55°C, these values would be 20 times as low). It would decrease to 29 s provided that hydroxylamine be only in the NH₂O form. Fast kinetics would thus require very basic media, which may however generate other difficulties such as the degradation of hydroxylamine in ammoniac, dinitrogen and dinitrogen monoxide (Nast and al., 1950; Bonner and al., 1978).

This analysis led us to take into account 3 reactions controlling significantly the processes kinetics in solution:

- iodine reduction by hydroxylamine;

\[ \text{NH}_3\text{OH}^+ + 2 \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + 4 \text{I}^- + 5 \text{H}^+ \]  \hspace{1cm} (1)

- nitrous acid reduction by hydroxylamine;

\[ \text{NH}_3\text{OH}^+ + \text{HNO}_2 \rightarrow \text{N}_2\text{O} + 2 \text{H}_2\text{O} + \text{H}^+ \]  \hspace{1cm} (2)

- iodide ions oxidation by nitrous acid.

\[ 2 \text{HNO}_2 + 2 \text{I}^- + 2 \text{H}^+ \rightarrow 2 \text{NO} + \text{I}_2 + 2 \text{H}_2\text{O} \]  \hspace{1cm} (3)

Reaction (3) was opposed to our objective of iodine and nitrous acid reduction into an inert compound N₂O because it regenerated iodine and nitrogen monoxide. It is thus important to minimize its kinetics while maximizing as much as possible those of reactions (1) and (2). The easily adjustable parameters to control the kinetics of these 3 reactions are: pH, temperature and initial concentration of hydroxylamine [NH₃OH⁺]₀. Their qualitative influence is summed up in Table 1.

**Table 1**: Effect of an increase in the parameters [NH₃OH⁺]₀, pH and temperature on the kinetics of reactions (1), (2) et (3).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>[NH₃OH⁺]₀</th>
<th>pH</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃OH⁺/I₂</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>NH₃OH⁺/HNO₂</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>HNO₂/I⁻</td>
<td>0</td>
<td>-</td>
<td>+</td>
</tr>
</tbody>
</table>

+ : acceleration  - : reduction in rate  0 : no effect

According to table 1, three strong points must be kept in mind:
the choice of the pH of the hydroxylamine solution will result from a compromise since, as noted above, the protons catalyze the reactions between nitrous acid and hydroxylamine or iodide ions, and inhibit; on the contrary, the reaction between iodine and hydroxylamine;

* the three reactions are accelerated by an increase in the temperature;
* an increase in the initial hydroxylamine concentration is a way to promote only reactions (1) and (2).

The optimization of these three parameters requires to quantify their effects on the kinetics of each reaction. We thus tried to model the reaction system I$_2$/I/HNO$_2$/NHOOH$^+$ by two ways successively:

* a phenomenological approach which used the rate laws established for the three reactions;
* an empirical approach which was based on the implementation of an experimental design (experimental research methodology) and the use of response surfaces.

### 3. MODELING OF THE REACTIONAL SYSTEM I$_2$/I/HNO$_2$/NHOOH$^+$: PHENOMENOLOGICAL APPROACH

#### 3.1 Setting in equation and numerical resolution

Are v1, v2 and v3 the rate of reactions (R-1), (R-2) and (R-3). Concentrations of I$_2$, I, HNO$_2$, NHOOH$^+$ and H$^+$ check the system of differential equations (E-1):

\[
\begin{align*}
\frac{d[I_2]}{dt} &= -v_1 + v_3 \\
\frac{d[I]}{dt} &= 2v_1 - 2v_3 \\
\frac{d[HNO_2]}{dt} &= 0.5v_1 - v_2 - 2v_3 \\
\frac{d[NHOOH^+]}{dt} &= -0.5v_1 - v_2 \\
\frac{d[H^+]}{dt} &= 2.5v_1 + v_2 - 2v_3
\end{align*}
\]

The rate laws of reactions (R-1) and (R-2) were established from our own experiments. For reaction R-3, the rate law proposed by Dozsa et al. (1976) was chosen. System (E-1) was solved numerically by implementing the method of Runge Kutta (fourth order).

#### 3.2 Results

Figure 2 makes it possible to confront the results of calculation with those of the experiments when the initial concentration of the protons was equal to 10$^{-1}$ or 10$^{-3}$ mol.L$^{-1}$. 

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Fig. 2: Modelling of the reaction system I$_2$/I$^-$/HNO$_2$/NH$_3$OH$^+$ using the established rate laws. Full line: calculated / points: experimental

[H$^+$]$_0$ = $10^{-3}$ mol.L$^{-1}$; [I$_2$]$_0$ = [NH$_3$OH$^+$]$_0$ = 5.55$x$10$^{-4}$ mol.L$^{-1}$, [I$^-$]$_0$ = 1.75$x$10$^{-2}$ mol.L$^{-1}$,

[HNO$_2$]$_0$ = 0 mol.L$^{-1}$, temperature 25°C, ionic strength 0.5 mol.L$^{-1}$

[H$^+$]$_0$ = $10^{-1}$ mol.L$^{-1}$; [I$_2$]$_0$ = 6.6$x$10$^{-3}$ mol.L$^{-1}$, [NH$_3$OH$^+$]$_0$ = 6.6$x$10$^{-3}$ mol.L$^{-1}$,

[I$^-$]$_0$ = 4.4$x$10$^{-7}$ mol.L$^{-1}$, [HNO$_2$]$_0$ = 0 mol.L$^{-1}$, temperature 25°C, ionic strength 0.5 mol.L$^{-1}$

The agreement between the model and the experimental results were excellent at pH = 3. In a more general way, modelling was true to the experiment for all the tests carried out at pH $\geq$ 2.

On the other hand, when the concentration of the protons was equal to 10$^{-1}$ mol.L$^{-1}$, the calculated plot diverged from the experimental results after the first minute of reaction. This poor correlation could result from an inappropriate kinetics description of reaction (R-3) since the rate law used for calculation was established in the pH range 2.5-5 and, consequently, was not taking into account the nitrous acid decomposition which occurred at pH < 2.5.

3.3 Conclusion

In the present state, the model made it possible to predict the reaction system behavior only when pH $\geq$ 2 at a temperature of 25°C. Its use to solve the problem of optimization would require, as a preliminary, to widen its range of validity to other temperatures and to establish experimentally the rate laws and stoichiometry of the reaction between iodide ions and nitrous acid in more acidic aqueous solutions. The great number of additional experiments required to complete such a work led us to modify our approach. At the opposite of the phenomenological one, a purely empirical model was investigated by implementing experimental research methodology (mathematical technique of optimal experimental design) in order to limit the number of tests while guaranteeing a good quality of information (Mathieu and al., 1997).

4. MODELING OF THE REACTION SYSTEM I$_2$/I$^-$/HNO$_2$/NH$_3$OH$^+$: EMPIRICAL APPROACH

The aim was to predict the response of the experimental system in any point inside the domain of interest without performing all the corresponding experiments (i.e., virtually, an infinite number of operating conditions. It would then make it possible to determine the regions of acceptable compromise where the system behaviour met the requirements that is to
say, in this particular case, to ensure a reduction of iodine and nitrous acid by hydroxylamine sufficiently fast to be at least as efficient as scrubbing with soda.

The chemical system was regarded as "black box" and only a relation of cause and effect was searched, connecting the variation of some parameters (called factors) and the response(s) of the system which characterise the result(s) obtained according to the pursued objective (Figure 3).

![Diagram of factors and consequences](image)

Fig. 3: Implementation of the experimental research methodology.

The factors taken into account were those which exhibited the strongest effects on the response(s) and they were identified on the basis of screening experiments. The relationship will be the mathematical model; it had only to represent the experimental response(s) in the domain of interest and to give a satisfactory estimate of their values. In most cases, the model is a polynomial the coefficients of which were calculated by carrying out a multilinear regression (least squares method). All calculations and analysis of the results (including variance analysis) are carried out a specific software “Nemrod” (Mathieu and al., 1986).

4.1 First design
4.1.1 Choice of the experimental responses and protocol

Two responses were chosen, noted $Y_1$ and $Y_2$, which corresponded to the reactions duration necessary to reach a 95% decrease in both of the concentrations of nitrous acid and iodine i.e.:

- $Y_1 =$ time such as $[I_2]_{total} = 0.05 [I_2]_0$ where $[I_2]_{total} = [I_2] + [I_i]$;
- $Y_2 =$ time such as $[HNO_2]_{total} = 0.05 [HNO_2]_{total}$ where $[HNO_2]_{total} = [HNO_2]^+ + [NO_2]$.

In practice, it was decided to consider the sum $(Y_1 + Y_2)$ to underscore the region where it was lower than a threshold value $S$ acceptable for the process. For reasons mentioned above, $S$ was fixed equal to 8s, residence time of the gas in the scrubber. From a practical point of view, the monitoring of iodine and nitrous acid concentrations in solution was performed by UV-visible spectrophotometry. The tests were carried out in a thermostated cell (3.8 mL in volume). The reagents, whose temperature was brought beforehand up to that required for the experiment operating conditions and whose pH was adjusted at the desired value with perchloric acid or soda, were introduced into the cell, following sequence:

(i) addition of 1.6 mL of iodine solution;
(ii) addition of 200 μL of sodium nitrite solution;
(iii) addition of 1.8 mL of hydroxylamine solution.
The spectrophotometric acquisition was started immediately after the last addition. Nitrous acid and iodine concentrations were calculated from the absorbance values at 288, 358, 372 and 467 nm by solving a linear equations system whose matrix form is:

\[
\begin{pmatrix}
A_{288} \\
A_{358} \\
A_{372} \\
A_{467}
\end{pmatrix} = \begin{pmatrix}
95 & 36200 & 7 & 13 \\
20 & 23784 & 56 & 25 \\
38 & 17740 & 57 & 18 \\
729 & 729 & 0 & 0
\end{pmatrix}\begin{pmatrix}
[I_2] \\
[I_3] \\
[HNO_2] \\
[NO_2^-]
\end{pmatrix}
\]

\[Y_1\] and \[Y_2\] are deduced from the plots of iodine and nitrous acid concentrations versus to time.

4.1.2 Choice of factors and experimental domain

Four factors were selected: pH, temperature, ratio of the initial concentration of nitrous acid to the initial one of iodine \([HNO_2]/[I_2]_0\) and ratio of the initial concentration of hydroxylamine to the initial one of nitrous acid \([NHOH^+]/[HNO_2]_0\). The lack of knowledge about the concentrations of nitrogen oxides in dissolution off-gas and its possible fluctuation with time made it useful to introduce as an additional factor, the initial concentration of nitrous acid. The initial concentration of hydroxylamine was related to that of nitrous acid (and not to that of iodine) in order to guarantee an excess of reducing reagent compared with nitrous acid in all the experiments, as it would take place if applied to reprocessing. The ionic strength was not included in the weighed up factors since it had relatively little influence on the kinetics when it was higher than 0.2 mol.L\(^{-1}\); moreover, its adjustment by salt addition was not realistic from an industrial point of view. The domains of interest for each factor are summarised in Table 2.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Experimental domain</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1-5</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 - 40°C</td>
</tr>
<tr>
<td>([HNO_2]/[I_2]_0)</td>
<td>4 - 200</td>
</tr>
<tr>
<td>([NHOH^+]/[I_2]_0)</td>
<td>2 - 20</td>
</tr>
</tbody>
</table>

Table 2: Experimental domain of interest.

They were inferred from the expected concentrations in the process but they were also conditioned by the experimental protocol. In all the tests carried out, iodine concentration was equal to 5.10\(^{-4}\) mol.L\(^{-1}\) (i.e. about four times lower than the solubility in aqueous solution at 25°C). The lowest initial concentration of nitrous acid \((2.10^3 \text{ mol.L}^{-1})\) was imposed by the limit of quantisation of the analytical method. Impossibility of carrying out a spectrophotometric monitoring when strong gas production \((\text{N}_2\text{O})\) led also to a limitation of the excess of nitrous acid compared to iodine to about 200 times, whereas it can reach 300 in the process.

In order to enable a comparison of the factors effects which were not expressed in the same unit, they had to be converted in coded variables defined as:

\[
x_j = \frac{U_j - U^0}{\Delta U_j}
\]

where \(x_j\) = value of the coded variable \(J\)
\( U_j = \text{value of the original variable J} \)
\( U_j^o = \text{value of the original variable for the center of the domain} \)
\( \Delta U_j = \text{variation step (variation of the original variable J associated with a one unit variation of the corresponding coded variable)} \)

### 4.1.3 Choice of model and experimental matrix

A second degree polynomial was postulated because of its simplicity and aptitude to describe responses with extrema:

\[
Y = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ij} X_i^2 + \sum_{i=2}^{4} \sum_{j=1}^{i-1} \beta_{ij} X_i X_j + \varepsilon
\]

\( X_i = \text{factors} \quad Y = \text{response} \quad \beta_i = \text{coefficient} \quad \varepsilon = \text{experimental error} \)

A regular Doehlert’s network was chosen (Doehlert, 1970) because of its high versatility. The number N of experiments to be performed for k factors, is: \( k^2 + k + 1 \); thus, in the present case, 21 experiments were necessary (4 factors).

### 4.1.4 Experimental design and results

The experiments performed and the results obtained are presented in Table 3.

<table>
<thead>
<tr>
<th>Essay n°</th>
<th>pH</th>
<th>[HNO₃]₀/µL</th>
<th>[NH₃OH]₀/µL</th>
<th>[HNO₂]₀/µL</th>
<th>T (°C)</th>
<th>( Y_1 ) (s)</th>
<th>( Y_2 ) (s)</th>
<th>( Y_1 + Y_2 ) (s)</th>
<th>log ( Y_1 + Y_2 )</th>
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</table>

The measures in the center of the domain was repeated 5 times in order to estimate the experimental variance.
It should be noted that $Y_2$ was equal to zero in most of the experiments: the reduction of iodine was generally almost immediate, except for some tests carried out at pH 1 or 2. The response $Y_1$ (19800 s) obtained for test 1, stood out, all the other measured values being lower than 365 s, in fact, the reduction of nitrous acid by hydroxylamine was very slow at pH 5. Varying to a large extent, the sum of the responses $Y_1+Y_2$ was poorly described by a polynomial model and, afterwards, the logarithm of $(Y_1+Y_2)$ was used; finally, the model was found to be:

$$
\log (Y_1+Y_2) = 1.5657 + 1.1911 \text{PH} - 0.6135 \text{HNO}_2 - 0.3533 \text{HA} - 0.4364 \text{TEMP} \\
+ 1.2727 \text{PH}^2 - 0.0442 \text{HNO}_2^2 + 0.0834 \text{HA}^2 - 0.2665 \text{TEMP}^2 \\
+ 0.7815 \text{PH}\times\text{HNO}_2 + 0.7782 \text{PH}\times\text{HA} - 0.4480 \text{HNO}_2\times\text{HA} \\
- 0.1287 \text{PH}\times\text{TEMP} - 0.5072 \text{HNO}_2\times\text{TEMP} - 0.2492 \text{HA}\times\text{TEMP} 
$$

standard deviation of the estimate : 0.0129
$R^2$ : 0.9753

where PH, HNO$_2$, HA and TEMP were the coded variables respectively corresponding to the original ones, pH, [HNO$_2$]$_0$/[I$_2$]$_0$, $[\text{NH}_3\text{OH}^+]$$_0$/[HNO$_2$]$_0$, T with the following relations:

$$
\text{PH} = \frac{\text{pH} - 3}{2} \\
\text{HNO}_2 = \left[\frac{[\text{HNO}_2]_0}{[\text{I}_2]_0}\right] - 102 * 0.866 \\
\text{HA} = \frac{[\text{NH}_3\text{OH}^+]_0/[\text{HNO}_2]_0}{9} - 11 * 0.816 \\
\text{TEMP} = \frac{T - 30}{10} * 0.791 
$$

Unfortunately, the test of validity of the model was not satisfied probably because the domain of interest was too large. This is confirmed by the examination of the residues

4.1.5 Conclusion of the first design

The examination of the experimental results revealed that the lowest responses values were all obtained when the initial pH of the solution was lower than 4, indicating that the optimum was located in the pH range 1-3. So, it was decided to design a second experimental matrix within this restricted domain for the pH. In order to limit as much as possible the number of new experiments by using again some of those performed previously, the algorithm of Fedorov was implemented.

4.2 Second design
4.2.1 Matrix elements and model

The response and factors were unchanged just as their variation ranges except the pH one (between 1 and 3), the relation connecting the original and coded variable becoming: $\text{PH} = (\text{pH} - 2)$. The postulated model was again a polynomial of the second degree. Experiments carried out at pH 1, 2 or 3 in the design according to Doehlert were preserved. Two additional tests, initially performed to validate the model, were added to the list. The algorithm of Fedorov (1972) makes it possible to “repair” the experimental matrix while adding to the preserved points, new points judiciously selected among a list of candidates; this procedure enabled to recreate missing information while keeping the qualities of the matrix. The
candidates points were those of a complete factorial matrix $3^4$ which was adapted to the spherical domain of the Doehlert's network. The starting point was a matrix made up of:
- the 18 preserved experiments of the initial Doehlert's matrix;
- the 2 additional experiments carried out for the validation of the first model;
- at least 2 experiments taken at random among the candidates points.

The new points were retained according to the quality of the matrix they completed. This quality is measured with a battery of complexes mathematical criteria, the details of which are out of the scope of this paper, and resulting in a global efficiency coefficient $G$ making it possible to select an optimal matrix.

The procedure was repeated for 22 experiments (i.e. two additional tests), then 23, 24, and up to 35 experiments; the matrix of 33 experiments represented a good compromise between the number of additional tests to be performed and the overall performance of the experimental design.

### 4.2.2 Experimental design and results

The new experimental design and the results obtained are summarized in Table 4. To the 33 experiments were added 5 additional tests carried out in the center of the new experimental domain.

It should be noted that the experiments carried out with a ratio $[\text{HNO}_2]/[\text{I}_2]$ equal to 4 (tests n° 30, 32, 48, 83, 85) led to a response $Y_1$ much higher than the other results obtained. Thus, to obtain a model which described at best the system in the area where the optimum is expected to be located, those five tests were not taken into account for the estimate of the coefficients of the model. Of course, it was checked that, in spite of this suppression, the experimental matrix kept satisfactory qualities ($G = 51\%$).

As mentioned before, the estimates of the polynomial coefficients were obtained by a multilinear regression:

$$
\log (Y_1+Y_2) = 0.9008 - 0.0581 \text{PH} - 0.9971 \text{HNO}_2 - 0.7241 \text{HA} - 0.4090 \text{TEMP} + 0.6332 \text{PH}^2 + 0.5551 \text{HNO}_2^2 + 0.4711 \text{HA}^2 - 0.0873 \text{TEMP}^2 + 0.3342 \text{PH}*\text{HNO}_2 + 0.2385 \text{PH}*\text{HA} + 0.1410 \text{HNO}_2*\text{HA} - 0.0319 \text{PH}*\text{TEMP} - 0.0940 \text{HNO}_2*\text{TEMP} + 0.0683 \text{HA}*\text{TEMP}
$$

standard deviation of the estimate: 0.0144  
$R^2$: 0.9743

Even if the test of validity of the model was still not satisfied, the discrepancies compared with the first model were reduced to a large extent. Moreover, since, roughly, this test indicated whether the difference between experimental and computed values of the response was ascribed only to the experimental error or not, the latter must be considered: in the present case, it was extremely small because of the experimental protocol (very good repeatability) so that the conditions required to pass the test were very restrictive. Otherwise, the examination of the residues showed that, unlike the first model, they were all uniformly distributed and smaller than in the first case; besides, when the response was lower than 10 s, the residues were all lower than 1 s.
### Table 4: New experimental design.

<table>
<thead>
<tr>
<th>Test n°</th>
<th>pH</th>
<th>pH [HNO₂]/[H₂O₂]</th>
<th>pH [NH₃OH⁺]/[HNO₂]</th>
<th>T (°C)</th>
<th>Y₁(s)</th>
<th>Y₂(s)</th>
<th>Y₁+Y₂(s)</th>
<th>log (Y₁+Y₂)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>102</td>
<td>11</td>
<td>30</td>
<td>13</td>
<td>11</td>
<td>24</td>
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<td>4</td>
<td>2</td>
<td>4</td>
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<td>30</td>
<td>175</td>
<td>57</td>
<td>232</td>
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<td>9</td>
<td>0,954</td>
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<tr>
<td>110</td>
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<td>11</td>
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<td>0</td>
<td>6,6</td>
<td>0,820</td>
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<tr>
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<td>102</td>
<td>11</td>
<td>30</td>
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<td>0</td>
<td>6,9</td>
<td>0,839</td>
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<td>102</td>
<td>11</td>
<td>30</td>
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<td>0</td>
<td>6,9</td>
<td>0,839</td>
</tr>
<tr>
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<td>102</td>
<td>11</td>
<td>30</td>
<td>6,6</td>
<td>0</td>
<td>6,6</td>
<td>0,820</td>
</tr>
<tr>
<td>114</td>
<td>2</td>
<td>102</td>
<td>11</td>
<td>30</td>
<td>7,2</td>
<td>0</td>
<td>7,2</td>
<td>0,857</td>
</tr>
</tbody>
</table>

- Preserved experiments of the first design
- Validation experiments for the first model
- Additional experiments according to the algorithm of Fedorov
- Tests in the centre of the new domain

### 4.2.3 Conclusion of the second design

The objective was not to predict the value of the response in any point of the domain of interest with an accuracy as high as possible, but only to determine the areas where the response was lower than a threshold value ensuring a sufficiently fast reduction of I₂ and HNO₂; this latter value was set at 8 s. From this point of view, the second model is quite
satisfactory as it is exemplified in table 5 which compares the values of experimental and calculated responses for 2 tests in the domain of interest.

Table 5: Comparison, for two tests, of the values of response determined experimentally and calculated with the model.

<table>
<thead>
<tr>
<th>test no</th>
<th>PH</th>
<th>[HNO₂]₀/[I₂]₀</th>
<th>[NH₃OH⁺]₀/[HNO₂]₀</th>
<th>T (°C)</th>
<th>Y₁ (s)</th>
<th>Y₂ (s)</th>
<th>Y₁+Y₂ (s) experimental</th>
<th>Y₁+Y₂ (s) Calculated</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2</td>
<td>200</td>
<td>10.2</td>
<td>25</td>
<td>4.6</td>
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<td>4.6</td>
<td>4.8</td>
</tr>
<tr>
<td>27</td>
<td>1.75</td>
<td>200</td>
<td>9</td>
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<td>5.1</td>
<td>0</td>
<td>5.1</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Thus this model was used to locate the acceptable area of compromise.

4.3. Exploitation of the model
4.3.1 Response surfaces curvature study

Three of the factors are fixed at their value corresponding to the centre of the domain (cross-section of the response surface). The effect on the response of a variation of the fourth factor over its range was illustrated on Figure 4. We thus used in the continuation model (E-VII-8) to seek the acceptable zone of compromise.

![Curvature study](image)

Fig. 4: Curvature study.

It can be noticed that:
- An increase in the ratios [HNO₂]₀/[I₂]₀ and [NH₃OH⁺]₀/[HNO₂]₀, like an increase in temperature, led the response to decrease, i.e. to accelerate the reduction of iodine and nitrous acid. However, the decrease was very small when the ratios above mentioned were higher than 0.5 in coded values i.e. 150 and 15 for the original ones.
An increase in the pH involved first a reduction then an increase in the response. The optimal value was close to 2. The effect of the pH and temperature on the response were in good agreement with the conclusions of the kinetics study (Table 1). Likewise, it appeared too that the increase in the concentration of hydroxylamine accelerated the reactions of reduction of iodine and nitrous acid. On another hand, the little effect of high hydroxylamine concentrations on the reaction rates cannot be explained from the kinetics rate laws, established for smaller reducing reagent concentrations. This discrepancy highlighted the existence of a limiting factor other than the concentration of hydroxylamine; however, whether it was due to the reaction mechanism or to an experimental artefact, it did not affect the feasibility of the method since it happened for response much lower than the threshold value. Otherwise, the role of the nitrous acid was, as for it, more difficult to predict it was involved in two reaction schemes which had antagonistic effects on the response: nitrosation of hydroxylamine and oxidation of the iodide ions.

### 4.3.2 Graphic determination of the optimal path

The plot of the optimal path (Myers, 1971) and (Box and al., 1987) made it possible to display the variations which the factors had to undergo in order to minimize the response as quickly as possible (Figure 5). To increase the factors $\frac{[\text{HNO}_2]_0}{[\text{I}_2]_0}$, $\frac{[\text{NH}_2\text{OH}]_0}{[\text{HNO}_2]_0}$ and Temperature compared to their values in the center of the domain was an efficient way or, on the contrary, to decrease the pH, this latter factor having however little influence. The optimal values of these four variables are collected in Table 6. Under these operating conditions, 95% of iodine and nitrous acid initially present were reduced within about one second.

#### Table 6: Values of the variables which minimize the response.

<table>
<thead>
<tr>
<th>Factor</th>
<th>pH</th>
<th>$\frac{[\text{HNO}_2]_0}{[\text{I}_2]_0}$</th>
<th>$\frac{[\text{NH}_2\text{OH}]_0}{[\text{HNO}_2]_0}$</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal Value</td>
<td>1.9</td>
<td>158</td>
<td>15</td>
<td>37°C</td>
</tr>
</tbody>
</table>

**Fig. 5:** Graphic study of the optimal path to minimize the response.
Table 7: Determination of the area in the experimental domain where $Y_1 + Y_2 < 8$ using isoresponse plots.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Fixed Factors</th>
<th>Figure</th>
<th>Comments</th>
<th>Area of interest ($Y_1 + Y_2 &lt; 8$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>$[\text{HNO}_2]/[\text{I}_2]=200$</td>
<td>9-a</td>
<td>- To increase the ratio $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$ in the range 2-15 without pH variation enabled to decrease the response. On the contrary, when the ratio was larger than 15, the response was quite constant. - When the ratio $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$ is set, a pH variation in the range 1.5-2.5 had little effect on the response.</td>
<td>Delimited by curve n°4 examples: * pH 2 [ \Rightarrow [\text{NH}_2\text{OH}^+]/[\text{HNO}_2] &gt; 7.5 ] * $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2] = 15$ [ \Rightarrow \text{pH} \leq 2.6 ]</td>
</tr>
<tr>
<td>$[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$</td>
<td>pH = 2</td>
<td>9-b</td>
<td>- To increase the ratio $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$ in the range 2-15 for a fixed value of $[\text{HNO}_2]/[\text{I}_2]$, enabled to decrease the response. On the contrary, when the ratio was larger than 15, the response decreased very much slowly. - To increase the ratio $[\text{HNO}_2]/[\text{I}_2]$ in the range 4-150 at $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$ constant, enabled to decrease the response. When the ratio is larger than 150, the response did not vary noticeably.</td>
<td>Delimited by curve n°5 examples: [ [\text{NH}_2\text{OH}^+]/[\text{HNO}_2] = 15 \Rightarrow [\text{HNO}_2]/[\text{I}_2] &gt; 95 ]</td>
</tr>
<tr>
<td>$[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$</td>
<td>$[\text{HNO}_2]/[\text{I}_2]=200$</td>
<td>9-c</td>
<td>- To increase the ratio $[\text{NH}_2\text{OH}^+]/[\text{HNO}_2]$ in the range 2-15 for a fixed temperature, enabled to decrease the response. On the contrary, when the ratio was larger than 15, the response did not vary noticeably. - To increase temperature in the range 20-40°C enabled to decrease the response.</td>
<td>Delimited by curve n°5 examples: * T = 25°C [ \Rightarrow [\text{NH}_2\text{OH}^+]/[\text{HNO}<em>2]</em>{\text{min}} = 7.5 ] * T = 35°C [ \Rightarrow [\text{NH}_2\text{OH}^+]/[\text{HNO}<em>2]</em>{\text{min}} = 5.3 ]</td>
</tr>
</tbody>
</table>
4.3.3 Study of the isoreponse plots

The plots of isoreponse (obtained by joining the points where the calculated response had the same value) was used to locate the areas of the domain where the reduction of 95% of iodine and nitrous acid was achieved in less than 8 s. Figure 6 exemplified a cross-section of isoreponse curves with two fixed variables. The cases where the temperature was equal to 25°C and the ratio [HNO₂]₀/[I₂]₀ equal to 200 was particularly interesting because these conditions were close to those which could be met in reprocessing (oxides of nitrogen in large excess compared to iodine, scrubbing carried out at ambient temperature). The results, which correspond to the shaded areas in Figure 6, are summed up in Table 7.

4.3.4 Conclusion of the model exploitation

The empirical study showed that hydroxylamine was able to reduce simultaneously and quickly iodine and nitrous acid in acidic solution. Thus, if the initial concentration of iodine was equal to 5.10⁻⁴ mol.L⁻¹, the ratio [HNO₂]₀/[I₂]₀ to 200, the ratio [NH₃OH⁺]₀/[HNO₂]₀ to 11 and the temperature to 25°C, only 4 s were needed to reduce 95% of iodine and nitrous acid initially present. The conditions that had to be checked by pH, hydroxylamine concentration, temperature and concentration are not too much restrictive (Table 8), which was crucial to enable an industrial application. The optimal pH was equal to 1.9, but fluctuations in the range 1-3 modified in moderation the response Y₁+Y₂ since the nitrous acid was in large excess compared to iodine (it would be the case in the process). In the same way, a variation of the ratio [HNO₂]₀/[I₂]₀ in the range 150-200 did not affect significantly the response. These results also indicated that it was useless to choose a ratio [NH₃OH⁺]₀/[HNO₂]₀ very much higher than 15, because the increase in the excess of hydroxylamine beyond this value allowed only a small acceleration of the reactions of reduction. Lastly, the increase in temperature was a mean to decrease the hydroxylamine concentration to be used. Thus, when the initial concentrations of iodine, nitrous acid and protons were respectively equal 5.10⁻⁴, 10⁻¹ and 10⁻² mol.L⁻¹, the lowest concentration of hydroxylamine which ensured the reduction within less than 8s of 95% of iodine and nitrius acid was equal to 0.75 mol.L⁻¹ at 25°C and 0.53 mol.L⁻¹ at 35°C.

**Table 8:** Influence of a fluctuation of pH, [HNO₂]₀/[I₂]₀ and [NH₃OH⁺]₀/[HNO₂]₀ on the response Y₁+Y₂.

<table>
<thead>
<tr>
<th>Reference</th>
<th>pH</th>
<th>[HNO₂]₀/[I₂]₀</th>
<th>[NH₃OH⁺]₀/[HNO₂]₀</th>
<th>Temperature (°C)</th>
<th>Y₁+Y₂ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH fluctuation</td>
<td>1.9</td>
<td>200</td>
<td>15</td>
<td>25</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>200</td>
<td>15</td>
<td>25</td>
<td>5.9</td>
</tr>
<tr>
<td>[HNO₂]₀/[I₂]₀ fluctuation</td>
<td>1.9</td>
<td>150</td>
<td>15</td>
<td>25</td>
<td>3.5</td>
</tr>
<tr>
<td>[NH₃OH⁺]₀/[HNO₂]₀ fluctuation</td>
<td>1.9</td>
<td>200</td>
<td>20</td>
<td>25</td>
<td>2.7</td>
</tr>
</tbody>
</table>

5. GENERAL CONCLUSION OF THE MODELLING

Two models of the reaction system I₂/T/HNO₂/NHOH⁺ were proposed. The first one, based on the rate laws of these three reactions, described well the experiment if the temperature was 25°C and the pH equal to or higher than 2. The kinetics laws for the reactions I₂/NH₃OH⁺ and HNO₂/NH₃OH⁺ which were established under these operating conditions were thus consolidated. However, the use of this model was limited by the narrowness of its validity domain. The second model, established on a wider experimental
Fig. 6: Use of isoresponse plot to locate the areas of the experimental domain where $Y_1+Y_2<8s$. 
domain, was an empirical one: it was a polynomial of the second degree whose coefficients were estimated from two optimised experiment matrices: the first of Doelherts’ network type and the second based on a factorial design and built using the algorithm of Fedorov. This model was used to determine the conditions favourable to a fast reduction of iodine and nitrous acid. Taking into account technique and economical constraints which led to operate at a temperature close to the ambient one, a pH close to 2, an hydroxylamine excess over nitrous acid equal to 15 represent a good compromise if the ratio $[\text{HNO}_2]/[\text{I}_2]$ was higher than 150. In addition, this operating point was relatively robust. The concentrations used in this work did not match exactly those which could be met in the process. Particularly, because of analytical procedure, the excess of nitrous acid compared to iodine had to be limited to 200 and the problem of extrapolation to higher values remained. This work was carried out directly in solution; the kinetics results obtained (time to reduce 95% of iodine and nitrous acid) were obviously not immediately transposable to the process. However, they showed that hydroxylamine could reduce simultaneously and quickly nitrous acid and iodine under conditions of concentration, acidity and temperature acceptable. The feasibility being acquired, the study is going to be continued by adopting an experimental configuration more representative of the process (continuous scrubbing in a column on a scale of 1/500, taking into account gas-liquide transfer).

6. APPLICABILITY OF HYDROXYLAMINE TO IODINE TRAPPING DURING SEVERE ACCIDENT MANAGEMENT

In the field of nuclear reactor safety and just as in the reprocessing one, hydroxylamine, instead of soda, could be of interest for iodine removal and NOx reduction in the containment during severe accident management.

6.1 Chemical reactions

As a reductant, hydroxylamine could help to keep iodine in the sump as iodide and thus to prevent formation of higher oxidation degree species and volatile compounds, even if the sump becomes acidic with pH as little as 1. In principle, hydroxylamine could be used in two ways: injected directly in the sump and/or in the sprayed solution in order to scrub the gaseous phase. It must be born in mind that soda just trap iodine by a disproportionation reaction into iodide and iodate and that, in acidic solution, the reverse reaction takes place (known as Dushman reaction): $\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \leftrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$, $K \approx 10^{47}$ at 25°C.

Concerning NOx, NO2 in the gas phase and nitrous acid (HNO2) in an acidic sump will be reduced into inert nitrogen protoxide (N2O) inhibiting the formation of these corrosive and oxidizing species; the reaction with soda just yields nitrite ion which give rise again to HNO2 and NOx if the sump becomes acidic.

Otherwise, hydrogen peroxide (H2O2) is gently reduced by hydroxylamine into nitrate (NO3-) when pH is lower than about 5.

Moreover, with pH up to 8 approximately, hydroxylamine and silver are not mutually exclusive to maintain iodine into aqueous solution.

Finally, maybe hydroxylamine would be also useful to reduce the volatile species RuO4 into RuO2 preventing Ru discharge outside the containment; however that may be, because of the lack of data about this problem, it will not be discussed here.
This new application of hydroxylamine is discussed below, stressing on the established knowledge and on that which must be enhanced to answer the question: is it possible to maximize the kinetics of reactions (1) and (2) (iodine and nitrous acid reduction by hydroxylamine; see above § 2) while minimizing reaction (3) (iodide ions oxidation by nitrous acid) under severe accident conditions just as it is for gas scrubbing in reprocessing? For the two cases, the easily adjustable parameters to control the kinetics of these 3 reactions are: pH and initial concentration of hydroxylamine \([\text{NH}_2\text{OH}^+\] \). Temperature can not be exactly controlled.

6.2 Comparison of the conditions met in the two cases: reprocessing and severe accident management

To replace soda by hydroxylamine to trap iodine in reactor containment during severe accident management is proposed on the basis of similarities between the physicochemical system met in such conditions and the one corresponding to dissolution off-gas scrubbing in nuclear spent fuel reprocessing, the latter case being studied extensively above. The similarities lie mainly on the qualitative composition of the atmosphere and aqueous solution but there are also some differences.

6.2.1 Composition and pH

In the sump, the large number of species resulting from the fuel and radiolysis leads to a very complex composition that is not easy to predict; from an initial basis of air (nitrogen and oxygen), water and hydrogen, the main reactive species in the gaseous phase are oxidizing (except hydrogen): nitrogen oxides, ozone, hydrogen peroxide, nitric acid, iodine compounds. On the quantitative point of view, to make clear a composition representative of the atmosphere is very difficult since, under radiation and because the high reactivity of the species involved, it is continuously altered and depends on the accidental sequence considered.

In the two cases, the concentrations differ to a large extent, particularly those of nitrogen oxides which are probably lower by far (about likely two orders of magnitude) than those met in reprocessing (about 3000 ppm in volume). Concerning iodine, the differences are probably much lower since:
- in solution, iodine concentration is lower than \(5 \times 10^{-5} \text{ mol.L}^{-1}\) in the sump while it ranges from \(10^{-3}\) to \(10^{-3} \text{ mol.L}^{-1}\) for dissolution off-gas scrubbing;
- in the gas phase, the concentration is a few ppm in volume while the order of magnitude at the scrubber inlet is about 10 ppm in volume.

The pH in the sump can range from 5 (acidic sump) to 9 (basic sump) according to the considered hypothesis while, for the scrubbing solution in reprocessing, it can be fitted more or less easily.

6.2.2. Temperature

The temperatures are quite different: less than 40°C in dissolution off-gas scrubbing and ranging potentially from 90 to 130°C during severe reactor accident in the sump; the walls and gaseous phase are at lower temperature than the sump, probably below 110°C. However, regardless of whether hydroxylamine is injected directly in the sump or in the

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sprayed solution, an increase in temperature is beneficial in terms of kinetics since the reactions are heat activated. Regarding organic iodine compounds, such an increase in temperature could modify dramatically the situation. Indeed, if the reaction is too slow to be taken into account during gas scrubbing at 25°C in reprocessing, on the other hand, around 100°C in case of severe reactor accident, the reaction rate rises by 500 (according to Arrhenius law; activation energy: 77.0 ± 9.7 kJ.mol⁻¹). In such conditions, the methyl iodide half life (initial concentrations: about 10⁻⁴ mol.L⁻¹ for CH₃I and 1 mol.L⁻¹ for hydroxylamine) would be only 12 s at pH 8; in view of the residence time in the containment, this value seems low enough to consider that iodoalkanes trapping by hydroxylamine is effective.

6.2.3. Hydrodynamics

The interaction between droplets and reactive gaseous components in the spray would be very bad compared to a scrubbing column; so, the gas-liquid transfer would be poor, just as with soda, but it would have no bad influence on the reduction reaction since, a fortiori compared to a column, the limiting step would be the transfer one.

6.2.4 First Conclusions

Considering the conditions and compositions of the sump and gaseous phase, it all looks very promising. According to the information collected above, the concentrations are probably lower than the ones met in dissolution gas scrubbing and, therefore, would require, at the most, the same order of magnitude in reducing reagent concentration that is to say rather diluted solution (lower than 0.1 mol.L⁻¹).

However, two main points which are deciding factors must be examined closely to make sure that none is prohibitive for this application of hydroxylamine; these points are:
- physical and chemical stability of hydroxylamine, i.e. thermal stability (in the range 90-130°C), radiation withstanding, chemical stability (in the pH range 5-9);
- compatibility with containment materials (concrete, steel, paintings, electric cables).

6.3. Stability of hydroxylamine

High temperature and radiation are typical of severe accident management in comparison to reprocessing gas scrubbing performed at about 25°C with a rather low radiation level.

6.3.1 Thermal and chemical stability (Bailar, 1973; Pembridge, 1979; US-DOE, 1998)

These two aspects can not be disconnected. Aqueous solutions of hydroxylamine nitrate (NH₂OH⁺ form used in reprocessing) are stable even at temperature much higher than 100°C under one atmosphere.

In basic aqueous solution, at pH higher than 10, hydroxylamine undergoes a decomposition (disproportionation) of the predominant basic form (NH₂OH) into N₂O, N₂ and NH₃. The reaction rate decreases with pH and nitrogen production prevails in strongly basic medium while nitrous oxide is the main product in more weakly basic solutions. However, diluted solutions are moderately unstable at room temperature; for example:
- from an initial hydroxylamine nitrate concentration of 0.2 mol.L⁻¹ in 0.1 mol.L⁻¹ soda, a loss of about 10% in the content is observed after 26 days and a full destruction within 12 months.
- from an initial hydroxylamine nitrate concentration of 0.153 mol.L\(^{-1}\) at pH 13.5 in soda, a loss of about 18% in the content is observed after 60 days.

This phenomenon is likely negligible in view of the order of magnitude of sequences duration during a severe accident management and the pH range in the sump.

In the same way, diluted nitric solutions of hydroxylamine nitrate are stable at room temperature; for instance, an hydroxylamine nitrate solution with 0.2 mol.L\(^{-1}\) in 0.1 mol.L\(^{-1}\) HNO\(_3\) does not exhibit any decrease in concentration after 2 years. Unlike, hydroxylamine nitrate is oxidized, through a complex autocatalytic mechanism, by concentrated nitric acid into nitrous acid which is reduced fairly rapidly by hydroxylamine nitrate into mainly nitrous oxide (with possibly nitrogen), the overall reaction being:

\[
4 \text{NH}_3\text{OH}^+, \text{NO}_3^- \rightarrow 3 \text{N}_2\text{O}↑ + 7 \text{H}_2\text{O} + 2 \text{HNO}_3,
\]

the rapid emission of large amounts of these two gaseous products can make the reaction explosive. The addition of a nitrous acid scavenger, like sulfamic acid, totally inhibits the reaction.

In fact, for hydroxylamine nitrate concentration lower than 10\(^{-2}\) mol.L\(^{-1}\), this reaction occurs only if the nitric acid one is higher than about 2.5 mol.L\(^{-1}\).

Hydroxylamine nitrate is typically purchased commercially and shipped as a solution up to 8 mol.L\(^{-1}\) (1.9 mol.L\(^{-1}\) for the use in spent fuel reprocessing); the pure solution, as purchased, is stable and can be stored indefinitely. In general, accidents involving hydroxylamine nitrate in nitric acid solutions are caused by inadvertent concentration of the chemical constituents through heating or natural evaporation, by addition of concentrated nitric acid, or through the action of catalyst as Fe\(^{3+}\).

Under reasonable operating conditions and a fortiori if used for reactor accident management, i.e. dilute solutions of pH higher than zero, hydroxylamine is a safe reagent which has the advantage over hydrazine, that it can not be converted into very unstable azide (N\(_3^-\)).

6.3.2 Radiation stability (Gould, 1962; Lefort and al., 1958 and 1961; Tarrago, 1960)

Studies were performed about the radiolysis of hydroxylamine aqueous solutions by gamma radiation (\(^{60}\)Co). At pH between 6 and 7, the main products are, with no air present (under vacuum), NH\(_4^+\), N\(_2\), N\(_2\)O and H\(_2\), while, under air at pH 4.4, they are NH\(_4^+\) and NO\(_3^-\).

Table 9 sums up some results, somewhat disparate, highlighting hydroxylamine sulphate behavior under radiation. The beneficial effect of nitrate in the solution must be noticed: the more nitrate concentration increases, the more hydroxylamine destruction rate is lowered; moreover, nitrate are proof against radiation. Nitrite ion behave towards hydroxylamine like nitrate.

When oxygen bubbles in a hydroxylamine solution during irradiation, the destruction rate is lowered compared to vacuum; under air, this small beneficial effect is mitigated. Anyway, the protective effect of nitrate and nitrite ions is enhanced.

Further investigations will be desirable particularly on hydroxylamine nitrate in diluted nitric acid; however, according to the data described above, it can be reasonably assumed that this medium is not very sensitive to radiolysis.
Table 9: Available data on hydroxylamine radiolysis in aqueous solutions by gamma radiation ($^{60}$Co).

<table>
<thead>
<tr>
<th>[HA]$_0$ (1) (mol.L$^{-1}$)</th>
<th>pH</th>
<th>Under air (Y/N/other)</th>
<th>[NO$_3$]$_0$ (2) (mol.L$^{-1}$)</th>
<th>Absorbed dose (10$^{18}$ eV.cm$^{-2}$)</th>
<th>HA destruction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 10$^{-3}$</td>
<td>6</td>
<td>N</td>
<td>0</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>5.5 10$^{-3}$</td>
<td>4.4</td>
<td>N</td>
<td>0</td>
<td>130</td>
<td>95</td>
</tr>
<tr>
<td>5.5 10$^{-3}$</td>
<td>4.4</td>
<td>N</td>
<td>0</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>N</td>
<td>5 10$^{-4}$</td>
<td>130</td>
<td>80</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>N</td>
<td>5 10$^{-3}$</td>
<td>130</td>
<td>55</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>N</td>
<td>0</td>
<td>20</td>
<td>15 (3)</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>Y</td>
<td>0</td>
<td>130</td>
<td>80</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>O$_2$</td>
<td>0</td>
<td>130</td>
<td>70</td>
</tr>
<tr>
<td>5 10$^{-3}$</td>
<td>4.4</td>
<td>Y</td>
<td>0</td>
<td>20</td>
<td>10 (3)</td>
</tr>
</tbody>
</table>

(1): Initial hydroxylamine concentration
(2): Initial nitrate concentration
(3): Initial nitrite concentration: 4.7 10$^{-4}$ mol.L$^{-1}$

6.4 Compatibility of hydroxylamine with containment materials

The use of hydroxylamine or its alkyl derivatives has been contemplated as corrosion inhibitors because they are O-binding reagents. So, it is a sign of good compatibility with steel (Lasher and al., 1995; Van Der Wissel, 1991) and metallic materials. As regards concrete, our experience with minerals in basic solutions in rather comforting. The same is true for paintings and polymers (electric cables insulators).

7. CONCLUSION

In the reprocessing framework, laboratory experiments have shown that, in acidic medium, hydroxylamine nitrate reduces both iodine into non-volatile iodide and nitrous acid into inert dinitrogen monoxide; moreover, the reactions are fast enough to be compatible with the gas residence time in a counter-current column. The rate controlling parameters were optimized by modeling of the I$_2$/T/HNO$_2$/NH$_3$OH$^+$ reactive system using the Methodology of the Experimental Research.

In the field of nuclear reactor safety, hydroxylamine could help to keep iodine in the sump as iodide, even if it becomes acidic (pH as little as 1). To introduce a reductant in the containment is of interest since this latter is rather oxidizing due to the large amount of water vapor produced in case of LOCA and to the radiolysis leading to oxidants like nitrogen oxides, ozone, hydrogen peroxide, nitric acid, iodine compounds. Together with silver in an acidic solution, hydroxylamine could help to keep iodine in the sump in the form of iodide ion with pH as little as 1 and to prevent formation of higher oxidation degree species and volatile compounds. Moreover, hydroxylamine could permit to get rid of NOx and H$_2$O$_2$ in some extent.

The compatibility of hydroxylamine with the structures in the containment and its behavior in the conditions met during a severe accident are rather promising as for this new
application. However, it would be like necessary to precise some data even they are encouraging:
- thermal stability up to 130°C,
- catalysis of the decomposition by the products resulting from the degradation of the fuel,
- stability under radiation.
That could be achieved by means of a relatively small experiments set.

As for the optimization of the reductant concentration (which could be of about 0.1 mol.L⁻¹), it will probably need to take into account the only known unsettled operating parameters, i.e. pH, hydroxylamine concentration and temperature. In the pH range 5-9, iodine reduction is very fast and nitrous acid destruction did not occur rapidly at room temperature but it could be very different in the range 90-130°C: a pH higher than 5 could be convenient for NOx reduction just as for iodine one. So, the optimization experiments set used for fuel reprocessing could not be transposed directly; it would have to be enlarged to the new temperature and pH ranges, after having decided to reduce or not nitrogen oxides.

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A MODEL TO SIMULATE THE REMOVAL OF CH$_3$I FROM AIRSTREAMS UNDER POST-ACCIDENT CONDITIONS BY CHARCOAL FILTERS

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ABSTRACT

Charcoal filters are installed in the Emergency Filtered Air Discharge System (EFADS) of Ontario Hydro’s multi-unit CANDU stations to minimize the release of airborne radioiodine in the event of a reactor accident. The performance of charcoal filters for removing radioiodine from airstreams has been studied under conditions associated with routine reactor operations, as well as under conditions similar to those expected following an accident. These studies have shown that a 20 cm-deep TEDA-impregnated charcoal filter is very effective in removing organic iodides from flowing air streams. These studies have also led to the development of a new physical model that can predict the time-dependent behaviour of iodine release from TEDA (triethylenediamine)-impregnated charcoal filters under post-accident conditions. This paper describes the charcoal filter model, the experimental studies performed to obtain appropriate values for the parameters used in the model, and the implications and significance of the model for accident simulation and management.

1. INTRODUCTION

Charcoal filters are installed in the Emergency Filtered Air Discharge System (EFADS) of multi-unit CANDU stations to minimize the release of airborne radioiodine in the event of a reactor accident. The charcoal used in the EFADS filters is highly activated, i.e., with a surface area of the order of 1000 m$^2$/g, and impregnated with triethylenediamine (TEDA). The performance of charcoal filters for removing radioiodine from airstreams has been studied extensively under conditions associated with routine reactor operations, as well as under conditions similar to those expected following an accident (Wren, 1991-1, Wren, 1991-2, Wren, 1999-1, Wren, 1999-2). These studies have shown that a 20 cm deep bed of the highly activated TEDA-impregnated charcoal has been shown to be very effective in removing CH$_3$I under postulated accident conditions of the EFADS. A decontamination factor greater than $10^{15}$ has been observed for a 20-cm deep bed of new and aged charcoal, where aged charcoal tested so far was charcoal aged in the EFADS up to 5 years (Wren, 1999-2). These experimental studies have led to the development of a new physical model that can predict the time-dependent behaviour of iodine release from TEDA-impregnated charcoal filters under post-accident conditions. This charcoal
filter model, the experimental studies performed to obtain appropriate values for the parameters used in the model, and the implications and significance of the model for accident simulation and management are presented here. Background information on the EFADS is presented first.

Multi-unit containments

For purposes of the present discussion, the significant features of a multi-unit containment of the CANDU design are the vacuum building and associated systems (used for pressure control within containment in the short term following a pipe break) and the EFADS which is used for pressure control in the longer term. The functions of the EFADS are to maintain containment pressures sub-atmospheric in the long term (after the vacuum reserve has been exhausted), and to provide a defined and monitored venting path for discharge from containment in the long term post-accident period. The general features of the EFAD system are described below.

Brief description of the EFAD system

The components of the EFADS are shown schematically in Figure 1. The EFAD system components are isolated from containment during normal reactor operation by double isolation valves. Aside from forming part of the containment boundary, these valves also protect the EFADS housing (which contains most of the EFAD system components) from the underpressure exerted within containment by the vacuum system when this system is initiated following a break. Without this protection, the EFADS housing would be susceptible to implosion, since it is not intended to withstand low absolute pressures. The primary function of the EFADS housing is shielding.

Within the EFADS housing are located, in the order that they would see flow from containment, the following components: (1) Roughing filter, (2) Demister, (3) Heater, (4) First HEPA filter bank, (5) Charcoal filter bed, (6) Second HEPA filter bank and (7) Blower.

The focus in this paper will be the charcoal filter bed, but other EFADS components have functions that are important for the charcoal. The demister and heater are intended to remove any water aerosols entering the EFADS piping from containment, and to ensure that the relative humidity of the air entering the charcoal bed is at 70% or less. This is necessary because the ability of the charcoal to remove and retain volatile iodine species can be impaired by high humidity conditions. The second HEPA filter downstream of the charcoal beds has the job of ensuring that no charcoal fines are released from the system. The EFAD system incorporates design features to ensure that there is sufficient air flow through the demisters and the charcoal filter to maintain the effectiveness of those components.

In order to quantify the capabilities of the EFAD system at removing volatile species of iodine from an air stream drawn from containment, a versatile model describing the behaviour of iodine species on the filter charcoal is needed. This model, and the theory and data underlying it, will now be described.
Fig. 1. Arrangement of Components in One Train of a Generic Emergency Filtered Air Discharge System (EFADS)
2. THE MODEL

A detailed description of the model has been published (Wren, 1999-1) and only a brief description is given here. The model, developed for the removal and retention of iodine from a flowing air stream by TEDA-impregnated charcoal under reactor accident conditions, is based on a one-dimensional convection-diffusion mass transport equation including adsorption and desorption of CH$_3$I on TEDA charcoal:

\[
\frac{\partial}{\partial t} C(z,t) = - V_L \frac{\partial}{\partial z} C(z,t) + D \frac{\partial^2}{\partial z^2} C(z,t) - \frac{\varepsilon}{\sigma_v} \frac{\partial}{\partial t} W(z,t) \tag{1}
\]

where $C(z,t)$ is the bulk-gas-phase concentration of CH$_3$I at time $t$ and at point $z$ along the depth of the charcoal bed (g/cm$^3$), $V_L(t)$ is the linear flow velocity through the packed bed (cm·s$^{-1}$), $D$ is the diffusion coefficient of CH$_3$I in air (cm$^2$·s$^{-1}$), $\varepsilon$ is the packing density of the charcoal bed (0.5 g·cm$^{-3}$), $\sigma_v$ is the void volume fraction, defined as the gas volume per unit volume of the charcoal bed (0.3), and $W(z,t)$ is the amount of CH$_3$I adsorbed per gram of charcoal at time $t$ and at point $z$ along the length of the charcoal bed (g·g$^{-1}$).

This is essentially a mass balance equation. The first two terms on the right-hand side of Equation (1) represent the changes in the CH$_3$I concentration in the gas phase as a result of convection and diffusion respectively; the last term represents the change that is due to its adsorption and desorption on charcoal. Under the high flow (about $V_L$ of 67 cm·s$^{-1}$) conditions expected in the EFADS following an accident, the diffusion term in Equation (1) can generally be ignored$^1$. Although it is included in our model, the mass balance term that is due to the radioactive decay will not be normally considered in the following discussion for simplification.

To solve the differential equations, the overall adsorption rate, i.e., the third term on the right-hand side of Equation (1), should be defined as a function of $z$, $t$, $C$ and $W$. Formulation of the adsorption-desorption term is where the differences among models generally occur.

The experimental data that are discussed in Sections 3 and 4 support the assumption that the adsorption-desorption of CH$_3$I on TEDA-impregnated charcoal occurs through two distinct adsorption processes; probably through physical adsorption followed by chemisorption on TEDA.

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$^1$ In the following discussion presented in the text, the diffusion term is ignored because its contribution to CH$_3$I behaviour on charcoal is expected to be small under high-flow conditions. However, the computer model includes the diffusion term, as defined in Equation (1). The diffusion coefficient of CH$_3$I in air at room temperature was reported to be $8.7 \times 10^{-2}$ cm$^2$·s$^{-1}$ (Krzemien, 1978). For the temperature dependence of the diffusion coefficient, it was assumed that it follows the dependence given by the Chapman-Enskog kinetic theory (Bird, 1960), i.e.:

\[
D(T) = 8.7 \times 10^{-2} \cdot \left( \frac{T}{298} \right)^{3/2}
\]
impregnants, with the rate of this chemisorption depending on the concentration of the physically adsorbed CH$_3$I:

$$\text{CH}_3\text{I}(g) \leftrightarrow \text{CH}_3\text{I}(p)$$

$$k_{A,p}$$

$$k_{D,p}$$

$$\text{CH}_3\text{I}(p) + \text{TEDA} \rightarrow \text{CH}_3\text{I}(c) \rightarrow \text{CH}_3\text{I}(g)$$

$$k_{A,c}$$

$$k_{D,c}$$

where g, p and c in parentheses and as subscripts represent gas, physisorbed and chemisorbed phases, and subscripts A and D represent adsorption and desorption respectively.

Desorption of chemisorbed CH$_3$I also appeared to occur because of the decomposition of the quaternary ammonium salts (TEDA-CH$_3$I). Pseudo-first-order decomposition reactions are common for quaternary ammonium salts. A model incorporating the two-step adsorption-desorption process was able to reproduce the asymmetric curves observed for CH$_3$I breakthrough from TEDA-impregnated charcoal beds (the results are presented later). This two-step process is the key difference between this model and other models.

These adsorption and desorption processes are formulated in the rate equations in our model as follows:

$$\frac{\partial W(z, t)}{\partial t} = \frac{\partial}{\partial t} W_p(z, t) + \frac{\partial}{\partial t} W_c(z, t)$$

$$\frac{\partial W_p(z, t)}{\partial t} = k_{A,p} \cdot \frac{\sigma_v}{\epsilon} \cdot C(z, t) \cdot \left(1 - \frac{W_p(z, t)}{W_p^0}\right) - k_{D,p} \cdot W_p(z, t)$$

$$- k_{A,c} \cdot W_p(z, t) \cdot \left(1 - \frac{W_c(z, t)}{W_c^0}\right)$$

$$\frac{\partial W_c(z, t)}{\partial t} = k_{A,c} \cdot W_p(z, t) \cdot \left(1 - \frac{W_c(z, t)}{W_c^0}\right) - k_{D,c} \cdot W_c(z, t)$$

The effects of temperature and relative humidity on the charcoal performance are incorporated in the model through their effects on parameters such as the adsorption capacities, $W_p^0$ and $W_c^0$, the adsorption and desorption rate constants, $k_{A,p}$, $k_{D,p}$, $k_{A,c}$ and $k_{D,c}$, and the diffusion coefficient, D. The present model assumes that the rate constants depend only on temperature, whereas the adsorption capacities depend only on relative humidity. Experiments performed to obtain these parameters are described below.

3. EXPERIMENTS

Experiments were performed to determine the dependence of the adsorption-desorption parameters on temperature and relative humidity. The experiments were designed to obtain these
parameters independently, consisting of four sets of tests: (1) CH$_3$I distribution following a short-term CH$_3$I loading at low concentrations, (2) CH$_3$I release during purging of a previously saturated bed, (3) CH$_3$I migration during long term purging and (4) full CH$_3$I breakthrough curves. The time profiles of the full CH$_3$I breakthrough curves were used to test the validity of the model as a whole.

3.1 Short-Term CH$_3$I Loading at Low Concentrations

Under the conditions of high gas flow velocities that are expected within an EFADS charcoal bed following an accident and also used in our experiments, convection will dominate, so the diffusion term in the mass balance equation can be ignored, and Equation (1) can be simplified to:

$$\frac{\partial}{\partial t}C(z,t) = -V_L\frac{\partial}{\partial z}C(z,t) - \frac{\varepsilon}{\sigma_v} \frac{\partial}{\partial t}W(z,t)$$  \hspace{1cm} (5)

At an early stage of loading when the charcoal surface is not covered extensively with CH$_3$I, the effects of saturation and desorption can be ignored and Equation (3) can be approximated to

$$\frac{\partial}{\partial t}W(z,t) = k_{A,p} \cdot \frac{\sigma_v}{\varepsilon} \cdot C(z,t)$$  \hspace{1cm} (6)

Under these conditions, the mass balance equation yields

$$C(z,t) = C_0 \cdot \exp(-k_{A,p} \cdot \frac{z}{V_L})$$  \hspace{1cm} (7)

$$W(z,t) = k_{A,p} \cdot \frac{\sigma_v}{\varepsilon} \cdot C_0 \cdot t \cdot \exp(-k_{A,p} \cdot \frac{z}{V_L})$$  \hspace{1cm} (8)

Other assumptions used to obtain these solutions are that the incident concentration of CH$_3$I(g) is constant with time, and that $k_{A,p}$ and the linear flow velocity are independent of $z$ and $t$.

According to Equation (7), the concentration of CH$_3$I(g) leaving the charcoal bed of a length $L$, $C(L,t)$, is independent of time, i.e.,

$$C_{eA}(t) = C_0 \cdot \exp(-k_{A,p} \cdot \frac{L}{V_L})$$  \hspace{1cm} (9)

Thus, the CH$_3$I concentration in the effluent would be constant with time during the early stages of loading. Equation (8) shows that, at any given time $t$, the distribution of adsorbed CH$_3$I along the length of the bed is exponential. The slope of a $\ln(W(z,t))$ versus $z$ plot at a given time would thus give the adsorption rate constant, $k_{A,p}$.

Equations (7) and (8) state that the adsorption rate constant, $k_{A,p}$, can be extracted from the measurements of (a) the CH$_3$I release from the charcoal bed or (b) the iodine activity distribution.
along the length of the charcoal bed. (For these experiments, the test conditions must satisfy the assumptions used in deriving the equations.) However, because of the very high adsorption efficiencies of the activated charcoals, the CH$_3$I release from a charcoal bed of any reasonable depth would be extremely small and the uncertainty in the adsorption rate constant determined from method (a) would be large. Many adsorption rate constants for CH$_3$I on activated TEDA charcoal reported in the literature were obtained this way.

In our laboratory, we have determined the adsorption rate constant as a function of temperature from the CH$_3$I distribution measurements (method (b)). To obtain $k_{ads}$ from these measurements, the total amount of CH$_3$I loading should be well below the adsorption capacity of the bed, and the loading should be performed over a short time period. Experimental conditions must also be consistent with the other assumptions used to obtain the equations; i.e., constant C$_0$ and $V_L$.

Experiments to determine the adsorption rate constant as a function of temperature were performed by loading small amounts of CH$_3$I, labelled with $^{131}$I, onto the charcoal bed. This was immediately followed by measurement of the $^{131}$I activity distribution along the depth of the bed using a scanning $\gamma$ detector. The experimental set-up and procedures have been described in detail previously (Wren, 1999-2), and only a brief description is given here. Typically, 3 to 10 mg of methyl iodide was loaded onto a charcoal bed, 5 cm in diameter, 2.5 cm in depth and 28 g in mass, over a 1 h period. During each test, the flow velocity, determined from the volumetric flow rate divided by the cross section of the bed, was kept constant at about 20 cm$\cdot$s$^{-1}$. This is the flow velocity that would be measured in a filter bed housing containing no charcoal, and is hereafter referred to as $V_{MT}$. The corresponding flow through a packed bed, referred to as $V_L$, is ~ 67 cm$\cdot$s$^{-1}$, assuming a void volume fraction of 0.3 for the charcoal bed. The flow was then interrupted, and the radioiodine activity distribution within the bed was measured immediately.

![Graph](image)

**Fig. 2.** The Iodine Activity Distribution Along the Depth of a Charcoal Bed Observed Immediately Following Loading with 0.01 g CH$_3$I. The activities near both ends of the charcoal bed were affected by the viewing volume of the detector.
A typical activity distribution observed in these tests is shown in Figure 2. These experiments were performed at 0% relative humidity and temperatures ranging from 25 to 90°C. The temperature range was chosen to cover the filter conditions following an accident of the EFADS of multi-unit CANDU reactors. The physical adsorption constant observed in this way showed an Arrhenius dependence on temperature. The activation energy for the physical adsorption of CH₃I on a charcoal surface was obtained to be 9 ± 2 kJ·mol⁻¹.

3.2. CH₃I Release During Purging of a Previously Saturated Bed

The rate equations that are applicable to the CH₃I release measurements during purging of a saturated bed can be derived by following steps similar to those given in Section 1. A detailed description of the derivation is not given here due to the limitation of space, but can be found elsewhere (Wren, 1999-1). It can be shown that the exit gas phase CH₃I concentration at an early stage of purging following a saturation can be approximated to (Wren, 1999-1)

\[
C_{\text{ex}}(t) = C_{\text{ex}}(0) \cdot \exp\left(-\left(k_{D,p} + k_{A,c}\right) \cdot t\right) = C_{\text{ex}}(0) \cdot \exp\left(-k_{A,c} \cdot t\right)
\]

for \(k_{A,c} \gg k_{D,p}\), and where \(C_{\text{ex}}(0)\) is the exit CH₃I concentration at \(t = 0\), i.e., at the onset of purging. Thus, the slope of the plot of \(\ln(C_{\text{ex}}(t))\) versus \(t\) observed at an early stage of purging yields the chemical adsorption rate constant, \(k_{A,c}\).

At later stages of purging when all physisorbed CH₃I is long since removed, desorption of chemically adsorbed CH₃I becomes the dominant process, and the exit CH₃I concentration is determined by (Wren, 1999-1)

\[
C_{\text{ex}}(t) = C_{\text{ex}}(0) \cdot \exp\left(-k_{D,c} \cdot (t - t_{p,c})\right)
\]

where \(t_{p,c}\) is the time at which the desorption of chemisorbed species becomes the dominant process. Thus the slope of the plot of \(\ln(C_{\text{ex}}(t))\) versus \(t\) observed at later times during purging would give \(k_{D,c}\).

In the experiments to obtain \(k_{A,c}\) and \(k_{D,c}\), methyl iodide, at a concentration in the range of 2 x 10⁻⁷ and 2 x 10⁻⁶ g·cm⁻³, was loaded onto a charcoal bed, 5 cm in diameter, 2.5 cm in depth and 28 g in mass, over about 7 h, at a linear flow velocity through the packed charcoal bed of 66 ± 7 cm·s⁻¹. The exit CH₃I concentration was measured as a function of time (i.e., CH₃I breakthrough curve, see also Section 3.4 and Section 4). When the exit CH₃I concentration reached the level of the inlet concentration, indicating that the bed was saturated, the loading was stopped but purging with laboratory air without CH₃I was continued. Since high concentrations were used in these experiments, the γ-detection method with ¹³¹I-labelled CH₃I was unnecessary, and an electron-capture detector was used to measure the CH₃I concentration (for detailed description, see Wren, 1999-2). These experiments were performed at 0% relative humidity and temperatures ranging from 25°C to 90°C.
The methyl iodide concentration observed during purging following saturation at 65°C is shown in Figure 3. The log of the exit \( \text{CH}_3\text{I} \) concentration as a function of time during purging shows two distinct slopes. The first slope gives the rate constant of \( k_{\text{A,c}} \), and the second slope gives \( k_{\text{D,c}} \) (see Equations (10) and (11)). These rate constants also followed Arrhenius temperature dependencies. The activation energy for the chemical adsorption of \( \text{CH}_3\text{I} \) on TEDA impregnants on the charcoal surface, \( \Delta E_{\text{A,c}} \), was observed to be 35 ± 5 kJ·mol\(^{-1}\) and the activation energy for the chemical desorption of \( \text{CH}_3\text{I} \), \( \Delta E_{\text{D,c}} \), was 50 ± 5 kJ·mol\(^{-1}\).

![Figure 3: Methyl Iodide Release As a Function of Time During Purging of a Previously Saturated Charcoal Bed at 65°C and 0% Relative Humidity.](image)

3.3. \( \text{CH}_3\text{I} \) Migration During Long-Term Purging

The rate of migration of \( \text{CH}_3\text{I} \) through the charcoal bed during purging following loading of small amounts of \( \text{CH}_3\text{I} \) strongly depends on the relative ratios of the adsorption and desorption rate constants for both physical and chemical processes. Therefore, once \( k_{\text{A,p}} \), \( k_{\text{A,c}} \), and \( k_{\text{D,c}} \) are determined, \( k_{\text{D,p}} \) may be obtained by simulating the \( \text{CH}_3\text{I} \) migration as a function of time during long-term purging, using the charcoal filter model.

For the experimental study, a TEDA-impregnated charcoal bed, 20 cm long and 5 cm in diameter, was pre-conditioned for 16 h at 68% relative humidity and 80°C. The bed was then loaded with 0.32 g of \( \text{CH}_3\text{I} \), labelled with \( ^{131}\text{I} \), for 1 h and then purged with laboratory air for 23 d. The \( V_{\text{MT}} \) during both loading and purging was 20 cm·s\(^{-1}\), which corresponds to \( V_L \) of 67 cm·s\(^{-1}\). The \( ^{131}\text{I} \) activity distribution was measured immediately after the \( \text{CH}_3\text{I} \) loading and periodically during purging. The results are shown in Figure 4. Even at this high temperature and relative humidity, \( \text{CH}_3\text{I} \) migration was observed to be very slow with the \( \text{CH}_3\text{I} \) peak moving only ~ 2 cm downstream over 23 d.
Because migration of CH$_3$I was so slow even at 80°C and even slower at lower temperatures, the data shown in Figure 4 were the only results that provided measurable migration of CH$_3$I. The observed CH$_3$I migration was reproduced using the full model consisting of Equations (1) to (4). The best fit was found with $k_{DP}$ of $5 \times 10^{-5}$ s$^{-1}$. Because data for the temperature dependence of this rate constant could not be obtained, the value obtained at 80°C will be used for other temperatures. The use of this value will underestimate the CH$_3$I removal and retention efficiency of TEDA-impregnated charcoal at lower temperatures.

Fig. 4. Observed Methyl Iodide Profiles for Migration Through a TEDA Charcoal Bed During Long-Term Purging Following a Small CH$_3$I Loading at 80°C and 68% Relative Humidity.

3.4 Breakthrough Curves for Adsorption Capacity

It was assumed that the adsorption capacities, $W_p^\circ$ and $W_c^\circ$, do not depend strongly on temperature. The relative humidity may, however, strongly affect the ideal adsorption capacities since water vapour, once adsorbed, may block pores and reduce the number of available TEDA sites. First, the overall effective adsorption capacity was determined from a breakthrough curve (experiments described in Section 3.2); for example by integrating the shaded area in Figure 5 and using absolute concentration rather than $C_{eq}/C_{in}$. (The relationship between the overall effective capacity and $W_p^\circ$ and $W_c^\circ$ are discussed later.) Experiments to determine the effect of relative humidity on the adsorption capacities for CH$_3$I on TEDA charcoal were performed at 298 K and relative humidities ranging from 0 to 75%. For these measurements, the charcoal bed was exposed typically to high inlet concentrations of CH$_3$I ($3.3 \times 10^6$ g·cm$^{-3}$) for a period of 2 h at a linear flow velocity of 67 cm·s$^{-1}$.

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Fig. 5. Observed CH$_3$I Breakthrough Curve at 50°C and 0% Relative Humidity. The loading concentration was $3.3 \times 10^{-6}$ g cm$^{-3}$. The shaded area shows the amount of CH$_3$I adsorbed upon saturation.

The overall effective adsorption capacity, $W_{\text{eff}}(R_h)$, measured as a function of relative humidity, $R_h$, is shown in Figure 6. The linear decrease in $\ln(W_{\text{eff}}(R_h))$ with $(\ln(R_h/100))^{-1}$ is consistent with a mechanism based on capillary condensation. That is, it is assumed that (1) at a given temperature and relative humidity, pores whose radii are less than $r_k$ will be blocked by condensed water, is determined by the Kelvin equation based on capillary condensation (Thomson, 1881), (2) the cumulative pore volume distribution is an exponential function of the average radius of the pores (a near-exponential distribution has been observed (Chang and Cho, 1985)), and (3) that the number of initially available adsorption sites is directly proportional to the cumulative pore volume not blocked because of capillary condensation. The overall effective adsorption capacity for a given $T$ and $R_h$ is, using these assumptions:

$$W_{\text{eff}}^o(T, R_h) = W_{\text{eff}}^o(T, 0\%) \cdot \exp\left(\frac{9.1}{T \cdot \ln(R_h / 100)}\right) \quad (12)$$

The relationship between $W_p^o$, $W_e^o$ and $W_{\text{eff}}^o$ is not clear. However, it is expected that they have the same relative humidity dependence because of capillary condensation. Therefore, we assumed that $W_p^o$ and $W_e^o$ would have the following dependencies on relative humidity:

$$W_p^o(T, R_h) = W_p^o(T, 0\%) \cdot \exp\left(\frac{9.1}{T \cdot \ln(R_h / 100)}\right) \quad (13)$$

$$W_e^o(T, R_h) = W_e^o(T, 0\%) \cdot \exp\left(\frac{9.1}{T \cdot \ln(R_h / 100)}\right) \quad (14)$$
Fig. 6. Dependence of the Adsorption Capacity on the Relative Humidity.

The adsorption capacities, $W_p^o$ and $W_c^o$, at 0% relative humidity are likely to depend on charcoal aging. At present, we do not have sufficient data to be able to quantify the aging process; we have been building up a data base on the effect of aging and the preliminary results indicate that the aging of charcoal in the EFADS has negligible impact on the adsorption capacity. For $W_p^o$, monolayer coverage with CH$_3$I of the measured BET surface area, 784 m$^2$.g$^{-1}$, is used in the current model. If we assume each CH$_3$I takes up an area of about 20 Å$^2$, then about 0.9 g CH$_3$I per g charcoal is required for monolayer coverage of the charcoal surface. For $W_c^o$, the amount of TEDA on charcoal was assumed to be 3 wt % and each TEDA molecule was assumed to provide two adsorption sites. The adsorption capacity, $W_c^o$, corresponding to 3 wt % TEDA, is 0.076 g CH$_3$I per g charcoal. Initially supplied with 5 wt % TEDA, it was conservatively assumed that non-uniformity of the TEDA impregnation on the charcoal and the aging of charcoal reduces its effective concentration for reaction with CH$_3$I.

4. MODEL SIMULATION

The mass transport model with the parameters determined by the four sets of experiments described above reproduced the time dependent behaviour of full CH$_3$I breakthrough curves very well. An example of the model simulation results is shown in Figure 7. (A better reproduction of the test can be obtained by increasing $W_c^o$.) Note that a very high CH$_3$I loading concentration, several orders of magnitude larger than those expected in the EFADS airstream following an accident, was used to obtain this breakthrough curve. The high loading was used in the
breakthrough measurements only to obtain the curves within reasonable time scales in the laboratories.

The CH$_3$I breakthrough from a TEDA charcoal bed shows an asymmetrical curve, supporting the assumption of a two-step adsorption-desorption mechanism. A one-step adsorption and desorption mechanism produces a symmetric breakthrough curve. The model, with the given uncertainties assigned to the parameters, is applicable in a temperature range of 25 to 150°C and a relative humidity range of 0 to 80%, and an CH$_3$I concentration range of 10$^{-9}$ to 10$^{-3}$ g·cm$^{-3}$. The model may be applicable outside these ranges, however, the uncertainties outside these ranges have not been established.

![Methyl Iodide Breakthrough Curve](image)

**Fig. 7.** Methyl Iodide Breakthrough Curve for a TEDA Charcoal Bed at 80°C and 0% relative humidity: (a) Circles, Experimental Data; and (b) Solid Line, Calculated Results. The loading concentration was 1 x 10$^{-6}$ g·cm$^{-3}$.

For radioactive isotopes, the mass balance and the adsorption-desorption equations contain the radioactive decay terms. All other physical properties, such as the adsorption and desorption rate coefficients, should be the same for all iodine isotopes. It is possible that the adsorption capacity of charcoal for CH$_3$I may be affected by the daughter products of iodine and may strongly depend on their adsorption characteristics. However, without data, this effect has been ignored. Also omitted from the model for the same reason is the effect of charcoal aging on the adsorption-desorption behaviour.
The model described in Sections 2 to 4 above has replaced an earlier model of the charcoal filter. The differences between these two models are described very briefly in the next section.

5. CHANGE FROM EARLIER MODEL

The earlier filter model was conceptually similar to a "stirred tank". In that earlier model, gaseous iodine species entering the filter with the air flow were removed from that air flow according to a given removal fraction or "trapping efficiency". This trapping efficiency was one of the primary user inputs which defined filter characteristics. Once removed from the air flow, iodine species were retained on the filter in an unspecified way, and there was no simulation of the spatial distribution of iodine within the volume of the filter material. Once iodine was removed from the air flow, it was simply retained within the volume of the charcoal.

Iodine species that had been removed from the air flow and were resident on the filter were subject to release from the filter by desorption. Desorption was dealt with by means of a rate constant, so that within each time interval a fixed fraction of the total amount of iodine on the filter was released. The numerical value of the desorption rate constant had to be determined by the analyst, depending on the specific EFADS design and the depth of the filter bed. A typical desorption rate constant was 1% per day.

These two parameters, trapping efficiency and desorption rate constant, constituted the user-defined portion of this filter model. No other user inputs were required. Each of the parameters could be varied at the beginning of a time period, but was then fixed for the length of that time period. The length of the time periods could be set arbitrarily by the user, and the length of any time period was not necessarily dependent on the length of any other time period. The ranges of both parameters had maximum and minimum values of 1.0 and 0.0 respectively, but too large values for the desorption rate constant could cause the code (in which the model was a component) to terminate the run on a convergence error.

In contrast, the new filter model (the version that includes all features) calculates iodine species removal from the airstream as a function of distance from the upstream face of the filter, and maintains a profile of iodine species concentration as a function of distance from the upstream face. Apart from filter bypass, there is no user input dictating iodine removal from the air stream, since this is calculated by the model. (No real filter is perfectly sealed, and some small amount of bypass leakage occurs. The maximum amount of bypass is a design characteristic and confirmation that bypass remains below this maximum is obtained by regular safety system tests.) Similarly, specifying the gross release of the iodine trapped on the filter is also taken out of the user's hands. The concentration profile of iodine species along the flow direction in the filter bed is similar to the chromatographic function. The model simulates the change in shape of this profile as a function of time. The practical end result is that there is virtually no desorption of iodine species from a deep (20 cm) filter bed. The movement of iodine through the depth of the bed, due to broadening and migration of the concentration profile, is slow enough that decay of (e.g.) I-131 will account for essentially all the inventory of iodine species on the filter before breakthrough at the downstream face can occur.
6. IMPLICATIONS FOR ACCIDENT SIMULATION AND MANAGEMENT

Significance of model for analysis

There are six areas where the new filter model has made an impact on analysis.

1. The model is constructed such that its primary performance features are determined by constants which are defined directly from experimental data. This avoids the task of having to estimate non-physical model features (particularly the desorption rate constant) from real data. In the past, these estimates had to be made such that the use of the data was not questionable, but at the same time the resulting model features did not include excessive conservatims.

2. The model makes it possible to reduce or even eliminate some types of user effect. Once the characteristics of the model have been set for a given filter design, user intervention to modify filter characteristics is generally not necessary. (Parametric changes input by the user may still be needed to explore unusual scenarios or for sensitivity work.)

3. The new model makes it possible to avoid the conservatism that was inherent in the earlier model due to physically unrealistic desorption of iodine species from the filter.

4. Because the model simulates the spatial distribution of iodine species along the flow axis within the charcoal bed, it provides a good basis for estimating radiation sources to be used in qualifying nearby items of equipment, sources to be used in filter bed heating calculations, and assuring that the filter bed is not saturating locally.

5. The model allows the inclusion of more process features that can be significant for filter operation. These include relative humidity, air flow velocity through the bed, and inlet air temperature.

6. The model rests on a good base of experimental data demonstrating the robustness of the model against variations in the factors mentioned above, but also robustness in the face of poisons such as organic compounds, oxides of sulphur and nitrogen, and other chemicals.

Impact on options for accident management

The model provides a more realistic estimate of the response of iodine on the charcoal filter to changes in process variables. The role of the filter model as an element to be used in determining accident management decisions is still being studied.

7. CONCLUSIONS

The charcoal filter in the EFAD system of a multi-unit CANDU containment is a significant barrier to release of iodine from containment following an accident. In conjunction with a much improved understanding of iodine behaviour in containment under accident conditions, the filter model described in this paper provides a more realistic estimate of the timing and mechanics of iodine retention on the EFADS charcoal. The model can also be used to assess the effects of conditions and process variables determined by events in containment and by modes of EFADS operation respectively. The role of this capability as an input to accident management decisions is still being studied.
ACKNOWLEDGEMENTS

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A STUDY OF THE EFFECTS OF RADIATION AND IMPURITIES ON THE GASEOUS IODINE PRODUCTION IN A CONTAINMENT DURING A SEVERE ACCIDENT

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ABSTRACT

In order to evaluate the effects of some impurities and of radiation on iodine behavior, NUPEC has been improving an analysis code, IOCAP (IQdine Chemistry Analysis based on physicochemical Phenomena in containment vessel), based on the IMPAIR-3 code developed by PSI. We consider IOCAP models of the radiolytic and chemical reactions caused by impurities for iodine. IOCAP code was verified using the RTF experimental results, and evaluated as to the effect of radiation and impurities such as silver and boron on the iodine behavior. The difference of the iodine behavior between with and without boric acid was small in this model. The gaseous iodine concentration with existence of silver in liquid phase decreased, because a large amount of iodine changed into AgI species in liquid phase. The effect of silver for gaseous iodine production was larger than the effect of pH control.

1. INTRODUCTION

A large amount of gaseous iodine was measured in uncontrolled pH and radiation condition in the systematical experiment of iodine behavior (Beahm, et al., 1992). The effect of pH is one of the important factor on gaseous iodine production, besides the pH are decreased by nitric acid production with radiation. On the other hand, in the FPT0 and FPT1 test results of PHEBUS Project, the gaseous iodine production in the steady-state containment vessel with acidic sump condition was very small compared with that in the primary circuit (Clement, et al., 1998). It was considered that the production of gaseous iodine in gas phase was influenced by the presence of silver, namely the ratio of Ag/I, in the containment. Since the effect of radiation and impurities such as silver and boron of the neutron absorber on iodine behavior is very complicated,
the production and the transport of gaseous iodine in the containment vessel during a severe accident have not been made clear yet. Therefore, it is important to make clear not only the iodine behavior in the primary circuit, but also the iodine behavior in the steady state containment vessel in order to evaluate accurately the gaseous iodine production behavior. In order to evaluate the effect of the impurities and radiation on iodine behavior, NUPEC has been improving an analysis code IOCAP (IODine Chemistry Analysis based on physicochemical Phenomena in containment vessel) based on the IMPAIR-3 code (Güntay and Cripps, 1992) developed by PSI. We consider IOCAP models of radiation and chemical reactions caused by impurities for iodine. The modeling and calculation methods for the effect of radiation and impurities are described in this paper. The verification of IOCAP code was evaluated using the RTF experimental results (Kupferschmidt, 1992) which is assigned in the international standard problem. Additionally, the effect of radiation and impurities on the iodine behavior was evaluated by the sensitivity analysis in actual plant scale.

2. MODELING SCHEME

In IOCAP code, the physicochemical behavior and the mass transfer of iodine species are modeled at the five locations in the steady-state containment vessel, that is (1) the gas phase, (2) the liquid phase, (3) the interface gas-liquid boundary, (4) the wall of containment vessel, and (5) the submerged wall of containment vessel.

![Fig. 1 Schematic iodine behavior treated in IOCAP code](image-url)
The schematic iodine behavior treated in IOCAP code are shown in Fig. 1. The physicochemical process of ①, ⑤ and ⑥ shown in Fig. 1, which are modeled in this work, are distinctive feature for IOCAP code. The whole formation mechanism of iodine species and their transport reactions in the containment vessel are modeled in the IOCAP code. Symbol ① indicates the release process of the chemical elements and the chemical compounds from the primary circuit to the containment vessel. Symbol ② indicates the iodine compounds transport process between liquid phase and gas phase. Symbol ③ indicates the organic and inorganic iodine reactions in both gas phase and liquid phase. Symbol ④ indicates the iodine compounds interaction with containment wall. Symbol ⑤ indicates the iodine reaction with impurities which are the material of core structures themselves except for fuel components. Symbol ⑥ indicates the radiation process to produce $\text{H}_2\text{O}_2$ and $\text{HNO}_3$ in both gas and liquid phases.

Speciation of the chemical species released from the primary circuit to the containment vessel as shown in symbol ① is input as boundary conditions which is calculated by the thermo-chemical calculation codes (Uchida, 1984). Eighteen chemical species calculated by the thermo-chemical calculation code are shown in Table 1. They were classified into eight stable groups. These groups composed of seven iodine species and Ag as shown in Table 1 were treated as initial iodine chemical forms in the containment vessel.

Table 1  Classification of initial iodine chemical forms

<table>
<thead>
<tr>
<th>Phase Condition</th>
<th>IOCAP</th>
<th>Thermo-chemical Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Phase</td>
<td>I$_2$</td>
<td>I$_2$, HOI, I, BI$_3$</td>
</tr>
<tr>
<td></td>
<td>I$^-$</td>
<td>CsI, HI, InI, CdI$_2$, TeI$_4$</td>
</tr>
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<td></td>
<td>CH$_3$I</td>
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<tr>
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<td>AgI</td>
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<td>I$_2$, BI$_3$</td>
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<tr>
<td></td>
<td>I$^-$</td>
<td>CsI, InI, CdI$_2$</td>
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<td></td>
<td>AgI</td>
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<td>Ag</td>
<td>Ag</td>
</tr>
</tbody>
</table>

3. MODELING OF RADIATION AND IMPURITIES

Radiation and impurities influence directly and indirectly the iodine behavior in the containment vessel. The radiolytic chemical species such as dissolved oxygen and hydrogen peroxide, react with the iodine chemical species, and nitric acid influences indirectly the iodine chemical forms. Impurities, such as silver and boric acid used in core control material, transported from the
primary circuit to the containment vessel, seriously affects the behavior of iodine. Therefore, the behavior of dissolved oxygen, hydrogen peroxide, nitric acid, and boric acid with iodine were modeled and installed in IOCAP code.

3.1 H$_2$O$_2$ PRODUCTION AND REACTION WITH IODINE

The hydrogen peroxide is produced by radiolysis of water. The reaction process between hydrogen peroxide and iodine is calculated by the following Eqs. (1), (2) and (3) (Burns, 1989).

\[
\begin{align*}
\text{I}^- + \text{H}_2\text{O}_2 & \rightarrow \text{HOI} + \text{OH}^- \\
\text{H}_2\text{O}_2 + \text{HOI} & \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^- + \text{H}^+ \\
\text{H}_2\text{O}_2 + \text{OI}^- & \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^-
\end{align*}
\]

and, HOI dissociates in according with Eq. (4).

\[
\text{K}_4 \\
\text{HOI} \rightleftharpoons \text{OI}^- + \text{H}^+ 
\]

OI$^-$ concentration in Eq. (3) was calculated by Eq. (5) based on Eq. (4).

\[
[\text{OI}^-] = \text{K}_4[\text{HOI}][\text{H}^+] 
\]

Where, dissociation constant K$_4$ in Eq. (5) is calculated by the following empirical Eq. (6) (Palmer, 1989).

\[
\log \text{K}_4 = 2800.48 + 0.7335 \text{T} - 80670/\text{T} - 1115.1 \log \text{T} \quad (\text{T in K}) 
\]

The production of H$_2$O$_2$ in radiation field D (kGy/s) was calculated by following empirical equation based on experimental data (Ishigure, 1986) with CsI solution.

\[
d[\text{H}_2\text{O}_2]/\text{dt} = 1.7 \times 10^{-4} \text{D}^{1.5} 
\]

3.2 PRODUCTION AND REACTION OF DISSOLVED OXYGEN

The reaction between dissolved oxygen and iodide is treated by Burns’s model. In this model, the oxidation reaction of iodide ion I$^-$ to iodide produces as a result of the both thermal and radiolytic effects.

\[
2\text{I}^- + 1/2 \text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O} 
\]

The reaction rate constant in Eq. (8) is extremely small in non-radiation field. In the IOCAP code, a variable reaction rate constant in radiation field D (kGy/s) are newly modeled. The reaction rate constant of I$_2$ and I$^-$ is defined, as follows.

\[
\frac{d[I_2]}{dt} = 1/2 \text{k(8)} [\text{I}^-]^{(1-n)} [\text{H}^+]^{n} \text{D} 
\]

\[
\frac{d[I^-]}{dt} = - \text{k(8)} [\text{I}^-]^{(1-n)} [\text{H}^+]^{n} \text{D} 
\]

\[
(0 < n < 1) 
\]

The reaction rate constant k(8) in Eq. (8) was calculated using the initial production rate Ror (mol/l/kGy) that was measured in an experiment of oxidation of iodide ion performed by Burns (Burns, 1986). The initial reaction rate constant k(8)$_0$ was calculated by Eq. (10) transformed from Eq. (9). The initial production rate (mol/l/kGy) of I$_2$ was

300
\[ k(8) = 2 \frac{\text{Ror}}{[\Gamma_0] \cdot [\text{H}^+]^n} \]

\[ \text{Ror} = \frac{d[I_2]}{dt} (\text{kGy/s}) = 1/2 \ k(8) [\Gamma_0] [\text{H}^+]^n \]

where, \([\Gamma_0]\) was initial concentration of \(\Gamma\) (mol/l), \([\text{H}^+]_0\) was initial hydrogen ion concentration (mol/l).

On the other hand, since the initial reaction rate was proportional to 0.7 power of the initial iodine ion concentration \([\Gamma_0]\) according to the experimental data (Furrer, 1987), \(n\) was considered to be approximately 0.3.

### 3.3 BORIC ACID EFFECT

The boric acid influences not only iodine chemical reaction but also hydrogen ion concentration. The boric acid is supplied from the primary circuit. The chemical reaction of boric acid with iodine is modeled as follows. The decomposition processes of iodine in liquid phase are well known as the following Eqs. (13) and (14).

\[ \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HOI} + \Gamma + \text{H}^+ \]  

(13)

\[ 3\text{HOI} \rightarrow \text{IO}^3^- + 2\Gamma + 3\text{H}^+ \]  

(14)

The boric acid influences the reaction rate constant in Eq. (14), and increases the reaction rate constant (Toth, 1984; Buxton, 1985) with the production of intermediate species. The effect of boric acid for reaction rate constant for iodine reaction is involved in the following Eqs. (15) and (16).

\[ 2\text{HOI} \rightarrow \text{IO}^2^- + \Gamma + 2\text{H}^+ \]  

(15)

\[ \text{IO}^2^- + \text{IO}^- \rightarrow \text{IO}^3^- + \Gamma \]  

(16)

The iodine interaction with boric acid is given by Eqs. (17) and (18), in which the intermediate species of boric acid could be assumed.

\[ \frac{kA_1}{\text{B(OH)}_3 + \text{IO}^- \rightarrow \text{B(OH)}_3\text{IO}^- \text{ (intermediate)}} \]  

(17)

\[ \frac{kA_2}{\text{B(OH)}_3\text{IO}^- + \text{HOI} \rightarrow \text{IO}^2^- + \Gamma + \text{H}^+ + \text{B(OH)}_3} \]  

(18)

The reaction rate constant in Eq. (17) and (18) is able to be estimated by the following empirical equation for Eq. (14) (Buxton, 1985).

\[ d[\text{IO}^3^-]/dt = 1/3 \ k(14) [\text{HOI}]^2 \]  

(19)

where, the reaction rate constant \(k(14)\) with boric acid in Eq. (19) is estimated by Eq. (20).

\[ k(14) = k_0 + k_A [\text{B(OH)}_3 + \text{B(OH)}_4] \]  

(20)

where, \(k_0\) and \(k_A\) are reaction rate constants without and with boric acid respectively (7.2 M\(^{-1}\)s\(^{-1}\) and 109 M\(^{-3}\)s\(^{-1}\)) and [B(OH)\(_3\)+B(OH)\(_4\)] is boric acid concentration.

### 3.4 NITRIC ACID PRODUCTION
Nitric acid reacts indirectly with the iodine species affecting by the hydrogen ion concentration. The production rate of nitric acid is able to be calculated using the G-values (Karasawa and M.Endo, 1996) and the dose rate. As shown in Fig.1, nitric acid produces from the radiolysis of gaseous nitrogen in the gas phase and dissolved nitrogen in the liquid phase. Nitric acid produced in the gas phase is assumed to be transferred immediately into the liquid phase. The increase of hydrogen ion concentration, that is nitric acid concentration in the liquid phase is determined by the nitrogen atom produced in the gas and the liquid phase. The production of nitric acid could be calculated with the G-values of nitrogen atom production of 0.007 in the gas phase and of 2.4 in the liquid phase using the Eq. (21) (Beahm, et al., 1992; Karasawa and M.Endo, 1996).

\[
d[HNO_3]/dt = 1.22 \times 10^{-7} \frac{G_g \cdot D_g \cdot V_g}{V_w} + 1.036 \times 10^{-4} f_N \cdot G_w \cdot D_w
\]  

(21)

where, G, D and V are G-values, dose rate (kGy/s) and volume, subscript g and w are gas and liquid phase, respectively, and fN is solubility of nitrogen gas in liquid phase.

3.5 HYDROGEN ION CONCENTRATION

It is well known that hydrogen ion concentration in liquid phase is one of the most important factor which strongly affects the chemical forms of iodine species. The effect of hydrogen ion concentration on the iodine speciation is considered in IMPAIR-3 code. The change of hydrogen ion concentration for radiation and impurities is treated as the separation effect irrespective of iodine reaction. The hydrogen ion concentration is calculated from the initial values of that depending on boric acid concentration, the concentration of nitric acid produced by radiolysis of nitrogen, and sodium hydroxide added in the liquid phase. The sodium hydroxide contributes to the increase in pH or decrease in the hydrogen ion concentration. Sodium hydroxide indirectly affects the chemical form of iodine species. Boric acid directly interacts with the iodine species as impurities, and also indirectly affects the iodine associated with changing the hydrogen ion concentration.

4. ANALYTICAL RESULTS

The validity of IOCAP model was evaluated by the comparison between analysis results and the RTF experimental results (Kupferschmidt, et al., 1992). The experimental result of the RTF3b test was selected in order to estimate the effect of hydrogen ion concentration. In addition, three cases of the parametric analysis were performed in the actual plant conditions in order to estimate the qualitative response of radiation effect and impurities model for iodine behavior.
4.1 EXPERIMENTAL ANALYSIS

Figures 2 and 3 show the comparison of molecular and ionic iodine concentration in water phase between RTF3b experimental result and analytical result. Figure 4 shows the result of the comparison of the molecular iodine concentration in gas phase. In the analysis, the pH was changed from 5.5 to 9.0 by the injection of sodium hydroxide solution in liquid phase during the period of 260,000 to 270,000 seconds. The reaction rate constant of I\textsubscript{2} deposition on the submerged wall was increased 200 times the original value of IMPAIR-3 code manual (Güntay and Cripps, 1992). The gaseous molecular iodine I\textsubscript{2} concentration in gas phase, the behavior of the I\textsubscript{2} and I\textsuperscript{-} concentration in liquid phase associated with pH change were well reproduced. This multiplier value was used in the following analysis.

![Fig. 2 Molecular Iodine Concentration in Liquid Phase](image)

![Fig. 3 Ionic Iodine Concentration in Liquid Phase](image)
4.2 PARAMETRIC ANALYSIS

The conditions of three preliminary calculations are shown in Table 2. The same reaction rate constants in parametric analysis were used as these adopted in the RTF3b test analysis. The initial element components were calculated based on 25GWD/t fuel burnup core inventory, considering core control materials components.

Table 2 Analysis conditions

<table>
<thead>
<tr>
<th>parameter</th>
<th>condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas phase volume</td>
<td>70000 m$^3$</td>
</tr>
<tr>
<td>Water phase volume</td>
<td>1700 m$^3$</td>
</tr>
<tr>
<td>Gas/water boundary surface area</td>
<td>250 m$^2$</td>
</tr>
<tr>
<td>Temperature</td>
<td>333 K</td>
</tr>
<tr>
<td>Initial pH</td>
<td>5.5</td>
</tr>
<tr>
<td>Dose rate</td>
<td>50 kGy/hr</td>
</tr>
<tr>
<td>Painted vessel wall surface area in gas phase</td>
<td>5500 m$^2$</td>
</tr>
<tr>
<td>Steel vessel wall surface area in gas phase</td>
<td>500 m$^2$</td>
</tr>
<tr>
<td>Concrete vessel wall surface area in gas phase</td>
<td>300 m$^2$</td>
</tr>
<tr>
<td>Painted vessel wall surface area in water phase</td>
<td>2.0 m$^2$</td>
</tr>
<tr>
<td>Steel vessel wall surface area in water phase</td>
<td>450 m$^2$</td>
</tr>
<tr>
<td>Concrete vessel wall surface area in water phase</td>
<td>50 m$^2$</td>
</tr>
</tbody>
</table>

Fig. 4 Molecular Iodine Concentration in Gas Phase
The components of chemical species for iodine and impurities were calculated by thermo-chemical calculation code (Uchida, 1984) under actual plant containment conditions. The chemical forms of boron and silver in containment vessel were mainly considered to be H₃BO₃ and Ag metal, respectively. The initial concentrations of iodine and impurities in containment vessel for three analyzed cases are shown in Table 3. The ratio of the concentration Ag/I in case No. 3 approximately corresponds to PHEBUS-FPT1 test result.

<table>
<thead>
<tr>
<th>element</th>
<th>case 1</th>
<th>case 2</th>
<th>case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (* mol/l)</td>
<td>5.88 x 10^-4</td>
<td>5.88 x 10^-4</td>
<td>5.88 x 10^-4</td>
</tr>
<tr>
<td>Ag (mol/l)</td>
<td>0</td>
<td>0</td>
<td>2.53 x 10^-2</td>
</tr>
<tr>
<td>H₃BO₃ (ppm)</td>
<td>0</td>
<td>2870</td>
<td>2870</td>
</tr>
</tbody>
</table>

* Initial chemical form is I-

Figures 5 and 6 show the analysis result of iodine behavior in gas and liquid phase for case No. 1. The case No. 1 corresponds to elemental composition without boron and silver in the actual plant scale. The pH slowly decreased by the production of nitric acid. The rapid increase in pH (5.5 to 9.0) with sodium hydroxide solution at 260,000 second induced the large change of iodine species concentrations similar to the result of RTF3b test. Gaseous iodine concentration reached steady state condition in about 320,000 seconds as shown in Fig.5. The time lag depends on the containment vessel volume. The concentration of molecular iodine I₂ in gas phase strongly depends on the pH condition in sump, and it decreased rapidly after pH change. It is considered that the decrease of other iodine chemical species case by the increase of I0₃⁻ ion in liquid phase by radiation.

Fig. 5  Iodine Behavior in Gas Phase without Boric Acid and Silver (case 1)
Fig. 6  Iodine Behavior in Liquid Phase without Boric Acid and Silver (case 1)

Figure 7 shows the effect of the existence of boric acid (case 2) in liquid phase on iodine behavior under the same hydrogen ion concentration changing (case 1).

Fig. 7  Effect of Boric Acid for Iodine Behavior in Liquid Phase
As the result of case No. 3 with boric acid and silver impurities, gas phase is shown in Fig. 8, and liquid phase is shown in Fig. 9. The ionic and molecular iodine species in acid condition extremely decreased as shown in Fig. 8. Other concentrations of iodine species in both gas and liquid phase are extremely smaller than that for case No. 1 as shown in Figs. 5 and 6. This is because a large amount of iodine changes into AgI species in liquid phase as shown in Fig. 9. Table 4 shows the molecular iodine concentrations in gas phase in the case of existence of silver and pH condition. Without silver the molecular iodine concentration at pH 4.0 is larger than that at pH 8.5. On the other hand, the molecular iodine concentration with silver at pH 4.0 is smaller than that at pH 8.5 without silver. Namely, the effect of silver on restricting gaseous iodine production is larger than that of pH control.

![Graph](image1)

**Fig. 8** Iodine Behavior in Gas Phase with Boric Acid and Silver (case 3)

![Graph](image2)

**Fig. 9** Iodine Behavior in Liquid Phase with Boric Acid and Silver (case 3)
Table 4  Molecular iodine concentration in gas phase (mol/l)

<table>
<thead>
<tr>
<th>existence of Ag</th>
<th>pH 4.0</th>
<th>pH 8.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>yes</td>
<td>$1.0 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>no</td>
<td>$3.0 \times 10^{-8}$</td>
<td>$3.0 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

5. CONCLUSION

The radiation and impurities effects on iodine behavior in a containment was modeled and installed in IOCAP code. Concerning the pH effect on the iodine behavior, the IOCAP was confirmed in comparison with the RTF3b experimental results. The concentration of molecular iodine I$_2$ in gas phase such strongly depends on the pH condition in sump as the molecular iodine concentration at pH 4.0 is about 6000 times larger than that at pH 8.5. The difference of the iodine behavior between with and without boric acid was small in this model. The gaseous iodine concentration under silver existence in liquid phase decreased both the acid and alkaline condition, since a large amount of iodine changed into AgI species in liquid phase. The effect of silver on restricting gaseous iodine production is larger than that of pH control.

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INTERNATIONAL STANDARD PROBLEM (ISP) NO. 41

Computer Code Comparison Exercise Based on a Radioiodine Test Facility (RTF) Experiment on Iodine Behaviour in Containment under Severe Accident Conditions

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ABSTRACT

The ISP No. 41 exercise resulted from a recommendation at the Fourth Iodine Chemistry Workshop held at the Paul Scherrer Institute (PSI), Switzerland in June 1996 for an International Standard Problem on iodine behaviour models. The test selected for the comparison was a Radioiodine Test Facility (RTF) experiment performed at AECL (Canada). The experiment was a two-stage test, conducted in a stainless steel vessel at 25°C and at a dose rate of 1.4 kGy-h⁻¹ which evaluated the effect of pH on irradiated aqueous solutions containing CsI.

This paper discusses the results of the ISP 41 exercise, with a primary focus on the evaluation and comparison of calculated results, and what they demonstrate about the aqueous iodine reaction subset within each model. The paper will also discuss the relative importance of mass transfer, surface adsorption and aqueous chemistry, and the sensitivity of each of the models to these phenomena. Finally, it will assess the applicability of the ISP 41 exercise to qualitative validation of the iodine models, and provide recommendations for continuing model evaluation.

1. INTRODUCTION

International Standard Problems (ISPs) are comparative exercises in which predictions of different computer codes for a given physical problem are compared with each other or with the results of a carefully controlled experimental study. The main goal of ISP exercises is to increase confidence in the validity and accuracy of the tools which are used in assessing the safety of nuclear installations. Moreover, they enable code users to gain experience and demonstrate their competence. At the Fourth Iodine Chemistry Workshop held at PSI, Switzerland in June 1996, it was recommended that an ISP be performed as ‘the basis of an in-depth comparison of the models as well as contributing to the database for validation of iodine codes’. COG (CANDU Owners Group), comprising AECL and the Canadian nuclear utilities, offered to make the results of a Radioiodine Test Facility (RTF) test available for such an exercise. The OECD/NEA
Committee on the Safety of Nuclear Installations (CSNI) has sponsored forty-five ISP exercises over the last twenty-four years, thirteen of them in the area of severe accidents.

The countries (organizations) which took part in the exercise were Canada (AECL), the Czech Republic (NRIR), France (IPSN), Germany (Siemens, GRS), Japan (JAERI), USA (Sandia), Spain (CIEMAT) and Switzerland (PSI). Participants were supplied by the Canadian team with information defining the physical boundary conditions (dimensions, volumes, and geometric surface areas of the vessel and the loops), and thermalhydraulic conditions for the experiment and provided with pH data measured as a function of time. They were asked to calculate various aspects of iodine behaviour, most notably, the concentration and speciation of iodine in the gas and aqueous phases, and the distribution of iodine at the end of the test (mass in aqueous and gas phases and on surfaces exposed to the gas and aqueous phases). This report presents a description of the RTF tests used for the exercise, a brief description of the models/codes used and the description and interpretation of the results.

2. DESCRIPTION OF THE RTF TEST

2.1 Radioiodine Test Facility

The intermediate-scale study on which the ISP-41 was based was performed in the Radioiodine Test Facility (RTF) at AECL’s Whiteshell laboratories. The RTF consists of a replaceable, cylindrical main vessel into which a $^{60}$Co radiation source can be placed. In 1992, when the data for this exercise was collected, the radiation source provided an absorbed radiation dose rate of about 1.4 kGy-h$^{-1}$ in the aqueous and gas phases. The main vessel of the facility can be partially filled with water and selected chemical additives can be added to the aqueous phase to simulate the sump water in containment following an accident. Electrical heaters around the outside of the vessel control the temperature of the vessel walls in contact with the gas phase up to 110°C and the water temperature up to 90°C. A test is generally initiated with an injection of $^{131}$I labelled CsI into the aqueous phase, to provide an initial aqueous iodide concentration of about $1 \times 10^{-5}$ mol dm$^{-3}$. This is followed by on-line and off-line monitoring of various species. At the end of a test, the iodine surface loadings are determined by washing the vessel, by measuring the $^{131}$I activity in the washes and by measuring the remaining activity on the surfaces. The final iodine activities on the coupons placed both in the gas and the aqueous phases during the tests are also used to determine and confirm the iodine surface loadings.

2.2 Experimental

An RTF test, conducted in two stages in a stainless steel vessel at 25°C was chosen for the exercise. In both stages, the initial pH was 10, followed by multiple, controlled, stepwise decreases in pH (to 7.2 in stage 1 and to 5.5 in stage 2). At the end of stage 1, the initial charge solution was discarded, the vessel was rinsed repeatedly to
remove adsorbed iodine and a fresh solution of CsI was added to commence stage 2. Operating conditions for Stage 1 and 2 of the ISP experiment are presented in Table 1.

Table 1  Experimental conditions for ISP-41 RTF experiments*.

<table>
<thead>
<tr>
<th>Vessel</th>
<th>316 Stainless Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose Rate</td>
<td>~ 1.36 kGy·h⁻¹</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C (± 3 °C)</td>
</tr>
<tr>
<td>Starting Concentration</td>
<td>9 × 10⁻⁶ mol·dm⁻³ CsI (± 10%)</td>
</tr>
<tr>
<td>Aqueous Volume</td>
<td>25 dm³ (± 10%)</td>
</tr>
<tr>
<td>Gas Volume</td>
<td>315 dm³ (± 10%)</td>
</tr>
<tr>
<td>Starting pH</td>
<td>~ 10 (± 0.3)</td>
</tr>
<tr>
<td>Aqueous Surface Area</td>
<td>52 dm²</td>
</tr>
<tr>
<td>Interfacial Surface Area</td>
<td>37 dm²</td>
</tr>
<tr>
<td>Gas Surface Area</td>
<td>220 dm²</td>
</tr>
</tbody>
</table>

* Note: Speciation of the ¹³¹I tracer prior to test start indicated 99.88% of the solution was in the form of I⁻ with 0.11% in the form of IO₃⁻ and 0.01% in the form of organic iodide.

3. DESCRIPTION OF THE MODELS

The models used by the participants were LIRIC (AECL), MELCOR-I (Sandia), IMPAIR (PSI, Siemens, GRS, and JAERI) and IODE (CIEMAT, IPSN and NRIR). A brief description of the models is provided as a background to the comparison of the calculations performed for the ISP-41 exercise.

3.1 Gas-Aqueous Interfacial Mass Transfer and Adsorption

All of the models used in the ISP-41 comparison treat mass transport and surface adsorption in a similar manner. Mass transport across the gas-aqueous interface is modelled in all cases using the model for diffusion through a stagnant film:

\[
\frac{dC_{aq}}{dt} = k_t \cdot \frac{A_{aq}}{V_{aq}} \cdot (H \cdot C_g - C_{aq})
\]  \hspace{1cm} (1)

\[
\frac{dC_g}{dt} = k_t \cdot \frac{A_{aq}}{V_g} \cdot (C_{aq} - H \cdot C_g)
\]  \hspace{1cm} (2)

where: \(C_{aq}\) and \(C_g\) are the aqueous- and gas-phase concentration of a given species (mol·dm⁻³), \(k_t\) is the overall (or interfacial) mass-transfer coefficient (dm·s⁻¹) (i.e., \(1/k_t = 1/k_{aq} + H/k_g\)), \(A_{aq}\) is the gas/aqueous phase interfacial area (dm²), \(V_{aq}\) and \(V_g\) are the aqueous and gas-phase volumes (dm³), and \(H\) is the partition coefficient, the ratio of the aqueous to gas phase concentration of the species at equilibrium (unitless).
Surface adsorption in all of the codes is treated as a reversible adsorption-desorption process. For example, the formulation in LIRIC for adsorption/desorption on gas phase surfaces is:

$$\frac{d[I_2]_g}{dt} = -v_{Ad} \frac{A_{gs}}{V_g} [I_2]_g \left(1 - \frac{[I_2]_s}{[I_2]_s^0}\right) + k_{Des} \frac{A_{gs}}{V_g} [I_2]_s$$

(3)

where $[I_2]_g$ and $[I_2]_s$ are the molecular iodine concentrations in the gas phase (mol·dm$^{-3}$) and on the surface (mol·dm$^{-2}$), respectively, $v_{Ad}$ is the deposition velocity (dm·s$^{-1}$), $k_{Des}$ is the desorption rate constant (s$^{-1}$), $A_{gs}$ and $V_g$ are the gas-phase surface area (dm$^2$) and volume (dm$^3$), respectively, and $[I_2]_s^0$ is the saturation capacity of the surface for I$_2$ (mol·dm$^{-2}$).

3.2 Aqueous Phase Iodine Chemistry

IMPAIR, IODE, LIRIC and MELCOR-I model hydrolysis of iodine in much the same manner, with the overall reactions being:

$$I_2 + H_2O = HOI + I^- + H^+$$

(4)

$$HOI = OI^- + H^+$$

(5)

$$3HOI = IO_3^- + 2I^- + 3H^+$$

(6)

where Reactions (4) and (5) are in rapid equilibria. It is only in the radiolytic reaction set that the mechanistic and empirical codes diverge to a great extent. In LIRIC and MELCOR-I, a mechanistic model is used for calculating the concentrations of the water radiolysis species that subsequently react with various iodine and organic species to produce volatile iodine species. Neglecting the radiolysis of organic species and the formation of organic iodides, LIRIC still contains about 300 reactions. The key ones are:

$$4.1 \text{H}_2\text{O} \xrightarrow{hv} 2.6 e_{ad}^- + 0.6 \cdot H + 2.7 \cdot \text{OH} + 0.7 \text{H}_2\text{O}_2 + 2.6 H^+ + 0.45 \text{H}_2$$

(7)

$$I^- + \cdot \text{OH} \rightarrow I^- + \text{OH}^-$$

(8)$^1$

$$I^- + I^- \rightarrow I_2$$

(9)$^1$

$$I_2(\text{aq}) + \text{H}_2\text{O} \rightarrow HOI + I^- + H^+$$

(10)$^1$

$$I_2(\text{aq}) + 2O_2^- \rightarrow 2I^- + O_2$$

(11)$^1$

$$I_2(\text{aq}) + \text{H}_2\text{O}_2 \rightarrow 2I^- + 2H^+ + O_2$$

(12)$^1$

where the coefficients in Reaction (7) are the G-values for the primary production from $\gamma$-radiolysis of water in units of molecules produced per 100 eV absorbed dose.

IODE and IMPAIR use two equations to model radiolysis of iodine species in the aqueous phase. In IODE, the equations are:

---

$^1$ Represents many reaction steps (i.e., more than one reaction is involved)
\[
2 \text{I}^- \xleftrightarrow{hv} I_2 \\
2 \text{IO}_3^- \xleftrightarrow{hv} I_2 + 3 \text{O}_2
\] (13) (14)

The pH dependence of molecular iodine formation in IODE is accommodated by incorporating [H\(^+\)] into the rate equation in the following manner:

Rate of I\(_2\) production by (13) = \(-d[I_2]/dt = -k_{13}[\text{I}^-][\text{H}^+]^nD + k_{13}[I_2]\),
Rate of I\(_2\) production by (14) = \(-d[I_2]/dt = -k_{14}[\text{IO}_3^-][\text{H}^+]^nD + k_{14}[I_2]\)

where D is the dose-rate in Gy\(\cdot\)s\(^{-1}\).

For IMPAIR, Reaction (13) is the same as that for IODE, with D expressed in kGy\(\cdot\)h\(^{-1}\); however instead of Reaction (14), iodate is irreversibly converted to iodide rather than to molecular iodine:

\[
\text{IO}_3^- \xrightarrow{hv} \text{I}^- 
\] (17)

The formation and decomposition of organic iodide and radiolysis of organic species are also treated quite differently in LIRIC than in IODE and IMPAIR. In LIRIC, the effect of aqueous organic species on pH, dissolved oxygen concentration and organic iodide formation are modelled by a series of reactions which have been developed from detailed mechanistic studies of methyl ethyl ketone [Wren, 1999]. Organic iodide formation is assumed to be primarily an aqueous phase process. Decomposition of organic iodides by hydrolysis is also incorporated into the model.

In IODE and IMPAIR organic iodide formation is modelled by using (CH\(_3\)I) as a generic organic iodide. It can be formed both by aqueous surface processes and by homogeneous aqueous and gas phase processes such as:

\[
I_2 + 2 \text{CH}_3\text{R} \rightarrow 2 \text{CH}_3\text{I} + 2\text{R} 
\] (18)

\[
2\text{CH}_3\text{I} \xleftrightarrow{hv} 2 \text{CH}_3\ast + I_2 
\] (19)

IMPAIR uses HOI as the reacting species as well, and in some versions, can differentiate between high molecular weight organic iodides (formed from CH\(_3\)R\(\ast\)) and methyl iodide. In IMPAIR, organic iodide formation on painted surfaces depends only on the deposited I\(_2\) and I\(^-\) (sump) concentrations. The concentrations of CH\(_3\)R\(\ast\) and CH\(_3\ast\) are not quantified, but are assumed to be in large excess. Homogeneous formation of organic iodide is modelled only for the sump, and the concentrations of the reacting species CH\(_3\)R\(\ast\) and CH\(_3\ast\) are provided by the user. Formation rate constants were derived from ACE/RTF Test 2A and 3B data.
4. RESULTS

Two sets of calculations were performed by each participant. In the first set of calculations, the details of which are reported in the Summary Report of ISP 41 [Ball, 1999], use of different adsorption/desorption rate constants and mass transfer coefficients by each of the participants made it difficult to compare the pool chemistry model in each code. It was therefore decided, at a meeting of ISP participants held in Ottawa in October 1998, that each participant should repeat the calculations using a standard set of rate constants for adsorption and mass transfer (these rate constants were recommended by AECL and are discussed in Section 5.1). By adopting this approach it was hoped that the radiolysis models, and the input rate constants for these models could be compared in a systematic manner. Repeating the calculations also eliminated concerns that evaluation of overall model performance would be unduly biased by the choice of adsorption/desorption rate constants, most of which were obtained from experiments performed at higher temperatures, where the overall adsorption of I₂ on stainless steel surfaces is smaller, and therefore underestimated the effect of adsorption at room temperature.

The total gas phase and aqueous phase iodine concentrations calculated in the second set of the exercise, are compared with experimentally observed values in Table 2. Calculation results for Stage 2 of the test are shown in Figures 1-4. Important features and discrepancies between the calculations are discussed below.

4.1 Total Concentration of Iodine in the Gas and Aqueous Phases

For the purposes of evaluating the results of this exercise, two overall criteria were used to determine whether the calculations provided a good fit to the data. These were:

1) Did the calculations reproduce the observed gas phase iodine concentrations to within an order of magnitude for all pH values?

2) Did the model reproduce (within 20%) the aqueous phase iodine concentration as a function of time?

A more rigorous criterion was chosen for the aqueous phase iodine concentration because its time dependent behaviour gives a clearer representation of what is happening to the iodine inventory than does the gas phase iodine concentration. The aqueous phase iodine concentration is also more critical in controlling overall iodine behaviour than is the gas phase concentration. It is therefore more important that the iodine models could adequately represent the aqueous phase concentrations.

Based on these criteria, only four out of nine of the second set of calculations could be considered to be a success. (See Figures 1 and 2 and Table 2). Most of the calculations significantly overestimated (by more than 30%) the final aqueous phase
concentrations. These cases likewise considerably underestimated the amount of iodine adsorbed on surfaces. Note that the evaluation criteria chosen were for the purposes of this exercise only, and do not reflect the criteria which would be used to evaluate the validity of the models for other purposes.

Table 2 Calculated vs. experimental iodine distribution at test end: 2nd calculation

<table>
<thead>
<tr>
<th></th>
<th>Stage 1 Percentage Iodine Inventory at Test End</th>
<th>Stage 2 Percentage Iodine Inventory at Test End</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas</td>
<td>Aq.</td>
</tr>
<tr>
<td>CIEMAT® (Case 1)</td>
<td>1.1 x 10^4</td>
<td>87.8</td>
</tr>
<tr>
<td>CIEMAT® (Case 2)</td>
<td>4.9 x 10^4</td>
<td>20.6</td>
</tr>
<tr>
<td>CIEMAT® (Case 3)</td>
<td>4.9 x 10^4</td>
<td>1.1</td>
</tr>
<tr>
<td>CIEMAT® (Case 4)</td>
<td>4.9 x 10^4</td>
<td>13.7</td>
</tr>
<tr>
<td>CIEMAT® (Case 5)</td>
<td>1.8 x 10^4</td>
<td>76.6</td>
</tr>
<tr>
<td>IPSN</td>
<td>2.1 x 10^4</td>
<td>88.9</td>
</tr>
<tr>
<td>NRIR</td>
<td>0.017</td>
<td>6.7</td>
</tr>
<tr>
<td>Siemens</td>
<td>8.6 x 10^3</td>
<td>70</td>
</tr>
<tr>
<td>GRS</td>
<td>1.6 x 10^3</td>
<td>76</td>
</tr>
<tr>
<td>PSI</td>
<td>2.0 x 10^4</td>
<td>100</td>
</tr>
<tr>
<td>JAERI</td>
<td>0.020</td>
<td>41.6</td>
</tr>
<tr>
<td>Sandia</td>
<td>.007</td>
<td>24</td>
</tr>
<tr>
<td>AECL</td>
<td>0.024</td>
<td>10.0</td>
</tr>
<tr>
<td>Experiment</td>
<td>.02</td>
<td>12.4</td>
</tr>
</tbody>
</table>

a Test end defined to be at 363 h, when the contents of the sump were drained.
b Case 1: k_{i3} = 1.7 x 10^3 Gy^1, k_{i3} = 2 x 10^5 s^1, n=0.5
Case 2: k_{i3} = 2.5 x 10^4 Gy^1, k_{i3} = 2 x 10^5 s^1, n=0.25
Case 3: k_{i3} = 2.17 x 10^5 Gy^1, k_{i3} = 2 x 10^5 s^1, n=0.1
Case 4: k_{i3} = 2.17 x 10^5 Gy^1, k_{i3} = 2 x 10^5 s^1, n=0.1
Case 5: k_{i3} = 2.17 x 10^5 Gy^1, k_{i3} = 2 x 10^5 s^1, n=0.1

4.2 Speciation and Distribution of Iodine

In the RTF experiment on which ISP-41 exercise was based, there was no significant source of organic impurities to promote organic iodide formation other than impurities in the I^1 tracer used to label the initial CsI solution. Consequently, most of the participants chose to ignore organic iodide formation, and those who did incorporate a nominal amount of organic or organic iodide as part of the initial conditions found that organic iodides did not contribute significantly to the calculated total gas phase iodine concentration. In the aqueous phase, all the calculations predicted that iodide was the predominant species. The fraction of aqueous iodine predicted to be in the form of iodate

\[ 2 \text{JAERI calculations assumed that high molecular weight organic iodides were present as an impurity in the aqueous phase at the beginning of the experiment. This led to a significant fraction of gaseous iodine at high pH being in the form of high molecular weight organic iodides in their calculations. The JAERI calculations in Figure 1 show only the fraction of iodine in the gas phase as I}_2. \]
differed fairly dramatically between the models, however in most cases less than 10% of the original iodine inventory is calculated to be in the form of iodate at the end of the test. Experimental results show that a maximum of 1% of the original iodide inventory was converted to iodate.

\[ \text{Figure 1} \ \text{Calculated (IMPAIR and LIRIC) vs. experimental results for Stage 2.} \]

(a) total amount of iodine (mol·dm\(^{-3}\)) in the gas phase, (b) total amount of iodine (mol·dm\(^{-3}\)) in the aqueous phase. For JAERI calculations, the fraction of the total gas phase concentration in the form of I\(_2\) was plotted.
Figure 2 Calculated (IODE and MELCOR-I) vs. experimental results for Stage 2.
a) total amount of iodine (mol·dm\(^{-3}\)) in the gas phase, b) total amount of iodine (mol·dm\(^{-3}\)) in the aqueous phase.

5. DISCUSSION

The large differences observed between the various calculations, even those performed using the same model, demonstrate that in most cases the models are extremely sensitive to input rate constants which are user defined. These sensitivities are discussed in the following sections.
5.1 The Effect of Adsorption/Desorption and Mass Transfer

One of the most significant differences between the various calculations was the amount of iodine that is predicted to deposit on surfaces (Table 2). To some extent this amount can be adjusted in each model by variation in the adsorption-desorption rate constants. Adjusting the adsorption/desorption rate constants improved the fit to the data in some cases, but it was not in itself sufficient to reproduce the experimental results. This became evident when many of the calculations greatly underestimated the amount of iodine adsorbed on surfaces, despite everyone using the same adsorption/desorption rate constants ($9 \times 10^3 \text{ dm-s}^{-1}$ and $9 \times 10^7 \text{ s}^{-1}$ for adsorption and desorption, respectively). In these cases, adsorption of $I_2$ on gas phase surfaces was limited by the rate of $I_2$ production in the aqueous phase, which was underestimated by the radiolysis models.

The use of the same interfacial mass transfer rate coefficient ($5 \times 10^4 \text{ dm-s}^{-1}$ for $I_2$) by most of the participants eliminated any influence that the choice of this value would have on the calculated gaseous iodine fraction, and the rate at which iodine was adsorbed on the gas phase surfaces. Nevertheless, under the conditions in which this experiment was performed, interfacial mass transfer would be fast relative to the predicted rate of change of aqueous and gas phase iodine species concentrations. The distribution of iodine would therefore be relatively unaffected by this parameter.

Examples of the effect of mass transfer on predictions of iodine volatility and the amount of iodine adsorbed on surfaces in IMPAIR can be seen in Figure 1, where calculations from GRS, who used a mass transfer coefficient of $6 \times 10^5 \text{ dm-s}^{-1}$ are compared to those of Siemens who used $5 \times 10^4 \text{ dm-s}^{-1}$. The participants used identical aqueous phase reaction and adsorption/desorption rate constants. Although the difference in the mass transfer coefficient had some effect on predicted gas phase iodine concentrations at high pH, the effect was very little at pH values less than 9. From this example, it is evident that although mass transfer and surface adsorption do have some effect on iodine volatility, it is the pool chemistry component of the codes that truly controls the models ability to predict iodine behaviour.

A final note regarding the choice of rate constants for adsorption/desorption and mass transfer is that there are some physical limitations on these rate constants. The adsorption rate constant can never exceed the gas phase mass transfer coefficient, since in the limiting case, adsorption on a surface can only be as fast as the species can reach the surface. A similar limit exists for the interfacial mass transfer coefficient whose value is limited by the individual rate constants for gas or aqueous phase mass transfer. The value used for interfacial mass transfer in this modelling exercise approaches this limiting value.

---

3 LIRIC calculations of RTF experiments typically use mass transfer coefficients of about $5 \times 10^4 \text{ dm-s}^{-1}$ for $I_2$. This value is high enough so that mass transfer is not the rate limiting step for accumulation of iodine in the gas phase, and approaches the limiting value for transfer across an aqueous/gas interface from a pool [Swarzzenbach]. It is also consistent with measured interfacial mass transfer coefficients on the order of $10^4 \text{ dm-s}^{-1}$ which were obtained in similar RTF experiments [Evans].
5.2 The Radiolysis Model

Calculations performed in this exercise demonstrated that even using standardized adsorption/desorption rate constants and mass transfer coefficients, there was a large difference between the various models, and different versions of the same model, in the predicted gas and aqueous phase iodine concentrations. This confirmed that the submodels for radiolysis of iodine in the aqueous phase is essential to the ability of any code to predict the volatility and distribution of iodine. This pool chemistry model is also the area in which there was the largest variation both in modelling approach (semi-empirical vs. mechanistic) and in user defined input.

A Comparison between the Semi-Empirical Models, IODE and IMPAIR

The rate constants used as input for the second set of calculations performed by IODE and IMPAIR are listed in Table 3. The sensitivity of the IODE model to the choice of these rate constants is presented in the calculation results performed by CIEMAT (Table 2). It is not surprising that the range of radiolytic rate constants in Tables 3 resulted in a wide range of predicted values for the concentrations of iodine. The range of values used for the rate constants demonstrates that the IMPAIR and IODE codes are still in the evolutionary stage where rate constants are being changed and optimized by the users to provide a best fit to data as that data becomes available. This emphasizes the need for a coherent data set over a large range of conditions, so that the semi-empirical models can be applied with greater certainty to accident conditions.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Radiolysis rate constants used in IODE and IMPAIR: 2nd Calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>k_{13} (mol•dm^{-3})^{a}</td>
<td>k_{13} (s^{-1})</td>
</tr>
<tr>
<td>IMPAIR PSI</td>
<td>3 \times 10^{-9} kGy^{-1}</td>
</tr>
<tr>
<td>IMPAIR Siemens</td>
<td>2.3 \times 10^{-4} kGy^{-1}</td>
</tr>
<tr>
<td>IMPAIR GRS</td>
<td>2.3 \times 10^{-4} kGy^{-1}</td>
</tr>
<tr>
<td>IMPAIR JAERI</td>
<td>4.0 \times 10^{-6} kGy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>1.7 \times 10^{5} Gy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>2.5 \times 10^{4} Gy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>2.17 \times 10^{4} Gy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>2.17 \times 10^{4} Gy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>2.17 \times 10^{4} Gy^{-1}</td>
</tr>
<tr>
<td>IODE CIEMAT^{b,c}</td>
<td>2.17 \times 10^{4} Gy^{-1}</td>
</tr>
<tr>
<td>IODE PSI</td>
<td>1.7 \times 10^{3} Gy^{-1}</td>
</tr>
</tbody>
</table>

{a} changed from the first calculations

{b} The rate constants k_{14} and k_{14} in IODE, used to represent 2I_{2} = I_{2} + 3O_{2} are set to be the same as k_{13} and n_{13}

{c} the user performed 5 calculations, varying both k_{13} and n to show model sensitivity.
A Comparison of the Mechanistic Models to the Semi-Empirical Models

The radiolysis models within the mechanistic codes LIRIC and MELCOR-I appear very different from those within the semi-empirical models. Nevertheless, the numerous reaction schemes in a mechanistic model can be condensed into a few representative reactions such as those in the semi-empirical models, without losing the information encoded in those reactions. The most important difference between mechanistic and the semi-empirical modelling, which are both fundamentally sound, is the method by which overall rate constants for the radiolytic oxidation and reduction of iodine species are chosen. In the mechanistic models, the rate constants are derived by solving a series of kinetic equations representing chemical reactions, whereas in the semi-empirical models, the rate constants are extracted from simulation of experimental data.

LIRIC predicts that, in the absence of adsorption, the concentration of iodine species in the aqueous phase from irradiated solutions of CsI will reach a pseudo-equilibrium concentration determined by the pH, dose-rate, and the concentration of impurities. An overall expression for the balance between oxidation of $\Gamma$ (Reactions (8) and (9)) and reduction of $I_2$ (Reactions (11) and (12)) can be written as:

$$\Gamma^{(aq)} \xrightleftharpoons[k_{20}]{k_{20}} I_2^{(aq)} \quad (20)$$

Reaction (20) is almost identical to Reaction (13) in the IODE/IMPAIR radiolysis model, from which a similar pseudo-equilibrium concentration of $I_2$ in the aqueous phase can be estimated. The pseudo-equilibrium concentrations of $I_2^{(aq)}$ calculated at various pH values for several versions of IODE and IMPAIR are presented in Table 4 where they are compared to the steady-state $I_2^{(aq)}$ concentrations predicted by LIRIC for the same conditions.

The concentrations shown in Table 4 represent the maximum amount of $I_2$, which can be present in the aqueous phase for a given set of conditions and/or oxidation and reduction rate constants. Since the calculations ignore organic iodide formation and neglect surface adsorption processes, the concentrations presented in Table 4 cannot be directly applied to a “real” system. Table 4 is however a useful starting point for comparison of radiolysis models. For example, a comparison between the steady-state [$I_2^{(aq)}$] concentrations calculated using LIRIC and IODE (CIEMAT) show that very similar concentrations are predicted at every pH. This is consistent with model calculations in Figure 2, which show that predictions from these two models agree reasonably well. However, a comparison of the aqueous $I_2$ concentrations for LIRIC and IMPAIR (PSI) shows that the latter would predict several orders of magnitude more $I_2$ than would LIRIC. This is not borne out by the actual model calculations shown in Figure 1. The lower gas phase iodine concentrations observed in the IMPAIR (PSI) calculations as compared to LIRIC or IODE (CIEMAT) result from the rate of production of $I_2$ in the aqueous phase being considerably smaller for IMPAIR (PSI). Therefore, although the equilibrium concentration of $I_2$ as predicted by IMPAIR (PSI) is larger than
for IODE (CIEMAT) or LIRIC, the rate at which the equilibrium is achieved is much slower. The rate of production of I₂ in IMPAIR is not sufficient to reproduce the experimental iodine behaviour, given that mass transfer and surface adsorption must also be considered.

**TABLE 4** Pseudo-equilibrium concentrations of I₂(aq) as a function of pH as predicted by IODE, IMPAIR and LIRIC when adsorption is ignored

<table>
<thead>
<tr>
<th></th>
<th>k₁₁₃ (mol·dm⁻³)ⁿ</th>
<th>k₁₃ (s⁻¹)</th>
<th>n₁₃</th>
<th>k₁₃·D·[H⁺]¹⁺</th>
<th>Calculated [I₂]ₚ as a function of pH (mol·dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMPAIR(PSI)</td>
<td>3.5 × 10⁻⁴ kGy⁻¹</td>
<td>2 × 10⁻⁷</td>
<td>0.35</td>
<td>7.5 × 10⁻⁷</td>
<td>3.4 × 10⁻⁵</td>
</tr>
<tr>
<td>IMPAIR(SIEMENS)</td>
<td>2.3 × 10⁻⁴ kGy⁻¹</td>
<td>2 × 10⁻⁷</td>
<td>0.4</td>
<td>1.0 × 10⁻⁴</td>
<td>4.5 × 10⁻³</td>
</tr>
<tr>
<td>IMPAIR(GRS)</td>
<td>2.3 × 10⁻⁴ kGy⁻¹</td>
<td>2 × 10⁻⁷</td>
<td>0.4</td>
<td>3.2 × 10⁻⁶</td>
<td>1.5 × 10⁻⁴</td>
</tr>
<tr>
<td>IMPAIR(JAERI)</td>
<td>4 × 10⁻⁶ kGy⁻¹</td>
<td>2 × 10⁻⁷</td>
<td>0.1</td>
<td>1.8 × 10⁻⁶</td>
<td>7.9 × 10⁻⁵</td>
</tr>
<tr>
<td>IODE(IPSN)</td>
<td>1.7 × 10⁻⁶ kGy⁻¹</td>
<td>2 × 10⁻⁵</td>
<td>0.5</td>
<td>8.4 × 10⁻⁶</td>
<td>2.1 × 10⁻⁶</td>
</tr>
<tr>
<td>IODE(CIEMAT)</td>
<td>2.5 × 10⁻⁶ kGy⁻¹</td>
<td>2 × 10⁻⁵</td>
<td>0.25</td>
<td>5.4 × 10⁻⁶</td>
<td>1.4 × 10⁻⁶</td>
</tr>
<tr>
<td>LIRIC</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>3.4 × 10⁻⁶</td>
</tr>
</tbody>
</table>

*a* An equilibrium constant of 5.1 × 10⁻¹⁹ mol²·dm⁻⁶ was assumed for I₂ + H₂O = HOI + H⁺ + I⁻.

*b* for IODE: \( \Sigma ([I_2]_{aq}) + [HOI]_{aq} = (k_{11}·D·[Gy]·s⁻¹)·[H⁺]¹⁺·[I⁻](aq) \) / \( 2 \times k_{11} \).

*c* for IMPAIR: \( \Sigma ([I_2]_{aq}) + [HOI](aq) = (k_{13}·D·[Gy]·s⁻¹)·[H⁺]¹⁺·[I⁻](aq) \) / \( k_{13} \times 3600 \text{ s·h}⁻¹ \)

*d* In LIRIC, rate of oxidation of iodide \( = 0.01 \text{ mol·dm}⁻³·s⁻¹ \), Reaction (8), I⁻ + ·OH = I + ·OH⁻ has a rate constant of about \( 10⁻⁶ \text{ mol·dm}⁻³·s⁻¹ \). When \([I] = 10⁻⁴ \text{ mol·dm}⁻³\), the ·OH concentration is \( 10⁻¹² \text{ mol·dm}⁻³\). From \([I_2](aq)\), and the rate of Reaction (8), the reduction rate (which includes thermal reactions) can be estimated.

Obtaining the correct pseudo-equilibrium I₂ concentrations at a given pH is only the first step in obtaining a good fit to any data set. For most systems, mass transfer and surface adsorption need to be considered. Reactions (20)-(22) are simple representations of the processes of: radiolytic interconversion of iodine species; mass transfer across the aqueous/gas interface; and adsorption of molecular iodine on gas phase surfaces.

\[
\begin{align*}
I^- (aq) & \rightleftharpoons k_{20} I_2 (aq) \\
I_2 (aq) & \rightleftharpoons k_{21} I_2 (g) \\
I_2 (g) & \rightleftharpoons k_{22} I_2 (ads)
\end{align*}
\]

From these reactions, it can be seen that processes such as interfacial mass transfer \((k_{21}[I_2](aq))\), compete with others such as reduction of I₂ in the aqueous phase, \((k_{20}[I_2](aq))\). For example, if the rate constant for interfacial mass transfer of I₂ is significantly larger than the rate of reduction of iodine in the aqueous phase, the ratio \(k_{20}/k_{21}\) would determine the concentration of iodine in the aqueous phase rather than the ratio \(k_{20}/k_{20}\). For this reason, the actual values for the rate constants corresponding to these processes must be well defined, and knowledge of the equilibrium constants or ratios \(k_{20}/k_{20}\) alone is not sufficient to predict iodine volatility. Establishing the absolute (or individual) values of the aqueous phase rate constants becomes even more critical in
more complex systems where other aqueous reactions of I\textsubscript{2} (e.g. with organic impurities or Ag) may occur and perturb the pseudo-equilibrium of Reaction (20).

A Comparison of the Mechanistic Models

As demonstrated in Figures 1 and 2, results from MELCOR-I (Sandia) compare very well to those from LIRIC (AECL). This is not surprising, since the models are very similar, and the rate constants for iodine reactions in the aqueous phase are very similar. The exception to the general good agreement between the two models is at high pH values, an observation which has yet to be rationalized.

6. CONCLUSIONS AND RECOMMENDATIONS

The experiments on which this ISP exercise was based were performed under controlled and limited conditions, and the evaluation of the iodine behaviour codes under these conditions cannot be directly applied to their ability to predict iodine volatility under accident conditions. The experiments were chosen as a starting point for evaluation of the various iodine behaviour codes because of their simplicity, in the hope that the very basic components of each code could be compared. This objective was realized. From this simple exercise a number of important points regarding the iodine behaviour codes were demonstrated, as summarized below.

1. The ISP exercise established that both the mechanistic and semi-empirical modelling approaches are fundamentally sound, and that all the models were capable of reproducing test results, given the appropriate input rate constants. It also demonstrated that choice of these constants is key to model performance. These input constants, in order of least to most important are:
   - mass transfer coefficients,
   - adsorption/desorption rate constants,
   - for the semi-empirical codes\textsuperscript{4}, radiolysis rate constants.

2. The variation in radiolysis rate constants used as input for the semi-empirical codes suggests that it is difficult to define these constants such that they can be used with confidence over a large range of different conditions. Important criteria for the choice of these rate constants are that they be defendable, and coherent with reality (i.e. they must be consistent with physical limitations and boundaries). Optimum values must be found to cover the entire range of the conditions of interest, or it must be demonstrated that these values can be extrapolated from a more limited set of

\textsuperscript{4} For the mechanistic models no user input is required for the radiolysis models. The assumption inherent in the mechanistic approach to modelling aqueous radiolytic reactions is that if the separate components of the radiolysis model (e.g. water radiolysis, reactions of iodine species) have been demonstrated to be valid over a wide range of conditions, and the relationship between the components is well understood, the entire model should be valid over the same range of conditions. This requires, of course, that mechanisms are correct, and the rate constants for individual reactions are well defined.
conditions. There are still some key reactions in the mechanistic models which are not well characterized over a large range of conditions. Thus the mechanistic models must be subjected to the same rigorous tests to determine if they perform well over the entire range of interest.

3. The sensitivity of model performance to input rate constants, as demonstrated by the wide spread in the calculation results from this exercise, is a reminder that one cannot blindly apply a model tested over a small range of conditions to conditions outside the tested range.

In conclusion, the exercise demonstrated that all the iodine behaviour codes could adequately reproduce the chosen experimental results. It also demonstrated that, for the most part, the codes are at the developmental stage where model performance is still extremely reliant upon the availability of suitable data, and the judicious choice of input rate constants. If the ultimate purpose of the iodine behaviour codes is for predicting iodine volatility under postulated reactor accident conditions, conditions which may be very different from the tested range of applicability of the codes, it is important that the developers and users of these codes make appropriate, defendable choices for these rate constants.

Evaluation of model performance using an RTF test performed at 25°C and under controlled thermal hydraulic conditions is not necessarily applicable to its performance under the more complex conditions which might be expected in severe accident scenarios. At the ISP meeting in Ottawa in October 1998, there was unanimous agreement however that this exercise provided a useful comparison between models, and a baseline for establishing the range of input values required for modelling iodine behaviour. There was support for performing additional exercises, which could provide a suitable framework for collaborative efforts towards complementary code development and validation. These exercises should also provide an opportunity for each of the participating code users to develop a strategy for determining input rate constants which are defensible over a wide range of conditions. It was recommended that more than one test be used for the next ISP, and that data obtained at higher temperature, and showing the effects of different surfaces (effect of organics) would be preferred. Possible sources of data include the RTF and CAIMAN test facilities.

REFERENCES

A SIMPLIFIED MODEL FOR CONTAINMENT IODINE CHEMISTRY AND TRANSPORT: MODEL DESCRIPTION AND VALIDATION USING STAINLESS STEEL RTF TEST RESULTS

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ABSTRACT

A model (IMOD-1.0) for the simulation of containment iodine chemistry and transport has been developed. The model consists of a small set of chemical reactions and transport phenomena which can be described by differential equations. IMOD-1.0 was created in response to a need for a compact model that is easy to understand and use, and can be readily incorporated into containment safety analysis codes. IMOD treats the transport and adsorption of iodine and adsorption of iodine onto surfaces in the same manner as LIRIC (Library of Iodine Reactions in Containment). However, in IMOD-1.0, the numerous rate equations for aqueous phase processes in LIRIC have been reduced to a pair of empirical reactions. Rate constants for these empirical reactions have been extracted from parametric calculations using LIRIC over a wide range of conditions. IMOD-1.0 is based on the full-scale mechanistic database, but has the advantages of a small model. The validation of this model has commenced, using Radiiodine Test Facility (RTF) data from a series of tests performed in stainless steel vessels. This paper describes the model, and presents simulation data compared to experimentally collected RTF data.

1. INTRODUCTION

We have constructed a simple iodine model, IMOD-1.0 (Iodine Module for Containment Codes) that can be used to determine iodine volatility in containment under postulated accident conditions. This simple model, developed from extensive sensitivity analysis of the comprehensive mechanistic LIRIC model (Wren, 1997), consists of two aqueous phase iodine reactions, aqueous iodine and surface interaction, aqueous-gas phase interfacial mass transfer, and iodine sorption on gas phase surfaces. The model has been validated with some of the experimental data obtained with stainless steel vessels in the Radiiodine Test Facility (RTF) (Wren, 1999-1). This report presents the validation of the model IMOD-1.0 using RTF tests, some of which were performed as part of the wok-in-kind under the COG/IPSN PHEBUS FP agreement.

2. DESCRIPTION OF IMOD 1.0

2.1 General Model Description

The simplified containment iodine chemistry and transport model, IMOD-1.0, groups iodine species into six categories: non-volatile and volatile iodine species in the aqueous phase (NONVOLI(aq) and VOLI(aq)), non-aqueous iodine species (NONAQI), iodine species in the gas
phase (VOLI(g)), iodine in condensing water film on surfaces (I(\text{con})), and iodine on the surfaces in contact with the gas phase (I(\text{ad})).

The reactions and the transport processes of these species in IMOD-1.0 are schematically presented in Figure 1.

![Diagram](image)

**Fig. 1** Iodine Pathways in IMOD-1.0: k represents a pseudo first order rate constant.

Reaction pathways and transport between these six groups of iodine species are formulated using simple first order differential equations. The reactions and mass transport processes considered in the first version of the model are:

1. two aqueous phase iodine reactions,
2. aqueous iodine and surface interaction,
3. aqueous-gas phase interfacial mass transfer of volatile iodine,
4. iodine sorption on dry surfaces in contact with the gas phase,
5. iodine sorption on condensing walls, followed by transport of condensate to the bulk water phase.

Each iodine reaction path in IMOD-1.0 represents many steps, so the first order rate constants for these reactions are overall or effective rate constants. They have been defined as a function of radiation dose, temperature, pH, type of surface, surface area, gas and aqueous volume, based on parametric studies of LIRIC.

### 2.2 Derivation of Rate Constants

The set of differential equations used to describe the processes in Figure 1 are listed in Table 1. The first order rate constants used in these differential equations are defined in Table 2. The rate constants in Table 2 have been derived from parametric calculations using the LIRIC data-base, or from experimental studies. A brief rationalization of some of the choices for these constants follows. A complete description is provided in the literature (Wren, 1999-1).
### Table 1  Differential Equations In IMOD-1.0*

<table>
<thead>
<tr>
<th>#</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>( \frac{d[NONVOLI(aq)]}{dt} = -k_f [NONVOLI(aq)] + k_b [VOLI(aq)] - k_{NIF} [NONVOLI(aq)] + k_{VIB} [NONAQI] )</td>
</tr>
<tr>
<td>B</td>
<td>( \frac{d[VOLI(aq)]}{dt} = -k_f [NONVOLI(aq)] - k_b [VOLI(aq)] - k_{VIF} [VOLI(aq)] + k_{VIB} [NONAQI] )</td>
</tr>
<tr>
<td>C</td>
<td>( \frac{d[NONAQI]}{dt} = -k_{NIF} [NONVOLI(aq)] + k_{VIF} [VOLI(aq)] - k_{NIB} [NONAQI] - k_{VIB} [NONAQI] )</td>
</tr>
<tr>
<td>D</td>
<td>( \frac{d[VOLI(g)]}{dt} = k_{MT} A_{int} \frac{V_g}{V_g} ([VOLI(aq)] - ([VOLI(g)] H VOLI)) )</td>
</tr>
<tr>
<td>E</td>
<td>( \frac{d[VOLI(aq)]}{dt} = k_{MT} A_{int} \frac{([VOLI(g)] H VOLI) - [VOLI(aq)])}{V_{aq}} )</td>
</tr>
<tr>
<td>F</td>
<td>( \frac{d[VOLI(g)]}{dt} = k_{AD} [VOLI(g)] \left( 1 - \frac{[I(ad)]}{SAT} \right) )</td>
</tr>
<tr>
<td>G</td>
<td>( \frac{d[I(ad)]}{dt} = k_{AD} \frac{V_g}{V_g} [VOLI(g)] \left( 1 - \frac{[I(ad)]}{SAT} \right) )</td>
</tr>
<tr>
<td>H</td>
<td>( \frac{d[I(ad)]}{dt} = k_{DES} [I(ad)] )</td>
</tr>
<tr>
<td>I</td>
<td>( \frac{d[I(con)]}{dt} = k_{cw} [VOLI(g)] \frac{V_g}{V_{con}} )</td>
</tr>
<tr>
<td>J</td>
<td>( \frac{d[VOLI(g)]}{dt} = -k_{cw} [VOLI(g)] )</td>
</tr>
<tr>
<td>K</td>
<td>( \frac{d[I(con)]}{dt} = k_{con} [I(con)] )</td>
</tr>
<tr>
<td>L</td>
<td>( \frac{d[[NONVOLI(aq)]]}{dt} = k_{con} [I(con)] \frac{V_{con}}{V_{aq}} )</td>
</tr>
</tbody>
</table>

* Note that the differential equations are grouped according to the type of processes. For example, the change in [NONVOLI(aq)] due to the aqueous phase reactions is formulated in Equation (A) and the change due to condensation in Equation (O). To obtain the overall change of [NONVOLI(aq)] the terms on the right-hand sides of Equations (A) and (O) should be added.

### Aqueous Phase Reactions

Rate constants for inter-convolution of volatile and non-volatile iodine species (\(k_f\) and \(k_b\) in Equations (A) and (B) in Table 1) were taken directly from analysis of LIRIC calculations performed at various conditions of pH, temperature and dose-rate. These calculations established that Reaction (1) below is the rate determining step for oxidation of iodide to molecular iodine (conversion of non-volatile iodide to volatile iodine) over a large range of conditions. The overall rate constant for conversion of NONVOLI(aq) to VOLI(aq), in IMOD 1.0 (\(k_f\)), was therefore defined as the product of the rate constant for Reaction 1, with the concentration of •OH radical (Equation (2)).
\[ \Gamma + \cdot \text{OH} \rightarrow \text{I}^- + \text{OH}^- \] (1)

The change in the NONVOLI(aq) concentration due to this reaction can be formulated as

\[ \frac{d[\text{NONVOLI(aq)]}}{dt} = k_1 \cdot [\cdot \text{OH}] \cdot [\text{NONVOLI(aq)]} = k_f \cdot [\text{NONVOLI(aq)]} \] (2)

The rate constant \( k_1 \) is \( 1.1 \times 10^{16} \text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1} \) (Wren, 1999-1). The concentration of \( \cdot \text{OH} \) as determined by LIRIC (Wren, 1999) has a linear dependence upon dose-rate \(([\cdot \text{OH}]_0 \text{ (mol}\cdot\text{dm}^{-3}) = 0.90 \times 10^{-12} \times D_r \), hence \( k_f \) \((\text{s}^{-1}) = (0.010 \pm 0.001) \times D_r \), where \( D_r \) is the absorbed dose rate in units of \( \text{kGy}\cdot\text{h}^{-1} \).

Sensitivity studies using LIRIC have also shown that for a given radiation field, pH, dissolved oxygen concentration and temperature, VOLI(aq) and NONVOLI(aq) will tend toward and remain in a near steady-state (Equation 3).

\[ K_{AgI} = \frac{[\text{VOLI(aq)]}}{[\text{NONVOLI(aq)]}} = \frac{k_f}{k_b}. \] (3)

From parametric calculations of the steady-state concentration of VOLI(aq) using the full LIRIC model and values of \( k_b \) defined as in Equation (2), the backward rate constant \( (k_b) \) used in IMOD-1.0, was calculated as a function of pH, temperature and dose rate (Table 2).

For the simulations of the tests in the presence of silver, the formation of AgI is accounted for in the aqueous phase reaction as

\[ \text{VOLI(aq)} \rightarrow \text{NONAQI (i.e. AgI)} \] (4)

where: \( k_{v_{AgI}} \text{ (s}^{-1}) = v_{Ag} (A_{Ag}/V_{aq}) \)

\( v_{Ag} \text{ (dm}^{-1}) \) is the deposition velocity of I\(_2\) on Ag

\( A_{Ag} \text{ (dm}^2) \) is the geometric surface area of the silver metal

\( V_{aq} \text{ (dm}^3) \) is the volume of the aqueous phase

The iodine interaction with Ag is considered to be irreversible, therefore the reverse of Reaction (4) was set to 0 (i.e. \( k_{v_{AgI}} = 0 \)). The same deposition velocity \( v_{Ag} \) was used for the simulation of PHEBUS RTF 3, which contained two "adsorption stages", and PHEBUS RTF 6 (see Section 3). These experiments contained 30 g and 200 g of Ag in the aqueous phase, respectively.

**Mass Transfer**

The interfacial mass transfer coefficient \( k_{MT} \) for high mixing and non-condensing conditions was obtained from a specifically commissioned RTF experiment performed under flow conditions typical of many RTF experiments (Evans, 1990). The temperature dependence of the individual \( (k_{maj}, k_{maj}) \) gas and liquid phase mass transfer coefficients was based on the known temperature dependence of the diffusion coefficients for species in the gas and aqueous phase. The PHEBUS RTF experiments were performed under less vigorous mixing conditions in the gas phase, with some tests performed under non-condensing and the others under condensing conditions. For the
non-condensing PHEBUS RTF tests, a gas phase mass transfer rate constant an order of magnitude lower than that for high mixing conditions was used. For the condensing PHEBUS RTF tests, the gas phase mass transfer rate constant was the same as that for the high mixing and non-condensing conditions, but an aqueous phase mass transfer rate constant an order of magnitude higher was used. These increases in the mass transfer coefficients are considered to be reasonable because an increase in the convection flow will result from condensation. It should be noted that a same mass transfer rate constant is used for a given set of conditions. (See Table 2).

### Table 2: Rate Constants And Parameters

<table>
<thead>
<tr>
<th>Constant</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_f$ (s⁻¹)</td>
<td>$(0.01 \pm 0.001) \cdot D_f \cdot (D_f \text{ in units of kGy-h}^{-1})$</td>
</tr>
<tr>
<td>$k_b$ (s⁻¹)</td>
<td>$k_b = A_b \cdot \exp(-\Delta E_b/RT) \cdot [H^+]^n \cdot [D]^m$</td>
</tr>
<tr>
<td></td>
<td>$n = (0.80 \pm 0.04) + (500 \pm 25) \cdot (1/T - 1/298)$</td>
</tr>
<tr>
<td></td>
<td>$A_b = (8 \pm 2) \times 10^{16}$</td>
</tr>
<tr>
<td></td>
<td>$\Delta E_b = 134 \pm 2 \times 10^3 \text{ J-mol}^{-1}$</td>
</tr>
<tr>
<td>$k_{NTF}$ (s⁻¹)</td>
<td>default = 0</td>
</tr>
<tr>
<td>$k_{NSF}$ (s⁻¹)</td>
<td>default = 0</td>
</tr>
<tr>
<td>$k_{VIF}$ (s⁻¹)</td>
<td>default = 0</td>
</tr>
<tr>
<td></td>
<td>$k_{VIF} = v_{Ag}(A_{Ag}/V_{aq})$ in the presence of aqueous phase silver, where $v_{Ag} = (0.010 \pm 0.005) \text{ dm}^{-3} \cdot \text{s}^{-1}$, and $A_{Ag}$ is the silver surface area in dm² ($A_{Ag}/V_{aq}$ has units of dm⁻¹)</td>
</tr>
<tr>
<td>$k_{maq}$ (dm·s⁻¹)</td>
<td>$7 \times 10^2 (T/298)$ for mixing and non-condensing conditions</td>
</tr>
<tr>
<td>$k_{mq}$ (dm·s⁻¹)</td>
<td>$7 \times 10^2 (T/298)$ for non-mixing and non-condensing conditions</td>
</tr>
<tr>
<td>$H_{VOLI}$</td>
<td>$\ln (H_{VOLI}) = \ln (H_{2259K}) + (-\Delta G_{VOLI}/R) \times (1/298 - 1/T)$</td>
</tr>
<tr>
<td>$H_{2259K}$</td>
<td>(79 ± 8)</td>
</tr>
<tr>
<td>$\Delta G_{VOLI}/R$</td>
<td>$(3600 \pm 200)$ or $\Delta G_{VOLI} = (30 \pm 2) \text{kJ-mol}^{-1}$</td>
</tr>
<tr>
<td>$k_{AD}$ (s⁻¹)</td>
<td>$v_{AD}(A_{Ag}/V_{aq}) = 1 \times 10^{-2}(A_{Ag}/V_{aq})$</td>
</tr>
<tr>
<td>$k_{DES}$ (s⁻¹)</td>
<td>$\ln \left( k_{DES} \right) = \ln \left( k_{DES(298K)} \right) + \left( \frac{\Delta E_{DES}}{R} \right) \left( \frac{1}{298} - \frac{1}{T} \right) $</td>
</tr>
<tr>
<td>$k_{DES(298K)}$</td>
<td>$(9 \pm 2) \times 10^7 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$\Delta E_{DES}$</td>
<td>$(74.6 \pm 1.5) \text{kJ-mol}^{-1}$</td>
</tr>
<tr>
<td>$k_{AD}$ (s⁻¹)</td>
<td>$v_{AD}(A_{Ag}/V_{aq}) = (7 \pm 2) \times 10^{-4} \text{ dm·s}^{-1}$</td>
</tr>
<tr>
<td>$k_{VOLI}$ (s⁻¹)</td>
<td>SAT(mol·dm⁻³) default = $2 \times 10^{6}$</td>
</tr>
<tr>
<td>$k_{con}$ (s⁻¹)</td>
<td>$F_{con}/V_{con}$</td>
</tr>
</tbody>
</table>

Note: $T$, $\phi$, $V_P$, $V_{aq}$, $V_{con}$, $A_{A}$, $A_{Ag}$, $F_{con}$ are defined by boundary conditions

*a $v_{Ag}$ was calculated assuming that $A_{Ag}$ was the geometric surface area of the silver. This simple assumption results in a deposition velocity which is artificially high, and faster than mass transfer should allow. However, this effect is negated when surface area is used again for the calculation of the first order rate constant (i.e., $v_{Ag}(A_{Ag}/V_{aq})$)*

*Used in the calculation of $k_{Mt}$:

$$
\frac{1}{k_{Mt}} = \frac{1}{k_{maq} + k_{mq}} + \frac{H_{VOLI}}{k_{AD}}
$$

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The partition coefficient, \( H \), for VOLI in IMOD-1.0 is defined to be that of \( I_2 \) (Wren, 1999-1). \( H \) is a thermodynamic equilibrium constant, therefore it is assumed to follow a simple Arrhenius temperature dependence as shown in Table 2. Because of this simplifying assumption which bases the overall partition coefficient for iodine only on \( I_2 \), IMOD 1.0 predicts iodine volatility less accurately if organic iodide formation in the aqueous phase is significant, which is likely to be the case with organic-painted vessels. Nonetheless, because of the wide ranges of types of organic iodides and their corresponding partition coefficients (Wren, 1999-2), the average partition coefficient of organic iodides that would be formed may be not that far off that for \( I_2 \).

**Adsorption/Desorption**

Among the reaction parameters in IMOD-1.0, the adsorption and desorption parameters are the most difficult to define. This is not because of the difficulty in formulating the iodine sorption process for a given surface, but because of the difficulty in defining the surface characteristics and surface area properly. This problem is less serious for smooth structures, such as painted carbon steel, whose surface area can be well defined using the geometric surface area and on which the iodine is deposited rather uniformly. For metal surfaces, however, iodine deposition may be initiated and localized on defect sites. Furthermore, the surface characteristics may change with adsorption, as a result of corrosion. The iodine adsorption/desorption on dry surfaces is included in IMOD-1.0 as a first order process (see Equations 6 and 7 in Table 2), with the adsorption rate constant \( k_{AD} \) further defined as:

\[
 k_{AD} = v_{AD} \left( A_s / V_g \right)
\]

where \( v_{AD} \) (dm\(^-\)s\(^-\)) is the adsorption rate constant per unit area per volume, referred to as the surface deposition velocity, \( A_s \) (dm\(^2\)) is the area of the surface exposed to the gas phase, and \( V_g \) (dm\(^3\)) is the volume of the gas phase.

For the simulations of the tests performed under non-condensing conditions, the iodine adsorption/desorption rate constants for electropolished and untreated stainless steel were chosen on the basis of experimental studies performed on the deposition of molecular iodine on stainless steel coupons (Wren, 1999-3). Where applicable, adsorption onto painted coupons in the gas phase was included in the calculations. This value was also chosen on the basis of experimental studies (Wren, 1997). Iodine desorption from painted coupons was not included because it is thought that adsorption on to epoxy painted surfaces is an irreversible chemisorption process.

The rate constant for absorption of iodine in condensing water films in IMOD-1.0 (\( k_{CW} \)) was extracted from simulations of the PHEBUS RTF 5 test (see Section 3). The transport of the condensing film from the wall to the bulk water, which maintains a steady state volume of the condensing film on the wall is included as a first order process. The rate of the first order transport of the condensing film (\( k_{con} \)) was experimentally determined from the volume flow rate of the film, \( F_{con} \), divided by the volume of the film \( V_{con} \). Iodine desorption from condensed water on walls was not included because iodine is quickly hydrolyzed to \( I^- \) upon contact with the condensing film.
3. VALIDATION OF THE MODEL

Predictions of the containment iodine model IMOD-1.0 have been compared against the results of various RTF tests performed in stainless steel vessels. The model simulation results for six RTF tests are described in this report. Three of these experiments were designed to examine the effect of a series of pH adjustments on iodine volatility from irradiated solutions of CsI at temperatures of 25 and 90°C. An additional three tests at 90°C examine the effects of condensing conditions, and/or the presence of Ag metal in the aqueous phase on irradiated aqueous solutions of CsI. Experiments performed at higher temperature also contained painted epoxy coupons in the gas phase and the aqueous phase.

Simulations of the RTF test results are described below. The experiments were simulated by solving the kinetics of the reaction schemes listed in Table 1 with the rate constants listed in Table 2. This was accomplished using FACSIMILE\(^1\), a commercially available numerical integration package for simultaneously solving coupled differential equations.

3.1 Description of the RTF Tests

The RTF itself, and typical RTF test procedure and test conditions are described in detail elsewhere (Ball, 1997). A summary of the conditions of the experiments used for this modelling exercise is presented in Table 3.

Table 3 RTF Test Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>P0T2</th>
<th>Phobus</th>
<th>Phobus</th>
<th>Phobus</th>
<th>Phobus</th>
<th>Phobus</th>
<th>Phobus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
<td>316L</td>
</tr>
<tr>
<td></td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Dose Rate (kGy-h(^{-1}))</td>
<td>~1.36</td>
<td>~0.9</td>
<td>~0.9</td>
<td>~0.8</td>
<td>~0.7</td>
<td>~0.8</td>
<td></td>
</tr>
<tr>
<td>Sump Temperature</td>
<td>25°C</td>
<td>90°C</td>
<td>90°C</td>
<td>90°C</td>
<td>90°C</td>
<td>90°C</td>
<td>90°C</td>
</tr>
<tr>
<td>Wall Temperature</td>
<td>25°C</td>
<td>110°C</td>
<td>110°C</td>
<td>110°C</td>
<td>80°C</td>
<td>80°C</td>
<td></td>
</tr>
<tr>
<td>Initial [CsI] (mol.dm(^{-3}))</td>
<td>9 x 10(^{-4})</td>
<td>1 x 10(^{-4})</td>
<td>1 x 10(^{-5})</td>
<td>1 x 10(^{-5})</td>
<td>1 x 10(^{-5})</td>
<td>1 x 10(^{-5})</td>
<td></td>
</tr>
<tr>
<td>Aqueous Volume (dm(^{3}))</td>
<td>25</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Gas Volume (dm(^{3}))</td>
<td>315</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
</tr>
<tr>
<td>Starting pH</td>
<td>10</td>
<td>9</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
<td>9</td>
</tr>
<tr>
<td>Surface Area(^a): gas(dm(^{2}))</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>220</td>
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<tr>
<td></td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
<td>52</td>
</tr>
<tr>
<td>Coupons(^c): gas(^d)</td>
<td>no</td>
<td>3@250 cm(^{2})</td>
<td>3@250 cm(^{2})</td>
<td>3@250 cm(^{2})</td>
<td>3@250 cm(^{2})</td>
<td>3@250 cm(^{2})</td>
<td>3@250 cm(^{2})</td>
</tr>
<tr>
<td>(aqueous)</td>
<td>no</td>
<td>8@19 cm(^{2})</td>
<td>8@19 cm(^{2})</td>
<td>8@19 cm(^{2})</td>
<td>8@19 cm(^{2})</td>
<td>8@19 cm(^{2})</td>
<td>8@19 cm(^{2})</td>
</tr>
<tr>
<td>Ag (grams)</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>32</td>
<td>no</td>
<td>no</td>
<td>200</td>
</tr>
<tr>
<td>Boric acid (mol.dm(^{-3}))</td>
<td>no</td>
<td>no</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>

\(^a\) vessel surface areas only (loop area excluded)

\(^c\) Hydrocentrofugon 901 Ripolin White-epoxy paint

\(^d\) Hydrocentrofugon 901 Ripolin White-epoxy paint

\(^1\) FACSIMILE - AEA Technologies, Harwell Laboratory, Oxfordshire, UK.
For the experiments performed in the absence of silver metal, the test observations can be summarized as follows:

1. the gas phase iodine concentration, \([I(g)]\), increased with a decrease in pH,
2. for a given pH and temperature the gas phase iodine concentration, \([I(g)]\), initially increased with time, and later followed a slow exponential (almost linear) decrease,
3. the total aqueous phase iodine concentration, \([I(aq)]\) and, where applicable the condensate iodine concentration, \([I(con)]\) slowly decreased exponentially with time, and
4. the gas phase iodine concentration was slightly larger under condensing conditions (PHEBUS RTF 5) than under non-condensing conditions (PHEBUS RTF 2).

The presence of Ag in the aqueous phase resulted in an exponential decrease in \([I(aq)]\), \([I(g)]\), and \([I(con)]\) which was much greater than that observed in the absence of Ag. The rate constant for this exponential decay decreased with an increase in pH.

3.2 Simulations and Discussion

3.2.1 RTF P0T2

The simulation results of P0T2 Stage 1 and 2 with IMOD-1.0, are shown in Figures 2 to 5. The calculated results are in good agreement with the observed gas and aqueous phase concentrations over a wide range of pH conditions at 25°C (within a factor of three for the gas phase concentration).

![Graph showing concentration vs. time and pH](image)

**Fig. 2** Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the gas phase, P0T2 Stage 1.
Fig. 3 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the aqueous phase P0T2 Stage 1.

Fig. 4 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the gas phase, P0T2 Stage 2.

Fig. 5 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the aqueous phase P0T2 Stage 2.
3.2.2 PHEBUS RTF 2A and 2B

These tests were performed at 90°C, under non-condensing conditions and in the absence of silver. The simulation results for the gas and aqueous phase iodine concentrations are shown relative to the experimental data in Figures 6 through 9.

The gas phase iodine concentrations at the beginning of Test 2B increased much more slowly than expected (Figure 8). The cause of this slow increase is not due to the accumulation of iodine in the gas phase being limited by the rate of interfacial mass because this slow change was not observed during sudden pH changes (cf. Figure 4). Adsorption of iodine on surfaces in the aqueous phase is also ruled out as a possible cause, because the adsorption of iodine on the surface would have drastically reduced the aqueous iodine concentration. The shape of the initial curve of the gas phase iodine concentration in Test 2B indicates that reactions such as;

\[
\text{VOLI(aq)} + \text{Impurity(aq)} \leftrightarrow \text{Iodine Complex(aq)} \quad (6)
\]

\[
\text{Impurity(aq)} \rightarrow \text{Decomposition Products} \quad (7)
\]

may be occurring in the aqueous phase. For example, I\(_2\) may react with organic impurities to establish a fast equilibrium with a non-volatile charge transfer complex, which could subsequently undergo radiolytic decomposition to release VOLI(aq), (and VOLI(g)). Alternatively, I\(_2\) may be reacting with active sites on the stainless steel surfaces in contact with the aqueous phase to form FeI\(_2\), which is readily dissolved in the aqueous phase to release I\(_2\). Assuming a finite number of active iron sites, this process would produce the same observed effect as the organic impurity scheme. At this point we do not have experimental data to confirm either of the explanations.

The proposed mechanism was tested in the simulation of the PHEBUS RTF test 2B. The simulation result suggests that a reaction such as proposed above may be required to explain the observed gas phase iodine behaviour at the beginning of the test.

![Graph showing calculated vs. experimental results for the total amount of iodine (mol·dm\(^{-3}\)) in the gas phase, PHEBUS RTF 2A.](image)

*Fig. 6* Calculated vs. experimental results for the total amount of iodine (mol·dm\(^{-3}\)) in the gas phase, PHEBUS RTF 2A.

\(^2\) One of the calculations shown in Figure 8 was obtained using \(1 \times 10^3\) dm\(^3\)·mol\(^{-1}\)·s\(^{-1}\) and \(2.5 \times 10^3\) s\(^{-1}\) for the forward and backward rate constant of Equilibrium (6) and \(8 \times 10^5\) s\(^{-1}\) for the decomposition rate of Reaction (7) and \(1 \times 10^3\) mol·dm\(^{-3}\) for the impurity level.
Fig. 7 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the aqueous phase, PHEBUS RTF 2A

Fig. 8 Calculated vs. experimental results for total amount of iodine (mol·dm⁻³) in the gas phase, PHEBUS RTF 2B

Fig. 9 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the aqueous phase, PHEBUS RTF 2B
3.2.3 PHEBUS RTF 5

The simulation results of PHEBUS RTF Test 5 performed under condensing conditions, are shown in Figures 10 and 11. The exponential decrease in the aqueous phase iodine concentration in PHEBUS RTF 5 is slower than that observed in the similar experiment RTF 2B. This is because the decrease in RTF 5 is due only to iodine adsorption on the painted coupons. In RTF 5, any iodine that adsorbs onto the condensed water film returns to the aqueous phase and therefore there is no net loss of iodine to the vessel walls.

As was observed in simulations of RTF2B, the calculated concentration of iodine in the gas phase and the condensate at the beginning of the test are higher than those observed. Similar reaction mechanisms (Reaction (6) and (7)) suggested for PHEBUS RTF 2B are also considered to be responsible for this case.

Fig. 10 Calculated vs. experimental results for the total amount of iodine (mol dm$^{-3}$) in the gas phase, PHEBUS RTF 2B

Fig. 11 Calculated vs. experimental results for the total amount of iodine (mol dm$^{-3}$) in the aqueous phase, PHEBUS RTF 2B
3.2.4 PHEBUS RTF 3 and PHEBUS RTF 6

The results of PHEBUS RTF Tests 3 and 6 are shown in Figures 12 to 15. With silver metal in the aqueous phase, the iodine reaction with silver dominated the behaviour of iodine in the aqueous phase.

In PHEBUS RTF 6, there was a significant delay between starting the test, and the onset of the exponential decrease of iodine in the aqueous phase. An explanation for this observation is that in both Tests 3 and 6, the silver wool was housed in a container made of stainless steel mesh. Because of the larger mass of silver used in RTF 6, as compared to RTF 3, there was more contact of Ag with stainless steel in the former. When AgI is in contact with iron, the following reaction is known to occur (Greenwood, 1985):

$$\text{AgI} + \text{Fe} \rightarrow \text{Ag} + \text{FeI}_2.$$  

(8)

FeI₂ dissolves easily in water, to release I⁻. The release of I⁻ from AgI was confirmed in separate controlled experiments in which AgI was placed in contact with Fe powder, stainless steel filings and stainless steel coupons. The overall impact of this reaction would be to delay the deposition of iodine on silver. The proposed mechanism was tested in the simulation of PHEBUS RTF 6 shown in Figures 14 and 15. The simulation included Reaction (8) until 25 h, after which reactive Fe is assumed to be exhausted. The mechanism appears to account for the iodine behaviour.

An important feature about the modelling of the Ag/iodine interactions in this experiment is that a simple mechanism, using direct interaction of silver metal with I₂ in the aqueous phase, and the same deposition velocity for both stages of RTF3 and for RTF6, adequately reproduced the results of both RTF3 and RTF6. This simple mechanism appears to explain the pH dependence of the reaction, and the observed decrease of aqueous phase iodine concentration very well, and it was not necessary to invoke the formation of AgO, or the reaction between silver metal and iodide ion.

![Graph showing calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the gas phase, PHEBUS RTF 3. Note that the increase in aqueous phase iodine at 21 h was due to an intentional second addition of CsI.](image)

**Fig. 12** Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the gas phase, PHEBUS RTF 3. Note that the increase in aqueous phase iodine at 21 h was due to an intentional second addition of CsI.
Fig. 13 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the aqueous phase, PHEBUS RTF 3. Note that the increase in aqueous phase iodine at 21 h was due to an intentional second addition of CsI.

Fig. 14 Calculated vs. experimental results for the total amount of iodine (mol·dm⁻³) in the gas phase, PHEBUS RTF 6.

Fig. 15 Calculated vs. experimental results for total amount of iodine (mol·dm⁻³) in the aqueous phase, PHEBUS RTF 6.
4. CONCLUSIONS

Simulation calculations of PHEBUS RTF tests using the simple iodine model, IMOD-1.0, have been performed as part of the validation of the model. The model can reproduce experimental results obtained under controlled pH conditions ranging from pH 4 to 9, and at temperatures of 25 and 90°C and iodide concentrations between $10^4$ and $10^6$ mol.dm$^{-3}$. Condensing conditions and rapid aqueous adsorption onto silver are also successfully simulated using this simple model. The gas phase iodine concentration is reproduced within a factor of two, except during the early transient periods. The model reproduced the iodine concentrations in the aqueous phase and in the condensate to within 20%. The model requires further development in some areas, particularly in organic iodide formation and pH prediction, and the effective rate constants will be refined to expand the applicability of the model to wider ranges of conditions and to minimize the uncertainties in the model predictions.

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SIMPLIFIED MODELLING OF IODINE BEHAVIOUR FOR SOURCE TERM ASSESSMENT OF FRENCH REACTORS

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ABSTRACT

In case of a severe accident with a core melt occurring in a Pressurized Water Reactor (PWR), iodine is released to the containment. The evaluation of the iodine behavior, including its chemical forms, is necessary for source term assessment, as iodine could be a major contributor to short term radiological consequences.

In order to evaluate the iodine source term, a review of available models was performed. This leads to a set of consistent assumptions relative to the different phenomena in which iodine is involved.

With the objective to be used for level 2 PSA source term evaluation, for which a large number of sequences have to be computed, a model based on these assumptions was elaborated.

Validation was then undertaken by comparing the results to closed form solutions, to separate effect tests and finally to integral experiments. With respect to the simplicity of the model, the results of the validation process are considered very satisfactory.

1. INTRODUCTION

In case of a severe accident with a core melt occurring in a Pressurized Water Reactor (PWR), iodine is released to the containment. The evaluation of the iodine behavior, including its chemical forms, is necessary for source term assessment, as iodine could be a major contributor to short term radiological consequences.

To determine the source term, it is necessary to know the quantity and chemical forms of iodine present in the gas phase. The aim of the work presented hereafter is to establish a simplified and fast running model which can be used in the frame of source term evaluation for level 2 PSA.
Due to the great complexity of its physical and chemical behavior in the reactor, it is not possible to model all the phenomena in which iodine is involved. The first task undertaken was then to define the phenomena having the most influence on the iodine source term. This conducted to the following list of processes to be studied:

- the release of gaseous species in the containment,
- the radiolytic oxidation of iodide in the sump,
- the formation of insoluble silver iodide in the sump,
- the sump-to-gas and gas-to-sump mass transfer of molecular iodine,
- the adsorption of molecular iodide on paints,
- the formation of organic iodides,
- the adsorption of iodine on concrete.

The following section summarizes the assumptions and models established for these phenomena. The analysis is based on experimental results, model evaluations and reference calculations performed using codes as IODE (Jacquemain, 1998) and INSPECT (Dickinson and Sims, 1996).

2. ASSUMPTIONS AND MODELS

Release of gaseous species in the containment

As iodine is a very volatile fission product, it is assumed that it is totally released from the fuel. But the forms under which this release is made is of course very important and sensitive on source term evaluation.

In many studies conducted to date, thermodynamical equilibrium calculations of simple systems such as (Cs-I-O-H) were considered. Other studies took into account kinetic aspects (Beahm et al, 1992, Wren 1983) but once more only on simple systems. More recently, equilibrium calculations including other species was made for conditions of the PHEBUS tests FPT0 and FPT1 (Götzmann, 1996). They showed that the carrying gas composition and the presence of species such as Ag, In, Cd and Mo may have a very significant impact on the amount of gaseous iodine release to the containment. In particular, in the presence of Mo under steam conditions, Cs$_2$MoO$_4$ is likely to be formed, thus reducing the quantity of Cs to react with I and increasing the release of gaseous iodine species.

During the course of the present study, equilibrium calculations were performed, for large and small break on the hot leg sequences. These calculations basically confirmed the trends established by Götzmann. They took into account a very complete system composed of (H-O-I-Cs-Br-Rb-Te-Sb-Sn-Se-Ba-Rh-Mo-Ag-In-Cd) for the 900 MWe PWRs. For the 1300 and 1450 MWe reactors, B and C were also included because a large part of the control rods is composed of B$_4$C.

Experimental results were also examined. On the one hand, results from VERCORS 4, under hydrogen, and VERCORS 5, under steam conditions, are qualitatively consistent with equilibrium calculations. Unfortunately, quantitative results could not be obtained because the post test iodine balance is not good. On the other hand, results from the PHEBUS FPT0 and FPT1 tests tend to show that the maximum gaseous iodine release is obtained during oxidation phases, that is to say under the maximum hydrogen content.
Based on the previous elements and more specifically on the results of the PHEBUS FP tests, which are definitely the most representative, it is assumed that the release of iodine in the containment is 95% under soluble aerosols and 5% under gaseous form. Due to the lack of information on this point, the gaseous species is supposed to be I\(_2\), although it is recognized that under hydrogen containing atmospheres, other species such as HI are likely to be formed. It is finally stressed that these assumptions are weakly established based on the existing knowledge, and that this point would deserve more attention in the future with respect to its impact on the iodine source term.

**Radiolytic oxidation of iodide in the sump**

The radiolytic oxidation of iodide has been studied in a large number of experiments during the past years. It is established that the radiolytic reactions are fast (Ishigure and Shiraishi, 1990). However, the relevant question for our application is whether molecular iodine production in the sump is rapid or not compared to the mass transfers.

In order to investigate this aspect, a study was conducted using the INSPECT code (Dickinson, 1998). This work showed that, for an irradiated iodide solution under representative conditions, if I\(_2\) is completely removed, the time required to re-establish equilibrium is in the order of a few minutes. These calculations are bounding cases because they correspond to an infinite mass transfer rate of I\(_2\). An example of the results is given in figure 1, for a solution with an initial concentration of I\(^-\) equal to 10\(^{-5}\) mol/l at 80°C, a pH equal to 5 and a dose rate of 1 kGy/h.

From these results, it was concluded that for our application it is adequate to assume that equilibrium is reached instantaneously, because typical time scale for mass transfer is much longer than that required to reach equilibrium.

![Graph](image-url)

**Figure 1:** I\(^-\) and I\(_2\) concentrations as a function of time for an irradiated solution with an initial concentration of I\(^-\) equal to 10\(^{-5}\) mol/l at 80°C, a pH equal to 5 and a dose rate of 1 kGy/h. I\(_2\) is removed at 80 minutes.
Taking into account the previous assumption, a correlation is required to estimate the steady-state concentration of molecular iodine. This correlation is based on a model proposed by Gorbovitskaya and Tiliks (1996) and experimental results of Burns and al (1990). It was also verified that the correlation gives results consistent with those of Lin (1979) at 25°C. The correlation is the following:

\[
[I_2] = 10^{-4} \sqrt{[I^-]} \exp\left(3.46 - 4.51 \times 10^{-2} T^2\right) \exp\left(-0.016 \left(pH^2 - 4.6^3\right)\right)
\]  

(1)

with \( T \) being the temperature in °C. This correlation is considered to be valid for iodide concentrations between 10⁻³ and 10⁻⁶ mol/l and for a pH value between 3 and 6. The application of the model leads to results exemplified in figure 2 for the 80-120°C temperature range at a pH of 4. Results are expressed in terms of conversion percentage defined as:

\[
100 \frac{[I_2]}{[I^-]}
\]  

(2)

for concentrations of iodide of 10⁻³, 10⁻⁴ and 10⁻⁵ mol/l.

The results show that the molecular iodine production strongly reduces as temperature increases and that the more diluted the solution is, the more efficient is radiolytic oxidation. These trends are consistent with the present understanding of the phenomena. The model was based on experiments at representative dose rates, which makes it applicable for reactor applications. However, it is pointed out that the model does not take into account the effect of dose rate which is its main deficiency.

![Figure 2: Conversion percentage of I⁻ to I₂ as a function of temperature at pH = 4 for initial concentrations of I⁻ equal to 10⁻³, 10⁻⁴ and 10⁻⁵ mol/l.](image)

**Formation of insoluble silver iodide in the sump**

It is now well established that silver can play an important role in the sump because of the formation of insoluble silver iodide from either I⁻ or I₂. This role was confirmed by the PHEBUS-FPT0 experiment (Jacquemain et al, 1997). Recent works have provided experimental data and modelling for the interaction of iodine with silver (Funke et al, 1996, Dickinson et al, 1999). This modelling has been introduced in the version 4.2 of the IODE
code. It has also been established that silver iodide is very likely to be stable under radiation (Belval-Haltier et al., 1997), although it is recognized that certain conditions have not been completely investigated and that work is still ongoing on that subject at PSI, Switzerland.

For the present work, the question to be addressed was whether or not the sump can be considered as a definitive trap for iodine. For this purpose, a parametric study was conducted using the IODE 4.2 code. Parameters investigated were the amount of silver in the sump and the percentage of oxidized silver, for both 900 MWe and 1300 MWe types of reactors which differ by the amount of silver in the control rods. It was concluded from this study that, with respect to the amount of molecular iodine released out of the containment building, the sump can be considered as an effective iodine trap for the 900 MWe but not for the 1300 MWe. Thus, sump chemistry can be disregarded for the former but not for the latter.

**Sump-to-gas and gas-to-ump mass transfer of molecular iodine**

A recent review on iodine interfacial mass transfers in the containment has been conducted (Evans et al., 1997). The authors recommend the use of the double film model for which the global transfer coefficients, $K$, with reference to liquid and $K_g$ with reference to gas, are expressed as:

$$K = \frac{1}{k_l + H/k_g}$$

$$K_g = \frac{1}{H/k_l + 1/k_g}$$

with $k_l$ and $k_g$ being the individual transfer coefficients in the liquid phase and in the gas phase respectively, and $H$ the partitioning coefficient. The partitioning of molecular iodine has been studied by many authors. We use the following relation (Lucas, 1982):

$$H = 231 \exp(1.65 \times 10^{-4} (T-571)(T-273))$$

with $T$ the temperature in K.

The determination of $k_g$ at 130°C for a non evaporating sump is based on the analysis of an experiment in the CAIMAN facility for which the pH is varied from 5 to 9. In this case, molecular iodine present in the gas phase is transferred to the sump at the time of the pH step. I$_2$ being hydrolysed instantaneously, it can be assumed that there is no resistance in the liquid, hence $K_g$ is equal to $k_g$. From the experimental results, $k_g$ was determined to be 2 $10^{-3}$ m/s. Theoretical considerations show that $k_g$ should vary proportionally to the cube of the gas temperature (Pugliarese, 1995). The following relation was then determined:

$$k_g = 3 \times 10^{-11} \ T^3$$

with $T$ in K. It was verified that this equation gives a value at 25°C consistent with those determined experimentally (Pugliarese, 1995). In case of an evaporating sump, it is assumed that $k_g$ is equal to the transfer velocity of water, with correction for the diffusion coefficient of the two species. An analysis was performed in the range 90-130°C for the liquid temperature with a gas temperature 20 degrees lower. It was concluded that $k_g$ is quasi constant in those conditions and is equal 4 $10^{-3}$ m/s.

For the determination of the $k_l$ coefficient, a study of the natural circulation flows in the sump due to the presence of fission products was performed. It showed that the flow velocity is of the order of 0.1 to 0.2 m/s for a 2000 m$^3$ sump (2 m high) and 0.04 to 0.06 m/s
for a 200 m³ sump (0.2 m high). This leads to values of $k$ equal to $9 \times 10^{-4}$ and $6 \times 10^{-4}$ m/s respectively at 130°C.

Adsorption of molecular iodine on paints

The adsorption velocity in the liquid phase was based on results of adsorption experiments with paints used in French reactors obtained by Lucas (1992) and Aujollet (1994) as well as on the analysis of results obtained in the CAIMAN facility. The different results were found to be consistent with each other, and a fit of the values for the adsorption velocity $k_{\text{ads}}$ gave the following relation:

$$k_{\text{ads}} = 10^{(0.02677-5.23)}$$

with $k_{\text{ads}}$ in dm/s and $T$ the liquid temperature in °C.

The adsorption velocity in the gas phase was studied by Belval-Haltier (1995) for representative reactor conditions. It was found that both the temperature of the carrying gas and the pre-conditioning temperature of the paint affect the adsorption velocity. If we assimilate the pre-conditioning temperature to the maximum temperature $T_{\text{max}}$ that the paint was exposed to, then the following relation can be established:

$$k_{\text{adg}} = -7.68 \times 10^{-4} T + 1.75 \times 10^{-3} T_{\text{max}} - 0.084$$

with $k_{\text{adg}}$, the adsorption velocity in dm/s, and $T$ (resp. $T_{\text{max}}$) the temperature (resp. the maximum temperature) of the gas in °C. This relation is valid in the 90-130°C temperature range only. It is also noted that the adsorption velocity can be influenced by condensation, but data are lacking for such conditions. However, it was verified on the results of one experiment conducted in the CAIMAN facility under condensing conditions that the adsorption velocity was consistent with the preceding formulation.

Formation of organic iodide

Organic iodides are of particular importance because they are not easily trapped on filters. For these species, several mechanisms of production have been identified: homogeneous or heterogeneous reactions, in aqueous phase or gas phase (Parsley, 1971). Among these mechanisms, PHEBUS-FP experiments showed that one of the most significant is the interaction of molecular iodine with paints in gas phase (Jacquemain et al., 1997, 1999).

By the time this work was conducted, only few experimental data on organic iodide production from painted surfaces in the gas were available. Furthermore, it was found that this topic was still under basic investigation and that no satisfactory model was established. It is also noted that since the interaction with iodine is very likely to depend on the structure of the paint, only results obtained with the paints used in French plants, or at least those for the same type of paint (epoxy), make sense in the context of our study.

The results of small scale experiments examined were those of Lucas (1992), Ventre and Albiol (1995), Marchand (1997), Belval-Haltier and Taylor (1999) and Baston and al (1998). Some results from the intermediate scale PHEBUS-RTF and CAIMAN experiments were also included in the analysis. Recent work showed that the organic iodide production is strongly dependant on surface concentration of iodine on the paint (Funke, 1999, Marchand and Petit, 1999). The data were then presented in terms of conversion percentage, defined as
100 times the ratio of the number of moles of organic iodide to the number of moles of iodine on the painted surface, as a function of the surface iodine concentration as in figure 3.

From that graph, it can be deduced that the conversion percentage is a decreasing function of the surface concentration. It is however not possible to directly derive a fit of these data which are relatively scattered. To be consistent with our overall model, we retained the assumption of a “conservative” conversion percentage value of 10%. This production is assumed to be instantaneous.

It is recognized that the assumptions made on this point are not satisfactory and that the uncertainty on the process will directly influence the results for plant evaluations. Models for organic iodide production are however proposed (Funke, 1999) and their possible use for reactor application must be studied.

![Conversion percentage of iodine to ICH₃ as a function of surface concentration on paint for different series of experiments.](image)

**Figure 3**: Conversion percentage of iodine to ICH₃, as a function of surface concentration on paint for different series of experiments.

Other routes for organic iodide production may exist. The first one is the interaction of iodine with paint in the sump. This process is not supposed to be dominant for the situations we examine because of the presence of silver in the sump which traps iodine.

Another possible production mechanism is the homogeneous interaction of methane with iodine in the containment atmosphere. Methane could be produced from the oxidation of boron carbide present in the control rods of the 1300 and 1450 MWe reactors. The degradation and oxidation of boron carbide control rods is presently not well known and this will be an objective for the upcoming PHEBUS-FPT3 test. Evaluations of the amount of CH₄ that can be produced were already done (Beahm et al, 1987). Similar evaluations performed with the GEMINI 1 code during the course of this study confirmed the dominating influence of the carrying gas composition. Boron carbide can be totally turned into methane in presence of excess hydrogen, which is very likely to be the case during the emission of volatile fission products. If we assume that methane and iodine concentrations in the containment are respectively of the order of 10⁻⁴ and 5 10⁻⁸ mol/l, then a literature survey showed that under
representative conditions the conversion of iodine to organic iodide can be of the order of 5%. However, the reaction of iodine with methane is relatively slow and with respect to our assumptions on heterogeneous reactions in the gas, this process can be neglected.

In conclusion, we think that the "conservative" assumptions we made on organic iodide production by interaction with paint in the gas phase account also for other production mechanisms.

**Adsorption of iodine on concrete**

1300 and 1450 MWe French plants are characterized by a double concrete containment. In case of leakage of the inner containment, iodine would escape and get in contact with bare concrete in the volume between the two containments before filtering. In order to finally estimate the release to the environment, the possible adsorption on concrete was studied.

For organic iodides, no data applicable to the situations expected in reactors were found in the literature. Considering the fact that organic iodides are moderately reactive species, we then assume that no adsorption occurs.

For molecular iodine, experiments were conducted under representative conditions (Cerf and Ventre, 1989). They showed that the adsorption velocity is about $10^{-3}$ m/s and that no desorption occurs.

3. **VALIDATION AND QUALIFICATION**

The assumptions presented in the previous section lead to a set of differential and algebraic equations which are solved using the FACSIMILE software.

After being set up, the model was assessed in consecutive steps. The first one was to compare the results to those of closed form solutions for simple problems. The second one was to calculate separate effects experiments. Both types of comparisons gave satisfactory results.

The model was then applied for the recalculation of intermediate scale experiments. Examples are shown for PHEBUS-RTF5 in figures 4 and 5 and for CAIMAN 97/04 in figures 6 and 7.

PHEBUS RTF5 is featured by an evaporating sump. The sump and gas temperatures are 90 and 75°C respectively. The value of the pH is 5. Calculated results for gas phase concentrations of molecular iodine and organic iodides are compared to experimental results. The calculated concentrations are overestimated. Both results generally lie within an order of magnitude with exception of the organic iodide concentration in the long term. This is not surprising with respect to the assumptions made for organic iodides production.
Figure 4: Experimental and calculated molecular iodine concentrations in the gas phase as a function of time for PHEBUS/RTF5.

Figure 5: Experimental and calculated organic iodide concentrations in the gas phase as a function of time for PHEBUS/RTF5.

The CAIMAN 97/04 test is featured by high temperatures in the sump (121°C) and in the gas (130°C). The pH is initially set to 5. The results compared are the iodine surface concentration on the painted plate in the gas phase and the organic iodide concentration. Both comparisons are satisfactory and the calculated results are away from the experimental ones by less than an order of magnitude. Again, the calculated organic iodide concentration is overestimated.
Figure 6: Experimental and calculated iodine surface concentration on the painted plate in the gas phase as a function of time for CAIMAN 97/04.

Figure 7: Experimental and calculated organic iodide concentration in the gas phase as a function of time for CAIMAN 97/04.

The final stage of assessment of the model was a comparison with the PHEBUS results. The aim was not to adapt the model to fit the experimental results, but rather to assess the complete set of assumptions for reactor applications by comparison to the most representative experimental results to date. The comparison for gaseous iodine concentration is shown in figure 8 for FPT0 and in figure 9 for FPT1.
**Figure 8:** Comparison of the total iodine concentration in the gas phase as a function of time between FPT0 experimental results and results calculated with reactor hypotheses.

**Figure 9:** Comparison of the total iodine concentration in the gas phase as a function of time between FPT1 experimental results and results calculated with reactor hypotheses.

It can be seen that the model is globally "conservative" with respect to PHEBUS results, particularly in the initial phase of FPT1.

With respect to its simplicity, the model is judged to be good when compared to experimental results of global experiments and adequate for reactor applications.
4. REACTOR APPLICATIONS

This section provides a sample reactor application for both 900 MWe and 1300 MWe types of reactors. The calculated situation is that of a simplified AB sequence (all temperatures are constant along the time period), which corresponds to a large break on the primary circuit with complete loss of safety injection and containment spray. Calculation conditions are summarized in Table 1. Calculated concentrations in the gas phase of both molecular iodine and organic iodides are represented in Figures 10 and 11.

**Table 1:** Calculation conditions for the AB sequence

<table>
<thead>
<tr>
<th></th>
<th>900 MWe</th>
<th>1300 MWe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Containment volume</td>
<td>50000 m³</td>
<td>70400 m³</td>
</tr>
<tr>
<td>Sump volume</td>
<td>195 m³</td>
<td>265 m³</td>
</tr>
<tr>
<td>Sump-gas interfacial area</td>
<td>800 m²</td>
<td>1160 m²</td>
</tr>
<tr>
<td>Sump painted surfaces area</td>
<td>1000 m²</td>
<td>1200 m²</td>
</tr>
<tr>
<td>Gas painted surfaces area</td>
<td>24200 m²</td>
<td>33000 m²</td>
</tr>
<tr>
<td>Mass of silver in the sump</td>
<td>114 kg</td>
<td>38.2 kg</td>
</tr>
<tr>
<td>Core iodine inventory</td>
<td>11 kg</td>
<td>15.7 kg</td>
</tr>
<tr>
<td>pH</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Liquid temperature</td>
<td>85°C</td>
<td>102°C</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>96°C</td>
<td>102°C</td>
</tr>
</tbody>
</table>

**Figure 10:** $I_2$ and $ICH_3$ concentrations in the gas phase as a function of time for the AB sequence on a 900 MWe French PWR.
Figure 11: I$_2$ and ICH$_3$ concentrations in the gas phase as a function of time for the AB sequence on a 1300 MWe French PWR.

Figure 10 also shows the influence of the choice of the maximum temperature for computing the adsorption coefficient on painted surfaces. In one case, this temperature was set equal to that of the gas, in the other case to 130°C. It can be seen that this has a large influence on the molecular iodine concentration in the short term, but it has virtually no influence on the organic iodide concentration.

Figure 11 also shows that molecular iodine concentration reaches an equilibrium as the adsorption is balanced by the emission from the sump. This is because the amount of silver in the sump is low. This in turn induces a very small increase of the organic iodide concentration in the long term.

5. CONCLUSION

A complete set of assumptions was formulated in order to model the iodine behavior in French PWRs in case of severe accidents leading to core melt and vessel rupture. These assumptions lead to a model in which the iodine behavior is dominated by reactions in the gas phase. Even if the proposed modelling takes into account the latest available results, some assumptions will need to be revisited when the knowledge improves. This is particularly the case for the amount of gaseous iodine initially released to the containment as well as for the production of organic iodides.

Time integration of the set of equation is performed using the FACSIMILE software. Comparison to experimental results gave satisfactory results with respect to the simplicity of the model. It was also shown that the set of assumptions is “conservative” with respect to the PHEBUS FP test results.
After including some complementary features, such as a modelling of spray, the presented model will be used for source term evaluation, mainly in the frame of the level 2 PSA.

6. REFERENCES


Belval-Haltier, E. and Taylor, P., 1999, Iodine Volatile Species Production from Painted Surfaces of the Reactor Containment during a Severe Accident. This workshop.


Marchand, C., Petit, M. 1999. Small Scale Experiments on Organic Iodide Production from Iodine - Painted Surface Interaction. This workshop.


IODINE BEHAVIOUR CALCULATIONS FOR A TMLB SEQUENCE.

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ABSTRACT

The chemical behaviour of iodine in containment during a TMLB sequence in a Spanish NPP has been analysed with IODE 4.0, a detailed chemistry code, and the results compared with the predictions of MAAP 3.0B, an integrated PSA code. The objective of the study is to estimate the impact that a detailed chemistry modelling would have in MAAP, by analysing the contribution of volatile iodine species to the aerosol leakage predicted by MAAP.

In order to make the comparison as straightforward as possible, thermal-hydraulic data calculated by MAAP 3.0B have been used as input for IODE. Nevertheless, the coupling between the codes presents some difficulties, and an analysis has been performed of the uncertainty due to the hypothesis made for data not calculated by MAAP. Additionally, some modifications have been made to the code IODE to reflect the improvement in the current understanding of iodine behaviour, but some areas of uncertainty still exist. Sensitivity calculations have been performed to check the effect of the degree of oxidation of silver aerosols, interfacial mass-transfer coefficients, and surface deposition rates. The results show that gaseous iodine release contributes to less than 20% to the release predicted by MAAP. A strong sensitivity of the results has been found towards the value of the pH of the sump and the modelling used for silver iodine interactions.

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1. INTRODUCTION

Due to the complexity of some phenomena and to the lack of validated models to describe some processes, it is generally accepted that there are still uncertainties in the capability of the codes to predict the source term in case of a severe accident. The present study is centred in the analysis of the chemistry of containment as modelled by MAAP, routinely used in PSA level II analysis. To assess the validity of the code, an accidental
sequence has been studied, and the results compared to the results of IODE, a detailed chemistry code.

According to the chemical modelling followed by MAAP (EPRI, 1996), iodine can be found in containment in the form of caesium iodine (CsI) aerosols, both suspended in the atmosphere and deposited on surfaces. IODE (Tarabelli, 1995) models volatile iodine species, giving an special importance to the equilibrium of the iodine species between the liquid and gas phase. Iodine can volatilise from the sump, due to production of volatile species by means of chemical reactions, not modelled in MAAP. It can be concluded that the chemistry modelled by MAAP is quite simplified. The comparison of the results of both codes for the same sequence could allow to estimate the uncertainty associated to the code MAAP.

2. DESCRIPTION OF THE SEQUENCE

The plant selected is a PWR of 2785 MWt, with a large dry containment. The sequence is a Station Blackout initiated by the loss of the 400 KV line. The accident follows the evolution characteristic of a TMLB sequence. The core is uncovered 2 hours after scram, and the vessel fails 1.2 hours later. The release of fission products takes place at high pressure. The ECCS and all the containment safeguards are assumed to be inoperative, which causes an increase of the pressure and temperature inside the containment, that would eventually lead to a containment failure after 48 hours if there is not intervention of the operators. During this time a 1% vol. leak flow rate is modelled. The contribution of this sequence to the total damage frequency is 0.35%, with a frequency of $0.2260 \times 10^{-6} \text{ year}^{-1}$ (Otero, 1997). The total contribution of sequences initiated by the loss of power of the 400 KV is $0.477 \text{ year}^{-1}$, which represents a 32.758% of the total damage frequency. This group does not include sequences initiated by a total loss of external power, which have a separate contribution of 10% to the total damage frequency.

From the chemical point of view, the key events in the accident are shown in table 1.

<table>
<thead>
<tr>
<th>Table 1.</th>
<th>Characteristic times of the sequence.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water arrival to the lower compartment</td>
<td>4880 s</td>
</tr>
<tr>
<td>Core uncover</td>
<td>6734 s</td>
</tr>
<tr>
<td>Maximum CsI liberation to the sump</td>
<td>11410 s</td>
</tr>
<tr>
<td>Maximum water mass in the sump</td>
<td>11460 s</td>
</tr>
<tr>
<td>Vessel Failure</td>
<td>11512 s</td>
</tr>
<tr>
<td>Drying* of the upper compartment sump</td>
<td>65700 s</td>
</tr>
<tr>
<td>Drying* of the lower and annular compartment sumps</td>
<td>43900 s</td>
</tr>
<tr>
<td>Maximum liberation of silver to the sump</td>
<td>70280 s</td>
</tr>
</tbody>
</table>

*The sump is considered dried when the water inventory is lower than 10 l.

3. MODELLING OF THE CODE MAAP

3.1 Nodalization of the Containment

The nodalization used by MAAP divides the containment in four compartments, each one composed of a sump and a gas phase. The upper compartment (A) is located above the operation plant. The lower compartment (B) is located below the operation plant. Although
the vessel is physically situated inside this compartment, it has a separate nodalization in MAAP, so that its modelling is independent of the lower compartment. The annular compartment (D) surrounds the lower compartment at the same level. Finally, the cavity (C) is located below the lower compartment. All the concrete surfaces are covered with an epoxide-type paint. Metallic surfaces correspond to the equipment, present in both the upper and lower compartments.

Table 2. Main Geometric features of the four compartments of the containment.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Volume of the Upper Compartment (A)</td>
<td>50437.8 m³</td>
</tr>
<tr>
<td>Distance from the operation plant to the highest point of the dome</td>
<td>48.3 m</td>
</tr>
<tr>
<td>Distance from the operation plant to the upper part of the cylindrical zone</td>
<td>28.3 m</td>
</tr>
<tr>
<td>Cylinder radius</td>
<td>20.0 m</td>
</tr>
<tr>
<td>Area of the operation plant</td>
<td>675.59 m²</td>
</tr>
<tr>
<td>Medium height of the metallic equipment in the upper compartment</td>
<td>21.68 m</td>
</tr>
<tr>
<td>Free Volume of the lower compartment (B)</td>
<td>4293.5 m³</td>
</tr>
<tr>
<td>Height of the lower compartment (B)</td>
<td>14.5 m</td>
</tr>
<tr>
<td>Deposition surface of the lower compartment (B)</td>
<td>420 m²</td>
</tr>
<tr>
<td>Medium height of the metallic equipment in the lower compartment</td>
<td>6.58 m</td>
</tr>
<tr>
<td>Free Volume of the Annular Compartment (D)</td>
<td>396.8 m³</td>
</tr>
<tr>
<td>Distance between the floor of the lower compartment and the floor of the annular compartment</td>
<td>0.0 m</td>
</tr>
<tr>
<td>Free Volume of the Reactor Cavity (C)</td>
<td>6987.8 m³</td>
</tr>
<tr>
<td>Distance from the bottom of the cavity to the floor of the lower compartment</td>
<td>8.47 m</td>
</tr>
</tbody>
</table>

3.2 Containment Sump

For illustration purposes, the maximum liquid level reached along the sequence in each compartment is shown in table 3. As the lower and annular compartments are located at the same height, the liquid level in both sumps is always equal.

Table 3. Maximum liquid level reached along the sequence in each compartment.

<table>
<thead>
<tr>
<th>Compartment</th>
<th>Liquid Level</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper Compartment</td>
<td>0.0338 m</td>
<td>6640 s</td>
</tr>
<tr>
<td>Lower Compartment</td>
<td>0.144 m</td>
<td>11500 s</td>
</tr>
<tr>
<td>Annular Compartment</td>
<td>0.144 m</td>
<td>11500 s</td>
</tr>
<tr>
<td>Reactor Cavity</td>
<td>1.428 m</td>
<td>20700 s</td>
</tr>
</tbody>
</table>

3.3 Chemical Modelling

Silver forms the 80% of the control rod alloy, with an initial inventory of 551.87 Kg. The initial iodine inventory is 14.60 kg., of which a 96.2% is retained in the primary circuit. Thus, the mass of iodine reaching the containment is 0.56 kg., in the form of caesium iodine (CsI) aerosols.

MAAP 3.0 divides fission products in 12 groups (Herrero, 1997). The only iodine species considered is CsI, which belongs to the second group, together with CsRb. It is assumed that all the available iodine is combined with the alkaline elements, due to the fact
that the molar ratio is approximately 10 to 1 (in favour of Cs). The remaining Caesium and Rubidium that are not combined with iodine are present as CsOH and RbOH respectively, composing the sixth group of fission products. The code considers that the species belonging to group 1 (noble gases), 2 (CsI and RbI) and 6 (CsOH and RbOH) can be volatile, provided that they present a non-negligible vapour pressure. For CsI this only occurs above 150°C.

The fission products of the 12 groups can be found in containment in three different states: vapour, aerosol and deposited. Noble gases exist only in vapour form, and the second and third states of their group correspond to inert aerosols. Once that in-vessel or ex-vessel liberation of the fission products has taken place, their chemical state is frozen, and is defined by the properties of the above mentioned groups. Given the dominance of CsI over RbI, the properties chosen to model the behaviour of the whole group are those corresponding to CsI.

Fission products can move among compartments. Gas circulation and water flow from one sump to another connected pool, by instance in the case of overflowing, is also allowed. It is assumed that if water is available, fission products are dissolved when deposited. That occurs, for instance, when aerosols reach a pool or are deposited on a steam-condensing surface. CsI deposited and dissolved in the liquid is transported along with water, for instance when there is a flow to another pool. However, it has to be kept in mind that the dissolution modelled by the code does not include a change in the chemical composition. This implies that the CsI that reaches the containment can be found in aerosol form, both suspended in the atmosphere or deposited in surfaces, but no volatile forms are allowed in this group for the conditions of the containment prevailing during this sequence, where the temperature is not high enough to produce a significant vapour pressure of CsI. In this sequence deposition of aerosols is mainly due to gravitational settling, other mechanisms contribution less than 10% to the overall deposition in containment.

Finally, MAAP 3.0B does not estimate the value of the pH of the liquid composing the sump.

4. THE CODE IODE

The objective of the code IODE 4.0 (Tarabelli, 1995) is to calculate the concentration of iodine species in the atmosphere and the sump and the amount of iodine that is irreversibly trapped by various surfaces (surfaces of the containment, silver from the control rods, etc.), produced in case of a severe accident in each compartment of a reactor containment.

IODE is a semi-mechanistic code which employs well-known mechanistic chemical reactions and uses a phenomenological approach for the modelling of complex reactions where the mechanistic approach is not reliable (radiolysis reactions, organic iodides formation). The code IODE models the thermal and radiolysis reactions of mineral species (I, I₂, HOI, IO₃, AgI) in the water solution, the formation and decomposition reactions of organic species (CH₃I is the only species considered) and the mass transfer of the volatile I₂ (sump-atmosphere interfacial mass transfer, adsorption on and desorption from surfaces, dissolution in condensed steam and washing-down to the sump) and CH₃I species (sump-atmosphere interfacial mass transfer, dissolution in condensed steam and washing-down to the sump).
4.1 Models of the code IODE 4.0.

Chemical Reactions

The code IODE 4.0 (Tarabelli, 1995) models semiempirically the chemical evolution of the system formed by a sump and a gaseous phase, by means of a set of 15 reactions, of which 13 occur in the liquid phase and 2 take place in the atmosphere of the containment:

In the gas phase:

(1) \( I_2 \) Oxidation (by ozone)
\[
2 \ I_2 + 4 \ O_3 \rightleftharpoons 4 \ IO_3^-
\]

(2) Organic Iodide formation
\[
I_2 + 2 \ CH_3R \rightleftharpoons 2 \ CH_3I + 2R
\]

In the liquid phase:

(3) \( I_2 \) Hydrolysis
\[
I_2 + H_2O \rightleftharpoons HOI + I^- + H^+
\]

(4) HOI Dissociation
\[
HOI \rightarrow OI^- + H^+
\]

(5) HOI Disproportion
\[
3 \ HOI \rightleftharpoons 3 \ I^- + 2 \ H^+
\]

(6) \( I^- \) Oxidation by Oxygen
\[
2I^- + \frac{1}{2} \ O_2 + 2H^+ \rightarrow I_2 + H_2O
\]

(7) Radiolytic \( I^- \) Oxidation
\[
2 I^- + h\nu \rightarrow I_2
\]

(8) Organic Iodide Formation
\[
I_2 + 2 \ CH_3R \rightleftharpoons 2 \ CH_3I + 2 \ R
\]

(9) Organic Radiolytic Decomposition
\[
2CH_3I + h\nu \rightarrow 2CH_3 + I_2
\]

(10) AgI Radiolytic Decomposition
\[
2AgI + h\nu \rightarrow 2Ag + I_2
\]

(11) AgI Formation
\[
I^- + Ag^+ \rightarrow AgI
\]

(12) \( CH_3I \) Hydrolysis
\[
CH_3I + H_2O \rightarrow I^- + CH_3OH + H^+
\]

(13) \( CH_3I \) Hydrolysis with OH
\[
CH_3I + OH^- \rightarrow I^- + CH_3OH
\]

(14) Radiolytic \( IO_3^- \) Reduction
\[
2 IO_3^- + h\nu \rightarrow I_2 + 3 \ O_2
\]

Besides, the code models organic iodide formation by interaction of iodine with surfaces.

4.2 Modifications to the code IODE 4.0

Inclusion of the Ag/I reaction.

A new modelling of silver/iodine reactions has been implemented in the code following the conclusions of a recent EC SCA (Dickinson, 1997), whose objective was to improve the current modelling of silver/iodine reactions in the sump (Herrero, 1996). The result of the project was a common expression of the rate constant for the reaction \( I^- + Ag \rightarrow AgI \), which occurs by means of a silver oxidation step.

Inclusion of a sedimentation rate of the \( IO_3^- \) generated in the gas phase.

Iodate (\( IO_3^- \)) evolution has been modified with respect to the original formulation in the code IODE 4.0 (Herrero, 1996). According to the code, \( IO_3^- \) is generated in the atmosphere of the containment by reaction (1) and remains in the gas phase. Studies performed by Vikis et al. (Vikis, 1990 and Vikis, 1985) show that molecular iodine (\( I_2 \)) can
react with ozone (O₃) to form various oxides (I₄O₉, I₂O₅) that in humid atmospheres can
generate oxyacids (HIO₃) by reaction with water. This reaction is totally shifted to the right
(towards the formation of IO₃). Based on these studies, it has been assumed that the IO₃⁻ is in
particulate form and a transfer rate from the atmosphere into the sump has been included in
the code, corresponding to particles of a medium diameter of 0.3 µm.

Despite the improvement in the modelling, a note of caution has to be made
concerning this reaction. The formation of IO₃⁻ in the atmosphere by reaction (1) follows a
first order kinetics with respect to molecular iodine, but is independent of the ozone
concentration. It is well known that ozone availability can be strongly affected by a complex
series of processes (surface interactions, containment geometry) that are not modelled by the
code, so that the kinetic expression is oversimplified (Jacquemain, 1998). This topic is the
object of current experimental research (Funke, 1999) aimed at improving the understanding
of this reaction under representative conditions.

**Inclusion of a time dependent rate for the silver input into the sump.**

In the original modelling of the code IODE, silver mass is entered as an initial input,
that decreases along the calculation as a consequence of the formation of silver iodide. The
previous modelling of the code only allowed the interaction of silver with I₂. This process,
while being very effective in reducing the concentration of I₂, did not influence significantly
silver concentration in the sump, due to the dominance of silver over iodine.

However, for the sequence under study, the release of silver occurs at a later time than
iodine liberation. The maximum of silver liberation to the containment takes place 70280 s,
while the maximum of iodine occurs at 11410 s, at the beginning of the sequence (see table
1). Additionally it has to be considered that the Ag/I reaction, whose kinetics is, in a broad
range of conditions, first order with respect to silver oxide, can produce a significant
depletion of the mass of silver oxide, which in turn, can be one or two orders of magnitude
smaller than the total mass of silver. As a consequence of both facts, for most of the duration
of the sequence, the ratio Ag:I is relatively low. For these reasons, the code has been modified
to include a silver input into the sump as a function of time.

**4.3 Data used in the code IODE 4.0**

Some of the data required to complete the input file for IODE match those produced
by MAAP as an output. Other data can be, directly or indirectly, deduced from them. Finally,
there are some variables necessary for a chemical analysis that MAAP 3.0B does not
consider, like the value of the pH of the sump, for instance. For these variables, if a certain
degree of uncertainty existed, a sensitivity calculation has been performed.

It has been assumed that the gas is homogeneously distributed among the different
compartments, and therefore the total free volume has been taken as the sum of the free
volumes. Thermalhydraulic conditions, such as gas and sump temperatures, total and partial
pressures, etc., are input as a function of time. They have been calculated by a mean average
of the results from MAAP, for the different compartments of the containment. When
variations among compartments existed, a weighted average has been taken. The
condensation flow rate has been obtained by adding the corresponding rates for the upper,
lower and annular compartment.
The containment sumps have been modelled by means of a single liquid volume, corresponding to the pools formed in the upper, lower and annular compartment. It has been assumed that the sump composition is homogeneous, justified by the existence of water flows among the compartments during most of the duration of the sequence. The liquid mass, temperature, composition and area of the surfaces in contact with the aqueous phase change as a function of time.

The cavity water has not been included in the total liquid volume because it does not contain a significant amount of CsI aerosols, due to the small deposition area of the compartment. Similarly, the water volume corresponding to the so-called containment sump has not been included in the calculation. This sump receives water (12.9 m³) at the beginning of the sequence, before the arrival of the fission products, and there are no water flows connecting it with other pools. The main function of this sump is to provide water for the containment safeguards (for instance, for spraying in recirculation mode), which are inoperative in this sequence.

The total surfaces (metallic and painted) and the sump-atmosphere interfacial area have been calculated by adding the corresponding ones for the upper, lower and annular compartments.

As a means to control the pH of the sumps in case of an accident, the plant is provided with 6 baskets of sodium trifosfate (TSP), located on the floor of the operation plant. This system substitutes the original design in which pH control was achieved by the addition of sodium hydroxide to the water injected by the spray system. It is estimated that dissolution of the TSP by the spraying water, and the mixing with the liquid in the sumps would result in a sump pH of approximately 8.5.

Two hypotheses have been made in the present study. In the first one it has been assumed that pH is effectively kept at values around 8.5, thanks to the dissolution of the TSP. In the second one, it has been followed the possibility that the TSP is not dissolved in the sump water, due to the spray being inoperative, or the lowering of the baskets not being achieved. For this case, an initial value of 5.5 has been assigned to the sump pH, which corresponds to the borated water used as a refrigerant. This value has been linearly decreased along the sequence to reach a value of 4.5 at 100000 seconds, reflecting the effect of the dissolution of nitric acid in the sump. Nitric acid can be produced by air radiolysis, which yields nitrogen oxides that in the presence of steam condensate and reach the sump (Ashmore, 1996). The first case can be considered a conservative estimate, as it is generally accepted that sump acidity (low values of the pH) promotes iodine volatility (Evans, 1997).

The dose rate has been calculated with the code MARS, at a height of 0.5 m from the floor. It has to be noted that the values obtained would have been higher had the dose rate been calculated closer to the floor.

Iodine arrival into the sump is reproduced by an initial input of iodine plus a time dependent function, which has been derived from the CsI aerosol settling rate in containment, taken from the results of MAAP. The total mass of caesium iodide (CsI) released to containment is 1.11 kg, i.e. 0.56 kg of iodine.
Silver input into the sump has been divided in 32 stages. In each of them, the arrival velocity has been approximated as the sedimentation rate of the inert aerosol material taken from the output of MAAP, averaged over the three compartments considered. At the end of the calculation, there are 58.6 Kg of silver in the sump. It has to be noted that the maximum input rate takes place at 72,000 s, when the calculation has finished. The silver specific surface, which enters the kinetic equation of the reaction Ag/I₂ is 1000 m² kg⁻¹.

The calculation performed with IODE begins at 11500 seconds, when the release of fission products to the containment takes place, and ends at 60000 seconds, when the water inventory of the sump has decreased to values lower than 10 litres.

5. CALCULATIONS PERFORMED WITH THE CODE IODE

5.1 Description of the Reference Case

Taking as an input the data presented, a reference calculation has been performed. Most of the constants used for this case (chemical reaction constants, mass transfer, etc.) correspond to the default values of the code (Tarabelli, 1995). Some modifications have been made following the findings of recent research projects, or reflecting the specific conditions of this sequence. The value of the constants that have been modified with respect to the default values of the code are shown in table 4.

Table 4  Mass transfer and surface deposition/desorption rate constants used for the reference case.

<table>
<thead>
<tr>
<th></th>
<th>Surface</th>
<th>Gas Phase</th>
<th>Liquid Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Constant</td>
<td>SS</td>
<td>10⁻⁴ m/s</td>
<td>1.4 10⁻⁶ m/s</td>
</tr>
<tr>
<td>Deposition Constant</td>
<td>Painted</td>
<td>7.1 10⁻⁴ m/s</td>
<td>4 10⁻⁶ m/s</td>
</tr>
<tr>
<td>Desorption Constant</td>
<td>SS</td>
<td>10⁶ s⁻¹</td>
<td>10⁻⁷ s⁻¹</td>
</tr>
<tr>
<td>Desorption Constant</td>
<td>Painted</td>
<td>6. 10⁻⁷ s⁻¹</td>
<td>2. 10⁻⁸ s⁻¹</td>
</tr>
<tr>
<td>Ag/I Reaction Rate Constant</td>
<td></td>
<td></td>
<td>2.10³ mm l mol⁻¹ s⁻¹</td>
</tr>
<tr>
<td>Ag/I₂ Reaction Rate Constant</td>
<td></td>
<td></td>
<td>10⁻¹ mm s⁻¹</td>
</tr>
<tr>
<td>I₂ Mass Transfer Rate</td>
<td></td>
<td>1.1 10⁻⁴ m/s</td>
<td></td>
</tr>
<tr>
<td>CH₃I Mass Transfer Rate</td>
<td></td>
<td>1.1 10⁻⁴ m/s</td>
<td></td>
</tr>
<tr>
<td>Degree of oxidation of silver aerosols</td>
<td></td>
<td>10 %</td>
<td></td>
</tr>
</tbody>
</table>

The value of the interfacial mass transfer constant chosen is relatively high (Evans, 1997), when compared to medium scale experiments, but may limit the volatilisation of iodine from the sump, considering that mass transfer is favoured in the conditions of this sequence, where there are significant temperature differences among liquid, gases and structures, and the sump is boiling for most of the duration of the calculation. This value has been the subject of a parametric study.

The value of the oxidation degree of the silver aerosols that reach the sump presents a high uncertainty due to the lack of data concerning silver oxidation in the conditions prevailing during a severe accident. In fact, only very recently it has been concluded that silver/iodine reaction does not take place significantly unless there is a previous oxidation step (Funke, 1996). The conditions of this sequence (high temperature and humidity, oxidising materials present both in the sump and the atmosphere) may favour a significant silver oxidation. The degree of oxidation used for the reference case has been set arbitrarily to 10%. However, this assumption is not conservative, due to the fact that the reaction between
silver oxide and iodide is very effective, causing the retention of iodine in the sump. As there is, unquestionably, a high uncertainty related to this value, a parametric study has been made changing this value between 0% and 10%.

5.2 Results of the Reference Case

At 60000 s the distribution of iodine in containment is shown in the next table.

<table>
<thead>
<tr>
<th></th>
<th>Iodine distribution (in kg.) in containment at 60000 s for the reference case.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaked to the environment</td>
<td>1.76 $10^{-7}$</td>
</tr>
<tr>
<td>Present in the sump</td>
<td>AgI 5.61 $10^{1}$</td>
</tr>
<tr>
<td></td>
<td>I$_2$ 4.75 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td>CH$_3$I 3.89 $10^{11}$</td>
</tr>
<tr>
<td></td>
<td>HOI 1.20 $10^{6}$</td>
</tr>
<tr>
<td></td>
<td>I$^{-}$ 6.56 $10^{8}$</td>
</tr>
<tr>
<td></td>
<td>IO$_3^{-}$ 7.55 $10^{5}$</td>
</tr>
<tr>
<td></td>
<td>Total 5.61 $10^{1}$</td>
</tr>
<tr>
<td>Deposited in the gas phase</td>
<td>SS 9.943 $10^{7}$</td>
</tr>
<tr>
<td></td>
<td>Painted 8.792 $10^{6}$</td>
</tr>
<tr>
<td></td>
<td>Total 9.786 $10^{6}$</td>
</tr>
<tr>
<td>Present in the atmosphere</td>
<td>I$_2$ 1.285 $10^{8}$</td>
</tr>
<tr>
<td></td>
<td>CH$_3$I 2.060 $10^{6}$</td>
</tr>
<tr>
<td></td>
<td>Total 2.78 $10^{5}$</td>
</tr>
<tr>
<td></td>
<td>IO$_3^{-}$ 2.568 $10^{5}$</td>
</tr>
<tr>
<td>Deposited in the liquid phase</td>
<td>SS 6.449 $10^{4}$</td>
</tr>
<tr>
<td></td>
<td>Painted 4.090 $10^{6}$</td>
</tr>
<tr>
<td></td>
<td>Total 4.100 $10^{6}$</td>
</tr>
</tbody>
</table>

As shown in figure 1, the initial iodide (I$^{-}$) concentration that is dissolved in the sump reaches values of $10^{-5}$ M, later decreased due to the equilibrium with I$_2$ and IO$_3^{-}$, governed by reactions (3) and (5) (section 4.1). For acidic conditions the equilibrium is shifted towards the formation of elemental iodine. Simultaneously, other competing mechanisms, such as the formation of organic iodides, deposition on walls, and transfer of volatile species to the containment atmosphere cause a decrease in the concentration of I$_2$ in the liquid phase, so that it always remains below $10^{-9}$ M.

In the gas phase, the most relevant feature is the importance of iodine adsorption on painted walls, which present a high surface. As shown in figure 2, the dominant volatile species is CH$_3$I, that in the code represents, generically, all the possible organic iodides. A source of uncertainty is related to this result. It is generally accepted that the modelling of organic iodide formation and destruction in the codes is not satisfactory, being currently the subject of experimental studies (Dickinson, 1997).

The leak of iodine to the environment is proportional to the leak rate from containment, and to the concentration of volatile species in the atmosphere. Figure 3 shows the mass of iodine leaked to the environment as a function of time. According to the predictions from MAAP, the leak of caesium iodide aerosols reaches a value below $3 \times 10^{1}$ gr of iodine at 60000 s. The comparison with the results from IODE, for the reference
calculation, shows that volatile iodine contributes less than a 1% to the total iodine leak. This result can be explained taking into account that most of the iodine that reaches the sump is trapped forming silver iodine, which is the dominant species formed. The formation of this species inhibits both the transfer of $I_2$ to the atmosphere of the containment and the formation of organic iodides. In a similar way, the deposition on painted surfaces has the effect of reducing the amount of volatile iodine in the gas phase available for leakage.

**Fig. 1** Evolution of the concentration of iodine in the sump for the reference case.

**Fig. 2** Evolution of the concentration of iodine in the gas phase for the reference case.

There is, however, a fundamental difference when comparing the aerosol leak (as predicted by MAAP) and the volatile iodine leak (calculated by IODE): the evolution with time. The mass of iodine aerosols suspended in the atmosphere of the containment is deposited on surfaces by several mechanisms (mainly gravitational settling). This deposition reduces the amount of aerosols available for leakage so that 90% of the release to the environment takes place before 41000 s. On the contrary, volatile iodine species are produced after aerosol deposition. The results of the calculation show that gaseous iodine concentration does not reach an stationary state, and iodine release increases with time.
Fig. 3 Mass of iodine leaked to the environment.

5.3 Parametric Studies

A series of parametric studies has been performed in order to estimate the effect of the uncertainty related to the input data of the code IODE. It has been considered that the factors with more influence in the results are the degree of oxidation of the silver aerosols, the evolution of the value of the pH along the sequence, the value of the mass transfer rates, the value of the deposition rates on surfaces and the modelling of silver/iodine interactions. The values of the parameters that differ form the reference calculation are shown in Table 6.

### Table 6. Values of the parameters used in the sensibility studies.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Degree of oxidation of silver</th>
<th>10 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>s01</td>
<td>Degree of oxidation of silver</td>
<td>3 %</td>
</tr>
<tr>
<td>s02</td>
<td>Degree of oxidation of silver</td>
<td>1 %</td>
</tr>
<tr>
<td>s03</td>
<td>Degree of oxidation of silver</td>
<td>0.5 %</td>
</tr>
<tr>
<td>Reference</td>
<td>pH (t_f-start)</td>
<td>5.5 - 4.5</td>
</tr>
<tr>
<td>s10</td>
<td>pH (t_f-end)</td>
<td>8.5 - 7.5</td>
</tr>
<tr>
<td>Reference</td>
<td>Mass transfer constant</td>
<td>1.1 \times 10^4 m/s</td>
</tr>
<tr>
<td>s21</td>
<td>Mass transfer constant</td>
<td>5.5 \times 10^3 m/s</td>
</tr>
<tr>
<td>s22</td>
<td>Mass transfer constant</td>
<td>5.5 \times 10^4 m/s</td>
</tr>
<tr>
<td>s23</td>
<td>Mass transfer constant</td>
<td>1.1 \times 10^3 m/s</td>
</tr>
<tr>
<td>Reference</td>
<td>Deposition Rate in gas paints</td>
<td>7.1 \times 10^4 m/s</td>
</tr>
<tr>
<td>Reference</td>
<td>Deposition Rate in liquid paints</td>
<td>4. \times 10^6 m/s</td>
</tr>
<tr>
<td>s31</td>
<td>Deposition Rate in gas paints</td>
<td>7.1 \times 10^5 m/s</td>
</tr>
<tr>
<td>s32</td>
<td>Deposition Rate in liquid paints</td>
<td>4. \times 10^7 m/s</td>
</tr>
<tr>
<td>Reference</td>
<td>Silver/iodine Reactions considered</td>
<td>Ag/I and Ag/I_2</td>
</tr>
<tr>
<td>s41</td>
<td>Silver/iodine Reactions considered</td>
<td>----</td>
</tr>
<tr>
<td>s42</td>
<td>Silver/iodine Reactions considered</td>
<td>Ag/I_2</td>
</tr>
</tbody>
</table>

5.4 Results of the Parametric Studies

Table 7 presents a summary of the results obtained for the sensibility calculations. In all the cases considered, at least 90% of the iodine reaching the containment is trapped in the
sump. On the contrary, the mass fraction of iodine that is released to the environment presents variations of 4 orders of magnitude, proving the influence of some parameters.

When considering the results, it has to be kept in mind that the reference case is not conservative. As a consequence, the mass of iodine leaked to the environment presents a strong increase with respect to the reference calculation for some of the cases considered. In general, it can be observed that the absolute values of the release are relatively small in all cases, due to the fact that only 3.8% of the bundle inventory of iodine reaches the containment and that the leak rate is 1% vol/day.

<table>
<thead>
<tr>
<th>Case</th>
<th>Leaked</th>
<th>Sump</th>
<th>Atmosphere</th>
<th>Atmospheric Deposits</th>
<th>Sump Deposits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>1.76E-07</td>
<td>5.614E-01</td>
<td>2.775E-05</td>
<td>9.786E-06</td>
<td>4.100E-06</td>
</tr>
<tr>
<td>c15</td>
<td>4.41E-05</td>
<td>5.273E-01</td>
<td>3.092E-02</td>
<td>1.713E-03</td>
<td>9.758E-04</td>
</tr>
<tr>
<td>s01</td>
<td>3.37E-07</td>
<td>5.613E-01</td>
<td>5.290E-05</td>
<td>1.791E-05</td>
<td>7.600E-06</td>
</tr>
<tr>
<td>s02</td>
<td>3.46E-06</td>
<td>5.599E-01</td>
<td>1.350E-03</td>
<td>1.096E-04</td>
<td>6.000E-05</td>
</tr>
<tr>
<td>s03</td>
<td>6.18E-06</td>
<td>5.581E-01</td>
<td>3.056E-03</td>
<td>1.470E-04</td>
<td>8.000E-05</td>
</tr>
<tr>
<td>s10</td>
<td>2.36E-09</td>
<td>5.613E-01</td>
<td>3.694E-07</td>
<td>6.817E-10</td>
<td>2.900E-10</td>
</tr>
<tr>
<td>s21</td>
<td>9.99E-08</td>
<td>5.614E-01</td>
<td>1.573E-05</td>
<td>5.531E-06</td>
<td>4.700E-06</td>
</tr>
<tr>
<td>s22</td>
<td>4.58E-07</td>
<td>5.613E-01</td>
<td>7.283E-05</td>
<td>2.467E-05</td>
<td>2.200E-06</td>
</tr>
<tr>
<td>s23</td>
<td>5.61E-07</td>
<td>5.613E-01</td>
<td>9.02E-05</td>
<td>2.976E-06</td>
<td>1.396E-06</td>
</tr>
<tr>
<td>s31</td>
<td>1.88E-07</td>
<td>5.614E-01</td>
<td>2.954E-05</td>
<td>2.005E-06</td>
<td>4.200E-06</td>
</tr>
<tr>
<td>s32</td>
<td>1.77E-07</td>
<td>5.614E-01</td>
<td>2.795E-05</td>
<td>9.863E-06</td>
<td>5.000E-07</td>
</tr>
<tr>
<td>s41</td>
<td>5.86E-05</td>
<td>5.004E-01</td>
<td>5.222E-02</td>
<td>2.392E-03</td>
<td>1.431E-03</td>
</tr>
<tr>
<td>s42</td>
<td>5.86E-05</td>
<td>5.004E-01</td>
<td>5.222E-02</td>
<td>2.392E-03</td>
<td>1.431E-03</td>
</tr>
</tbody>
</table>

As expected (Dutton, 1995), there is a major influence of the value of the sump pH in the results. The comparison between the reference case (low pH) case s10 (high pH) shows that the release decreases in 2 orders of magnitude when pH control is achieved.

A strong variation is also observed when considering different models for Ag/I interactions, as can be observed in figure 4. The mass of iodine leaked if Ag/I interaction is not included in the calculation increases by a factor 300 with respect to the reference case. In this calculation, where a 10% oxidation of silver was assumed, the ratio of silver oxide that enters the sump to total iodine is 10:1. This ratio is smaller during the first hours of the calculation, because iodide and silver releases occur at different times. In the intermediate case of a 0.5% of silver oxidation, only 0.3 Kg of silver oxide are available to react with I⁻, so that the ratio silver oxide/iodine is less that 1. In this case, all the silver oxide reacts with iodide and the release to the environment is higher that in the reference case by a factor 35. In general, within the range of 0.5%-3% of silver oxidation, the release of iodine to the environment is strongly related to the kinetics of the silver/iodide interaction.
Fig. 4  Mass of iodine leaked to the environment. Effect of the Ag/I modelling.

Iodine transfer from the sump to the gas phase is the result of two processes. First, the production of volatile species in the sump, by means of the hydrolysis and oxidation reactions. Later, the transfer of these compounds through the liquid-gas interface. The velocity of the global process can be limited both by the production rate in the sump or by the interfacial mass-transfer constant. In the reference case, an intermediate situation occurs. As the leak to the environment is proportional to the mass of gaseous iodine present in the atmosphere, an increase or decrease in the mass transfer rate has the direct consequence of increasing or decreasing, respectively, the total iodine leaked, as can be observed in figure 5.

Fig. 5  Mass of iodine leaked to the environment. Effect of the mass transfer rate.

By comparison, the influence of decreasing the value of the deposition constants is less significant, as can be observed in table 7.
6. CONCLUSIONS

The analysis of a TMLB sequence shows that the release of volatile iodine species to the environment contributes in less than a 20% to the release predicted by MAAP in all the cases studied. MAAP considers that iodine can be found in containment as a CsI aerosol, so that IODE results have to be added to the leak predicted by MAAP. The overall gaseous leakage is very sensitive to assumptions made in the chemistry modelling.

The results show, as expected, a significant decrease in the total release of volatile iodine if pH control of the sump is maintained throughout the sequence. The mass of iodine released from containment in the case of a high pH is three orders of magnitude smaller than the aerosol iodine release calculated by MAAP. If pH were to fall to 4.5, the release could represent a 20% of the iodine aerosol mass. However, the inclusion of the Ag/T reaction reduces this contribution. The results are very sensitive to the degree of oxidation of the silver aerosol reaching the sump, for which no complete databases exist. The mass of gaseous iodine leaked increases in a factor 300 if silver/iodide interaction is not modelled, and a factor 35 if a 0.5% silver oxidation is assumed, with respect to the reference case, in which a 10% oxidation was chosen.

Other factors, such as the value of the interfacial sump-atmosphere mass transfer rate, have less influence in the overall iodine leaked, causing variations of less than one order of magnitude. Finally, a decrease of the deposition rate constants on painted surfaces does not have a significant impact in the results.

The evolution with time of the release as predicted by MAAP follows the trend of the aerosol concentration in the atmosphere, with a maximum rate in the first hours of the accident, when aerosols reach the containment, decreasing later as a consequence of deposition processes. On the contrary, volatile iodine is produced after deposition has occurred. With the modelling used, the gas phase iodine concentration does not reach a steady state, this resulting in iodine being pumped from the sump into the atmosphere for the duration of the sequence.

The sequence has been studied under the assumption that during the first 48 hours containment integrity is maintained, there is no intervention of the operators and the electric power is not recovered. If an accident management measure is to be taken, it should be kept in mind that the composition of iodine in the atmosphere is predominantly CsI aerosols during the first hours and gaseous organic iodide in the long term. This is also the case with respect to the release to the environment. There are various factors, out of the scope of this study, which could affect the amount and composition of the release, like a late resuspension from the primary circuit, the effect of an increase in the leak rate from containment, or the effect of accident management measures, like containment venting (Powers, 1998). No quantitative predictions have been calculated in this work, but it can be estimated that if, for instance, sprays were available only for a limited period during the first hours, the release of aerosols would be much smaller. As the uptake of organic iodine by sprays is much less effective than for aerosols or elemental iodine, it is possible that the release of gaseous iodine would not be significantly affected by spray operation, and it could become the main contribution to the release.
ACKNOWLEDGEMENTS

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IODINE SOURCE TERM CALCULATIONS FOR THE DUKOVANY VVER-440/213 NPP

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ABSTRACT

Selected severe accident sequences from the Probabilistic Safety Assessment (PSA) study for the Dukovany Nuclear Power Plant (NPP) were analyzed for the iodine source term to the environment. The Dukovany VVER-440/213 (Czech Republic) is a LWR which is characterized by a six-loop pressurized primary circuit, a bubble condenser pressure suppression system, and a containment building comprised of rectangular hermetic rooms. As the design leak for such a type of containment is relatively high, release of higher amounts of iodine can be expected even for those postulated accidents where the containment function is not challenged (no containment failure neither bypass). If the possibility of the formation of volatile iodine species is taken into account, the concern is whether the iodine release to the environment will not be substantially higher than the release estimated in the PSA study. The progression of a severe accident has been analyzed by a fully integrated NPP Dukovany MELCOR model and the longer term formation of volatile iodine species in containment has been modeled by the modified version of the IODE code. This paper describes the approach taken to model the iodine behavior in the accident, presents some results for the iodine source term, and presents also results of some sensitivity calculations for the most important parameters from the point of view of the accident management.
1. INTRODUCTION

At a core melt accident in LWR, the radioiodine is expected to be released from the RCS to the containment primarily in the form of CsI on aerosol particles. Upon contact with water in containment, CsI will dissolve in this water to form a non-volatile I⁻ anion. Under radiation conditions, this non-volatile species can be oxidized to volatile molecular iodine, I₂, and can also further react to various organic iodides, some of them also volatile (Wren, 1996). All the volatile species will be relatively quickly partitioned to the gas phase. The airborne iodine can be potentially released to the environment either through containment leaks or through the failed containment. Thus, in the case when the aerosols are successfully removed from the containment atmosphere to the sump by the engineered safety systems or by natural processes, the formation of gaseous iodine species becomes a risk-significant issue. This could be particularly important at some later phase of an accident because “given sufficient time the containment atmosphere will naturally cleanse itself from aerosols to an important extent” (Powers, 1999) which is not the case for gaseous species.

The most important of the recognized accident management measures for mitigating the gaseous iodine is maintaining the sump water pH high (approximately more than 8). One of the other possibilities is using chemical additives to spray solution (hydrazine in the Dukovany NPP for both the spray solution and the bubble condenser water) which can reduce volatile I₂ in water to non-volatile I⁻. The analyses presented here are focused on assessing the sensitivity of the gaseous iodine behavior to the most important containment parameters from the point of view of the severe accident management, namely sump pH and containment sprays function. The influence of the painted surfaces in the containment which can serve as a trap for molecular iodine has also been addressed.

The estimates of the iodine release to the environment at an accident can be obtained by modeling the iodine behavior with the integral source term codes, such as MELCOR and MAAP (Dutton, 1996). For Dukovany PSA Level 2 purposes, MELCOR code was used (Rydl, 1997). The iodine behavior was modeled as if all the iodine was in the form of CsI throughout the accident (kind of a default in the code). This assumption results in iodine containment behavior being dictated by aerosol behavior and the iodine release to the environment is then determined by the release of aerosol particles bearing CsI. For the reasons given above this approach could lead to some underestimation of the iodine release to the environment. It is particularly important for those cases where the containment fails late in the accident or where the release occurs from the intact containment through small leaks (important for containments with high design leaks such as VVER-440) or filters in which aerosols can be trapped more easily than volatile iodine species. The latter case was studied in this work to assess the contribution of the gaseous iodine release to the total iodine release from the VVER-440/213 containment with particular respect to the gaseous iodine release at the late phase of the accident (up to 5 days). The progression of an accident has been analyzed by a fully integrated NPP Dukovany MELCOR model (Dienstbier, 1996) and the longer term formation of volatile iodine species in containment has been modeled by the modified multicompartar version of the IODE code (Gauvain, 1996).

The Dukovany VVER-440/213 (Czech Republic) is a LWR which is characterized by a six-loop pressurized primary circuit, containment building comprised of rectangular hermetic rooms, and a bubble condenser pressure suppression system. Containment sump is located in steam generator (SG) compartments which house the primary system and which are connected by a horizontal corridor to the bubble condenser tower. The bubble condenser is a large
reservoir of water (~1300m³) consisting of 12 floors of shallow water pools designed to suppress the pressure increase accompanying a LOCA. This water can also be pushed to the SG compartments either as a result of the rapid pressure increase above the pools (e.g. H₂ burns at a severe accident) or on purpose by an operator when there is a need for water during the accident (e.g. for ECC systems in recirculation).

For the iodine behavior analyses a sequence from the group of the SB-OUT sequences (steam line break outside containment) was selected because these sequences are the main contributors to the total Core Damage Frequency in the Dukovany PSA Level 1 study (Patrik, 1998). Accident progression after the core damage (mainly the spray functions and operator interventions) was modeled to be the likely progression based on the PSA Level 2 analyses (Bradley, 1998). The selected sequence is not only a representative of the likely sequences but it is also somewhat typical for the postulated accident progression in VVER-440/213 containment, especially because almost all the condenser water was emptied to the SG compartments during the accident as a result of hydrogen burns. As there was no ECCS water loss from the sump, the total water volume in SG compartments was large enough to overflow to the reactor cavity after RPV failure. It filled up slowly about 2/3 of the total cavity volume. Thus, in cavity, a lot of gaseous iodine species could be formed which could then escape to the containment atmosphere. The impact of these processes on the iodine source term has been studied in this work using the multicomartment features of the IODE code.

Both the likely scenario where the containment sprays were working all the time and the scenario without sprays have been modeled with MELCOR to have some background for assessing the total impact of the sprays on iodine source term (influence of the containment pressures and temperatures, aerosol wash-out from the atmosphere). Detailed IODE analyses of the volatile iodine species formation and behavior for various pH profiles have been performed for the likely scenario (with the sprays on) and the impact of the sprays on gaseous iodine was assessed by the sensitivity calculations on the relevant spray effects modeled by IODE.

All the conclusions drawn from the results of our simulations are striving to be, to some extent, generic. Some of those conclusions are believed to be applicable also to modeling of the iodine accident behavior in different containment designs (PWR). As for the concrete numbers characterizing in this work the iodine accident behavior at Dukovany, these cannot be used directly as a base for the accident management planning at this NPP. The reason is that all the geometrical input data and a lot of other input data were only a rough approximation to the real plant data and they were not approved by the plant staff.

2. IODINE VOLATILITY IN VVER-440/213 CONTAINMENT AND ITS MODELING WITH THE IODE CODE

The most important processes which determine the iodine volatility are the aqueous iodine chemistry, mass transfer of the volatile iodine species from the water phase to the containment atmosphere and the sorption of the iodine species on various surfaces both in the gas phase and in the water phase. Iodine chemistry in gas phase is not so much important (Weaver, 1996). The homogeneous gas phase reaction of I₂ with ozone was neglected based
on the rationale given in Powers (1999): this process should not be so much important as the concentration of ozone that would be required to make a significant impact on the airborne iodine would have to be quite large owing to the slow rate of homogeneous gas phase reactions.

Volatile species, I₂ and organic iodides, will form in water and then will be rapidly transferred to the atmosphere according to their respective partition coefficients. Under radiation conditions, the most important processes in water which will oxidize non-volatile I to I₂ and reduce I₂ back to I are the reactions with water radiolysis products. As these radiolysis products reach rapidly the steady state concentrations for given conditions (pH, dose rate, amount and character of some impurities in water, etc.), the iodine species concentrations will also reach some pseudo-equilibrium rapidly (Ball, 1999). As was shown in ISP-41 exercise, the IODE code is capable (in the absence of I₂ sorption on surfaces exposed to the aqueous phase or other fast aqueous I₂ depletion reactions) to predict the pseudo-equilibrium concentrations of aqueous iodine species quite well. Thus, the default IODE radiolytic reaction model recommended for calculations under reactor conditions (cf. IODE Release 4.0 Reference Report) was used for modeling the I₂ formation. On the other hand, it was decided to change slightly the IODE model of the organic iodide (RI) behavior. The reason was that the results of our simulations of some ACE RTF tests with the default IODE model of organic iodide formation were not satisfactory. In the new model, for the average partition coefficient of all the organic iodides the same value has been used as for the molecular iodine (Wren et al., 1999). For the formation of the organic iodides via reaction I₂ + RH → RI, a constant sump water concentration of the organic material (of the order of 10⁻⁶) was assumed. The average hydrolysis reaction rate of all the organic iodides (for the hydrolysis reaction RI → ROH + I) was assumed to be the same as the hydrolysis reaction rate of iodomethane.

Mass transfer of the volatile iodine species from the sump to the containment atmosphere at an accident is not likely a rate limiting process which could influence the amount of gaseous iodine in the atmosphere (obviously the more this would be true for a boiling sump). Thus, in our simulations with IODE, the mass transfer was modeled to be so fast that any faster transfer would not increase the iodine volatility.

The sorption of molecular iodine on the epoxy painted walls of the SG compartments has also been modeled. In accordance with the recommendation of the IODE code manual, the irreversible adsorption of I₂ only on surfaces exposed to the gas phase has been assumed. The value of the adsorption coefficient, k_{ADS}=10^{4} m/s, is also based on the recommendation in the IODE manual.

2.1 Modeling Assumptions

pH evolution

Prediction of the sump pH profile at an accident is very difficult as it can be influenced by a great variety of materials: pH control additives with basic reaction, organic acids formed from the dissolved organic compounds, big amounts of CCl₄ aerosols with basic reaction, boron compounds, primary system additives, atmospheric species such as CO₂, etc. For the Dukovany plant where there is no sump pH control it was assumed that the pH evolution looks like this: During the first 10 hours (beginning at the time when the iodine interactions in water
started) the pH changed from initially basic values, pH=8.5, linearly to pH=6 and then slowly (again linearly) to pH=5 at the end of the sequence. Our estimate is based on quite a simplistic application of the experimental results\textsuperscript{a} to very complex interactions at a real plant. This estimate is believed, at least, not to be non-conservative. As for the acidic region, the estimate for the uncontrolled sump water gave similar pH values (5-6) also for large LOCA at PWR (Dutton, 1996 and Stephenson 1992). To compare the results for the different pH evolution scenarios, also the sequence with the constant sump pH=7 was analyzed with the IODE code.

At the Dukovany plant, hydrazine which is added to both the condenser tower water and to spray solution is used as an additive which may reduce volatile molecular iodine and which also can increase pH. Both these effects were neglected in the calculations because the experimental work of Bartonicek et al. (1990) has shown that under severe accident conditions at Dukovany hydrazine would be relatively quickly oxidized by the atmosphere oxygen and also it would decompose by radiation.

**Containment Sprays**

The IODE code is capable of modeling the interaction of the spray droplets with gaseous iodine as described, for instance, in works of Albert et al. (1987) and Hyder (1990). However, this phenomenon has not been modeled because all the time when this may be of any interest the sprays are working in recirculation mode and thus they have the same chemical composition as the sump water where the gaseous iodine is being generated. For Dukovany, this is likely to be the case quite often. Thus, generally, this type of gaseous iodine interactions could be important only for the cases where there is a possibility to alter the spray water chemistry by adding agents later in the accident (when sprays are in recirculation mode).

On the other hand, other type of the interaction with the gaseous iodine could be important and this is entraining of the gaseous iodine by the steam massively condensing on the spray droplets. This also can be modeled by the IODE code and it has proved to have an impact on iodine volatility in our simulations.

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\textsuperscript{a} Important, long term effect on pH can be expected from various organic acids which will be formed under radiation conditions from the dissolved components of the containment wall paints (Wren et al., 1999). For the epoxy paints which cover the SG compartment walls in Dukovany, similar sump pH profile was expected as that shown in figure 3 of the above mentioned work.
3. RESULTS

The analyzed SB-OUT sequence, with the sprays working all the time, starts with a main steam header rupture (secondary steam line break outside containment) and subsequent loss of the secondary heat removal. High pressure injection (HPI) is initiated immediately but the RCS pressure stays very high so the operator starts the feed&bleed procedure by switching the containment sprays on and opening the PORV. After opening the PORV, the signal for LPI is created, and the accident would have been stopped if it was not for the common cause failure of HP and LP ECCS at some later time after automatic switchover to recirculation. The core melt accident initiated such a way leads to reactor pressure vessel (RPV) failure at low pressure followed by an expulsion of the molten core to the cavity. Before the vessel failure, the fission products can escape from the RCS to the containment through the opened PORV. The containment leak is modeled as an equivalent hole in the SG compartments.

<table>
<thead>
<tr>
<th>time (hrs)</th>
<th>event</th>
</tr>
</thead>
<tbody>
<tr>
<td>~0</td>
<td>Main Steam Header (MSH) rupture + loss of feedwater</td>
</tr>
<tr>
<td>1</td>
<td>HPI signal from MSH rupture, reactor scram, RCP trip</td>
</tr>
<tr>
<td>1h 25min</td>
<td>containment sprays manually started</td>
</tr>
<tr>
<td>1h 26min</td>
<td>PORV opened</td>
</tr>
<tr>
<td>1h 40min</td>
<td>containment overpressure signal: containment isolated, LPI signal</td>
</tr>
<tr>
<td>~2</td>
<td>switchover to recirculation</td>
</tr>
<tr>
<td>2h 45min</td>
<td>common cause failure of HP and LP ECCS</td>
</tr>
<tr>
<td>5h 50min</td>
<td>core uncoverty starts</td>
</tr>
<tr>
<td>~7</td>
<td>1500K in core upper region</td>
</tr>
<tr>
<td>8h 30min</td>
<td>core support plate failure</td>
</tr>
<tr>
<td>~9</td>
<td>CCI starts</td>
</tr>
</tbody>
</table>

MELCOR prediction of the amount of iodine released from the degraded fuel to the RCS before the vessel failure is approximately 55% of the iodine inventory which looks reasonable. Almost all of the iodine still remaining in the core debris, when the debris had fallen onto the concrete cavity basemat, was released quickly after core-concrete interaction (CCI) had started. Subsequently, a lot of this iodine (~1.5kg) escaped from the dry cavity to the other containment volumes (including SG compartments) being driven by overpressure from CCI. The iodine distribution among different volumes in containment after 5 days (as predicted by MELCOR) is shown in Tab. 2. The total CsI mass in SG compartments is shown in Figure 1.

<table>
<thead>
<tr>
<th>volume</th>
<th>fraction of the iodine fuel inventory</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG compartments</td>
<td>40%</td>
</tr>
<tr>
<td>cavity</td>
<td>25%</td>
</tr>
<tr>
<td>RCS</td>
<td>25%</td>
</tr>
<tr>
<td>condenser tower shaft,</td>
<td>almost all of the rest of iodine</td>
</tr>
<tr>
<td>condenser tower and neighboring volumes</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Iodine distribution in containment at the end of MELCOR calculation
As the sprays are working, most of the aerosol mass (including aerosols with CsI) is quickly removed from the containment atmosphere and is collected in the sump. The cumulative source of I to the sump and resulting total iodine concentration in the sump water are given in Figure 2. After the condenser tower water had been emptied in a stepwise manner to the sump (mostly as a result of hydrogen burns -MELCOR prediction), the amount of water in sump was so high that it began to overflow to cavity, filling up slowly about 2/3 of the total cavity volume. The water overflow to cavity begins at ~20hrs. The iodine (~0.5kg), residing at the bottom of the cavity at this time, dissolves in water and yields the total aqueous concentration which is approximately 4 times higher than the total aqueous iodine concentration in the sump.

The total airborne iodine mass in both the CsI and gaseous forms in containment atmosphere is shown in Fig. 3. It can be seen that after approximately 30hrs there is more volatile iodine species in the atmosphere than CsI with the exception of short period at about 60hrs
corresponding to high release of aerosols from RCS to SG compartments (MELCOR prediction). The volatile species in the containment atmosphere are, according to modified IODE, mostly organic iodides (cf. Fig. 4). Resulting iodine leak to the environment is shown in Fig. 5. At about 100hrs the total release of gaseous iodine exceeds that of iodine in CsI form. The total release to the environment in Fig. 5 represents something less than 0.01% of the iodine fuel inventory.

Figures 3 and 4. Iodine in SG compartments atmosphere

Figure 5. Iodine release to the environment

The effect of the volatile iodine species which were formed in cavity water (rapidly partitioned to the cavity atmosphere and transferred to the containment atmosphere) on the total gaseous iodine release from the containment can be estimated from the comparison shown in Fig. 6. There can be seen that the transfer from cavity to containment atmosphere represents an amount of gaseous iodine which is much higher than the amount of gaseous iodine partitioned from the containment sump. However, the integral amount of gaseous iodine coming from cavity is not higher than that coming from sump because the interactions in cavity which could form the volatile species began only after there had been some water there (~20hrs).
The influence of a potential mechanism of the gaseous iodine removal from the atmosphere can also be seen in Fig. 6. It is the effect of the steam condensation on the spray droplets driving the gaseous iodine forms from the atmosphere eventually to the sump water. The IODE code predicts that the effect of the steam condensation is one of the dominant effects influencing the gaseous iodine behavior when there are steam condensing conditions. However, according to the IODE manual, the experimental data up to date are not sufficient to validate such models and so the model must be used carefully. Anyway, our understanding is that this effect could really be important for the removal of the gaseous iodine from the containment atmosphere.

Figure 6. Volatile iodine species flow rates to and from the SG compartments atmosphere (total amount of iodine in all volatile forms transferred per second)

![Graph showing flow rates to and from the SG compartments atmosphere](image)

3.1 Effects of the sump water pH and the containment sprays

The effect of the sump water pH on the gaseous iodine leak to the environment was studied by comparing the results for different pH profiles. One profile (pH= 8.5→6→5) is our best estimate for the sump pH evolution under accident conditions at Dukovany (cf. paragraph 2.1) and the others are profiles with a constant pH. Because the effect of the steam condensation as calculated by IODE (cf. previous paragraph) is very strong, pH sensitivity calculations have been performed for both the case with the steam condensation and without it. In figures 7-12 the results for pH= 8.5→6→5 are compared to the results for the constant pH=7.
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Fig. 7 and 8. Gaseous iodine concentration in the containment atmosphere

STEAM CONDENSATION

<table>
<thead>
<tr>
<th>Concentration (mol/l)</th>
<th>time (hrs)</th>
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<tbody>
<tr>
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NO STEAM CONDENSATION

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<tr>
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</table>

Fig. 9 and 10. Iodine deposition onto gas phase surfaces

STEAM CONDENSATION

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<thead>
<tr>
<th>Mass (kg)</th>
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NO STEAM CONDENSATION

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<thead>
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<tbody>
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Fig. 11 and 12. Gaseous iodine leak to the environment

STEAM CONDENSATION

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NO STEAM CONDENSATION

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<th>time (hrs)</th>
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<tbody>
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<td>80</td>
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<tr>
<td>1.0E-07</td>
<td>100</td>
</tr>
<tr>
<td>1.0E-08</td>
<td>120</td>
</tr>
</tbody>
</table>

If the sprays are working and the effect of the steam condensation is calculated by IODE then the impact of the pH changes is less important (cf. figures 11 and 12). Even if the IODE code highly overestimates the effect of the steam condensation, the cumulative impact of the sprays on the gaseous iodine release to the environment could be also that high (cf. last paragraph in this chapter). For sequences without sprays, the differences in the gaseous iodine release for the two pH profiles are of a factor of 3 (Fig. 12). The same is true about the sequences with sprays where the absolute iodine leak is much less (Fig. 11). This means that the gaseous iodine release to the environment could be three times higher for our best-estimate pH profile of the sump water than for the constant pH=7. If the sump pH was low (pH=5) from the very
beginning of the sequence the corresponding iodine release would be only slightly higher than for pH=8.5→6→5. If it was possible to hold the pH high (~≥8.5) for the whole time the total gaseous iodine release would be much less than that with constant pH=7 (approximately by an order of magnitude).

The higher is the amount of molecular iodine I$_2$ in the containment atmosphere (most of the time I$_2$ represents something less than 10% of the total gaseous iodine in the atmosphere —cf. figures 7 and 8) the more of it will be irreversibly adsorbed on the epoxy painted walls of the containment (figures 9 and 10). There is no remarkable steam condensation on the containment walls neither with the sprays on (according to MELCOR all the steam condenses on the spray droplets) nor without it. This means that there are no water films on walls and that the only I$_2$ interaction on and with the containment surfaces is the irreversible sorption process as described in chapter 2.

Figures 13 and 14. Containment pressure and CsI release to the environment

The net impact of the containment sprays on the total iodine release to the environment comprises the effect of the removal of the airborne iodine from the atmosphere and the suppression of the containment pressure. The impact on the particulate matter (aerosols) in the containment atmosphere can be seen in figures 13 and 14. The total CsI release to the environment for the sequence with sprays is almost by 2 orders of magnitude lower than for the sequence without sprays. Mitigation of the aerosol release will be particularly important at the early phase of an accident. Keeping the low pressure in the containment (or even underpressure in the intact containment) could have great impact on the iodine source term also in late accident stages. As for the removal of the gaseous iodine from the atmosphere, our results obtained with IODE suggest this: If we have sprays to condense the steam in the containment then the gaseous iodine leak could be much lower than for the case without condensation even if we neglect the other mitigative effects of the sprays.

4. CONCLUSIONS

Iodine source term to the environment has been calculated for the representative of the dominant severe accident scenarios at the Dukovany NPP. The important objective of the work was to assess the contribution of the release of volatile iodine species (I$_2$ and organic iodides) to the total iodine release. For the iodine leak from the intact containment, when containment sprays are working, it has been found that the release of gaseous iodine is comparable to that of iodine in CsI form (aerosol release). At the beginning of the accident the total iodine release was represented almost exclusively by the CsI release, then the gaseous iodine release was slowly increasing and at a very late stage of the accident (~5 days) it even exceeded the CsI release. The total release for this sequence, however, represents only a very small fraction
of the iodine fuel inventory (less than $10^{-4}$). The aerosol releases calculated by MELCOR are likely to be conservative because the retention of the particulate matter in the containment leak path is neglected. Thus, the ratio of the gaseous iodine release to the CsI release could be even higher.

The most important mechanism of the volatile iodine species formation were reactions of dissolved I with water radiolysis products in the sump water. By these reactions, I can be oxidized to volatile I$_2$ and this can react with organic materials in the sump to form organic iodides. Both I$_2$ and organic iodides are relatively rapidly partitioned to the gas phase according to their respective partition coefficients. The modified version of the IODE code predicts that at the late stages of an accident the organic iodides are the prevailing volatile species in the containment atmosphere. However, the model of the organic iodide formation is maybe too simple and it would need to be looked at. In vicinity of the containment walls, molecular iodine may interact with the epoxy painted gas phase surfaces and may be irreversibly retained in the paint. For the assumed value of the adsorption constant, the mass of the retained I$_2$ does not represent a remarkable fraction of the total iodine mass in the containment. The impact of the retention in the paint on the gaseous iodine leak to the environment is thus not high.

pH sensitivity calculations have confirmed the well-known fact that the gaseous iodine release could be substantially mitigated by maintaining the sump water pH high (approximately more than 8). As for the containment sprays interactions with gaseous iodine, our simulations do not seem to indicate that the spray droplets could chemically interact with it. The timing of the severe accident scenarios at Dukovany dictates that most of the time during which the volatile iodine species are being formed the sprays are working in recirculation mode. The spray water thus has the same chemical composition as the sump water where the volatile iodine species are being generated. On the other hand, the IODE code simulations suggest that the massive steam condensation on the spray droplets can drive substantial amounts of the gaseous iodine from the containment atmosphere to sump. The steam condensation model in the code, however, has not been validated yet. Anyway, the sprays will have a great impact on the total iodine release, especially through the wash—out of the particulate matter (aerosols) from the containment atmosphere. The sprays are also capable of maintaining a low pressure or even underpressure in the containment, lowering thus the driving force for the fission products release to the environment.

In the simulations with the multicompartment IODE code it was found that for a postulated severe accident at Dukovany high amounts of volatile iodine species can be formed not only in the sump but also in other volumes neighboring the SG compartments. For instance, the total amount of the volatile iodine species coming to the containment atmosphere from cavity could be even higher than that coming from the sump.

Modeling gaseous iodine behavior such a way as presented in this paper brings numerous problems with it. It was very difficult to keep track of some of the accident phenomena for the IODE code runs. There is no feedback between IODE and MELCOR and many things cannot be modeled at all (e.g. interactions of gaseous iodine with aerosols). The remedy for this would be an integral code capable of modeling the most important gaseous iodine related phenomena. Some simplified methods would also be needed for estimations of the sump pH evolution based on the interactions of all the important materials in the containment.
ACKNOWLEDGMENTS

This work is sponsored by the Ministry of Industry and Trade of the Czech Republic. We would like to thank Dr. J.C. Wren and her colleagues for providing us with the model of the organic iodides formation and a lot of other useful information and recommendations. We also gratefully acknowledge the contributions of Mr. S. Hustak and Dr. B. Bartonicek.

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IODINE MANAGEMENT IN THE FINNISH NPPs

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ABSTRACT

In a severe accident at a BWR, a large amount of chlorine might be released from the synthetic rubbers, used as insulation material of the electrical cables, due to irradiation and heating. In order to maintain the iodine retention capability the sodium thiosulphate concentration of the filter will be increased. A large amount of chlorine, which could be converted to HCl in the containment, would reduce the pH of the water pools and wet surfaces. This may lead to formation of significant amount of molecular as well as organic iodine. Another source of organic iodine may be reactions between boron carbide in control rods, steam and iodine in the degrading core. The filter of the containment venting system is capable of effectively arresting iodine in particular and elemental form. For retention of organic iodine, the retention capability is less effective and uncertain. TVO is planning to enhance the retention of iodine with a containment pH control system. The pH would be controlled by 50% NaOH solution in the containment spray from external source that starts after transition to the emergency operating procedure for severe accidents. Simultaneously the lower drywell is flooded from the wetwell. The pH control covers thus all water volumes in the containment. The system modifications are planned for the year 1999.

The Loviisa VVERs have large amounts of borax in the ice of their ice condenser containments, and therefore the sump water is alkaline in most of the sequences with leakages into the containment. Furthermore, mixture of hydrazine and potassium hydroxide solution is added into the containment spray water in order to remove volatile iodine from the containment atmosphere. After the beginning of a loss-of-coolant-accident, the sump water becomes basic rather soon due to the borax in the ice condenser ice. The formation of nitric acid in the radiation field in the containment atmosphere and the hydrochloric acid from cable fires in some accident sequences are not a threat to the sump pH. In the containment bypass sequences, the ice might not be involved in the possible formation of water pools in the leak path. Thus, the pool pH would probably be acidic, and in case of high aerosol retention in the water pools the volatile iodine species might be dominating the release. According to the PSA level 2 for the Loviisa NPP, these sequences contribute only little to the total risk, and the cases with only little aerosol retention in the water pools are dominating the bypass sequences.
1. INTRODUCTION

1.1 Olkiluoto BWRs

Teollisuuden Voima Oy owns and operates two ABB Atom BWR plant units at the west coast of Finland. About 20 years ago, when the Olkiluoto nuclear power plant was taken into operation, the design of the two units represented the most modern nuclear technology and fulfilled the safety requirements of that time. Over the years, both nuclear technology and safety requirements have undergone evolution and development.

Plenty of design modifications have been introduced to Olkiluoto 1 and 2 since the commissioning in order to keep the plant units technically up-to-date. Provisions for severe accidents were backfitted in the plant units Olkiluoto 1 and 2 already in the SAM project (Severe Accident Mitigation) which was finished in 1989. The main modification was containment filtered venting system. The filter was installed by Siemens. The purpose of the filter is to avoid ground contamination by release of radioactive substances due to a postulated severe accident.

An extensive modernisation program (MODE) was carried out in Olkiluoto 1 and 2 during the period of 1994 – 1998. The MODE had the following main goals:

- Reviewing safety features and enhancing safety, when feasible,
- improving the production related performance,
- finding factors limiting the plant life time and eliminating them, when feasible, and
- enhancing the expertise of the utility staff and improving productivity.

The MODE consisted about 40 separate subprojects. The safety review was carried out mainly in the following areas:

- Design basis review
- Severe accidents
- Modernisation Final Safety Analysis Report
- Modernisation Probabilistic Safety Assessment

The work carried out in the MODE project regarding severe accidents is a continuation to the SAM project. Iodine retention was one of the issues investigated in the MODE project.

In a severe accident, with conservative assumptions a large amount of chlorine could possibly be released from the synthetic rubbers, used as insulation material of the electrical cables, due to irradiation and heating. Chlorine in molecular form or hypochlorite would behave in the thiosulphate solution of the filter like iodine. The iodine retention capability of the filter would thus be reduced. In order to maintain the iodine retention capability the sodium thiosulphate concentration of the filter will be increased.

A large amount of chlorine, which might be converted to HCl, in the containment, will reduce the pH of the water pools and wet surfaces. The origin of the chlorine is the synthetic rubbers used as insulation in cables. This might lead to significant amount of molecular as
well as of organic iodine. Another source of organic iodine may be reactions between boron carbide in control rods, steam and iodine in the degrading core.

The filter of the containment venting system is capable of arresting iodine effectively in particular and elemental form. For retention of organic iodine, the retention capability is less effective and uncertain. TVO has investigated the possibilities to enhance the retention of iodine by containment pH control system. The system installation is planned for the year 1999. Iodine chemistry will be one of the research topics in the starting Nordic Nuclear Safety Research program, subproject SOS-2.3 Severe accidents.

1.2 Loviisa VVERs

Fortum Power and Heat Oy (former Imatra Voima Oy) owns and operates two VVERs at Loviisa. The thermal power of the reactors is 1500 MW per unit and the containments are Westinghouse-type ice condenser containments. The containment is divided into upper compartment (the main volume of the containment) and lower compartment (the steam generator room), which are connected with two ice condenser sections with the total amount of around 835 000 kg of ice. The design absolute pressure of the containment is 1.7 bar, which is relatively low compared to most of the Western NPPs.

Despite the low design pressure of the containment, the severe accident management strategy for the Loviisa NPP does not include filtered containment venting, but the containment integrity is maintained by avoiding energetic events and ensuring the long-term containment cooling. The critical safety functions in this approach are (Tuomisto 1996):

- Manual depressurisation of the primary circuit leading to a low pressure sequence,
- successful hydrogen burn mitigation by mixing the containment atmosphere and removing the hydrogen from the containment in a controlled manner,
- maintaining the reactor pressure vessel integrity by external cooling of the vessel, and
- avoiding the containment over-pressurisation with the containment external spray system.

The mixing of hydrogen is performed by forcing the ice condenser doors open, which creates a global convective loop flow from the lower compartment through one of the ice condensers up to the upper compartment, and further downwards the other ice condenser back to the lower compartment. During a severe accident, the main part of the low-volatile fission products, including iodine, are released during or shortly after the hydrogen production, and therefore the fission products are assumed to be mixed throughout the containment, as well.

At maximum, a containment leakage of 0.2% of the containment gas inventory per day at the design pressure of 1.7 bar is allowed. If this requirement is fulfilled, only small amounts of fission products are escaped from the containment. If the air ventilation stack is in operation and the activity level in the exhaust air increases, the gas flow is switched to the filter line with four sequential filters: prefilter – HEPA filter – potassium iodide (KI) impregnated active carbon filter – HEPA filter. The minimum requirement for the particle removal efficiency of new HEPA filters is 99.97% and the efficiency is expected to increase while ageing. The requirement for the efficiency of active carbon filters in use is at minimum 99% for removal of methyl iodide (CH₃I) and the efficiency of I₂ removal is thus expected to be at least 99.9%.
These filters are not designed especially for severe accidents, but when the total amount of fission products deposited into the filters remains relatively low, they can be expected to function as designed.

2. CONTAINMENT FILTERED VENTING SYSTEM AND IMPACT OF CHLORINE IN THE FILTER

During a severe accident at a BWR, a large amount of chlorine (Cl\textsubscript{2}) and hydrochloric acid (HCl) might be released by irradiation and heating from the synthetic rubbers used as insulation material of the electrical cables. Most of the released chlorine hydrolyses within the water pools to hydrochloric and hypochlorous acid (Siemens 1998). The total amount of chlorine in the insulation material is 1400 kg. From that about it is conservatively assumed that 700 kg are released to the containment during a severe accident sequence: 470 kg in lower drywell (all the cables) and 230 kg in upper drywell (25% of cables in upper drywell).

The containments are equipped with filtered venting system to control containment pressure and temperature in severe accident. The filters are of Siemens design. The filter contains a 0.2% sodium thiosulphate and 0.5% sodium hydroxide solution. The solution volume is about 20 m\textsuperscript{3}. The filter of the containment venting system is capable of arresting iodine effectively in particular and elemental form. For retention of organic iodine the retention capability is less effective and uncertain.

The chlorine released from the cables into the containment may consist of the compounds HCl, Cl\textsubscript{2}, HOCl, HClO\textsubscript{3} etc. Chlorine can only reach the Siemens filter via the gas phase. This means that the chlorine can be transported either in small droplets as dissolved Cl\textsubscript{2} and the corresponding hydrolysis products as ClO\textsuperscript{-} and Cl\textsuperscript{-} or in gaseous as volatile HCl, Cl\textsubscript{2} and HOCl. It is assumed that when venting starts, the droplet concentration is such low that nearly all chlorine is transported in gaseous form.

The concentration of Cl\textsubscript{2} in the gas phase shortly before the pressure reduction is determined by the overall distribution coefficient of chlorine (ratio of chlorine concentration in the water and in the gas phase). As the concentration of molecular chlorine in the gas phase is several orders of magnitude smaller than in the water phase and as molecular chlorine hydrolyses in water, the resulting chlorine gas phase concentration is very low. However, with decreasing pH value of the water pools in the containment the concentration of molecular chlorine increases.

In the case of hydrochloric and hypochlorous acid the transfer rate via the gas phase is practically zero because chemically formed salts such as NaCl and NaOCl in the water pools are non-volatile. Even in acid water pools the concentrations of hydrochloric and hypochlorous acid in the gas phase are very low compared to the Cl\textsubscript{2} concentration.

It follows that via the gas phase practically only molecular chlorine is released to the filter. Hypochlorite and hypochlorous acid react in the water pools to form non-volatile salts, or compounds that are low-volatile compared to Cl\textsubscript{2}. The chemical behaviour of chlorine in the gas and the water phase is affected by high radiation field, high temperature (> 100 °C) and containment pH value.
The original sodium thiosulphate concentration in the filter is 0.2% by weight. TVO will install a containment pH control system. This system would rely on manual operator actions and diesel engine mounted pumps having a certain failure probability. If the water pools within the containment are pH controlled the amount of 64 kg of thiosulphate is more than sufficient for converting and therefore retaining all iodine and chlorine released to the filter. Volatile chlorine released from the insulation material of the electrical cables is converted in alkaline solutions to non-volatile chlorine compounds such as NaCl etc. However, it is conservatively assumed that 5% of the released Cl₂ (35 kg or 500 mol) will enter the Siemens filter. A realistic value will be > 1%. In addition, the release of I₂ is 0.75 kg. In this case, a minimum of 35 kg of sodium thiosulphate is needed in the filter.

If the water pools of the containment are not alkaliised (no pH control system), the pH of the containment will decrease to values below 5. At such low values and under irradiation it has to be assumed that more than 50% of the released chlorine will be converted in a realistic timespan to molecular Cl₂. With decreasing pH value the conversion to molecular Cl₂ increases. At least, it has to be assumed conservatively that all chlorine released from the cables to the containment will be released to the Siemens filter. This means that the filter shall contain 620 kg sodium thiosulphate to fix all molecular chlorine. In addition, it is conservatively assumed that all iodine from the containment will be released to the filter. That is about 15 kg of iodine. This means that in addition to the amount of 620 kg, further 32 kg of thiosulphate has to be dissolved in the filter solution. If the water pools within the containment are not pH controlled, the amount of thiosulphate needed is thus 700 kg leading to the concentration 3.5% in the filter.

The design basis for increasing sodium thiosulphate concentration in the filter has conservatively been selected the failure of the containment pH control system. The thiosulphate concentration will be increased to 3.5%.

The pH in the Siemens filter decreases due to the reaction of molecular chlorine and iodine with thiosulphate, which reacts to form HCl or HI. In the case of pH controlled containment, 36 kg of HCl is formed. If the pH value is not controlled, it is assumed that 720 kg of HCl is formed. A pH reduction has no significant consequences for the iodine and chlorine removal capacity because thiosulphate is able to fix these elements in an acid solution.

The solubility of sodium thiosulphate is high. TVO has tested thiosulphate solution of 8.5% by weight for one year in laboratory conditions and no stability problems have been observed (TVO, 1999). TVO has also tested the iodine retention capability of 3.5% thiosulphate solution with presence of chlorine. According to the results, the iodine is arrested in the solution.

3. RETENTION OF IODINE IN CONTAINMENT

3.1 Containment pH control

According to NUREG-1465 (1995) at least 95% of iodine entering the containment is in the form of CsI with the remaining 5% as molecular iodine plus organic iodine compounds with not less than 1% of each as molecular and organic iodine. Once the iodine enters containment, however, additional reactions are likely to occur. In an aqueous environment, as expected for BWRs, iodine is expected to dissolve in water pools or plate out on wet surfaces in
ionic form as $\Gamma$. Subsequently, iodine behaviour within containment depends on the time and pH of the water solutions. Because of the presence of other dissolved fission products, radiolysis is expected to occur and lower the pH of the water pools. Without any pH control, the results indicate that large fractions of the dissolved iodine will be converted to molecular iodine and be released to the containment atmosphere. However, if the pH is controlled and maintained at a value of 7 or greater, very little (less than 1%) of the dissolved iodine will be converted to molecular iodine. Organic compounds of iodine, such as methyl iodine, CH$_3$I, can also be produced over time largely as a result of molecular iodine reactions with organic materials.

A postulated large amount of chlorine, which could be converted to HCl in the containment, would reduce the pH of the water pools and wet surfaces. The origin of the chlorine is the synthetic rubbers used as insulation in cables. This may lead to formation of significant amount of molecular as well as of organic iodine. Another source of organic iodine may be reactions between boron carbide in control rods, steam and iodine in the degrading core. These reactions require further investigation.

Organic iodine is not readily removed by containment sprays or filter systems. In a severe accident, organic iodine would be released to environment through the filtered venting system. The retention capacity of filter for organic iodine is significantly poorer than for particulate and molecular iodine.

NUREG-1465 concludes that where the pH is not controlled to values of 7 or greater, significant fractions of molecular iodine, as well as organic iodine may be expected within containment.

According to the severe accident management procedures of Olkiluoto 1 and 2, the lower drywell would be flooded with water from wetwell prior to vessel breach. Containment is filled with water from external water source with a capacity of 25 kg/s to 100 kg/s. pH control system would be connected to this containment water filling system.

TVO has been planning to enhance the retention of iodine with a containment pH control system. The pH would be controlled by 50% NaOH solution that would be delivered to the containment when containment spray is supplied from external source during the accident. The containment spray from external source starts after transition to the emergency operating procedure for severe accidents. Simultaneously lower drywell is flooded from wetwell. The pH control covers thus all water volumes in the containment. The water treatment plant already normally uses the 50% NaOH solution.

A new NaOH tank will be installed. Part of the NaOH is reserved for the containment pH control. The rest would be used in the normal operation. The required NaOH volume is about 1.1 m$^3$ (Siemens, 1997) to neutralise the containment water pools regarding the HCl generated by pyrolysis and radiolysis of cable materials. The amount of HCl generated is 20 kmol. The initial water mass in containment is 3,180,000 kg. The solution is gravity driven into the raw water system near fire extinguishing sprinklers, from where the solution is delivered into the containment during containment water filling.

The total amount of chlorine that is conservatively assumed to be released from the cables is 700 kg; 470 kg in lower drywell (all the cables) and 230 kg in upper drywell (25% of cables in upper drywell).
The possibilities to deliver NaOH as fast as possible into the containment will be investigated. Lower drywell will be flooded from wetwell prior to the NaOH supply and the lower drywell water pool pH should be kept above 7.

Combustion engine pumps may be required to refill the new tank from the existing large NaOH tanks (20 m³).

The maximum capacity of one containment water filling train is about 100 kg/s. With the booster pump the capacity is 25 kg/s.

The pH control system will be installed during 1999.

3.2 Organic iodine

VTT Chemical Technology and VTT Energy investigate the possibilities to improve retention of organic iodine. The filter of the containment venting system is capable of arresting iodine effectively in particular and elemental form. For retention of organic iodine the retention capability is less effective and uncertain. The purpose is to find means to improve the existing filter so that they are capable of trapping the organic iodine compounds and of preventing iodine to form organic compounds. Possible means are the oxidation of molecular iodine by modifying the chemical composition of the filter or by using catalytic oxidation.

The study will be funded by Nordic Nuclear Safety Research, VTT, STUK and TVO. The work starts with literature study. Experiments will be performed.

4. IODINE MANAGEMENT AT LOVIISA

The iodine management at the Loviisa NPP is based on avoiding acidic sump water during the accident in order to prevent effective formation of volatile iodine species.

The ice in the ice condensers contains large amounts of borax (Na₂B₄O₇·10 H₂O) with the total boron concentration of 2000 ppm, which corresponds to the sodium tetraborate (Na₂B₄O₇) concentration of 9.3 g/kg. The water solution of sodium tetraborate is clearly basic with the pH of over 9 at 25 °C (Kroschwitz 1992). The pH of the solution does not change significantly over a wide range of concentrations, but the high concentration makes the solution well buffered. At higher temperatures, the pH of the solution decreases, but still remains close to 9 (Kotowski 1966). The total amount of ice is at least 835 000 kg, and thus the amount of sodium tetraborate is approximately 7800 kg or 39 kmol at minimum.

During a severe accident, the ice condenser doors are forced open to create a global convective loop flow in order to ensure effective hydrogen mixing in the containment. Due to the strong steam condensation in the ice condensers, aerosols are removed from the flow through diffusiophoresis. The aerosol removal efficiency depends on several parameters, e.g. on the flow rate and the amount of ice. Without steam, the particle retention may be very low, but with steam the retention is tested to be more efficient (Ligotke et al. 1991). Nevertheless, in the Loviisa containment, the removal in the global loop is estimated to be more efficient than the removal by gravitational settling in the upper compartment of the containment. As the ice is alkaline, only a fraction of the iodide from the aerosols is converted to iodine. The ice removes also volatile iodine from the flow through the ice condenser (Malinowski 1970).
The containment spray system is equipped with injection from a separate tank containing 5 m$^3$ of 5% hydrazine (N$_2$H$_4$) and 20% potassium hydroxide (KOH) solution. The injection into the spray water is carried out with two pumps with a capacity of 1.6 m$^3$/h each. These chemicals increase the spray water pH in order to remove volatile iodine from the containment atmosphere. The total spraying capacity is around 500 kg/s, and when the spray water is taken from the emergency core coolant (ECC) tank with boric acid concentration of 12 g/kg, the spray water pH becomes around 7.5.

It is estimated that a large complete cable burn around the pressuriser at Loviisa would produce 246 kg or 6.7 kmol of hydrochloric acid (HCl). If the burn takes place at very early stages of the accident, HCl concentration in the sump water may decrease the sump pH drastically. However, as ice starts to melt the sump pH increases, and the overall effect of HCl becomes minor.

Nitric acid (HNO$_3$) is formed in the radiation field in the containment gas phase. Assuming the G-value of HNO$_3$ formation in air to be 2 / 100 eV and the dose rate of 3 Gy/s in the whole containment atmospheric volume of 57 000 m$^3$, the nitric acid formation rate becomes approximately 42 mmol/s or 2.6 g/s. The pH of the sump water starts to decrease significantly when the amount of nitric acid exceeds 50 kmol. With the production rate above, this would appear after 15 days of irradiation or after a total dose of 4 Mgy. However, this dose exceeds the expected total dose during one year after a severe accident, and therefore the constant irradiation rate of 3 Gy/s is much too high for a prolonged duration, although it may represent the radiation level in the early phases of the accident.

Figure 1 shows the calculated sump pH behaviour during a severe accident at the Loviisa NPP. The time behaviour does not correspond to any specific accident sequence, but rather represents different phases in the calculations. Five different calculations have been performed with different assumptions on the available emergency core coolant (ECC) water and chemicals within it. In the calculations, the following assumptions are used:

0...10 min  160 000 kg of primary coolant (9.3 g/kg of boric acid; 3.4 mg/kg of NH$_3$; 16 mg/kg of KOH) and 160 000 kg of water from accumulators (12 g/kg of boric acid) is injected into the sump. (In all cases)

1...10 min  246 kg of HCl is released into the sump. (In cases B, C and D)

10 min...1 h  900 000 kg of ECC water (12 g/kg of boric acid) is injected into the sump. (In case C only)

1...1.5 h  900 000 kg of spray water (12 g/kg of boric acid; 75 mg/kg of NH$_3$; 423 mg/kg of KOH) is injected into the sump. (In case D only)

0...10 h  The ice melts totally with a constant rate. (In all cases)

In addition, in case E a constant irradiation rate of 3 Gy/s in the gas phase (57 000 m$^3$) is applied. In other cases, a more realistic irradiation profile with time dependency is assumed resulting in the total dose of around 3 Mgy during one year. Furthermore, in case of the containment spray (case D) the hydrazine added to the spray water is assumed to thermally decompose to ammonia (NH$_3$) completely. The sump water temperature is assumed to be 100 °C.
Figure 1  Sump water pH at the Loviisa NPP during a severe accident. The time behaviour does not refer to any specific accident sequence, but rather represents different phases in the calculations. A - No water from the ECC tank, no HCl. B - No water from the ECC tank, HCl. C - ECC tank added to sump water, HCl. D - ECC tank added to sump water with spray chemicals, HCl. E - No water from the ECC tank, no HCl, high constant radiation level.

According to the calculations, it appears that in the sequences where ice is melted into the sump, the pH remains rather high. This indicates that an only small amount of iodine is converted to volatile species. The calculations show very low pH levels of the sump water in cases B, C and D during the first hour, but this is only a result of the computational arrangement. In reality, the ice melts more rapidly in the early phases of the accident, and when the main iodine release from the core starts after the core uncovering, approximately half of the ice has melted. In the calculations shown here, this corresponds to the point at five hours. At this point, the pH level is clearly above 7, which should prevent major I$_2$ formation in the sump. Even if the gas phase yield of HNO$_3$ of 2 / 100 eV was slightly underestimated, it would not change the overall results.

These calculations suggest that the sump water might become acidic after around ten months (case B and C). However, the most important radionuclide of iodine is $^{131}$I, which has the half-life of approximately eight days. Therefore, a decay time of three months, for example, is long enough to decrease the iodine radioactivity to such a low level where major radiological consequences resulting from iodine can be avoided.

The pH may not be controlled in those severe accident sequences where ice is not melted into the water pools in the leak path. These sequences include several bypass sequences, but according to the Level 2 PSA for the Loviisa 1, the aerosol releases in many of these sequences are already very large. Therefore, the pH control would not decrease the iodine release very much, if at all. The pH control of the water pools in the leak path is expected to decrease the source term significantly if the leakage has to go through the water pool. However, these sequences contribute only little to the total risk. Thus, when considering the iodine control during severe accidents at the Loviisa NPP it is adequate to study only the containment sequences and the situations presented above.
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Making Practical Use of Iodine Knowledge in Severe Accident Management Strategies: A U.S. Industry Perspective

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Background

The U.S. industry approach to severe accident management is outlined in NEI Report 91-04, Severe Accident Issue Closure Guidelines\(^1\) and reported at the final meeting of the CSNI Senior Experts in Severe Accident Management meeting held in June 1995.\(^2\) The approach taken by U.S. utilities was to establish an appropriate degree of personnel preparedness to identify degraded core conditions and containment plant damage states, and then assess and select one or more mitigative strategies to achieve a stable plant condition. We believe the current plant design and operating practices are sufficiently robust as to not require the backfitting of engineered solutions that could mitigate hypothetical, stylized severe accident conditions.

In such an approach, the developers focused on what is known about severe accident phenomena, the ruggedness of the fission product barriers, potential atypical uses of plant systems and components, and mitigation measures. The knowledge base used to develop severe accident management guidance (SAMG) implemented at the U.S. plants reflects severe accident phenomenological research developed through about the early 1990s.

\(^1\) See reference 1
\(^2\) See reference 2
Almost all operating plants in the U.S. have completed implementation of SAMGs in accordance with the instructions in NEI 91-04. The industry expects that the NRC will declare very soon that the issue is resolved for U.S. plants.

Although the initial implementation phase is completed and the regulatory interest is resolved, there remains an ongoing obligation under the industry formal position to identify, assess and incorporate, as appropriate, new severe accident knowledge. NEI is the focal point for receiving such new information and assuring that it is appropriately considered by the industry experts, whether they reside at the NSSS vendors, EPRI, utilities or engineering consulting firms. The research findings regarding iodine composition and behavior is an example.

Specifically regarding iodine, there appears to be three fundamental insights derived from past severe accident research:

- Iodine in the primary system and containment exists primarily as compounds of cesium, silver, or other elements rather than as elemental iodine. Thus iodine is mainly in the form of particulate (i.e., aerosol) as opposed to a gas.

- The aerosol form of iodine is generally more readily retained in containment than the gaseous form. Unlike gaseous iodine, removal of particulate iodine from the containment atmosphere is not sensitive to chemical additives. Further, maintaining a neutral pH or higher in the containment sump will prevent iodine, once removed to the sump, from reevolving to the containment atmosphere.

- Significant retention would be expected in primary system and adjacent piping (e.g., upper internals, coolant system piping, main steam piping of BWRs, PWR steam generators) rather than release to containment or the environment for most severe accident sequences.

The insights noted above are reflected in the severe accident management strategies and bases first established in the EPRI Technical Bases Document\(^3\) and refined in the NSSS Owners Group vendor-specific severe accident management guidance\(^4\) (SAMG).

Changes in our understanding of the form and distribution of iodine in the containment has led the U. S. nuclear industry to revisit the value of the existing post-TMI-2 post accident sampling system (PASS). This system emerged as one of many post-TMI operations and systems improvements. Some of these improvements, such as symptom-based accident management procedures, have made the U.S. plants more capable of dealing with abnormal plant events and

\(^3\) See references 3 and 4
\(^4\) See references 5 through 7
severe accident scenarios. The PASS system, however, has for years been judged by many to be a costly, unnecessary system.

Following implementation of the SAMGs, two industry Owner’s Groups are pursuing regulatory relief from PASS and specifically the elimination of the radioisotope assessment procedure for evaluation of core damage, and elimination of in-containment radioisotope measurement for use in emergency planning. The primary basis for this shift is a better understanding of severe accident progression and the confidence that SAMGs and in-plant instruments are more effective in providing timely information on core status and event progression than would PASS samples. For severe accidents, plate-out and iodine distribution issues compromise the usefulness of remotely obtained iodine samples. Also, in the early stages of a core damage accident when the core damage assessment is not useful, personnel considerations may limit the ability to obtain and analyze multiple samples in a timely manner.

Concurrently under NRC staff review are a Westinghouse Owners Group (WOG)-sponsored topical report entitled Core Damage Assessment Manual (CDAM), and an application of the CDAM at the Wolf Creek Nuclear Power Plant. A similar submittal by the Combustion Engineering Owners Group (CEOG) is expected to follow successful completion of the WOG effort.

What about information from subsequent research?

When assessing the need for or value of new research information, one must be careful to ask the question: Would it matter to the design of future plants, to regulation of current plants, or to the operating staff of current plants utilizing the SAMGs? In the case of SAMGs (the subject of this paper), based on the objectives the industry set for its SAMG, is the new information significant from a practical, operations-oriented or event-response perspective? Or, is the compilation of increased scientific knowledge, while interesting, really not of much value to a plant staff attempting to stabilize degraded, severe accident-type conditions?

Aspects of severe accident management that appear to be relevant to this discussion of what to do with an increased knowledge base regarding iodine composition and behavior are the following:

- **Remaining Uncertainties in SAM**—is there enough to be gained by further research on iodine such that the current elements of SAM would be changed? Or, is our knowledge base sufficient to have reasonable confidence that the considerations for diagnostics, strategy assessment, and subsequent recommended actions are appropriate / adequate and therefore does not support additional research?

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5 See references 8 and 9
From the perspective of severe accident management, additional analytical capability on the evolution and distribution of iodine is unnecessary. SAMGs are developed with sufficient robustness so as to deal with the impact of iodine releases. To supplement the SAMGs, the CEGO is encouraging its member utilities to utilize I-131 discriminating capability in their field measurements. These field measurements would ensure that sufficient information is available to the emergency response team to make informed decisions with regard to continued evacuations.

Consequently, the U.S. industry is unaware of uncertainties in SAM which are so important as to justify further iodine research.

- **Which SAM Strategies Would Change**—what in the SAMG would be different? Is it likely that plant-specific implementing procedures would be revised? The U.S. approach has long endorsed the need for instructions that are less rigid than typical normal or emergency operating procedures, what we refer to as **guidance**.

We believe operator actions to control airborne fission products will remain the same. That is, use the sprays to remove airborne iodine. Sufficient evidence is available to confirm that spraying is an effective means of removing both elemental iodine and particulate from the containment atmosphere. Also, adjustment of the pH of the containment sump to prevent conversion of iodine to a more volatile state is recognized as an effective means of maintaining low airborne iodine levels in containment.

Protective Action Recommendations (PARs) will be influenced by the extent of iodine releases, however, the process for establishing these PARs will remain the same. If intentional releases are required to regain control of the plant and bring it to a controlled, stable condition, the form of iodine would not play a role in the selection of the strategies.

There is little capability to measure iodine except through grab samples. The U.S. industry view is that considering the inherent time delays for sampling and analyses, this is only useful after the plant has been stabilized and is not useful for active accident management.

- **Organizational Issues**—are there insights regarding iodine form and quantity that require a different tact to be taken by the plant emergency response staff? Does it require a different expertise, methods and tools for issuing protective action recommendations than that typically provided in current Emergency Response Organization?
The emergency response staff is capable of responding to potential accidents with a wide spectrum of iodine releases. Thus, knowledge that significant levels of iodine are being or may be released from the containment is important for emergency planning considerations. However, this release may be effectively evaluated based on an assessment of the event progression and fission product release paths (using the SAMGs) coupled with field surveys including I-131 monitoring.

No new information is considered to be necessary for this task to be successfully completed. Consequently, we are unaware of how iodine research could affect these organizational issues.

- **What are the implications on personnel training**—would the insights from the iodine research require modification in the content and conduct of SAM training and drills necessary to achieve the desired level of performance?

Existing Emergency Plans are sufficient to deal with small and large levels of radiation release from containment. Plans will not be improved by increased knowledge of iodine form, release mechanisms or transport. Uncertainties in the event are such that field monitoring would likely be needed to confirm analytically derived expectations.

We would of course be very interested in any required modification to training since SAM is a knowledge-based activity and training is a very important element of the overall ability to provide an adequate response. However, we have not identified where such modifications would be required.

- **Finite resources need to be applied judiciously**—is there enough risk-reduction benefit from applying this knowledge that warrants the cost of implementing it? The U.S. industry view is that if one believes that current plant design and operating practices provide adequate protection of the public from severe accidents, then providing “additional protection” must be carefully considered against the anticipated costs and possible detriment to other aspects of safe plant operation.

Resources should be applied to prevent and mitigate events; not on the tracking or response to esoteric, low probability scenarios. Since evolution and deposition of iodine is an after-the-fact issue from the perspective of severe accidents and the ability to control the event is limited to use of a few components, the risk reduction benefit of increased knowledge of the ideal iodine transient response is of far less value than the ability to monitor off-site iodine releases. And, even the ability to monitor off-site iodine releases is still of lower value than the ability to avert the accident.
Conclusion

Key conclusions are as follows:

- The U.S. industry supports acquiring and maintaining a substantial knowledge base on subjects as complex and important to safety as fission product iodine behavior during a severe accident, and notes that a substantial knowledge base currently exists.

- Industry is generally unaware of SAM-related issues in the U.S. which would require major iodine research programs to resolve.

- Because there are limited resources and competing demands for these resources, additional research should be carefully defined to address necessary safety improvements and should be subject to some type of peer review from the users of the research results before it is undertaken.

References

1. NEI 91-04, Revision 1, Severe Accident Issue Closure Guidelines, November 1994.

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IODINE BEHAVIOR UNDER BWR SEVERE ACCIDENT CONDITIONS

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ABSTRACT

The effects of pH and irradiation dose and organic paint material on the formation of volatile iodine species, I₂ and CH₃I, were investigated experimentally in order to understand the behavior of iodine in containment in a BWR severe accident. The experimental results were compared with simulation results obtained by iodine chemical model based on IMPAIR. Experimental results showed the dependence of pH and dose and water temperature on the formation of volatile iodine species, I₂ and CH₃I. IMPAIR simulation results for experiments were within one order of difference of experimental results. MAAP, IMPAIR and the water pool pH calculation code were used to simulate the iodine behavior under BWR severe accident conditions. The preliminary simulation results showed that the total amount of volatile iodine species in the wetwell gas space is below the order of 10⁴ of the initial iodine inventory at 72 hours after an accident.
1. INTRODUCTION

In a light water reactor severe accident, accident management for core debris cooling and heat removal from containment are the top priority in order to mitigate the accident and prevent a large release of fission product out of containment. Based on the experience of the TMI-2 accident, a large part of iodine in degraded fuel is thought to be released as CsI, which is aerosol and involatile and water-soluble. Suspended CsI aerosol will be moved to suppression pool water by scrubbing at exit of relief valve quenchers and vent pipes and containment spray using fire pump, considering BWR accident management (See Figure 1).

According to former studies on iodine behavior, it is generally accepted that molecular iodine, \( I_2 \), will be formed from radiolytic oxidation of I in the pool water, and radiolytic oxidation depends on the pH of the pool water. And, it is accepted that organic iodine, \( CH_3I \), will be formed from \( I_2 \) deposition on epoxy paint surface. \( I_2 \) and \( CH_3I \) are volatile and could be easy to release from containment.

In view of accident management, our concerns are rates and dependency of these volatile iodine species formation. To examine the above concerns, experiments were done by irradiating CsI solution with/without painted SUS plate. And experimental analyses were done for these experiments. We also tried iodine behavior analysis under BWR severe accident conditions. The scheme of our experimental and analytical approach is shown in Figure 2. In this paper we describe our experiments and experimental analysis and iodine behavior analysis under BWR severe accident conditions.

![Figure 1](image1.png)  
**Figure 1**  Schematic Diagram of Accident Management Related to Iodine Behavior (BWR)

![Figure 2](image2.png)  
**Figure 2**  Scheme of Experimental and Analytical Approach to examine iodine behavior under BWR SA Conditions
2. EXPERIMENTAL

2.1 Experimental Apparatus and Experimental Conditions

The experimental apparatus is shown in Figure 3. It consisted of two parts: a gamma irradiation facility and a measurement system. Sample CsI solutions in an irradiation vessel were irradiated by Co-60. The irradiation vessel was made of stainless steel (SUS) with inner surface coated with Teflon. An electrical heater was installed in the irradiation vessel to control solution temperature. A painted SUS plate was installed in some experimental cases. The concentration of iodine chemical forms sampled from gas phase and liquid phase was measured by gas chromatograph and ion chromatograph. The pH of solution was measured.

In Table 1 experimental parameters are shown and compared with BWR SA conditions.

![Figure 3 Schematic Diagram of the Experimental Apparatus](image)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>BWR SA Conditions</th>
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</thead>
<tbody>
<tr>
<td>Dose (kGy)</td>
<td>0, 0.3, 1.5, 15</td>
<td>0 ~ 1000</td>
</tr>
<tr>
<td>Initial Iodine Concentration (mol/l) (CsI)</td>
<td>$10^4$</td>
<td>$\sim 10^5$</td>
</tr>
<tr>
<td>Volume ratio Gas/solution</td>
<td>2</td>
<td>$\sim 2$</td>
</tr>
<tr>
<td>Temperature (deg-C)</td>
<td>20 (RT), 90, 120</td>
<td>$\sim 130$</td>
</tr>
<tr>
<td>pH of CsI solution</td>
<td>3 and 7</td>
<td>Changed alkali to acidic due to nitric acid production</td>
</tr>
</tbody>
</table>
2.2 Experimental Results and Experimental Analysis

Figure 4 shows the effect of irradiation dose on the concentration of I₂ and CH₃I in gas phase at pH7 and pH3 with RT of water temperature. Figure 5 shows the effect of water temperature on the concentration of I₂ and CH₃I in gas phase and on the I₂ deposition amount on painted plate surface. IMPAIR simulation results for experimental analysis are also plotted in the same figures.

There is a dose dependence, a pH dependence and a water temperature dependence.

Regarding the dose dependence, the concentrations of I₂ and CH₃I in gas phase increase with the increase of dose up to 2 kGy. But after 2 kGy, the concentrations decrease. This reason is not clear. However, it is speculated that radiolytic oxidation due to OH radical is dominant up to 2 kGy, thereafter the production of H₂O₂ due to radiolysis of water works as a reductor. Further study is necessary to explain this dependency.

Regarding the pH dependence, it can be seen from the experimental results that high pH leads to lower rate of radiolytic oxidation.

Regarding the water temperature dependence, it can be seen that high temperature leads to high water solubility of I₂ and low deposition amount of I₂ on painted surface. It is speculated that CH₃I concentration increased with the increase of temperature because the decrease of I₂ deposition amount on painted surface increased effective reaction area to produce CH₃I.

IMPAIR simulation results are within one order difference of experimental results. Thus, IMPAIR could be used for iodine behavior analysis of BWR.

![Graphs showing the effect of radiation dose on the concentration of I₂ and CH₃I in gas phase, and the effect of water temperature on the concentration of I₂ and CH₃I in gas phase and the deposition amount on painted surface.]

**Figure 4** Effect of Radiation Dose on the Concentration of I₂ and CH₃I in Gas Phase
(Water temperature : RT)
Figure 5  Effect of Water Temperature on the Concentration of I₂ and CH₃I in Gas Phase and on the I₂ Deposition Amount on Painted Surface. (pH : 7, Dose: 1.5kGy)

3. ANALYSIS

3.1 Iodine Behavior Analysis in a Typical BWR Severe Accident Sequence

The iodine behavior in a typical BWR primary containment vessel (PCV) during a severe accident has been evaluated by calculating the pH value in the suppression pool water and analysing the chemical and physical processes in the drywell and wetwell for the thermal-hydraulic and fission product conditions provided by the MAAP computer code. The accident sequence chosen was a low pressure core melt sequence in a BWR-5 1100MWe Mark-II plant and the accident management after reactor pressure vessel (RPV) failure was considered.

3.2 Analytical Method

The analytical method of iodine behavior in a BWR PCV is illustrated in Figure 6. This method consists of five calculation parts and is encoded as a computer system. The parts are described in the following.

Part 1: Thermal-Hydraulics and Fission Products Calculation

MAAP code (FAI, 1990) is used for calculating the thermal-hydraulics and fission products responses during a severe accident. The iodine species is modelled only for CsI in MAAP. In this method, MAAP outputs such as the thermal-hydraulics conditions in the PCV, the fission products decay heat distributed in the PCV regions, and CsI and CsOH mass deposited on suppression pool are used for evaluating the iodine behavior.
**Part 2: Dose Rates Calculation**

The absorbed dose rates are calculated at the water pools in the pedestal, the drywell, and the wetwell, and at the drywell and wetwell atmospheres for the evaluations of the nitric acid formation in the water pools and the iodine chemistry in the PCV regions. These dose rates are computed from the decay heats, fluid volumes, and the absorbed material density in each region, which are results of the thermal-hydraulics and fission products calculation by MAAP.

It is assumed that the decay heat by fission products deposited in a water pool is totally absorbed in the water (Weber, 1991)

\[
D = \frac{Q_{dec}}{V \cdot \rho}
\]  

where \(D\) is the dose rate (Gy/s), \(Q_{dec}\) is the decay heat in a pool (W), \(V\) is the water volume (m\(^3\)), and \(\rho\) is the water density (kg/m\(^3\)).

It is assumed that the absorption fraction of the decay heat by the core debris deposited on the pool bottom, such as the pedestal floor, is 10%.

In the drywell and wetwell atmosphere calculations, assuming that the region is a sphere with uniform radioactive source, the atmosphere absorption efficiency is given by:

\[
f = 1 - e^{-\text{ir}}
\]  

where \(\text{ir}\) is the absorption coefficient (1/m), and \(R\) is the radius of sphere (m).

**Part 3: Nitric Acid Formation Calculation**

The nitric acid formation and transport are considered for the suppression pool pH calculation. The rate equation of nitric acid in a water pool is given by:

\[
\frac{dN_i}{dt} = GD_i V_i \rho_i + \sum_j \frac{W_{j,i}}{V_j} N_j - \sum_k \frac{W_{i,k}}{V_i} N_i
\]  

where \(N_i\) is moles of nitric acid in a water pool (mol), \(G\) is the g-value of nitric acid formation \((7.048 \times 10^{-10} \text{ mol/J})\) (Beahm, 1992), \(W_{j,i}\) is the inlet water flow (m\(^3\)/s), and \(W_{i,k}\) is the outlet water flow (m\(^3\)/s). Subscript \(i\) is the target water pool, \(j\) is the donor pool, and \(k\) is the acceptor pool. The moles of nitric acid in the suppression pool is given by integrating three equations for water pools in the pedestal, the drywell, and the wetwell.

**Part 4: Suppression Pool pH Calculation**

It is assumed that the suppression pool pH is governed by the nitric acid radiolytically generated and CsOH transported from the primary system. Assuming that all reactions which determine the pool pH occur rapidly, the pool pH is calculated using the SOLGASMIX-PV code (Bemann, 1977) which determines the equilibrium state by finding the minimum free energy.
Part 5: Iodine Chemistry and Iodine Species Transport Calculation

The analytical models of iodine chemistry and iodine species transport in the PCV are shown in Figures 7 and 8, respectively. The iodine chemistry model treats $I_2$, $CH_3I$, $IO_3^-$ and $I^-$ as iodine species. The CsI deposited on the suppression pool predicted by MAAP is treated as $I^-$ in the iodine chemistry calculation. In the wetwell, the iodine species concentrations in water and gas spaces are calculated by the chemical kinetics model based on the IMPAIR 3 (Güntay, 1992), and the following phenomena are considered: iodine hydrolysis, radiolysis, and methyl reactions in the suppression pool, iodine oxidation by radiolytically formed ozone in the gas space, and organic iodide formation from paint wall in both spaces. The mass transfer of volatile iodine species such as $I_2$ and $CH_3I$ between water and gas spaces is calculated by the partition coefficient and the mass transfer constant. In the drywell, iodine species concentrations in gas space are calculated by considering the same reactions in the wetwell gas space. The iodine species transport between the drywell and wetwell gas spaces is evaluated by the gas flows though the vent pipes and the vaccum breakers. At the opening the suppression pool vents, the scrubbing of aerosol iodine such as $IO_3^-$ through the pool is calculated using the decontamination factor of MAAP results. Also, the removal of iodine species in gas space by the spray is considered by the stagnant film model (Grist, 1982) for volatile iodine species and using the removal rate calculated by MAAP for aerosol iodine. The iodine species removed by the drywell spray are carried to the suppression pool with the spray flow. The rate equations representing these iodine phenomena are solved using the IMSL IVPRK routine based on the Gear method.

![Figure 6 Schematic Diagram for Evaluating Iodine Behavior in a BWR PCV](image-url)
Figure 7  Iodine Chemistry Model

Figure 8  Iodine Species Transport Model in a BWR PCV
3.3 Analytical Result

The selected sequence is assumed to be initiated by a transient causing closure of main steam isolation valves (MSIVs) followed by a loss of high pressure injection systems. The RPV is successfully depressurised by the automatic depressurization system (ADS), but low pressure injection systems are assumed to be unavailable, resulting in core melt and then RPV failure under low pressure condition. After RPV failure, the alternative water injection to the pedestal region and drywell spray adjusting as mitigative countermeasures for severe accident are assumed to be operated, and after that, the emergency core cooling (ECC) systems and the residual heat removal (RHR) system are assumed to be successfully recovered.

Results of this sequence predicted by MAAP are shown in Figures 9 through 11.

Figures 9 and 10 show the PCV pressure and the temperature responses for a 72-hour transient time, respectively. Just after RPV failure, at about one and a half hours, the steam generation due to rapid quenching of the core debris on the pedestal floor by falling water remained in the RPV lower plenum causes almost noncondensable gases in the drywell to be purged to the wetwell gas space, resulting in a PCV pressure rise. The PCV pressure gradually increases also after the core debris quenching, because the steam generates continuously due to the core debris cooling by the alternative water injection system to the pedestal region operated for preventing the core-concrete attack and this steam flows to the wetwell, causing the suppression pool temperature to rise. When the drywell pressure reaches 0.57 MPa, which is one and a half times the design pressure, at about 10 hours, the alternative drywell spray system is turned on and the PCV pressure decreases. For the purpose of accident management, this drywell spray is intermittently operated corresponding to the drywell pressure level with the intention of minimizing the compression of the wetwell gas space as the alternative spray system adds the cooling water from the external water source to the PCV. The PCV pressure and the drywell gas temperature are maintained well below the failure criteria by these mitigative actions. Once the ECC systems and the RHR system are recovered at about 28 hours, the core debris is cooled by the ECC injection water and the PCV atmosphere is cooled by the RHR spray, resulting in an immediate decrease in the PCV pressure and temperature. Since the suppression pool cooling is available, a safe, stable state is attained.

Figure 11 shows the distribution of CsI mass fraction to the initial inventory in the PCV. Nearly all of CsI in the fuel matrix is released before RPV failure. Of which, about one-fourth is convected into the suppression pool through the safety relief valves (SRVs) and the remainder is initially deposited on the structures of the RPV. At RPV failure, some amount of the deposited CsI in the RPV revaporizes and enters the drywell and suppression pool. After the alternative drywell spray initiation, the CsI in the drywell is convected into the
suppression pool with the spray water, causing an increase in the amount of CsI in the suppression pool.

The suppression pool pH transient predicted in this sequence is shown in Figure 12. Just after accident initiation, the pH value slightly decreases as the pool temperature rises due to entering of steam through the SRVs and the dissociation of water accelerates. When the core melt starts and volatile fission products enter the suppression pool, the pH value increases because of CsOH entering the pool. After RPV failure, the pH value gradually decreases since the nitric acid is produced by the irradiation of suppression pool. The nitric acid produced in the pedestal water is transported to the suppression pool, and the pool temperature continues to increase. Once the suppression pool cooling starts at about 28 hours, the pH value increases due to the decreasing of pool temperature and becomes above 7.0.

The fraction of iodine species in the wetwell and drywell gas spaces to the initial iodine inventory is shown in Figures 13 and 14, respectively. The CsI result in this figure was calculated by MAAP. The deposited CsI in the suppression pool predicted by MAAP is treated as I in the water space for this iodine chemistry calculation. The I in the suppression pool is converted to I₂ by the hydrolysis and radiolytical oxidation. Also, the I and the converted I₂ reacts with the paint wall, resulting in the formation of CH₃I. These volatile iodine species formed in the pool water transfer to the wetwell gas space. In the gas phase, the I₂ is converted to IO₃⁻ by radiolytically formed ozone and the CH₃I is also formed by reacting with the paint wall in the gas space and also is radiolytically decomposed to I₂. When the alternative drywell spray is started to operate at about 10 hours and the vacuum breakers open intermittently, the iodine species in the wetwell gas space flow to the drywell and react in the drywell gas space and with the paint wall. The fraction of CsI in the gas spaces predicted by MAAP reaches a maximum just after RPV failure and then decreases due to the natural removal mechanism. The predominant iodine species in the wetwell gas space before the RHR spray is IO₃⁻ which is an aerosol iodine species, followed by I₂. Also in the drywell gas space, the predominant iodine species is CsI aerosol, which is calculated by MAAP, released by revaporization from RPV. Once the RHR spray in the drywell and wetwell starts at about 28 hours, aerosol iodine species are rapidly removed from the gas spaces and I₂ becomes to be predominant. The total amount of volatile iodine species in the PCV gas space is predicted to be below the order of 10⁻⁴ of the initial iodine inventory at 72 hours.
Figure 9  PCV Pressure

Figure 10  PCV Temperature
Figure 11  Fraction of CsI Distribution

Figure 12  Suppression Pool pH
Figure 13  Fraction of Iodine Species in Wetwell Gas Space

Figure 14  Fraction of Iodine Species in Drywell Gas Space
4. CONCLUSIONS

Experimental results obtained using irradiating CsI solution with/without painted SUS plate showed the dependence of pH and dose and water temperature on the formation of volatile iodine species, $I_2$ and $CH_3$I. It was seen that high pH leads to lower rate of radiolytic oxidation.

IMPAIR simulation results for experiments are within one order difference of experimental results. It was judged that IMPAIR could be used for iodine chemistry analysis of BWR.

MAAP, IMPAIR and the water pool pH calculation code were used to simulate the iodine behavior under BWR severe accident conditions. The preliminary simulation results showed that the total amount of iodine species in the wetwell gas space is below the order of $10^4$ of the initial iodine inventory at 72 hours after an accident.
5. REFERENCES


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