PROCEEDINGS OF THE THIRD CSNI WORKSHOP
ON IODINE CHEMISTRY IN REACTOR SAFETY

September 11-13, 1991 Tokai-mura, Japan

March 1992

(Ed.) Kenkichi ISHIGURE*, Masakatsu SAEKI,
Kunihisa SODA and Jun SUGIMOTO

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Proceedings of the Third CSNI Workshop on Iodine Chemistry in Reactor Safety
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The Third CSNI Workshop on Iodine Chemistry in Reactor Safety was held at Tokai Research Establishment of Japan Atomic Energy Research Institute at Tokai-mura, Ibaraki-ken, Japan, on September 11 to 13, 1991. About 60 experts attended the Workshop from 10 countries and 2 international organizations.

In the Workshop, 29 papers were presented in five sessions on various aspects of iodine chemistry in reactor safety, such as radiolytic and surface reactions of iodine species, fundamental and integral tests, modeling and code developments.

The information exchanged and the discussions followed resulted in extended and promoted understanding of iodine behavior in accidents of light water reactors and also gave a large expectation for the further progresses coming in the future.

Keywords: Proceedings, Workshop, Iodine Chemistry, Reactor Safety, Radiolytic Reaction, Surface Reaction, Iodine Species, Iodine Behavior, Reactor Accidents, Light Water Reactor

* Department of Chemistry
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CSNI主催第3回原子力安全におけるヨウ素化学ワークショップ論文集
1991年9月11～13日、東海村

日本原子力研究所東海研究所燃料安全工学部
石榑 順吉*・佐伯 正克*・早田 邦久・杉本 純

（1992年1月24日受理）

OECD/CSNI主催の第3回原子力安全におけるヨウ素化学ワークショップが日本原子力研究所東海研究所で1991年9月11から13日にかけて開催された。このワークショップには、10ヶ国2国際機関から専門家約60名の出席があった。

ワークショップでは、ヨウ素種の放射線分解及び表面における反応、基礎及び総合実験、解析モデルとコードの開発など、原子力安全におけるヨウ素化学に関する合計29の論文が5つのセッションにおいて種々の観点から発表された。

ワークショップにおける情報交換と発表後の討論により、軽水炉の事故時のヨウ素挙動に関するより深い理解が得られるとともに、今後の研究の進展に対しても大きな期待が寄せられた。
Proceedings of

The Third CSNI Workshop on Iodine Chemistry in Reactor Safety

Organized under the auspices of the
OECD Nuclear Energy Agency,
Committee on the Safety of Nuclear Installations

and

Hosted by the Japan Atomic Energy Research Institute

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M. Saeki
K. Soda
J. Sugimoto

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Foreword

The Third CSNI Workshop on Iodine Chemistry in Reactor Safety was held at Tokai-mura in Japan on September 11 to 13, 1991, being hosted by the Japan Atomic Energy Research Institute. About 60 experts attended this Workshop from 10 countries and 2 international organizations including two specialists from U.S.S.R. for the first time, and 29 papers were presented in five sessions on various aspects of iodine chemistry in reactor safety, such as radiolytic and surface reactions of iodine species, fundamental and integral tests, modeling and code developments.

The information exchanged and the discussions followed greatly extended and promoted our understanding of iodine behavior in accidents of light water reactors and also gave a large expectation for the further progresses coming in the future.

It should be emphasized that a most important and unique forum has been established through the Workshop for exchanging information and collaboratively solving the important problems in the field of the iodine chemistry in nuclear reactor safety.

As the chairman of the programme committee of this Workshop, I express my sincere thanks to all the speakers and chairmen for their excellent contributions, all the members of the programme committee, that is, Dr. W. Morell (Germany), Dr. R.L. Ritzman (U.S.A.), Dr. M. Saeki (Japan), Dr. H.E. Sims (U.K.), Dr. K. Soda (Japan), Mr. L. Soffer (U.S.A.), Dr. J. Sugimoto (Japan), Dr. A.C. Vikis (Canada) and Dr. J. Royen (OECD) for their cooperation in the preparation of the programme.

I also like to acknowledge Dr. T. Yamashita, Dr. M. Nakashima, Mr. K. Hashimoto, Mr. N. Yamano, Mr. A. Hidaka, Ms. M. Abe and Ms. H. Kurosawa for their help in administration and operation of the Workshop.

K. Ishigure (University of Tokyo)
Chairman, Third CSNI Workshop
on Iodine Chemistry in Reactor Safety
At the Workshop, an effort was made to integrate all information for better use by safety analysts. There is no doubt that a lot of information on iodine behaviour has been accumulated, but in many cases this information needs to be co-ordinated and well organised for safety analyses of nuclear reactors. It is essential that the results of laboratory studies and integral experiments together with modelling activities are well co-ordinated. Therefore, the goal was:

- to review the knowledge and understanding of the chemistry of iodine of relevance to the prediction of its behaviour in nuclear reactors during a range of operational and accident conditions;

- to define those areas of chemistry which are important but poorly understood and require further study.

As shown by the conclusions of the Workshop, there is no doubt that this objective was widely attained.

It is my pleasure to thank JAERI, on behalf of NEA, for the hospitality generously offered to this Workshop; special thanks are due to Dr. K. Soda, Dr. M. Saeki and Dr. J. Sugimoto who have invested a lot of work and effort in the preparation of the meeting. We also would like to express our gratitude to the members of the Programme Committee, Professor K. Ishigure (Chairman of the Workshop), Dr. K.-H. Neeb (represented by Dr. W. Morell), Dr. R.L. Ritzman, Dr. M. Saeki, Dr. H. Sims, Dr. K. Soda, Mr. L. Soffer, Dr. J. Sugimoto, Dr. A.C. Vikis. Their efforts and advice have strongly contributed to the success of the Workshop.

J. Royen
CSNI Secretary
THIRD CSNI WORKSHOP ON IODINE CHEMISTRY IN REACTOR SAFETY

SUMMARY AND RECOMMENDATIONS

The third CSNI Workshop on Iodine Chemistry in Reactor Safety was held at Tokai-mura, Japan on September 11 to 13, 1991. It was hosted by the Japan Atomic Energy Research Institute (JAERI). About sixty experts attended the Workshop, from ten countries and two international organizations; these included for the first time two experts from the U.S.S.R. Twenty-nine papers were presented in five sessions on various aspects of iodine chemistry in reactor safety.

Examination of the programs of the three Iodine Workshops held so far, shows that the trends in research and development in this field have shifted significantly since 1985:

1. from homogeneous to heterogeneous systems,
2. from inorganic to organic iodide species,
3. from fundamental to integral tests, and
4. from scientific to engineering approaches.

These observations have important consequences for further developments in this area, as reflected in the following conclusions and recommendations:

1. Substantial progress has been made in understanding and predicting the behaviour of iodine in the containment building of a reactor following an accident, such as a loss-of-coolant accident. Collaboration between scientists and engineers in designing and analyzing integral and fundamental tests is necessary for further progress in this field.

2. In spite of recent progress, fission product chemistry is still one of the main contributors to source term uncertainties; further research is needed in this field; in particular in the areas of organic compound interactions and surface effects.

3. Dialogue between safety analysts and chemists is essential to identify the importance to risk of chemical phenomena and to prioritize safety issues involving fission product chemistry.

4. Much of the homogeneous solution chemistry is understood; particularly important exceptions are rates and mechanisms for iodine hydrolysis, hydrogen peroxide reactions and the role of organics.

5. Interactions between iodine vapour and bulk material aerosols can occur and have significant effects on iodine compound and transport.

6. Iodine volatility within containment increases with decreasing pH, but, in the presence of radiation, it is not sensitive to the initial aqueous iodine species.
There is further need for the development/validation of existing models and codes against realistic integral tests. However, separate effects experiments must also be performed to both guide and help rationalize the data for the large integral tests.

A variety of surface interactions involving iodine can and probably will affect its transport and volatility in accident situations. Dealing with surface reactions was identified as one of the most significant uncertainties in models and codes.

Suspended CsI aerosols can be oxidized to iodine during hydrogen burns under dry condition. However, modest steam concentration (10%) suppresses CsI oxidation to I$_2$. Additional research on this issue was recommended.

Intervention remains an important issue. It has been shown that high pH is favourable, but the minimum pH required to suppress volatility is still uncertain.

An evaluated kinetic database is being issued and should be maintained. Some efforts should be devoted in the future to assess the temperature dependence of the reactions included in this database. Also, a sensitivity analysis should be conducted to reduce the number of chemical reactions to the most important ones.

Studies should be broadened to examine fission products other than iodine that are important to risk such as cesium and tellurium. It is recommended that the next Workshop, if held, should also focus on these fission products. The need for and the scope of another Workshop should be reviewed in two years time.

The following is a summary of papers presented at the meeting, including several points of direct relevance to reactor safety:

Probabilistic safety assessment (PSA) is an important and effective tool to identify areas of uncertainties associated with source term evaluation of a nuclear reactor accident and to prioritize research areas. It was pointed out at the Workshop that fission product chemistry, particularly modelling of organic compound interactions and surface interactions, is one of the sources of uncertainties; further research is needed in this area. Codes need improvement in modelling fission product behaviour as well. However, the relative importance of each phenomenon to nuclear safety should be carefully examined before detailed investigations are initiated. Therefore, a dialogue between safety analysts and researchers in chemistry is essential in order to identify and prioritize safety issues regarding fission product chemistry.

National and international programs carried out in the past have been extremely valuable; future programs will also be of importance, not only in the OECD area, but also in the rest of the world. At the Workshop, a lot of work done in Canada, Japan and the United Kingdom was presented. The ACE program focused on several key uncertainties such as radiolysis effects, hydrogen combustion effects, interactions with aerosols and interactions with surface coatings. The Commission of the European Communities (CEC) also conducted extensive research on fission product chemistry primarily under the PHEBUS-FP program. Regulatory application of the current technology may lead to a revision of source term criteria in U.S.A. It was agreed at the Workshop that worldwide communication among safety experts is clearly useful to further
reduce risk of a nuclear reactor accident.

Papers on homogeneous chemistry covered effects of silver on radiolytic methyl iodide formation and destruction; also effects of pH, organic materials and their concentration on radiolysis of iodine solution. An analytical description of the mass transfer and kinetics aspects of the JAERI VITA facility was presented. This was followed by a related paper on effects of radiolysis in boiling solutions, where mass transfer is also important. Another paper gave valuable measurements of rate constants for reactions of OH radical with I\(^-\), the reaction of H\(_2\)O\(_2\) with the hydrolysis products of I\(_2\) and the rate of reaction of I\(_2\) with OH\(^-\).

The conclusions were that much of the homogeneous solution chemistry of iodine was understood. Particularly important exceptions are rates and mechanisms of iodide hydrolysis, and of reactions of H\(_2\)O\(_2\) with molecular iodine and its hydrolysis products. The key area of uncertainty is now the role of organic solutes on the pH behaviour, organic iodine production and inorganic iodine behaviour in a radiation field. The combination of mass transfer with reaction was shown to be important to the rate of evolution of iodine as well as the partition coefficient.

Papers on chemistry at surfaces including vapor-aerosol interactions showed that surfaces can have an important impact on iodine behaviour in severe accident environments. A useful experimental technique for determining the kinetics of vapor-aerosol reactions was described and data for the reaction of iodine with cadmium and silver were given. An approach for interpreting data on organic iodide formation at surfaces was also presented. Three papers showed the value of performing separate effects laboratory experiments to help plan and rationalize integral tests. These papers also confirmed the advantage of maintaining alkaline pH conditions in water reservoirs to limit iodine volatility and associated surface interaction effects. New measurements of the rate of I\(_2\) deposition on epoxy paint were presented and rationalized using semi-empirical expressions. It was concluded that a considerable amount of new data are available showing trends in surface processes and effects which can now be used to improve and validate iodine models and codes.

Five papers regarding integral experiments conducted in Canada, the FRG, the U.K. and the U.S. were presented. Results from the ACE program showed that the importance of maintaining high pH in controlling low iodine volatility in containment. Once the solution becomes acid, iodine volatility is only slightly decreased if the solution is changed to alkaline. This has important implications for a strategy of pH control within containment and implies that the pH must be kept alkaline from the beginning. Measured iodine aerosol deposition rates in a large steel vessel were rapid, with about 98% of the mass removed with a removal half-time of 40 minutes. Conversion of CsI aerosol to I\(_2\) was measured under hydrogen combustion conditions. With no steam present, about 15% of the CsI was converted to I\(_2\), whereas, when 10% steam was present, less than 0.5% of the CsI was converted. Evidence was seen of chemical reactions of CsI and CsOH with H\(_2\)BO\(_3\) to form CsBO\(_2\) and HI. In addition, iodine release was measured for iodine dissolved in water in high pressure tubes. Under pipe rupture conditions, less than 1 % of the iodine was released from a compartment. This finding has application to steam generator tube rupture accidents.

Most prominent amongst the conclusions/recommendations of the Second CSNI
Workshop on Iodine Chemistry was the wish to test our models and codes against large-scale, realistic, integrated tests. Thanks to a number of national and international activities during the last three years, the above wish has been largely fulfilled as evidenced by the number of papers presented on this topic. Such tests provided the basis for further development of the IMPAIR-2 code, which now includes an iodine/aerosol interaction submodel and improved submodels for dealing with the iodide reactions, high molecular weight organic iodides, and deposition/revolatilization. Data from the University of Tokyo, Oak Ridge National Laboratory, AECL Research, and AEA Technology were used to test the INSPECT code. The LIRIC model was further developed and tested using data from the Radioliodine Test Facility (RTF) and a preliminary organic radiolysis submodel was developed through a U.K./Canada collaboration. Finally, the ACE-RTF program provided an opportunity for a code comparison exercise for the INSPECT, LIRIC, IMPAIR, IODE and TRENDS codes. In addition to the predictive capabilities of codes, their usefulness in identifying areas of uncertainty in iodine chemistry was demonstrated during the session.

A first attempt was made to apply the iodine code IMPAIR-2 to a source term analysis for a LWR plant. For this purpose the IMPAIR-2 code was inserted into a code-package system. The thermo-hydraulic boundary conditions calculated with the codes in the package give input data to the IMPAIR-2 computation of the iodine behaviour for every compartment. An encouraging first approach was made to model the efficiency of containment spray systems by considering the effects of chemical reactions on mass transfer rates. As a next step the spray removal method should be included into the containment iodine codes. In order to arrive at a European standardized basis for modelling the iodine behaviour in calculations of radiological consequences of design basis accidents, the CEC has initiated studies to integrate the different boundary conditions in the existing PWRs and their influence on iodine behaviour (from the release from the fuel to the release to the environment). Uncertainties regarding the volatility of aqueous HOI were discussed.
1. Session I
NATIONAL AND INTERNATIONAL PROGRAMMES
1.1 OVERVIEW OF SEVERE ACCIDENT RESEARCH IN JAPAN

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ABSTRACT

An overview of Japanese activities of LWR severe accident research is presented, covering various fields and topics of experimental and analytical study on severe accident phenomena. Also reviewed are some procedural measures under consideration for managing severe accident at LWR plant based on the knowledge and methodology developed in this activities.

1. INTRODUCTION

In the nuclear power plant licensing procedure in Japan, the safety examination on basic design is performed based on relating laws and guidelines whose requirements on safety design are prescribed within the framework of design basis accident. Accordingly, severe accident which is more severe but far less unlikely than the design basis accident is not explicitly considered in this procedure.

In recent years, however, it has become widely recognized as important to understand the safety margin of the plant system against severe accident and prepare procedural measures for managing its course and mitigating its consequences. These additional measures are usually called as accident management measures. It is needless to say that research to understand the severe accident is essential for this task since these activities are only possible through wise utilization of theory and knowledge base accumulated in the course of severe accident research.

From this viewpoint, Nuclear Safety Commission of Japan has continuously encouraged and reviewed the accumulation of the theory and knowledge base of severe accident and tried to reflect them upon the nuclear safety policy for regulating the design and operation of nuclear power plant. In other words, the current position of Nuclear Safety Commission on severe accident can be summarized in the following way;

(1) The knowledge of severe accident is one of the most important basis for the formulation of safety design criteria, siting criteria, and guideline for emergency planning.

(2) Industry and research organizations should perform severe accident research in order to identify important phenomena associated with severe accident, to develop analytical tools for source term analysis and risk estimation, and to find ways for preventing and mitigating severe accident through design and/or accident management.

(3) Plant operator should have knowledge of severe accident and reflect it upon the plant management so as to be able to properly cope with beyond design basis accident including severe accident.

A major organization pursuing severe accident research in Japan is JAERI, which is promoting this research in accordance with the governmental nuclear reactor safety research plan [1]. Nuclear Power Engineering Center also performs several large scale demonstration
tests related to the severe accident condition in the plant. In the following chapters, current status of severe accident research being performed mainly by these organizations is summarized, dividing them in experimental and analytical study with some emphasis on fission product behaviour and its effect on severe accident source terms. Also enclosed is a review of activities aiming at improving accident management measures based on these study.

2. EXPERIMENTAL STUDIES ON SEVERE ACCIDENT

Various in-vessel and ex-vessel experiments have been planned and performed so as to obtain basic knowledge on severe accident phenomenology including fission product behaviour which is essential for the safety evaluation of the accident. In the following, present status of experimental research on fuel damage and melt progression, fission product release and transport, component and containment integrity and the demonstration of the effectiveness of accident management procedures is summarized briefly.

2.1 Fuel Damage and Melt Progression

Japan's activities in the filed of experimental investigation of in-vessel melt progression relies largely upon international research collaboration such as the Cooperative Severe Accident Research Program (CSARP), the TMI-2 R&D Program in USA, the CORA experiment in Germany, the LOFT program of OECD and the PHEBUS program in France. Analyses of data in these large scale experiments have provided us significant insight into the core melt progression process during a severe accident. The TMI-2 debris examination which has started at JAERI in 1991 is also a study in this category.

In order to better understand and interpret the data of such large scale experiments, it is useful to perform experiments for identifying each specific effects or phenomena. From this viewpoint, JAERI has performed fuel damage experiment by using the Nuclear Safety Research Reactor (NSRR) and study on the interaction of fuel with control rod and structural material components using the apparatus shown in Figure 1.

As for the reactor pressure vessel failure due to the attack of molten core, the mechanism remains still to be clarified. The TMI-VIP program is expected to provide useful information for the reduction of the uncertainty in this mechanism. Structural analysis of the reactor pressure vessel has been already performed at JAERI to interpret the data obtained in the TMI-VIP program.

Ex-vessel melt progression after the vessel failure plays an important role in determining the timing of the containment failure and source terms. Important phenomena in this ex-vessel melt progression phase include core-concrete interaction and melt cooling in the containment. Hydrogen generation and burn process in the containment may also be affected by these ex-vessel melt progression phenomenon. The Anticipated Load and Performance of a Containment in a Hypothetical Accident (ALPHA) program at JAERI focuses on the clarification of phenomena related to the ex-vessel melt progression, especially core-concrete interaction and molten core coolability in a containment. Steam explosion is also studied in this program since this phenomenon in a containment may have an influence on the integrity of reactor vessel and the containment as well[2]. Schematic diagram of the ALPHA test facility is shown in Figure 2 and in Table 1, summarized is the major capability of the facility.

2.2 FP Release and Transport

Research efforts in the field of iodine chemistry in Japan focus mostly on the establishment of both general database and analytical model for iodine behaviours in various conditions, covering reaction rate, formation of organic and volatile iodine, and effect of coolant boiling upon them. Reaction rates of iodine chemistry in the aqueous phase are measured by pulse radiolysis method at University of Tokyo. Formation of organic iodine in the radiation field is experimentally studied at JAERI with small scale test apparatus shown in Figure 3. The effects of radiation, pH, and impurities upon the formation have been experimentally clarified. It has been found that the formation of volatile iodine is also
suppressed by the existence of AgI in water. Basic reaction kinetics of iodine, cesium and tellurium with structural material components such as Fe, Ni and Cr are investigated by using the apparatus illustrated in Figure 4. The effect of coolant boiling on oxidation of iodide ions was investigated at Hitachi Ltd. It was pointed that the oxidation increased as the void fraction increased due to coolant boiling.

At JAERI, fission product release and transport have been studied mostly from the viewpoint of supplementing the large scale integral experiment data such as those obtained from the CSARP program and the PHEBUS FP program. A new test is planned in order to study the fission product release from a fuel of a test assembly at high temperature of 2800 C under various conditions ranging from oxidized to reduced environment. Figure 5 presents the schematic diagram of the facility for this experiment.

The efficiency of pool scrubbing is one of the dominant factors influencing source terms in severe accidents. Therefore the experimental facility for pool scrubbing investigation (EPSI) shown in Figure 6 was fabricated at JAERI to quantify this efficiency. Experimental results obtained so far have indicated that the pool scrubbing is extremely effective in removing fission products even at elevated temperature and pressure [3].

NUPEC is now promoting a test program to study the trapping of radioactive material in the leakage path of a containment such as electric penetration assembly (EPA) and an equipment hatch. In this program, iodine trapping effect in the leakage path will be investigated under simulated severe accident conditions. Test will be done on organic seal materials such as epoxy resin and silicon resin which are to be used in these penetrations as an insulator or a gasket. It is assumed in designing the tests that the leakage path grows at these organic part when temperature and pressure increase beyond the design limit in severe accident condition. The test program consists of a bench scale test for surveying parameters which dominantly affects the efficiency of iodine trapping in the leak path and a large scale test which is useful for the confirmation and the evaluation of the iodine trapping effect in more realistic setting. In the latter test, therefore, a test assembly simulating the actual situation in the operating plant will be utilized.

2.3 Component and Containment Integrity

Integrity of the containment has become focus of attention especially since the Chernobyl accident for which no strong containment of the western type existed. In the case of severe accident, the degradation of the containment function is associated with the ex-vessel phenomena such as steam explosion, hydrogen burn, excessive pressure and/or temperature in the containment.

Effect of dynamic pressure to the containment was studied at JAERI by the analysis using the finite element analysis code. The result indicated that the containment would maintain its integrity even if the dynamic pressure reach 4 to 5 times of the design pressure [4]. Leak rate tests at high pressure and temperature have been carried out in ALPHA test program at JAERI to characterize the failure mechanism of the penetrations for instrument cables and power cables. Experiments conducted so far show no leakage resulting from high pressure. NUPEC is promoting a proving test program on containment integrity. The program includes hydrogen mixing and distribution tests, hydrogen burning tests, and tests to measure failure pressure of steel containment vessel (SCV) and prestressed concrete containment vessel (PCCV) [5].

2.4 Effectiveness of Accident Management Schemes

Accident management has become an important issue from the viewpoint of prevention and mitigation of a severe accident. ROSA-V program is now planned at JAERI to focus on accident management during transients and accidents. Experiments will be conducted to demonstrate the effectiveness of various accident management measures by using the modified ROSA-IV facility. On the other hand, ALPHA program pays an attention to the ex-vessel phase of accident management scheme such as spraying water on top of molten core material
for the termination of further core degradation and scrubbing and/or filtering for the mitigation of consequences of severe accidents. Experiments are in progress by using the EPSI facility.

3. ANALYTICAL STUDIES ON SEVERE ACCIDENT

As suggested by Nuclear Safety Commission, it is important to develop analytical tools for the assessment of severe accident and utilize them to perform PSA and plan effective accident management. In the following, the present status of severe accident analysis code development in Japan is reviewed and some insight from the utilization of such codes, recent result of PSA for Japanese LWRs and the recent activities of government and utilities with respect to accident management are given.

3.1 Code Development

The development and assessment of codes for severe accident analysis has primarily been pursued at JAERI. JAERI has developed THALES code package for level 2 PSA studies of both BWR and PWR. In addition, JAERI has developed detailed mechanistic codes such as MUFLAR, HORN and REMOVAL for the analysis of experimental data and the verification of the THALES code. MUFLAR is a two-dimensional core damage progression analysis code. HORN is a code which is capable of predicting the chemical form of fission products along the release path. REMOVAL is an aerosol analysis code which has been validated through the analysis of the LACE experiment.

At the same time, several organizations have introduced such integrated code as SCADAP/RELAP5 or MELCOR and carried out their assessment by applying them to TMI-2 accident and large scale tests such as PBF/SFD, CORA and PHEBUS/SFD.

3.2 Recent Level-1 PSAs for LWR Plants

Probabilistic Safety Assessment (PSA) is recognized as the convincing tool to support the deterministic safety assessment method and assist the regulatory activities of nuclear power plants. From this viewpoints, the governmental organizations and industries are collaborating for the development and application of PSA methodologies in recent years. Among them, JAERI has been developing PSA methodology and conducting level 1 and 2 PSAs for Japanese LWR model plants. The purposes of this activity are to find out a possible problem in actually applying the whole PSA methodology developed to a plant and also to utilize the findings obtained through the analysis for the resolution of generic safety issues.

Japan Institute of Nuclear Safety (JINS) of NUPEC has been conducting level-1 and level-2 PSAs for typical Japanese BWRs and PWRs since 1987. The initiating events selected in these assessments were limited to the internal event such as a loss of coolant accident (LOCA) and abnormal operational transients during high power operation. In these study, small event trees and large fault trees were constructed. The data base of component failure rates was mainly composed of IREP and LER data while data on initiating events, off-site power loss, emergency diesel generator (EDG) failure rate and recovery rate of failed offsite power were based on Japanese experiences. The result has indicated that the core damage frequency of Japanese LWRs are far less than the value of 10^-5 /RY which is a goal set for new plant by IAEA INSAG. The major reason for this lies in the fact that the frequency of initiating event and unreliability of electric power source including EDG are less than those experienced in most of other countries.

3.3 Preliminary Level-2 PSA and Assessment of Source Term

As for level -2 PSA , the result suggests that the frequency of containment failure is about one order of magnitude less than that of severe core damage, though the study should be recognized as preliminary since it is premature to determine the uncertainties in the source term evaluation.
In order to understand the sources of uncertainty in source term evaluation, source term evaluation codes used in level 2 PSA in Japan such as THALEAS/ART of JAREI, STCP of NRC, and MAAP of IDOCOR were compared. They are significantly different from each other in several key models for fission product release and transport. These are models for fission product release during core/concrete interaction, chemical form of fission products, fission product release from containment during energetic events, aerosol retention, gaseous fission product retention and revaporation, agglomeration of aerosol, pool scrubbing, interaction of fission product behaviour with thermo-hydraulics etc. To understand the impact of these differences, comparisons have been made among calculated results of 4 standard problems [6]. These problems are TQUV (transient followed by total loss of core cooling function) and TB(station blackout ) sequences of 1100 MWe class BWR-5 with Mark II containment and TMLB (transient followed by loss of feed water as well as all AC power) and S2HF (small break LOCA followed by the failure of ECCS recirculation and containment spray).

Tables 2 and 3 show the distribution of CsI at the end of calculation (30 to 70 hrs depending on codes) for BWR TQUV and TB sequences, respectively. Table 2 indicates that MAAP code gives the largest environmental release for TQUV sequence among these three codes. This is explained by the fact that this code has the most comprehensive FP revaporation model in which the redistribution of heat source accompanied with the FP transport is taken into consideration. This table also shows that most of CsI is located in the reactor coolant system (RCS) in the case of THALES/ART code and in the wetwell in the case of STCP code. In the case of MAAP code, however, most of CsI is located in the drywell. This difference of MAAP result from others is caused by the occurrence of containment failure just after the penetration of pedestal concrete and the difference in FP revaporation model aforementioned. In TB sequence, all the codes predict very small environmental release. Most of CsI is retained in the RCS in the case of THALES and STCP, while it is in the wetwell in the case of MAAP.

Tables 4 and 5 show the CsI distribution at the end of calculation (160 hours) for PWR TMLB and S2HF sequences, respectively. In TMLB sequence, all the codes calculates that most of CsI is released in the reactor vessel. However, most of CsI released is retained in the primary system in the case of MAAP and in the case of THALES/ART, most is released in the containment. As for the fraction of environmental release, STCP gives the smallest number which is far smaller than those obtained by THALES and MAAP codes because it lacks FP revaporation model. In S2HF sequence, MAAP code gives the largest source terms and the largest FP retention in the primary system. This is because in MAAP evaluated is the revaporation of CsI in the primary system as well as in the containment.

In summary, this study shows that the source terms are significantly influenced by models for natural circulation of gas in the PWR primary coolant system, debris relocation and channel blockage, debris dispersion after RPV failure, core / concrete interaction, fission product retention in RCS, pool scrubbing, release of nonvolatile fission products during core/concrete interaction and revaporation of volatile fission products, although their sensitivity depends on the specific plant and accident sequence.

Recently, JAERI has developed THALES-2 code to model, among others, fission product revaporation in severe accidents of BWRs with Mark-I and Mark-II containment by coupling thermo-hydaraulics and fission product transport models. A few test run of THALES-2 code for BWR small LOCA without ECCS sequence indicates that the effect of revaporation on the source terms depends on the chemical form of FP as well as the containment failure time, the temperature of reactor coolant system at the time of containment failure and the type of concrete used[7].

4. RESEARCH AND PREPARATION FOR ACCIDENT MANAGEMENT

4.1 Preparation of Accident Management Measures
Accident management include, as defined by IAEA INSAG report, preplanned and ad hoc operational practices which, in circumstances in which the design specifications of the plant are exceeded, would make optimum use of existing plant equipment in normal and unusual ways to restore control. Various measures can be considered for this purpose, ranging from special operation procedures, special equipment, special communications and so on. The effective use of these many measures is considered to increase when their utilization are prepared beforehand.

Under the guidance of MITI, the electric utilities have already developed procedures to cope with the unexpected events which have not been considered in the event-based operational procedures prepared for managing transient and accident conditions in the past. These are so-called symptom-based procedure, an improved version of the emergency operating procedures specifically designed for the management of beyond design basis events and/or events of which causes are not identified by operators. This kind of procedure is considered effective from the viewpoint of cognitive process of operators in preventing the progression of such events and situations to severe core damage.

Currently, a special committee is established in NSC to review the need for measures for keeping the integrity of containment vessel in the case of severe core damage and the measures to vent the containment and ignite the hydrogen, in particular, in the light of the results of level-1 and level-2 PSAs. Considering the extremely low frequency of severe core damage and the ensuing containment failure evaluated so far, the installation of venting system and igniters do not seem to improve the plant safety significantly. However, uncertainty in phenomenology in severe accident makes it difficult to definitely conclude the discussion in that way.

4.2 Research on Accident Management Strategy

Analytical study of accident management was performed at JAERI with emphasis on the effectiveness of intentional depressurization and reflooding of damaged core. Findings from such analysis will be further investigated experimentally to confirm and quantify the effectiveness of such strategy using ALPHA, ROSA-V and EPSI facilities.

Several analytical studies have been performed at JAERI to improve the knowledge base for the consideration of accident management strategy. One of them is a level-2 PSA conducted for 1,100 MWe-class BWR-5 with MARK II containment using the THALES/ART code developed at JAERI[8]. According to this analysis, a large number of accident sequences which led to containment overpressure failure can be categorized, except for ATWS sequences, into three groups by the similarity in the timing of containment failure after core melt initiation, as shown in Figure 7: these are (1) sequences with successful high pressure injection but loss of decay heat removal, (2) sequences with successful low pressure injection but loss of decay heat removal and (3) sequences without ECCS injection. Evaluated source terms were found to be strongly dependent on this time interval as well as the location of containment failure since this interval corresponds to the time available for natural deposition of aerosol.

Figure 8 shows the contribution of each accident scenario family to the core damage frequency, to the containment failure frequency and to the product of iodine release fraction and containment failure frequency. Any of these indices indicates that the functionality of residual heat removal system is the most important risk reduction factor. It is interesting to note that LOCA sequences are also dominant contributors as transient sequences when the products of iodine release fraction and containment failure frequency is considered, although from the view point of core damage frequency, only accident sequences initiated by transient are the dominant contributors. It should be noted however that the results shown here are rather tentative due to a limited plant data and insufficient modelling in the code.
5. CONCLUSION

The licensing procedures in Japan do not explicitly require the analysis of severe accidents, although their prevention is the first priority of design, construction and operation of a nuclear power plant. The TMI-2 and the Chernobyl accidents, however, demonstrated that severe accidents could occur and led us to pursue severe accident research in Japan in order to quantify the safety margin of nuclear power plant against this accidents and to study the measures to control their course and mitigate their consequences. According to the results of the research on severe accidents which has been initiated and pursued by the government research organizations and industries in Japan, current generation reactors in Japan seem to well satisfy the internationally agreed safety requirements and have reasonable safety margin against severe accident conditions well beyond the design basis.

Findings from the recent studies of PSA, however, indicates that severe accident source terms evaluated still have large uncertainties mainly come from the uncertainties associated with fission product chemistry. Therefore, it is important to continue experimental and analytical research of severe accident and fission product behaviour in particular, for further enhancement of our knowledge base in this field. This enhancement will surely contribute to the enhancement of the manageability of severe accident and nuclear reactor safety, in general.

References


Table 1: Major Dimensions and Capabilities of ALPHA

<table>
<thead>
<tr>
<th>Location</th>
<th>Volume (m$^3$)</th>
<th>Height (m)</th>
<th>Diameter (m)</th>
<th>Design Pressure (MPa)</th>
<th>Design Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
<td>5.7</td>
<td>3.9</td>
<td>2</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 2: Distribution of Csi at the End of Calculation (BWR TQUEV Sequence)

<table>
<thead>
<tr>
<th>Location</th>
<th>THALES/ART</th>
<th>STCP</th>
<th>MAAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCS</td>
<td>9.4×10^{-1}</td>
<td>2.9×10^{-1}</td>
<td>1.6×10^{-2}</td>
</tr>
<tr>
<td>Drywell</td>
<td>2.8×10^{-4}</td>
<td>2.0×10^{-3}</td>
<td>6.7×10^{-1}</td>
</tr>
<tr>
<td>Wetwell</td>
<td>5.7×10^{-2}</td>
<td>7.0×10^{-1}</td>
<td>1.5×10^{-1}</td>
</tr>
<tr>
<td>Debris</td>
<td>0.0</td>
<td>2.0×10^{-10}</td>
<td>0.0</td>
</tr>
<tr>
<td>Reactor Building</td>
<td>1.8×10^{-4}</td>
<td>8.7×10^{-7}</td>
<td>8.3×10^{-2}</td>
</tr>
<tr>
<td>Environment</td>
<td>4.2×10^{-8}</td>
<td>1.2×10^{-4}</td>
<td>8.3×10^{-2}</td>
</tr>
</tbody>
</table>

Table 3: Distribution of Csi at the End of Calculation (BWR TB Sequence)

<table>
<thead>
<tr>
<th>Location</th>
<th>THALES/ART</th>
<th>STCP</th>
<th>MAAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCS</td>
<td>8.3×10^{-1}</td>
<td>6.7×10^{-1}</td>
<td>1.5×10^{-1}</td>
</tr>
<tr>
<td>Drywell</td>
<td>4.2×10^{-3}</td>
<td>1.8×10^{-2}</td>
<td>3.0×10^{-2}</td>
</tr>
<tr>
<td>Wetwell</td>
<td>1.6×10^{-1}</td>
<td>3.1×10^{-1}</td>
<td>8.2×10^{-1}</td>
</tr>
<tr>
<td>Debris</td>
<td>3.4×10^{-3}</td>
<td>2.8×10^{-4}</td>
<td>0.0</td>
</tr>
<tr>
<td>Reactor Building</td>
<td>1.9×10^{-7}</td>
<td>9.8×10^{-4}</td>
<td>1.1×10^{-3}</td>
</tr>
<tr>
<td>Environment</td>
<td>5.3×10^{-5}</td>
<td>9.2×10^{-4}</td>
<td>8.4×10^{-5}</td>
</tr>
</tbody>
</table>

Table 4: Distribution of Csi at the End of Calculation (PWR TMLB' Sequence)

<table>
<thead>
<tr>
<th>Location</th>
<th>THALES/ART</th>
<th>STCP</th>
<th>MAAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary System</td>
<td>1.1×10^{-3}</td>
<td>0.73</td>
<td>0.69</td>
</tr>
<tr>
<td>Containment</td>
<td>0.99</td>
<td>0.27</td>
<td>0.28</td>
</tr>
<tr>
<td>Debris</td>
<td>2.0×10^{-4}</td>
<td>0.032</td>
<td>0.0</td>
</tr>
<tr>
<td>Environment</td>
<td>0.014</td>
<td>1.6×10^{-4}</td>
<td>0.033</td>
</tr>
</tbody>
</table>

Table 5: Distribution of Csi at the End of Calculation (PWR S2HF Sequence)

<table>
<thead>
<tr>
<th>Location</th>
<th>THALES/ART</th>
<th>STCP</th>
<th>MAAP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary System</td>
<td>0.016</td>
<td>0.039</td>
<td>0.34</td>
</tr>
<tr>
<td>Containment</td>
<td>0.98</td>
<td>0.96</td>
<td>0.51</td>
</tr>
<tr>
<td>Debris</td>
<td>0.0</td>
<td>1.5×10^{-3}</td>
<td>0.0</td>
</tr>
<tr>
<td>Environment</td>
<td>8.8×10^{-4}</td>
<td>9.5×10^{-4}</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Fig. 1. Fuel Component Interaction Test Apparatus

Fig. 2. Schematic Diagram of ALPHA

Fig. 3. Schematic Apparatus for Separating Organic Iodine Species from Irradiation Sample
Fig. 4. Schematic Diagram of the Test Apparatus or Reaction Kinetics Experiment

Fig. 5. Schematic of Out-of-Oile Fission Products Release Test Facility

Fig. 6. Schematic Diagram of EPSI

Fig. 7. Source Terms Calculated by THALES/ART
**Fig. 8 Relative Importance of Accident Sequences**

**Designators**
- A: Large break LOCA with equivalent diameter of greater than 6 inches.
- B: Failure of electric power to engineered safety features.
- P: Failure of safety/relief valves to reclose after opening.
- Q: Failure of normal feedwater system to provide core make-up water.
- S1: Medium LOCA with an equivalent diameter of 2 inches to 6 inches.
- S2: Small LOCA with an equivalent diameter of 1/2 inches to 2 inches.
- T: Transient event.
- TI: IORV (Inadvertent Opening of Relief Valves) event.
- U: Failure of high pressure core cooling system or reactor core isolation cooling system to provide core make-up water.
  - U1: Failure of high pressure core spray
  - U2: Failure of core isolation cooling system
- V: Failure of low pressure core cooling system.
  - V1: Failure of low pressure core spray
  - V2: Failure of low pressure injection
- W: Failure to remove residual heat.
DISCUSSION

Weber
In your pool scrubbing experiments, do you consider only aerosol materials, or are gaseous iodine species studied also?

Kondo
We only consider aerosol materials. The reason is that it is considered that the major form of iodine released from core to the primary system under severe accident condition is to be CsI aerosol.

Tennankore
What is the Japanese policy on severe accident?

Kondo
The rules say nothing on the severe accident. However, it is implicitly understood that the goal of safety regulation is firstly to prevent the occurrence of severe accident and secondly to accommodate to some extent the consequence of severe accident with design margin of the plant to the design basis accident. One of the objective of PSA is to review such capability of plant in severe accident.
1.2 OVERVIEW OF THE ACE IODINE PROJECT

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ABSTRACT

The ACE iodine project is a multi-component research program with international sponsorship that was designed to generate data on several issues which were viewed as being important to the analysis of iodine behavior in containment during severe accidents. The principal phenomena investigated include radiolysis, hydrogen combustion, aerosol interactions, and surface coating (paint) interactions in a combination of laboratory experiments, intermediate scale tests, a large-scale containment vessel experiment, and supporting studies. The experimental design of the separate components of the program are summarized and the key results obtained in these studies are described. The significance of this body of new information to the problem of predicting iodine behavior in containment during severe accidents is also discussed.

1. INTRODUCTION

The Advanced Containment Experiments (ACE) program is a cooperative research effort that is sponsored by an international consortium of organizations from nineteen countries in Asia, Europe, and North America. It involves experimental work on filter performance, iodine behavior, and corium concrete interactions. The scope of the iodine behavior work was gradually developed through consultation with a group of iodine chemistry specialists from the consortium membership. In general, it was determined that experimental studies were needed to address several issues which were viewed as being important in modeling volatile iodine species generation and removal in containments during potential severe accidents. The issues of concern were aqueous solution radiolysis effects, hydrogen combustion/deflagration effects, bulk aerosol interaction effects, and organic surface coating (paint) interaction effects. The types of studies that were performed ranged from exploratory to near confirmatory. The project was made up of four basic elements; (1) laboratory scale separate effects-experiments, (2) intermediate scale multi-effects tests, (3) a large scale combined-effects experiment, and (4) various supporting studies. Details and major findings from each of these elements will be described in the subsequent sections of this paper.
2. EXPERIMENTAL

2.1 Laboratory Studies

Three different laboratory scale experimental efforts were conducted during the overall iodine project to obtain data on individual parameter effects and to investigate new phenomena. One series of bench-scale experiments were performed at the AECL Whiteshell Laboratories to evaluate the separate effects of epoxy-painted surfaces, solution pH, gamma radiation, temperature, initial iodine speciation, and time on aqueous iodine chemistry. The experiments were done in three phases as shown by the test matrix in Table 2-1. Small glass vessels (50 ml) were used in batch-type experiments. Key parameters measured during the tests included the liquid/gas total iodine partition coefficient, painted surface/liquid or painted surface/gas iodine distribution coefficients, and liquid and gas phase organic iodide concentrations. Some supplementary studies were done to obtain additional data on iodine interactions with epoxy paint.

Another series of laboratory experiments were conducted at Oak Ridge National Laboratory (ORNL) to examine the reactivity of potential aerosol materials toward vapor iodine forms, determine sorption rates, and measure surface loadings. The iodine forms used consisted of elemental iodine, methyl iodide, and hydrogen iodide which were exposed to various powdered materials, representing possible aerosol components, in a simple once-through flow system. Iodine uptake was measured for different exposure times and temperatures. Recovered samples were analyzed for iodine species, and companion thermochemical calculations were done to assist interpretation of the results.

The third set of laboratory scale experiments, which were also performed at ORNL, were designed to investigate the chemistry associated with cesium iodide decomposition in hydrogen flames. The work utilized a rather simple apparatus consisting of a specially designed hydrogen burner with an off-gas collection/analysis system and other supporting equipment. Hydrogen combustion flame temperatures were mapped and the type and yield of iodine products were determined when small quantities (several micromoles) of cesium iodide powder were introduced directly into various locations of the stationary flames.

2.2 Intermediate Scale Tests

The intermediate scale experiments were composed of a series of radiolysis effects tests in the Radiodine Test Facility (RTF) and a set of hydrogen deflagration effects tests in the Containment Test Facility (CTF). Both facilities are located at AECL-Whitesell Laboratories.
The RTF consists of a 0.35 cubic meter vessel equipped with gas and liquid circulation/sampling loops, a Co-60 radiation source giving dose rates of 1-2kGy/hr, and associated equipment enabling operation from room temperature up to about 80°C. The objective of the tests was to follow the time dependent behavior of iodine under a range of conditions in order to provide a body of data for evaluating and improving existing accident analysis models and codes. A schematic diagram of the RTF is shown in Figure 2-1, and the test matrix is given in Table 2-2. The parameters varied in these multi-effects tests included radiation dose, initial aqueous phase iodine speciation, aqueous phase pH, and painted or unpainted vessel interior. The gas phase to liquid phase volume ratio was held at ten to one. Each test was run for several days during which gas and aqueous phase iodine concentrations, iodine speciation, and system conditions (pH, temperature, pressure, etc.) were measured regularly. The vessel interior was freshly cleaned, painted, and cured before each of the first three tests. The paint used was a reactor accident qualified coating; specifically, Keeler and Long No. 4500 epoxy-amine self-priming surface enamel.

The CTF is a 6.3 cubic meter spherical steel vessel that has been used to conduct numerous hydrogen combustion experiments over a wide range of conditions. For the ACE tests the facility was equipped with a pneumatic device for dispersing several grams of fine cesium iodide powder into a pre-mixed hydrogen containing atmosphere in the vessel. The gas mixture was then ignited, and following the resulting deflagration, the atmosphere was sampled and the samples analyzed chemically for the presence of oxidized forms of iodine (elemental iodine and iodate). A diagram of the equipment is shown in Figure 2-2, and the test matrix is given in Table 2-3. The principal objective of the tests was to determine what effect steam would have on the stability of suspended cesium iodide during energetic hydrogen burns.

2.3 Large-Scale Experiment

A three-part experiment was conducted at the Containment Systems Test Facility (CSTF) to evaluate the effectiveness of volatile iodine sinks (i.e., bulk aerosols, painted surfaces and water reservoirs) at large scale. The CSTF, which is located at the Hanford site near Richland, Washington, consists of an 852m³ containment vessel with associated aerosol generation equipment and all the auxiliary facilities needed to conduct containment behavior experiments. A schematic diagram showing the principal equipment used in the ACE test is given in Figure 2-3. The containment vessel was insulated on the outside and internal surfaces were painted with the same epoxy coating as used in the laboratory and intermediate scale ACE experiments.
The experiment was carried out over a period of about four days with the containment vessel closed and pressurized by steam addition to about 240 kPa. The vessel gas temperature was maintained at about 100°C by continued steam addition to make up for heat losses. Condensed water drained into a pool at the bottom of the vessel which contained common additives to fix the pH. A diagram of the test sequence is given in Figure 2-4. On day one, about 1 kg of mixed CsOH and MnO aerosol was rapidly introduced into the vessel followed immediately by release of about 100 g of HI. The decline in the airborne concentration of all three components was followed with Maypack and other samplers for one day. On day two, the same sequence was performed except I₂ rather than HI was released and sampling continued for about two days. At that point, the pH of the water pool was changed from 5.6 to about 8.5 and the test continued another day with sampling. Thermal-hydraulic parameters were measured throughout the experiment and wall condensate, pool water, and deposition coupon samples were periodically collected. Highly sensitive chemical analysis procedures were specially developed for determining the iodine content of these samples since use of radioactive iodine in the test was prohibited.

2.4 Supporting Studies

Several additional activities were organized to compliment the experimental studies in the iodine project. The most important was a code comparison and data review/assessment effort. Test problems were designed for calculation by five different iodine behavior codes to reveal similarities and differences and to evaluate their potential for predicting the major features of multi-effects experiments such as the RTF and CSTF tests. In addition, a group of iodine chemistry specialists was organized for the purpose of reviewing existing information and recommending research needed to resolve important iodine behavior issues. Another activity involved a survey of methods for measuring iodine in various types of solid, liquid and gas samples that would result from performing large and intermediate scale experiments. Chemical speciation determinations as well as elemental analyses were emphasized. In addition, the various ACE members were requested to provide results of independent research being done on iodine behavior at their local laboratories as work-in-kind contributions to the project. Such contributions could be either experimental data or the results of analytical studies.

3. RESULTS

The major results obtained from the various studies outlined above will be described in this section. Detailed results from individual studies are described and discussed in five companion papers which have been prepared for the current Third CSNI Iodine Workshop.(1-5)

The laboratory scale experiments produced several findings of significance to the understanding of iodine behavior in severe accident environments. The bench-scale series indicated that at room temperature and in the presence of a radiation
steady state iodine volatility was independent of whether the initial aqueous species was I⁻ or I₂. These experiments also confirmed the observation made by other workers that the total iodine partition coefficient varies strongly and in direct proportion to aqueous pH. This dependence, which was maintained to total doses approaching 200kGy, gave partition coefficients in the range of 10⁵ to 10⁶ at pH = 9 and in the range of 10² to 10³ at pH = 4.5. In addition, the presence of epoxy paint in the irradiated systems did not affect the overall iodine volatility although some iodine sorption by the paint took place (generally greater under acid pH conditions). The hydrogen burner experiments showed that no significant chemical interactions can be expected for aerosol materials in stationary hydrogen-air flames until the material has been vaporized. Cesium iodide that is vaporized is unstable in hydrogen flames with the iodine redistributing between the -1, 0, and +5 oxidation states. In addition, both hydrogen iodide and organic iodides are readily oxidized to I₂ in hydrogen-air flames.

Some of the results of the intermediate scale experiments were similar to those from the bench-scale series. For example, the radiolysis experiments in the RTF at 60°C gave steady state iodine volatilities which were independent of the initial aqueous species. The iodine partition coefficients showed about the same spread with pH in the stainless steel vessel test (RTF-4) but somewhat less spread with pH in the painted vessel tests (RTF-2 and -3; i.e., values ranging from 10⁴ to 10⁵ at pH = 9 and ranging from 10² to 10⁴ at pH = 5-6). In addition, appreciable deposition of iodine on epoxy painted surfaces occurred during the acidic conditions in RTF-3 but not during the alkaline conditions of RTF-2. In RTF-3 the wall in contact with the gas phase was the dominant deposition surface and little change in iodine loading occurred when the pH was made alkaline late in the test. Organic iodides were observed to be minor contributors to steady state total iodine in the RTF tests; of the order of 1% at acid conditions and about 0.1% at alkaline conditions in the presence of the 1-2kGy/hr radiation field, epoxy painted surfaces, and at 60°C. In the stainless steel vessel (RTF-4) these yields were lower but only by about a factor of 4. The hydrogen combustion experiments in the CTF produced appreciable elemental iodine (15% or more) when the atmosphere was dry but no measurable elemental iodine when 10% steam was present. This occurred in near stoichiometric hydrogen-oxygen mixtures producing peak flame temperatures in excess of 2500°C.

The principal finding from the large-scale experiment at the CSTF was that both HI and I₂, which were introduced as vapors into the aerosol filled containment vessel, were removed from the atmosphere at the same rate as the aerosol material. Maypack samplers found less than 2% of the total iodine in nonparticulate form. The aerosol material experienced significant particle growth due to its hygroscopic nature which produced relatively rapid removal (t₁/₂ = 40-45 min) from the vessel atmosphere by gravitational settling.
Finally, the results of iodine code comparison calculations showed that present codes are in agreement with each other in some respects but differ in other respects. Points of agreement include the predicted major iodine species, overall iodine volatility, importance of pH, and importance of painted surfaces as iodine sinks. Areas of difference included the modeling of organic iodide formation, predictions of iodine deposition on dry and wet surfaces, and predictions of minor aqueous species concentrations. The group of iodine chemistry specialists exchanged views periodically about how to resolve these differences. This process is not yet complete.

4. DISCUSSION/CONCLUSIONS

The observation in the bench-scale work and in the RTF experiments that iodine volatility was essentially independent of which aqueous species was used initially is a valuable finding with respect to design of experiments as well as for accident analysis purposes. It indicates that the chemical system is reasonably well behaved with strong driving forces for reaching equilibrium compositions. Thus, initial speciation does not have to be an experimental parameter nor a particular concern in iodine model development. This insight was applied in designing the RFT-4 test where only one initial iodine species, cesium iodide, was used.

The other major findings described in the previous section have similar important implications with respect to the practical issues of estimating and/or controlling iodine behavior in severe accidents. Perhaps the most significant result is the observed sensitivity to aqueous phase pH in the presence of a strong radiation field. The data as a whole demonstrate three clear advantages of starting with an alkaline (pH = 8-9) system: (1) low overall volatility of iodine, giving partition coefficients in the range of $10^4$ to $10^5$; (2) low levels of organic iodine species even when relatively large amounts of epoxy paint materials are present (on the order of 0.1%); and (3) low iodine concentrations on vessel surfaces. Under acid conditions (pH = 4-6), the total partition coefficient should drop by a factor of about 100, the organic iodine level should rise by a factor of about 10 (but remain a small fraction of the total iodine), and appreciable iodine buildup on vessel surfaces should be expected. This last result may, depending on the nature of the interaction with the surface material(s), constitute a significant delayed source of volatile iodine when/if the system "equilibrium" should be disturbed. Obviously, if alkaline conditions can be established and maintained in the accident environment, the task of limiting and predicting iodine volatility is considerably simplified.

The experimental work on the issue of the stability of cesium iodide aerosol during hydrogen combustion events was clearly exploratory. Nevertheless, the CTF results demonstrated that a modest steam partial pressure prevented decomposition of the iodide during and after energetic deflagrations. Perhaps the hygroscopic salt absorbed sufficient water to avoid evaporation of the cesium iodide during the brief passage of the high temperature flame front. This explanation would reconcile the CTF observations with those from the laboratory scale hydrogen burner.
experiments. However, fundamental studies to determine the specific physical and chemical mechanism of the interactions taking place could not be done. It is evident that cesium iodide stability in these situations does depend on the specific ambient conditions and extrapolation of the ACE results to dissimilar conditions is not recommended.

The large-scale experiment at the CSTF clearly showed that a reactive aerosol at gram/cubic meter concentrations is a very effective sink for both HI and I₂ such that these iodine species, which may exist as vapors initially, soon behave as particulates. Since the transport properties of particles are different from those of vapors, this finding has important implications for models or computer codes which seek to predict the time dependent behavior of iodine in containment vessels during severe accidents. The capability to treat the vapor-aerosol interaction and its effects should be present in the model/code. Both theory and experiment show the interaction process is quite rapid and the factor which will determine its overall impact is the amount of aerosol present compared to the amount needed to absorb all of the vapor iodine species. Again, experimental work has shown that strongly alkaline materials such as CsOH have large capacities for I₂ or HI while weakly alkaline or neutral materials such as MnO have limited capacities.

Findings from the iodine code comparison calculations are encouraging but it is apparent that more model development and testing is needed to treat additional phenomena and to produce more uniform and accurate prediction of key experiments. Iodine specialists from the ACE membership have agreed that considerable uncertainty exists about how to model organic compound interactions and how the various surface (wet and dry) interactions should be treated. The potential list of compounds and surface types is so large that a serious effort to generalize, group, approximate, or otherwise simplify the issue is needed. When a practical approach has been developed and implemented, the ACE experiments and other existing work should be used to test the strength and accuracy of the methodology.

ACKNOWLEDGEMENT

The work reported in this paper was supported by the ACE project which is a consortium of organizations from 19 countries in Asia, Europe, and North America. The author wishes to acknowledge the valuable assistance of the members of the ACE Technical Advisory Committee in planning the content of the Iodine Project and the dedicated efforts of the technical and support personnel from the several research organizations who successfully carried out the research plan in a timely and professional manner.
REFERENCES


Table 2-1
Test Matrix for Bench-Scale Experiments

<table>
<thead>
<tr>
<th>Phase</th>
<th>Test</th>
<th>Radiation kGy/hr</th>
<th>Temp °C</th>
<th>Iodine Species (a)</th>
<th>pH</th>
<th>Coupon (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2</td>
<td>0</td>
<td>25</td>
<td>CsI</td>
<td>8.5-9.0</td>
<td>No/Yes</td>
</tr>
<tr>
<td>3/4</td>
<td>0</td>
<td>25</td>
<td>CsI</td>
<td>4.5-6.0</td>
<td>No/Yes</td>
<td></td>
</tr>
<tr>
<td>5/6</td>
<td>0</td>
<td>25</td>
<td>I₂</td>
<td>8/5-9.0</td>
<td>No/Yes</td>
<td></td>
</tr>
<tr>
<td>7/8</td>
<td>0</td>
<td>25</td>
<td>I₂</td>
<td>4.5-6.0</td>
<td>No/Yes</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9/16</td>
<td>Same as Phase 1 but at 80°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>17/24</td>
<td>Same as Phase 1 but at 1kGy/hr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) Iodine concentration = 10⁻⁵M  
(b) Epoxy painted steel coupon

Table 2-2
Test Matrix for RTF Tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Initial Iodine Species(a)</th>
<th>Initial pH</th>
<th>Radiation Source, KCl</th>
<th>Vessel Surface</th>
<th>Other Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CsI, CH₃I, I₂</td>
<td>9</td>
<td>0</td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CsI, CH₃I, I₂</td>
<td>9</td>
<td>8.5</td>
<td>Epoxy</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>CsI, CH₃I, I₂</td>
<td>5.5</td>
<td>8.5</td>
<td>Epoxy</td>
<td>pH change (b)</td>
</tr>
<tr>
<td>4</td>
<td>CsI</td>
<td>9</td>
<td>8.5</td>
<td>Stainless Steel</td>
<td>pH change (c)</td>
</tr>
</tbody>
</table>

(a) Separate stages for each initial species  
(b) Increase to pH9 on day 5 in each stage and hold for one day  
(c) Decrease to pH5.5 on day 6 and back to pH9 on day 10.

Table 2-3
Test Matrix for CTF Hydrogen Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>H₂L, %</th>
<th>Steam, %</th>
<th>Air, %</th>
<th>CsI, g/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td>80</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>0</td>
<td>71</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>10</td>
<td>61</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
<td>0</td>
<td>71</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>10</td>
<td>65</td>
<td>10</td>
</tr>
</tbody>
</table>
Figure 2-1 Diagram of the Radioiodine Test Facility

Figure 2-2 Arrangement Drawing of the CTF for Hydrogen Combustion Effects on Dispersed Cesium Iodide
Figure 2-3 Diagram of the CSTF Test Arrangement

Figure 2-4 The CSTF Iodine Experiment Test Sequence
DISCUSSION

Kupferschmidt (Comment)
Data on organic iodide % are correct but it should be pointed out that even though organic iodides are minor species compared to total iodine. They are nearly always the dominant volatile species in the gas phase.

Ritzman
Your point is generally correct but accident consequences are proportional to fission product release fractions. The point of the statement in the paper is to caution that the absolute magnitude of the volatile fraction is an important parameter.

Evans
Will further experimental information be required before the interaction of iodine with aerosols in a radiation field? Can it be incorporated into the existing iodine codes?

Ritzman
Off hand I cannot think of any critical data that would be needed. If the implied concern is with the potential for acidifying alkaline hydroscopic aerosols, this is not likely during the time period the aerosol remains suspended because the period is relatively short compared to acid production rates.

Kupferschmidt (Comments)
1) Although the fraction of iodine as organic iodides was less than 1% in the ACE RTF and bench-scale studies, it is important to note that except for the pH 5.5 stainless steel RTF test, organic iodides dominated the gas phase (> 75%).

2) With regard to your comments on the effect of organics, I agree that we cannot study in detail the role of all possible organics on iodine chemistry. However, by investigating the reactions of selected organics with iodine and water radiolysis products, a better understanding of the effect of organics should be possible. These investigations should include the study of various classes of organic compounds (i.e., alkane, aromatic, ketone, etc.)
1.3 IODINE CHEMICAL FORM IN LWR REACTOR ACCIDENTS: REGULATORY PERSPECTIVES IN THE UNITED STATES

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ABSTRACT

Recent technical evaluations of the likely chemical form of the iodine released from the reactor coolant system into the containment, done under the auspices of the Nuclear Regulatory Commission, are reviewed for their implications for the present assumptions in US licensing actions. The present assumptions are contained in Regulatory Guides 1.3 and 1.4, both of which are based on Technical Information Document (TID)-14844. The NRC intends to update those assumptions for use in licensing actions for advanced LWR reactors. With NRC approval, existing and evolutionary plants may be allowed to use updated insights from this research in licensing actions. The plans for modifications of existing guidance and the schedules for such changes will be discussed.

1. INTRODUCTION AND BACKGROUND

Radionuclide releases, that is, the type, quantity, timing and energy characteristics of the release of radioactive material from reactor accidents ("source terms") are deeply embedded in the regulatory policy and practices of the U.S. Nuclear Regulatory Commission (NRC). For almost thirty years the NRC's reactor site criteria [1] have required for licensing purposes that an accidental fission product release from the core into the containment be postulated to occur and that its radiological consequences be evaluated assuming that the containment remains intact but leaks at its maximum allowable leak rate.

In this regard, iodine fission products and the chemical form of iodine have played a key role. The characteristics of the "source term" into the containment, which must be distinguished from a release to the environment, is contained in Regulatory Guides 1.3 and 1.4 [2,3], but is derived from the 1962 report TID-14844 [4], and consists of 100% of the core inventory of noble gases and 50% of the iodines (half of which are assumed to deposit on interior surfaces very rapidly). These values were based largely upon experiments performed in the late 1950's involving heated irradiated UO₂ pellets. One percent of the remaining "solid" fission products was also included in TID-14844, but was dropped from consideration in Regulatory Guides 1.3 and 1.4.

Regulatory Guides 1.3 and 1.4 specify that the iodine is assumed to be instantaneously available for release, and also specify that the iodine chemical form is assumed to be predominantly (91 percent) in elemental (I₂) form, with 5 percent assumed to be particulate iodine and 4 percent assumed to be in organic form. These assumptions have significantly affected the design of engineered safety features, which have largely been optimized to remove elemental iodine. In addition, containment isolation valve closure times have also been affected by these assumptions.

Use of the TID-14844 release has not been confined to an evaluation of plant mitigation features such as sprays and filtration systems and site suitability alone. The regulatory applications of this release cover a wide
range, including the basis for (1) the post-accident radiation environment for which safety-related equipment should be qualified, (2) post-accident habitability requirements for the control room, and (3) post-accident sampling systems and accessibility.

In contrast to a specified source term for design basis accidents, severe accident source terms first arose in probabilistic risk assessments (e.g., Reactor Safety Study, WASH-1400 [5]) in examining accident sequences which involved core melt and where containments could fail. Severe accident source terms represent mechanistically determined "best estimate" releases to the environment, including estimates of failures of containment integrity. This is very different from the combination of the non-mechanistic conservative release to containment postulated by TID-14844 coupled with the assumption of very limited containment leakage used for Part 100 siting calculations for design basis accidents. The worst severe accident source terms resulting from containment failure or containment bypass can lead to consequences that are much greater than those associated with a TID-14844 release into containment and where the containment is assumed to be leaking at its maximum leak rate for its design conditions. Indeed, some of the most severe source terms arise from some containment bypass events, such as "event V".

Although severe accident source terms have not been mandated in individual plant licensing safety evaluations in the USA, they have had significant regulatory applications. Source terms from severe accidents (beyond-design-basis accidents) entered into regulatory consideration and usage shortly after the issuance of WASH-1400 in 1975, and their usage was accelerated by the aftermath of the Three Mile Island accident in March 1979. Current applications rely to a large extent on the results of WASH-1400 and include (1) part of the basis for the sizes of emergency planning zones for all plants, (2) the basis for staff assessments of severe accident risk given in plant environmental impact statements, and (3) part of the basis for staff prioritization and resolution of generic safety issues, unresolved safety issues, and other regulatory analyses. Source term assessments based on WASH-1400 methodology appear in many probabilistic risk assessment studies performed to date.

Source term estimates under severe accident conditions began to be of great interest shortly after the Three Mile Island (TMI) accident when it was observed that only relatively small amounts of iodine were released to the environment compared with the amount predicted to be released in licensing calculations. This led a number of observers to claim that severe accident releases were much lower than previously estimated.

A major NRC research effort began about 1981 and has been under way since then to obtain a better understanding of fission product transport and release mechanisms in LWR's under severe accident conditions. This research effort [6] has included a very large and extensive staff and contractor effort, involving a number of national laboratories as well as nuclear industry groups, which resulted in the development and application of a group of computer codes [7], the Source Term Code Package (STCP), Figure 1, to examine core-melt progression and fission product release and transport in LWRs. Work by the NRC staff has also included significant review efforts by peer reviewers, foreign partners in NRC
research programs, industry groups, and the general public. The STCP methodology on severe accident source terms has been reflected in the issuance of NUREG-1150 [8] which provides an assessment for five US nuclear power plants.

The purpose of this paper is to review some regulatory implications of recent technical evaluations of the chemical form of iodine released into the containment and to discuss these in the context of regulatory initiatives regarding severe accidents and LWR source terms that are currently underway in the United States.

2. RESEARCH INSIGHTS REGARDING FISSION PRODUCT RELEASES INTO CONTAINMENT

As a result of the NRC’s research effort to obtain a better understanding of fission product transport and release mechanisms in LWR’s under severe accident conditions, [9] the STCP emerged as an integral tool for analysis of fission product transport in the reactor coolant system (RCS) and containment. The STCP models release from the fuel with CORSOR [10] and fission product retention and transport in the RCS with TRAPMELT [11]. Releases from core-concrete interactions are modeled using the VANESA code [12]. Depending upon the containment type, NAUA, SPARC [13] or ICODEF [14] are used to model the transport and retention of fission product releases from the RCS and from core-concrete interactions into the containment, with subsequent release of fission products to the environment consistent with the state of the containment.

Improved modeling of severe accident phenomena, including fission product transport, has been provided by the recently developed MELCOR code [15]. At this time, however, an insufficient body of calculations is available to provide detailed insights from this model.

Using the NRC developed STCP, the NRC has sponsored studies [16,17] which have analyzed the timing, magnitude and duration of fission product releases. Based on these studies, the general release phases and typical duration times associated with a severe reactor accident for a pressurized water reactor (PWR) can be categorized as shown in Table 1. Typical core inventory release fractions associated with these phases which appear within containment are shown in Tables 2 and 3 for high pressure and low pressure accident sequences, respectively.

![Figure 1. Source Term Code Package](image-url)
Table 1. Release Phases of a Severe Accident

<table>
<thead>
<tr>
<th>RELEASE PHASE</th>
<th>DURATION, hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant Activity Release</td>
<td>10 to 30 seconds</td>
</tr>
<tr>
<td>Gap Activity Release</td>
<td>0.1 - 0.5</td>
</tr>
<tr>
<td>Early In-Vessel Release</td>
<td>0.7 - 3.0</td>
</tr>
<tr>
<td>Ex-Vessel Release</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Late In-Vessel Release</td>
<td>10</td>
</tr>
</tbody>
</table>

From these tables, it can be seen that initially there is a release of coolant activity associated with a break in the reactor coolant system. Assuming that this cannot be accommodated by the reactor coolant makeup systems (including emergency core cooling systems), fuel failure would occur with a release of the activity located in the gap between the fuel pellet and the fuel cladding. As the accident progresses, fuel degradation commences resulting in a loss of fuel geometry accompanied by gradual melting and slumping of core materials to the bottom of the reactor pressure vessel. During this period, the early in-vessel release phase, virtually all the noble gases and significant fractions of the volatile nuclides such as iodine and cesium, are released into containment. The amounts of volatile nuclides released into containment during the early in-vessel phase are strongly influenced by the pressure within the RCS during core degradation. High pressure sequences result in significant retention and plateout of volatile nuclides within the RCS, while low pressure sequences result in relatively little retention within the RCS and consequently higher releases into containment.

If failure of the reactor pressure vessel occurs, two additional release phases then occur. Molten core debris released from the reactor pressure vessel into the containment will interact with the concrete structural materials of the cavity below the reactor. As a result of these interactions, significant quantities of the less volatile nuclides may be released into containment. Ex-vessel releases are strongly influenced by the type of concrete in the reactor cavity. Limestone concrete decomposes to produce greater quantities of CO and CO₂ gases than basaltic concrete. These gases, will in turn, sparge significant quantities of the less volatile nuclides, such as barium and strontium, and small fractions of the lanthanides, as well. Large quantities of non-radioactive aerosols may also be released as a result of core-concrete interactions. The presence of water in the reactor cavity overlying any core debris can significantly reduce the release of ex-vessel releases (both radioactive as well as non-radioactive) into the containment, either as a result of cooling the core debris, or at least by scrubbing the releases and retaining a large fraction in the water. The degree of scrubbing will depend, of course, upon the depth of any water overlying the core debris. Simultaneously, and with a generally longer duration, late in-vessel releases of some of the volatile nuclides not previously released during the early in-vessel phase will also occur and be released into containment.
Table 2. Core Fractions Released into Containment under High RCS pressure.

<table>
<thead>
<tr>
<th>NUCLIDE</th>
<th>Gap Release</th>
<th>Early In-Vessel</th>
<th>Ex-Vessel</th>
<th>Late In-Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe, Kr</td>
<td>0.05</td>
<td>0.95</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.05</td>
<td>0.14</td>
<td>0.22</td>
<td>0.12</td>
</tr>
<tr>
<td>Cesium</td>
<td>0.05</td>
<td>0.11</td>
<td>0.30</td>
<td>0.08</td>
</tr>
<tr>
<td>Tellurium</td>
<td>$10^{-4}$</td>
<td>0.05</td>
<td>0.23</td>
<td>0.04</td>
</tr>
<tr>
<td>Strontium</td>
<td>$10^{-6}$</td>
<td>0.01</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td>Barium</td>
<td>$10^{-6}$</td>
<td>0.02</td>
<td>0.09</td>
<td>0</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>0</td>
<td>$3 \times 10^{-3}$</td>
<td>0.027</td>
<td>0</td>
</tr>
<tr>
<td>Cerium</td>
<td>0</td>
<td>$4 \times 10^{-3}$</td>
<td>0.018</td>
<td>0</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>0</td>
<td>$1 \times 10^{-3}$</td>
<td>0.015</td>
<td>0</td>
</tr>
</tbody>
</table>

* Values shown for limestone concrete

Table 3. Core Fractions Released into Containment under Low RCS pressure.

<table>
<thead>
<tr>
<th>NUCLIDE</th>
<th>Gap Release</th>
<th>Early In-Vessel</th>
<th>Ex-Vessel</th>
<th>Late In-Vessel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xe, Kr</td>
<td>0.05</td>
<td>0.95</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Iodine</td>
<td>0.05</td>
<td>0.40</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td>Cesium</td>
<td>0.05</td>
<td>0.30</td>
<td>0.34</td>
<td>0.08</td>
</tr>
<tr>
<td>Tellurium</td>
<td>$10^{-4}$</td>
<td>0.15</td>
<td>0.30</td>
<td>0.04</td>
</tr>
<tr>
<td>Strontium</td>
<td>$10^{-6}$</td>
<td>0.03</td>
<td>0.14</td>
<td>0</td>
</tr>
<tr>
<td>Barium</td>
<td>$10^{-6}$</td>
<td>0.04</td>
<td>0.11</td>
<td>0</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>0</td>
<td>$8 \times 10^{-3}$</td>
<td>1 $\times 10^{-3}$</td>
<td>0</td>
</tr>
<tr>
<td>Cerium</td>
<td>0</td>
<td>0.01</td>
<td>0.017</td>
<td>0</td>
</tr>
<tr>
<td>Lanthanum</td>
<td>0</td>
<td>$2 \times 10^{-3}$</td>
<td>0.017</td>
<td>0</td>
</tr>
</tbody>
</table>

* Values shown for limestone concrete

3. RECENT EVALUATION OF IODINE CHEMICAL FORM IN CONTAINMENT

Oak Ridge National Laboratory (ORNL), under the auspices of the NRC, has recently completed a study on iodine chemical forms and behavior entering the containment from the reactor coolant system, and its subsequent behavior in-
containment in an aqueous environment. Since the NRC intends to consider the information in this report for regulatory updating of accident source terms, the report has recently been issued [18] in draft form for public comment. This effort is also the subject of another paper [19] being presented at this conference, and will be discussed only briefly here.

The ORNL results indicate that iodine entering the containment is at least 95% CsI. 5% is I plus HI, with not less than 1% as either. Once iodine enters containment, however, additional reactions may occur. In an aqueous environment, as expected for LWRs, iodine is expected to dissolve in water pools or plate out on wet surfaces as I-. Subsequently, iodine behavior within containment depends upon the pH of the water solutions. Because of the presence of other dissolved fission products, radiolysis as a result of nitric acid formation is expected to occur and lower the pH of the water pools. Without any pH control, ORNL results indicate that large fractions of the dissolved iodine will be converted to elemental iodine and be released to the containment atmosphere. Organic iodine will then be produced slowly over time from the elemental iodine available. On the other hand, if pH control is available and the pH is maintained at a value of seven or greater, very little (less than one percent) of the dissolved iodine will be converted to elemental iodine.

It is important to keep the conditions associated with the ORNL results clearly in mind. These results suggesting that only small fractions of the total iodine in containment would be in elemental form apply only for those cases where the pH is controlled to levels of 7 or greater. Significantly greater quantities of elemental iodine may be expected within containment where there is no control of the pH. Finally, although severe accidents involving early containment failure might initially release CsI to the environment, conversion to elemental iodine would be expected to occur during atmospheric transport, since there is no pH control for offsite releases.

4. REGULATORY INITIATIVES UNDERWAY IN US

Design basis accident source terms have been used in the USA for licensing purposes in three distinct ways, namely: (1) for siting evaluations as required by 10 CFR Part 100, (2) to assess the effectiveness of plant mitigation systems, and (3), to define the radiological environment conditions for certain plant systems. At the present time, the NRC is pursuing several regulatory initiatives to incorporate insights from updated severe accident source terms. These are discussed below.

A. Revision of NRC Reactor Site Criteria

Present U.S. reactors have been sited and designed based on their ability to cope with a group of postulated accidents, the so-called design basis accidents. The ability of the plant to withstand these events, as well as their radiological consequences must be shown to be acceptable in order for the plant to be licensed. Reactor siting also reflects consideration of accidents beyond the design basis, since the Statement of Considerations published when 10 CFR Part 100 was issued noted that accidents beyond the design basis, or severe accidents, were a factor in establishment of the population center distance as a siting requirement.
Although U.S. siting criteria require an exclusion area and a low population zone (LPZ), and also require that the nearest population center be no closer than one and one-third times the outer radius of the LPZ, it is important to recognize that numerical criteria for these site parameters (other than they must not result in the dose guideline values stated in Part 100 being exceeded) are not provided. Rather, the sizes of the exclusion area and LPZ are regulated indirectly by the credit given for fission product cleanup systems such as sprays and filter systems as well as the allowable containment leak rate. Hence, siting dose calculations actually have affected plant design, particularly fission product cleanup systems related to iodine, more than siting. Although the original report TID-14844 stated that the procedural method resulted in distances roughly reflecting "current" siting practices, TID-14844 did not give credit for fission product cleanup systems. After the introduction of such systems, the NRC staff implemented conservative assumptions in granting credit for such systems in order to maintain siting distances roughly equivalent to those approved for early plants. In addition, Part 100 provides no criteria on population density other than those associated with the population center distance.

At the present time, better guidance on U.S. reactor siting criteria can be found in Regulatory Guide 4.7 [20]. This document provides guidance, but not requirements, on acceptable site parameters. It notes that for typical plant engineered safety features, an exclusion area distance of about 0.4 miles and an LPZ radius of about three miles have usually been found to satisfy the dose guidelines of 10 CFR Part 100. The guide also states that reactor sites should have a population density at plant startup of less than 500 persons per square mile out to a distance of 30 miles from the site (total population within a circular area divided by the area of the circle), and that the projected population density during the plant lifetime should not exceed 1000 persons per square mile over the same distance. Applicants proposing sites in excess of these values should pay special attention to alternative sites having lower population densities. It is estimated that about half a dozen existing U.S. reactor sites have population density values that are in excess of the values listed in Regulatory Guide 4.7. All of these sites were reviewed and approved prior to the issuance of Regulatory Guide 4.7 in 1975.

Because siting dose calculations are not strongly influencing siting in the U.S., and because improved source term insights are important in understanding how future plants should be designed to cope with potential severe accidents, a revision of the NRC's reactor site criteria (10 CFR 100) is being undertaken. The reactor site criteria are to be revised to remove source term and dose calculations for siting purposes and to add exclusion area size and population density criteria directly into Part 100. These criteria are expected to be similar to those given in Regulatory Guide 4.7. It is important to note that this rule change is not expected to substantively change existing U.S. siting practice since it is already controlled largely by the guidance of Regulatory Guide 4.7. At the same time, Appendix A to Part 100, containing site seismic criteria, is also being revised to reflect our latest understanding in this area.

Source term and dose criteria will continue to be important for plant design; hence, an interim revision of 10 CFR 50 will be carried out in parallel and will contain the present source term (i.e., that from TID-14844). These proposed rule changes are expected to be issued for comment by early 1992.
A final revision of 10 CFR 50 to incorporate updated source term and severe accident insights will then be undertaken, with a proposed rule for comment presently scheduled to be issued by September 1992.

B. Technical update of TID source term

Severe accident research insights have confirmed that although the TID-14844 release is very substantial and has resulted in a very high level of plant capability, nonetheless, based upon the large amount of information obtained on severe accidents since the publication of TID-14844 almost thirty years ago, the present recipe is no longer compatible with a realistic understanding of severe accidents. It has both conservative and non-conservative aspects. The assumption of an instantaneous appearance of a large fraction of the core inventory of noble gas and iodine isotopes within containment has long been recognized as highly conservative, but until the application of a modern methodology with the capability of examining the timing of individual severe accident sequences involving core degradation, it was difficult to arrive at more defensible values. It has also become clear that neglect of other important nuclides released into containment, such as cesium, may be non-conservative. Use of the TID-14844 prescription in its present form may force plant designers to include design features that may not enhance safety and that focus, instead, upon certain aspects of the prescription (e.g., very rapid closure of certain containment isolation valves and filter designs emphasizing removal of elemental iodine). Similarly, use of the present prescription may cause designers not to focus on other important aspects of plant accidents (e.g., release of cesium and potential containment failure under severe accident conditions).

The NRC is currently in the process of reviewing designs for future nuclear power plants and the NRC staff has been directed to apply these important research insights towards resolution of key issues associated with the licensing of these designs. At the present time, work is underway within the NRC to prepare and issue a technical update of the present source term derived from TID-14844 and contained in Regulatory Guides 1.3 and 1.4 making use of current severe accident research insights. This effort is expected to be reflected in changes in the timing of the release, the composition and magnitude of fission product releases into the containment, and the chemical form of the iodine fission products. A draft of an updated report replacing TID-14844 is expected to be transmitted by the NRC staff to the Commission by about the end of 1991, with publication for comment scheduled by about early 1992. Although this updated source term report is expected to be applied toward licensing of future light water reactor plants, insights arising from this study are also expected to be made available for voluntary use by existing reactor licensees.

Rather than an instantaneous release into the containment, as currently given, the revised formulation is expected to be stated as a series of fission product releases into containment, each one associated with a particular phase of an accident or group of accidents. Hence, the revised formulation is expected to begin with the release of coolant activity, followed by release of activity in the fuel gap, release of fission products associated with gross fuel degradation prior to reactor vessel failure, and finally, release of fission products from core-concrete interactions as well as late in-vessel
revolatilization. A conceptualization of such a revised source term is shown in Figure 2.

![Diagram: Concept of Revised Source Term]

Figure 2. Concept of Revised Source Term

Additional nuclides other than the noble gases and iodine are expected to be given consideration. For example, preliminary indications are that the fraction of core inventory of cesium released into the containment is generally comparable to that of iodine. In addition, some tellurium and smaller fractions of the remaining nuclides are also expected. Ex-vessel releases are expected to be given consideration, as well. These would add additional nuclides such as strontium and barium. It is expected that the presence of water in the reactor cavity would play an important role in scrubbing of releases from any core-concrete reactions. In addition, other processes capable of introducing large aerosol loads into containment, such as high pressure melt ejection (HPME), may also require consideration.

A portion of the area in Figure 2 which schematically shows releases after vessel failure is drawn as shaded. This is because it is not yet clear whether addition of these releases would result in a source term into containment that is less than or greater than that presently given in TID-14844.

5. REGULATORY IMPLICATIONS OF REVISED IODINE CHEMICAL FORM

Although regulatory positions arising from updated source term insights remain to be developed, some preliminary implications of the ORNL results...
regarding iodine chemical form as well other severe accident insights can be seen at this time. A few of these are discussed briefly below.

5.1 Containment Spray Systems

Virtually all US PWR's employ containment spray systems. This system serves a dual purpose; namely, containment cooling and pressure suppression in the event of a postulated loss-of-coolant accident, plus use as a containment atmosphere cleanup system to reduce the inventory of fission products as well. Until relatively recently, spray systems were designed to remove elemental iodine only and NRC guidance strongly encouraged the use of a chemical additive, typically NaOH, simultaneously with spray injection to enhance the removal of elemental iodine.

After review of available experimental data, the conclusion was reached that removal of elemental iodine by a fresh solution having little or no dissolved iodine was not sensitive to the pH of the solution. After spray recirculation, however, the pH of the solution was determined to be important [21] in order to avoid the evolution of elemental iodine in solution, with a pH level of 7 or greater effectively preventing the evolution of elemental iodine. NRC guidance [22] was changed relatively recently to reflect this. Models were also added to allow for removal of elemental iodine by natural deposition processes and spray removal of aerosol particulates.

This revised guidance, generally conservative in the amount of removal credit allowed for the spray system, should be reviewed in the face of new insights regarding iodine chemical form.

5.2 Engineered Safety Feature Filtration Systems

At the present time, virtually all U.S. nuclear power plants employ safety-related filtration systems. These are typically employed in most control room habitability systems to provide adequate radiological protection for operators against postulated accidents, are required for mitigation against a postulated spent fuel handling accident and may also be employed in those plants having secondary containments (e.g., boiling water reactors) to control offsite releases of postulated accidents. Regulatory guidance on the design of such systems [23], indicates that high efficiency charcoal adsorbers (with elemental iodine removal efficiencies of 95 percent or greater) are employed, in addition to particulate filters. Assuming that the pH is controlled, post accident, revised insights on iodine chemistry calls into question the need for such high efficiency charcoal adsorbers. Indeed, some have contended that our revised knowledge renders charcoal filtration unnecessary.

The NRC staff is currently reviewing this complex issue and has not yet reached a technical position. Nevertheless, it may be useful to examine some key questions affecting this issue in light of revised insights on iodine chemical form discussed here and elsewhere in this conference. Since control room filtration systems take air from outside containment prior to entry into the control room, a key question is the degree of elemental iodine evolution which might occur during typical transport times for any leakage from the containment to the control room air intake (assuming appropriate pH control within
containment) and re-evolution of elemental iodine from particulate iodine trapped on prefilters.

Present regulatory assumptions used in analyzing the postulated spent fuel pool accident [24] are that virtually all the iodine released from the fuel-clad gap will be retained in the pool water. However, the spent fuel pool is not currently required to have any pH control and long term conversion to elemental iodine and re-evolution from the pool surface might occur. The degree of such conversion is currently unknown since a key question here is the pH time history in the spent fuel pool, given a postulated spent fuel accident. Since safety-related filters equipped with charcoal adsorbers to retain elemental iodine are required for present plants, re-evolution of elemental iodine, if it occurs, is not a concern for present plants.

Finally, for filtration systems within containment, several questions which have a strong bearing on this issue must be addressed, even assuming pH control. These are (1) to what degree will CsI retained on particulate filters decompose to evolve elemental iodine?, and (2) what effect would hydrogen burns have upon the chemical form of iodine within containment? Based upon preliminary information, CsI retained on particulate filters as an aerosol appears to be chemically stable provided that it is not exposed to moisture. Exposure to moisture, however, would lead to CsI decomposition and production of iodine in ionic form (I\(^-\)), which, in turn, would lead to re-evolution of elemental iodine. Filtration systems designed in accordance with present US guidance are equipped with demisters to remove significant moisture before it reaches the charcoal adsorber part of the filter train. However, an additional concern is that the demisters themselves may trap some CsI aerosol.

Resolution of these questions is being pursued in order to improve regulatory guidance for these issues.

5.3 BWR Suppression Pools

Boiling water reactors (BWR's) in the US currently employ suppression pools for steam pressure suppression to cope with the postulated loss-of-coolant accident. Until recently, no credit was permitted for iodine scrubbing by the suppression pool in calculating radiological consequences as required by 10 CFR Part 100. However, analyses of severe accident sequences [25], have shown that the suppression pool is effective in scrubbing some of the most important radionuclides, such as iodine, cesium, and tellurium which are largely released in the in-vessel phase. For the Peach Bottom plant, a BWR with a Mark I containment, decontamination factors (DF) ranging from 1.2 to 4,000 with a median value of 80 were calculated. Depending on the timing and location of containment failure, the suppression pool may also be effective in scrubbing core-concrete releases as well.

Current NRC guidance [26] has been revised to recognize this research and suppression pools may be credited with iodine retention in analyses by reactor licensees. Some limitations in the use and application of this credit should be noted, however. Although licensees may take credit for scrubbing of iodine fission products in the suppression pool to reduce the filter efficiency of safety-related filtration systems, they are not permitted to use the credit for
suppression pool scrubbing to eliminate a safety-related filtration system where it was previously required. Similarly, licensees may not use scrubbing by the suppression pool to increase the allowable primary containment leak rate.

What are the implications of the ORNL findings on iodine chemical form with regard to BWR suppression pools? Although decontamination factors for the suppression pool are large, a key question is whether iodine trapped in the pool will be re-evolved? Re-evolution of iodine was judged to be important in accident sequences in which the containment had failed and where the suppression pool was boiling. There is presently no requirement for pH control in BWR suppression pools. Hence, it is not clear whether suppression pools would scrub substantial amounts of iodine in the early phases of an accident, only to re-evolve it later as elemental iodine. It may well be that additional materials likely to be in the suppression pool as a result of a severe accident, such as cesium borate or cesium hydroxide and core-concrete decomposition products, would counteract any reduction in pH due to radiolysis and would assure that the pH level was sufficiently high to preclude re-evolution of elemental iodine. This question, unfortunately, has not been sufficiently studied to have a definitive answer. It is important to note that this is not a matter of concern for present plants since all BWR's are required to have safety-related filtration systems designed to cope with large quantities of elemental iodine. Hence, even if the suppression pool were to re-evolve significant amounts of elemental iodine, this would be retained by the existing downstream filtration system.

6. CONCLUSIONS

Iodine fission products and the chemical form of iodine released into containment have played a major role in U. S. regulatory criteria. Plant features required to mitigate accident releases, such as filtration systems and containment spray systems, have been optimized to cope with iodine, particularly iodine in elemental form. As a result of modern research insights we now recognize that our improved understanding of the chemical form of iodine within containment should be applied to provide better guidance to designers as well as information to operators which reflects these results. In addition, we must also recognize that consideration should be given to other significant fission products, in addition to iodine, which are released as a result of a severe accident. The NRC is proceeding on a program to incorporate these insights into its regulatory structure.

REFERENCES


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DISCUSSION

Sims

There is considerable uncertainty in effects of pH on recreation of radiolytic iodine production. Neither rates of reactions nor mechanisms are satisfactorily known. This is a problem for modellers and some laboratory data are misleading.

Soffer

We will be interested to review those data.
1.4 THE CANADIAN PROGRAMME ON IODINE CHEMISTRY IN REACTOR SAFETY

R.J. Fluke¹, G.M. Frescura¹, N.H. Sagert², K.N. Tennankore², and A.C. Vikes²

ABSTRACT

The Canadian program on iodine chemistry in reactor safety provides information needed to quantify and minimize iodine release to the environment following a postulated reactor accident. This comprehensive program consists of fundamental studies, bench-scale "separate-effects" experiments, and intermediate-scale "all-effects" integrated tests, to address the chemistry of iodine in the containment system, in-core studies, to address the high-temperature chemistry of fission products in UO₂ fuel, and iodine abatement studies. Large-scale test data are obtained by participation in international projects such as ACE and PHEBUS-PP. The main focus of the program is the development and validation of the LIRIC model and database, used to predict iodine behaviour in various postulated accidents. The rationale for the program, its main elements, and recent progress are reviewed in this document.

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1. INTRODUCTION

The Canadian program on iodine chemistry in reactor safety provides information needed to quantify and minimize iodine release to the environment following a reactor accident. It includes comprehensive studies of the chemistry of iodine (and other related fission products) in the reactor cooling system and in the containment building of CANDU(*) reactors under accident conditions. These studies form part of the reactor safety program in Canada, which addresses various safety issues including hydrogen combustion, aerosol transport, high-temperature fuel and fuel-channel behavior, and the thermalhydraulic behaviour of the CANDU multi-channel reactor cooling system. These programs are funded by AECL Research and Canadian electric utilities (Hydro Quebec, New Brunswick Power, and Ontario Hydro) through the CANDU Owners Group (COG). The work is conducted by AECL Research at the Whiteshell and Chalk River laboratories, and through contractors such as the University of Toronto. Also, some of the information needs are met by liaison, information exchange and participation in international projects, such as ACE and PHEBUS-PP.

This document summarizes the rationale and scope of the Canadian program on iodine chemistry in reactor safety. It describes the main elements of the program and gives highlights of recent progress.

2. BACKGROUND OF THE CANADIAN PROGRAM

2.1 Rationale and Scope

The Canadian program on iodine chemistry in reactor safety has evolved from our reactor licensing requirements, reactor and containment design features, and public safety concerns. To license a reactor in Canada, the electric utility has the responsibility to provide a submission to the regulatory authority, the Atomic Energy Control Board (AECB). This submission includes an accident analysis in which iodine release calculations are performed using a conservative model. The AECB does not specify a detailed methodology, it is the utility's responsibility to justify the use of any such models by providing the necessary data to support the adequacy of the models.

The iodine model must also take into account the unique design features of both single-unit and multi-unit CANDU reactors and their containment systems. For example, fuel ejection from a failed channel, while the reactor is at full power, is considered a design-basis accident in Canada. Although a single-unit CANDU reactor uses a containment building not unlike that of a pressurized-water reactor (PWR), a multi-unit CANDU containment features a large vacuum building that quickly suppresses the loss-of-coolant-accident (LOCA) blowdown pressure, providing several days of subatmospheric holdup. In the longer term, after the vacuum reserve is depleted, emergency filters provide a well-controlled and monitored release path. More generic accident conditions, which generally apply to boiling-water reactors (BWRs) and PWRs, are also relevant to the CANDU reactor.

(*) CANada Deuterium Uranium, Registered Trademark of AECL
These conditions include a large containment building with a pool of water ranging from high to low pH, various types of paint, organic materials, and high radiation fields. Thus, conditions can vary over a wide range and must be accounted for in the model and database.

Recently, more realistic estimates of iodine release have been needed, both to provide assurance of public safety and for emergency preparedness considerations. To encompass these issues, the Canadian program has included an evaluation of accident management strategies such as venting of the containment through a filtered pathway which includes charcoal filters for the removal of volatile iodine species.

In summary, because of licensing requirements, the unique and generic design features of CANDU, and public safety concerns, the Canadian program on iodine chemistry in reactor safety is developing a realistic model of iodine behaviour that accounts for the long-term behaviour of iodine, its transport in containment, and the effectiveness of emergency filter systems and other abatement strategies. Data from this and other programs around the world are used to develop and validate the iodine behaviour model used by electric utilities for accident analysis and licensing.

2.2 Developing the Canadian Program

Early licensing calculations of iodine release were based on conservative estimates of its volatility, using empirical information from sources such as the 1958 accident at Windscale. Since it was necessary, for water reactors, to model interactions of volatile species with containment surfaces and the water pool, the program began by examining the chemistry of I₂, CH₃I and other organic iodides, and less well characterized species such as HOI.

The TMI-2 reactor accident [1], along with a large body of experimental and theoretical results, indicated that previous licensing assumptions were too conservative and that potential radiiodine releases in water-cooled power reactors were far less than previously assumed, because of the inherent chemical behaviour of iodine. However, the uncertainties raised as a result of the TMI-2 accident, led to the need for well-documented and realistic estimates of iodine release. Without a fundamental understanding of iodine behaviour, it could not be shown that the low iodine release observed at TMI-2 was typical for a wide range of conditions. Thus, the Canadian program expanded to investigate in-core high-temperature iodine behaviour under CANDU fuel-channel conditions, to confirm that iodine would be released in the form of CsI, which would dissolve on contact with water to form the relatively unreactive and involatile aqueous iodide. The program also placed new emphasis on aqueous iodine chemistry to determine the range of stability of aqueous iodide.

By the mid-1980s, our fundamental studies had produced an improved database of the thermal chemistry of iodine, which was used to determine chemical forms and concentrations of gaseous and aqueous iodine species in the reactor cooling system and the containment building [2-6]. These studies provided further underlying support for the claim that our licensing assumptions were indeed conservative. However, uncertainties remained about the effects of surfaces and organic materials under the influence of radiation. Also, the fundamental approach, although necessary, was not seen as providing an early solution to the need for more realistic models. Thus, a new approach was initiated in Canada with the construction of the Radiiodine Test Facility (RTF) [7]. This new strategy includes integral "all-effects" testing in the RTF, a bench-scale program and, of course,
continuation of our fundamental program. The main focus is the development and validation of the LIRIC (Library of Iodine Reactions in Containment) model and database [8,9].

As discussed in Section 4, RTF tests to date have confirmed and/or added to our understanding of iodine behaviour under accident conditions. However, such tests have also shown phenomena unexplained by the current model, a finding consistent with one of the objectives set for the RTF, which was to identify any phenomena that may not be revealed in a solely fundamental approach. Because of the RTF findings, a rationalization plan was recently implemented, which places more emphasis on the following: (a) accelerating the development of LIRIC to account for the results of the RTF tests; (b) more bench-scale studies to examine the reasons for the phenomena observed in the RTF; and (c) a review and evaluation of our thermodynamic and kinetic data on iodine.

In the following sections, the main elements of the Canadian program on iodine chemistry in reactor safety are summarized and some of the key findings are presented.

3. LIRIC MODEL AND DATABASE

A key element of the Canadian program is the development and validation of the LIRIC model and database to predict iodine behaviour for various accident scenarios. More detailed information on LIRIC has been published earlier [9] and an update is presented in a companion paper. In summary, LIRIC includes about 150 thermal and radiolytic chemical reactions in the aqueous phase. Specifically, LIRIC includes thermal reactions of the various iodine chemical forms, reactions dealing with the radiolysis of water, and reactions of the iodine species with the products of water radiolysis. In addition to the chemical reactions, LIRIC includes data for modelling the mass transfer of iodine species between air and water, and their deposition to and desorption from painted surfaces in contact with either the aqueous or the gaseous phase. Also, the model includes the mass transfer of other gases such as $\text{H}_2$, $\text{O}_2$, and $\text{CO}_2$ between the aqueous and gaseous phases, which is shown to be very important to the overall chemistry of iodine.

To simulate various reactor accidents using the LIRIC model and database, we developed the MITIMAKS (Modelling of Interfacial Transfer Interactions in Mass Action Kinetic Simulation) code, a modification of the MAKSIM code, used to model chemical reaction kinetics [10], to allow for mass transfer. The LIRIC model has also been implemented using the AEA Technologies package FACSIMILE/CHERMAT [11] and this is currently the preferred approach. An example of a LIRIC calculation is shown in Figure 1, where the concentrations of the various iodine species in the aqueous and gas phases, and the partition coefficients, are given as a function of time. The initial conditions for this calculation are similar to those for a typical RTF test: dose rate 0.26 Gy/s, pH 9.0, iodide concentration 10 mmol dm$^{-3}$, and organic impurity 1.0 mmol dm$^{-3}$.

In recent tests with the RTF, we observed a high volatilization of aqueous iodide when organic materials with a high radiation field were present (see Section 4). To account for these observations, a preliminary submodel was added to LIRIC to account for the radiolytic production of organic iodides and the radiolytic decomposition of organic materials to form organic acids and $\text{CO}_2$, which in turn increase the acidity and, consequently, the formation of iodine and organic iodides.
In future versions of LIRIC, we expect to add thermal and radiolytic reactions in the gas phase, temperature effects and surface reactions, such as reactions of iodine with the various paints used on concrete and steel surfaces.

4. RADIOIODINE TEST FACILITY

To further develop and validate the LIRIC model, we constructed the RTF, shown in Figure 2 [9]. The RTF is being used to conduct a series of intermediate-scale integrated tests on iodine behaviour under a variety of reactor accident conditions. These tests are designed to examine the effect of different containment surfaces, radiation, temperature, water chemistry, and impurities on iodine volatility. Potential accident management techniques are also being examined. Average gamma-radiation fields up to about 2 kGy·h⁻¹ are provided by a 315-TBq cobalt-60 source. On-line instrumentation allows direct monitoring of a number of key variables, such as total iodine concentrations in the liquid and gas phases, pH, temperature, and redox potential. Analytical facilities, such as HPLC, gas chromatography, species-selective sorbents and extraction techniques (coupled with radiocounting), enable us to obtain detailed information on chemical forms of iodine during the course of the test.

Phase I of the RTF program has been completed [12]. Phase I was a series of tests, with and without radiation, in which the starting form of iodine was aqueous CsI and the vessel was carbon steel coated with zinc primer paint. All Phase I tests demonstrated that carbon steel surfaces coated with zinc primer paints were an important sink for iodine. Generally, between 45 and 66 percent of the total iodine inventory introduced into the main vessel was found to adsorb onto surfaces. In all cases, the iodine was strongly adsorbed and not readily removed when washed repeatedly with distilled water or solutions of hydrazine. Adsorbed iodine was highest (2 to 5 μg·cm⁻²) on aqueous wetted surfaces and the degree of adsorption did not appear to depend on the presence of radiation. However, we found that radiation from the 315-TBq cobalt-60 source resulted in an increase, by more than two orders of magnitude, the amount of iodine deposited on surfaces exposed to the gas phase. (Adsorption on surfaces exposed to either the aqueous or the gas phase was not important in a reference test conducted using a stainless steel vessel.)

Another important feature observed in the Phase I program was the predominance of organic iodides. Depending on the experimental conditions, organic iodides amounted to between 70 and 95 percent of the total airborne iodine concentration. In tests conducted using the cobalt-60 source, the controlled addition of an organic impurity such as methyl ethyl ketone (MEK), a common paint solvent, resulted in an increase of the total airborne iodine concentration by more than an order of magnitude over a period of several hours. Sudden reductions in pH and dissolved oxygen concentration, presumably due to oxidation of MEK to the corresponding acids, were also observed. As expected, without radiation, the addition of MEK had no significant impact on iodine volatility or the partition coefficient for various conditions examined in one of the Phase I tests. Overall, without MEK, the partition coefficient was in the range 10⁵ to 10⁶. The addition of about 1 mmol·L⁻¹ MEK resulted in a reduction of the partition coefficient to 10⁴ at steady state.

Tests to assess the effectiveness of either adding hydrazine or increasing the pH to reduce the gas-phase iodine concentration showed no effect. Under the conditions of the experiment, most gas-phase iodine was
in the form of organic iodides, on which neither alkali nor hydrazine has a significant effect. Furthermore, hydrazine decomposed rapidly in the presence of radiation.

We have recently completed Phase II and initiated Phase III and IV of the RTF experimental program. Phase II consisted of two tests, each conducted over a four-week period, using a 10-μmol.dm⁻³ CsI solution in a zinc-primed, vinyl-coated carbon steel vessel. Studies were done with and without radiation. Each test consisted of several stages to study the effect of various chemical and physical conditions on iodine volatility. The first test, conducted with radiation, exhibited unusually high concentrations of iodine in the gas phase and a sharp decrease in pH. This was not observed in the absence of radiation. In the radiation test, the addition of MEK increased iodine volatility slightly but the addition of hydrazine had little or no effect. The vinyl surface had a strong affinity for iodine and 90 percent of the available iodine was absorbed by the surfaces, mostly at surfaces exposed to the gas phase.

Phase III - Test 1 studied iodine partitioning in a polyurethane-coated carbon steel vessel, without radiation. Phase IV - Test 1 was also conducted without radiation, using a zinc-primed, epoxy-coated carbon steel vessel. In both cases, the iodine partition coefficients were very high (10⁵ to 10⁶).

In summary, the RTF tests to date have shown a number of interesting phenomena that have confirmed and added to our understanding of iodine behaviour under accident conditions. For example, in the presence of organic impurities such as MEK, radiation produces organic iodides, which are generally more volatile than inorganic forms of iodine. However, radiation may also play an important role in iodine volatility by actually enhancing the removal of iodine from the gas phase under certain conditions. Also, the addition of modest amounts of base does not always lower iodine volatility when the dominant form of iodine is organic iodides. Finally, this series of tests showed that surfaces painted with a zinc primer can act as a significant sink for iodine, thereby serving as a passive system for mitigating iodine volatility.

5. BENCH-SCALE STUDIES

The main objective of the bench-scale program is to rationalize the results of integral tests and identify issues requiring resolution at the fundamental level. This is achieved by conducting scoping experiments to screen information on separate phenomena and potential mechanisms. Two areas of current study involve containment surface materials, such as paints, and various organic materials known to affect iodine behaviour under high radiation fields. For example, early tests conducted in the RTF with an inorganic zinc-primer-coated vessel demonstrated that painted surfaces could play a passive safety role by providing a large sink to retain iodine. This phenomenon was examined in bench-scale tests, where it was found that the zinc primer surface reduces I₂ to iodide. However, this iodide can be incorporated into the primer surface only if that surface undergoes oxidation. Bench-scale tests have also demonstrated that organic materials react with iodine to form organic iodides, and that the radiolytic decomposition of organic materials can reduce the pH of the solution, through the formation of acidic compounds such as carboxylic acids and, possibly, CO₂. The drop in pH favours more I₂ production. However, tests have also shown that this increase in volatility can be reduced, even in the presence of radiation and organic materials, if a high
pH is maintained.

6. FUNDAMENTAL STUDIES

The key objective in our program of fundamental studies on iodine chemistry is to establish the mechanisms and associated parameters required to model the behaviour of iodine in the containment system of a CANDU reactor under accident conditions. Present work includes studies to determine the rate constant of the reaction of OH radicals (generated by the radiolysis of water) with aqueous I₂. This work is aimed at resolving literature [13,14]. Studies of the radiation chemistry of moist air-iodine systems are also being conducted to assess the extent of radiation-induced oxidation of airborne iodine [15]. The latter studies are intended to assess the role of radiation in suppressing volatile iodine forms via conversion to iodine oxides that are soluble in water. A third project, about to begin, will measure the rate of reduction of methyl radicals in iodide solutions. In the presence of radiation, this reaction appears to convert aqueous iodide to volatile organic iodide (CH₃I) [16].

7. IN-CORE HIGH-TEMPERATURE CHEMISTRY

To predict the chemical forms of iodine that could be released into the containment building, it is important to understand the high-temperature chemistry of iodine and relevant fission products in the fuel and the reactor coolant system under postulated reactor accident conditions. In past studies, we have used chemical equilibrium methods to calculate the chemical speciation of iodine and cesium for various Cs/I/O/H mixtures as a function of temperature [3]. To understand and account for the behaviour of iodine-132, which is a daughter of tellurium-132, we have recently extended our calculations to Te [12,17]. The release of tellurium from fuel depends on cladding oxidation, since tellurium is retained by the cladding until the zirconium is oxidized. We are using chemical equilibrium calculations to model this release and to determine the volatility of tellurium under reactor accident conditions. We have compiled a thermodynamic database for the tellurium-zircaloy system. An important parameter in the Te-Zr-Sn database is the activity coefficient of tin in zirconium. Since this activity coefficient is low, tin metal in the presence of zirconium is thermodynamically unstable with respect to the formation of an alloy. The activity coefficient of tellurium in zirconium is not available but we have estimated values for the thermodynamic data of some Zr-Te compounds.

On the experimental front, we are using a Knudsen cell/mass spectrometer system to obtain thermodynamic data (enthalpies and Gibbs energies) for cesium telluride (Cs₂Te) and cesium tellurite (Cs₂TeO₃) at high temperatures [18]. We have recently equipped this system with a radiofrequency-heated Knudsen cell, which enables us to achieve temperatures up to 3100 K. Work now in progress is examining the Cs/CsI/UO₂ system to assess the effect of cesium uranate formation on cesium and iodine volatility. A study of the vaporization of a mixture of one percent CsI in UO₂ was initiated. The enthalpy of vaporization of CsI from this mixture was 470 kJ mol⁻¹, much higher than that obtained from mixtures of CsI with cesium uranate. Experiments to measure the vaporization of a mixture of one percent RbI in UO₂ were also done for comparison.
8. IODINE ABATEMENT

CANDU multi-unit containment systems feature an Emergency Filtered Air Discharge System, for long-term control of radionuclide releases following an accident. Deep-bed filters containing TEDA-impregnated activated charcoal, used to remove iodine from the discharge, would accumulate a large inventory of iodine that would have to be retained by the charcoal beds for several weeks. Since the performance of the charcoal beds affects iodine release, calculations must adequately represent this performance, which includes not only a removal efficiency, but also the subsequent migration of iodine through and desorption from the charcoal beds.

In the first phase of this program, experiments were conducted to characterise the long-term post-LOCA performance of charcoal filters. Both KI and TEDA-impregnated commercial charcoal was evaluated, since both types were used at Ontario Hydro nuclear generating stations; presently, only TEDA-impregnated charcoal is used. The removal efficiency and retention of I\textsubscript{2} and CH\textsubscript{3}I were measured as a function of bed depth, temperature, relative humidity, radiation, aging and the presence of potential "poisons", including NO\textsubscript{x}, SO\textsubscript{2}, H\textsubscript{2}, NH\textsubscript{3}, and MEK. A second phase is under way to develop a model for the time-dependent migration and release of iodine species through a charcoal filter.

In addition, we have explored the technical and economic feasibility of a conceptual photochemical system for removing organic and inorganic radioiodines during venting of the reactor containment following an accident. The system under consideration uses ultraviolet light to convert organic iodides to molecular iodine and ozone, which reacts with iodine to form solid iodine oxyacids that can be removed from air by aqueous scrubbers or particulate filtration techniques [19]. Alternatively, the fixation of iodine by reaction with ozone can be eliminated and, once the organic iodides are converted to molecular iodine, the latter can be removed easily, even by substantially degraded charcoal filters. The proposed system would increase the efficiency and long-term reliability of charcoal filters used in emergency applications and, where venting systems are not equipped with iodine scrubbers, would provide an effective means of radioactive iodine removal.

9. ACKNOWLEDGEMENT

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10. REFERENCES


FIGURE 1: An RTF Run with a Dose Rate of 0.26 Gy·s⁻¹, an Initial pH of 9.0, an Initial Iodide Concentration of 10 μmol·L⁻¹ and the Organic Impurity of 1.0 μmol·L⁻¹. Figure 1(a) shows some of the species present in the aqueous phase [I₂ (-----), HOI (----), RI (---), I₂O₃ (---)] and I₂ at the wall/aqueous interface (-o-o-). Figure 1(b) shows some species in the gas phase [I₂G (---), HOI (-----), Light Organic Iodides (---), Heavy Organic Iodides (---)] and I₂ at the wall/gas interface (-o-o-).
FIGURE 2: Diagram of the Radioiodine Test Facility.
FIGURE 3: Measured Partition Coefficient as a Function of Time for the RTF Run Modelled in Figure 1.

DISCUSSION

Sims (Comment)
The RTF data show an important area of work which has so far not have sufficient attention and that is the effect of mass transfer between phases in chemical systems. It is the competition between volatilization and homogeneous reaction which determines release fraction.
1.5 ACTIVITIES OF THE COMMISSION OF THE EUROPEAN COMMUNITIES IN THE AREA OF IODINE CHEMISTRY IN SEVERE REACTOR ACCIDENTS

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September 4, 1991

Abstract

The principal activities of the Commission of the European Communities (CEC) in the area of iodine chemistry in severe nuclear reactor accidents are reviewed. These are mainly carried out in conjunction with partner organisations as part of a programme of Shared Cost Actions. Fundamental thermochemical data have been measured and assessed for a number of compounds or systems of importance in predicting the behaviour of fission products in the primary circuit. The Falcon programme of integral and separate-effects experiments has examined the transport and deposition of fission products under reasonably representative accident conditions, with particular emphasis on containment iodine chemistry. The most important activity is through involvement with the Phebus-FP programme of in-pile integral tests, which will involve detailed examination of the fuel bundle, primary circuit, and containment phenomena. These experiments will be modelled using various computer codes. The development of an integrated European severe accident code package (ESTER) is also supported.

1 Introduction

The behaviour of iodine in a severe nuclear reactor accident is probably one of the most important factors which can affect the magnitude and radiobiological impact of the source term to the environment. Iodine can form highly volatile species under accident conditions, which could result in a large release to the environment. Given that it is also

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relatively easily metabolised, a release of iodine could result in a significant risk to the public.

The Commission of the European Communities (CEC) is involved in a number of programmes which examine the transport and deposition of fission products in the unlikely event of a severe accident in a light-water reactor (LWR). These studies are concerned with core degradation, primary circuit, and containment phenomena, all of which involve examination of some aspects of the behaviour of iodine. These programmes are carried out either directly by the CEC at JRC-Ispra or in collaboration with other organisations through a series of Shared-Cost Actions (SCAs).

The programmes can be divided into four principal areas of investigation:

1. **Fundamental data measurement and assessment.** This currently involves the measurement and assessment of thermochemical data to be used in primary circuit modelling codes, but later studies may include some examinations of high-temperature reaction kinetics.

2. **Small- and intermediate-scale experiments.** These are concerned with both separate-effects studies and integral experiments (Falcon) which are used to examine the behaviour of fission products under representative accident conditions.

3. **Large-scale experiments.** This is almost entirely concerned with the Phebus-FP programme of integral experiments [to be conducted jointly with the Commissariat à l’Energie Atomique (CEA)].

4. **Code development and validation.** Many codes are used to model different accident phenomena, including those associated with equilibrium chemistry and material transport in the primary circuit (e.g., VICTORIA, RAFT), and the dynamics of iodine species in the containment (e.g., INSPECT, IODE, and IMPAIR-2). Data from the experimental programmes are used to test, develop, and validate them. The development of an integrated code package (ESTER) is also planned.

The aim of this paper is to highlight the areas most closely associated with the behaviour of iodine in a severe accident.

2 **Fundamental Data Measurement and Assessment**

Primary circuit modelling codes, such as VICTORIA[1], require a comprehensive and accurate thermochemical data base to enable both high-temperature (upper plenum, hot-leg) and low-temperature (steam generator, cold-leg) vapour-aerosol and vapour-vapour chemical reactions to be modelled. These codes use a Gibbs free energy minimisation routine to determine the thermodynamically favourable reactions and thus calculate vapour and aerosol compositions. The VICTORIA data base currently contains thermochemical data for 25 elements and for 167 condensed- and vapour-phase species.

In January 1990, a meeting of specialists[2] was held under the auspices of JRC-Ispra and in collaboration with Winfrith Technology Centre to define additional systems that may be important in primary circuit chemistry and the requirements for thermochemical data measurements and assessments. These requirements have provided the bases for
two phases of SCAs with ECN-Petten (phases 1 and 2), AEA Technology (phases 1 and 2) and the Free University of Brussels (phase 2), of which the second phase is currently underway[3]. This programme involves close collaboration between the three laboratories so that thermochemical data for the 41 systems defined by the specialists meeting could be measured and assessed.

The following iodine-containing systems were examined as part of phase 1 of the SCA:

\[
\text{In-I : InI(c), InI(g), InI}_2\text{(c), InI}_3\text{(c), InI}_3\text{(g), In}_2\text{I}_6\text{(g)},
\]

\[
\text{Cd-I : CdI(g), CdI}_2\text{(c), CdI}_2\text{(g), CdI}_4\text{(g), Cs}_2\text{CdI}_4\text{(c), Cs}_2\text{CdI}_4\text{(g), CsCdI}_3\text{(g)}.}
\]

Whilst it is not proposed to discuss the results obtained for all of these systems, the CsI-CdI\(_2\) system is particularly interesting, because this system has been neglected in severe accident studies.

There is evidence[4] which suggests that caesium iodide will react with either cadmium or cadmium iodide at elevated temperatures to form ternary compounds such as CsCdI\(_3\) or Cs\(_2\)CdI\(_4\),

\[
\text{CsI(g) + CdI}_2\text{(g) }\rightarrow\text{ CsCdI}_3\text{(g)},
\]

\[
2 \text{ CsI(g) + CdI}_2\text{(g) }\rightarrow\text{ Cs}_2\text{CdI}_4\text{(g)}.}
\]

The study was conducted in two phases. The first examined the condensed phase behaviour of Cs\(_2\)CdI\(_4\) and involved the construction of a phase diagram for the behaviour of the CsI-CdI\(_2\) system (Figure 1). The second involved a preliminary mass spectrometry study of the CsI-CdI\(_2\) system at high temperatures. A quantitative study of the variation of relative ion intensities with temperature was made. For the following two equilibria

\[
\text{CsI(g) + CdI}_2\text{(g) }\leftrightarrow\text{ CsCdI}_3\text{(g)},
\]

\[
\text{CsI(g) + CsCdI}_3\text{(g) }\leftrightarrow\text{ CsCdI}_4\text{(g)},}
\]

the relative ion intensities were taken to be directly proportional to the partial pressures. Therefore, it was possible to calculate the enthalpy change [\(\Delta H(T)\)] for each reaction using the Van't Hoff equation. These were found to be \(-40.0 \pm 4.2\) and \(-32.0 \pm 3.3 \text{ kJ/mole}\), respectively, over the temperature range from 600 to 1000 K.

3 Small- and Intermediate-Scale Experiments

The main activity of the CEC in the area of small- and intermediate-scale experiments has been conducted through two SCAs with Winfrith Technology Centre in the area of multi-component aerosol behaviour. These programmes have involved both integral tests conducted in the Falcon facility and separate-effects studies. The first phase of the programme[4] involved integral tests with simulant and trace-irradiated fuels which were primarily of a phenomenological nature, and separate-effects experiments to investigate interactions of cadmium aerosols with I\(_2\), CsI, and Te vapours. The second phase[5] involved integral tests conducted under conditions more representative of those predicted for a severe accident, separate-effects studies to examine boric acid and control-rod aerosol
behaviour, code analysis of the integral tests, and instrumentation assessment. Many of these activities are of direct relevance to the forthcoming Phebus-FP tests (cf. Section 4).

The main features of the Falcon facility are shown in Figure 2. In the second phase, the complexity of the tests increased with the progression of the test matrix (Table 1) with the addition of control rod alloy and boric acid to the primary circuit and the inclusion of paint and an aqueous sump in the containment. The additions to the containment were specifically aimed at studying two important phenomena, namely the formation of organic iodides on painted surfaces and the retention of iodine by an aqueous sump. One wall of the containment vessel was coated with the same paint as that used in the Sizewell B pressurised water reactor under construction in the UK. The sump was buffered either to an initial pH of 5 or 8. A variety of on-line and post-test analysis techniques were used in the studies, including gamma-ray spectroscopy (on-line and post-test), iodine speciation filters (Mepacks), and inductively coupled plasma mass spectrometry (ICPMS). The results highlighted several important phenomena:

1. Retention of iodine on the painted wall was significantly enhanced compared with unpainted surfaces (typically by a factor of 10).

2. The principal component of the gasborne iodine was initially aerosol but after 48 hours more than 50 % was vapour-phase iodine (CH\textsubscript{3}I and I\textsubscript{2}).

3. There was considerable retention of iodine in the aqueous sump with the highest concentrations observed at pH 8.

The above results were specifically concerned with iodine behaviour, but clearly other iodine-related effects such as the influence of boric acid were also observed during the programme.

4 Large-Scale Experiments

Probably the Commission's most important activity in the area of severe accident research is its involvement in the Phebus-FP programme[6, 7] conducted in conjunction with the CEA. The experimental programme will comprise six tests (FPT-0 to -5) in which fresh (FPT-0) or high burn-up (FPT-1 to -5) fuel will be irradiated in situ for between 9 to 14 days under normal PWR conditions and then heated, in the same position up to UO\textsubscript{2} melting. Each test will be designed to simulate a specific beyond-design-basis-accident sequence in an LWR (e.g., TMLB, V). Fission products will be released from the core region through a system representing the reactor coolant system and steam generator to the containment vessel (Figure 3). The release and transport of material will be monitored and characterised using a number of on-line and post-test analysis techniques such as gamma-ray spectroscopy, mass spectrometry, impactors, sequential coupons, and iodine speciation samplers. The results will provide data with which to test and develop severe accident codes (cf. Section 5) as well as giving an important insight into accident phenomena.

The study of containment iodine behaviour is an important objective of the Phebus-FP programme. The experimental sequence, therefore, includes a fission-product release phase of one to two hours and then a containment test phase for aerosol depletion and
iodine chemistry measurements during two to four days. Four main criteria will be used to analyse variations in iodine behaviour:

1. the degree of radiolysis,
2. sump pH,
3. organic paints,
4. temperature.

The degree of radiolysis will play a key role in determining the iodine chemistry in the containment. Small-scale experiments such as Falcon have so far not been able to address this process, and although the ACE/RTF tests have provided useful data, they cannot be considered to be integral in nature. It is currently proposed to conduct the Phebus-FP tests with low-, or medium-iodine concentrations although the exact dose rates have not yet been determined.

The pH of the aqueous sump will also be varied according to the test so that a range of accident conditions will be covered. It has been postulated that there will be greater retention of iodine in an alkaline sump and this effect will be investigated further.

Surfaces coated with organic paints typical of those used in operational reactors will be incorporated into the tests. This will involve coating surfaces which will remain dry during the tests, those which will condense water, and those which will remain partially immersed in the sump (probably in the form of coupons). Each test will be conducted with a single type of paint to prevent problems arising from the assignment of specific phenomena to individual paints. The tests should enable the role of paints in containment iodine chemistry to be assessed better, particularly with respect to retention and the formation of volatile organic iodides.

These studies of iodine chemistry in the containment will require instrumentation[8] which is dedicated to measuring iodine in the gas phase and in solution both on-line and post-test. The gas-phase behaviour will be monitored using modified Maypack iodine speciation samplers. These will comprise sections which will separate the aerosol, organic, and inorganic fractions which can then be counted. It is currently envisaged that this will be analysed post-test but the feasibility of on-line measurements, made in conjunction with gamma-ray spectroscopy, are also being assessed. The iodide concentration in the sump will be measured using an ion specific electrode and this technique may be extended to include other species. Other techniques which are not specific to iodine such as on-line and post-test gamma-ray spectroscopy, and post-test analyses of sequential conforms, will also provide useful information on iodine behaviour.

5 Code Development and Validation

A large number of severe accident codes are available for use within the framework of the activities of the CEC. Data from the experimental programmes described in the preceding sections will be used in their development and validation. Not all the codes emphasize iodine chemistry, even though iodine compounds play a significant role. The codes are divided into two groups: those that consider equilibrium chemistry, thereby
determining the equilibrium concentration of iodine compounds in the presence of other species by minimising the Gibbs free energy, and those that calculate the dynamics and time-evolution of iodine species in the primary circuit and the containment.

5.1 Equilibrium Chemistry

The Commission is involved in the development and validation of a number of computer codes that calculate equilibrium speciation of fission products and their chemical interaction with aerosols and structure surfaces. It is expected that they will be primarily applicable to modelling the speciation and transport of fission products and aerosols in the primary circuit, where thermal hydraulics conditions ensure the validity of the chemical equilibrium assumption.

The main emphasis is in the development of aspects of VICTORIA[1], via an SCA with AEA Winfrith Technology Centre, and in its application for the description of fission-product behaviour in the primary circuit for the Phebus experiments. VICTORIA is a mechanistic code that calculates chemical interactions between fission products, aerosols, carrier gases, and structures. It follows fission product release from the fuel, and the transport of the ensuing equilibrium species through the primary circuit to the containment. Currently, it is used to calculate species deposition on the primary circuit and eventual fission product release into the containment for FPT-0.

VICTORIA determines the compounds present in a given nodalisation cell via a constrained Gibbs free energy minimisation. The Gibbs free energy for each species is approximated by a cubic polynomial over a large temperature range (400 K to 2500 K). The coefficients are stored in a data base, which is under expansion and assessment (cf. Section 2). Even though most of the chemical considerations are based on the well-mixed, equilibrium assumption, an effort is being made to incorporate kinetics effects, especially in the interaction of vapours with structures. Iodine is not treated differently from other species: the data base contains 14 gaseous iodine compounds (CsI, BaI, BaI\(_2\), I, I\(_2\), HI, SrI, SrI\(_2\), SnI\(_2\), FeI\(_2\), FeI\(_4\), BI, BI\(_2\), BI\(_3\)) and 5 condensed-phase species (CsI, BaI\(_2\), SrI\(_2\), SnI\(_2\), FeI\(_2\)).

Control-rod iodine compounds are not included in the data base, although experiments[4] suggest that their interaction with iodine considerably alters iodine deposition and transport. Specifically, Falcon experiments[4] suggest that boric acid interacts with CsI to form highly volatile HI and relatively involatile CsBO\(_2\), by

\[
\text{CsI}(g) + \text{HBO}_2 \rightarrow \text{CsBO}_2(c) + \text{HI}(g).
\]

Similarly, the following reaction is believed to modify Cs deposition,

\[
\text{CsOH}(g) + \text{HBO}_2 \rightarrow \text{CsBO}_2 + \text{H}_2\text{O}(g),
\]

since CsOH is much more volatile than CsBO\(_2\).

Thermodynamic measurements have been made for some control-rod iodine compounds (cf. Section 2), but they have not been included in the data base. Furthermore, some kinetics effects are also being studied; a model for the kinetics of CsOH interaction with stainless steel surfaces has been developed, but it has not yet been implemented.
VICTORIA has been used to model a number of Falcon experiments and to distinguish the nature of iodine compounds deposited onto structures. These experiments will be used in validating the various theoretical models included in the code.

Another code in use at JRC-Ispra is RAFT[9], which is similar to VICTORIA, in that it calculates equilibrium speciation via a free energy minimization, and then considers transport through the primary circuit. However, the nucleation models in the two codes differ. The data base for RAFT is smaller, it includes 67 species, out of which four are gaseous iodine species (CsI, I, I₂, and HI) and one condensed (CsI). RAFT is also used in the calculation of aerosol and vapour interaction, and deposition in the primary circuit of Phebus for FPT-0.

An SCA has been initiated[10] for the use of SOLGASMIX[11], a code that determines equilibrium concentrations via a different numerical scheme. It has been used to identify the chemical species that originate in the core region, after release from the fuel, and to determine the most representative species that can be used as input for transport codes. Its data base considers 13 elements, 90 chemical species with 10 gaseous iodine species and 3 condensed-phase. Detailed presentations of iodine speciation under a variety of thermal hydraulic conditions of severe accidents have been given.

The codes described in this section are not specific to iodine but they determine equilibrium concentrations in systems where many competing reactions co-exist. Hence, they provide useful insight in the nature of iodine species that are thermodynamically favourable in a highly reactive environment. It is expected that they give a reasonable approximation to speciation in regions of the primary circuit where the temperatures are high and the effluent gas velocities moderate.

5.2 Chemical Kinetics

5.2.1 Primary Circuit Modelling

Chemical-kinetics effects become important at low temperatures and for small concentrations. Specifically, they are important when the residence time of the reactive species in a volume is less than the equilibration time. Moreover, they are important in interactions of fission products with aerosols and surfaces. A number of SCAs concentrate on the development and validation of kinetics models, with emphasis on the behaviour of iodine species.

A group at the Universidad Politecnica de Madrid (UPM) has been developing a model[12] for the dynamics of compounds containing four elements—O, H, I, and Cs—under various conditions of temperature and mass-flow rates. Eighteen iodine gas-phase reactions and one condensed-phase (gas-surface) reaction are included in the model. Reaction rates are calculated by the Activated Complex theory. The two ensuing unspecified parameters, the activation energy and the frequency prefactor, are either determined experimentally or theoretically estimated. The resulting differential equations are solved by the computer code FACSIMILE[13].

The kinetics model was used to study the kinetics of iodine and caesium in the primary circuit under conditions specified for FPT-0. They conclude that, depending on the duration of the simulation, for high concentrations CsI attains its equilibrium value, whereas CsOH and HI do not. Conversely, for low concentrations, CsOH attains its equilibrium
value, whereas CsI and HI do not. Equilibrium concentrations compare favourably with those predicted by SOLGASMIX.

A similar calculation was performed by IKE, Universität Stuttgart[14]. Some discrepancies were noticed, but they are attributable to the different chemical reactions considered and, more importantly, to the absence of the irreversible surface reaction in the IKE simulation.

The UPM contract has been extended to couple the kinetics of tellurium to that of caesium and iodine, and to validate the models using experimental results from a series of experiments: MARVIKEN, LACE, ACE, Falcon. Moreover, their study will contain a detailed presentation of nucleation models.

5.2.2 Containment Modelling

At the JRC-Ispra two codes that describe the kinetics of iodine species in the containment are being investigated and used: IMPAIR-2[15] and IODE[16].

IMPAIR-2 models the chemical behaviour of different iodine compounds in a volume with gaseous and aqueous phases as a function of time. The code serves principally in the investigation of iodine in a containment sump and the accompanying atmosphere during a severe-reactor accident. Twenty chemical reactions are considered, including chemical reactions of fission-product iodine in aqueous solutions and at liquid-gas interfaces. The modelling of inorganic reactions is considered to be adequate, whereas that of organic reactions needs to be improved. IMPAIR-2 models the reactions of water-radiolysis products with inorganic iodine species, heterogeneous organic reactions on "dry" surfaces, inorganic reactions in the gas phase (which are important, but have not been validated). Eventually it will also consider interactions between gaseous iodine species and aerosols. Furthermore, it models multi-compartment containment, necessary for the study of stratification.

IODE, which forms part of the system of severe accident codes ESCADRE, provides a chemical kinetics model for the behaviour of iodine in the containment. At the moment it considers 22 chemical reactions.

The development of models to follow vapour-aerosol interactions and iodine chemistry includes a contract with AEA Harwell Laboratory to modify and develop INSPECT. INSPECT is a mechanistic code specific to iodine chemistry that models the dynamics of iodine species. Since it does not rely on empirical correlations, it is flexible and applicable over a wide range of conditions. It considers 29 chemical reactions, but incorporation of new chemical reactions is relatively easy. Part of the envisaged modifications is the inclusion of interactions of iodine with non-aqueous aerosols. It is planned that the code will be coupled to a containment code (e.g. CONTAIN), to provide a comprehensive description of fission product chemistry and aerosol behaviour.

Preliminary comparisons[17] of IMPAIR-2, INSPECT, and IODE results for an ACE/RTF experiment suggest that the codes are in overall agreement for iodine gas-phase partitioning, the effect of surfaces, organics, mass transfer, and pH, and on the effect of major sinks. However, major differences were noticed in the detailed speciation of iodine.
5.3 ESTER

The Commission's ultimate aim in developing and validating the previously described codes is to couple them with a reliable thermal-hydraulics code in a uniform and consistent code, named European Source TERm code package. The code package ESTER will be used in the analysis of the radiological source term in LWR severe accidents, and in the analyses of integral tests like the Phebus experiments. It is envisaged to be a mechanistic best estimate code that will calculate the following coupled phenomena:

1. Release of fission product vapours and aerosols from the reactor core or the fuel rod bundle.
2. Transport, deposition, and resuspension of fission products in the reactor primary cooling system.
3. Transport and deposition of fission products in the containment.

6 European Severe Accident Chemistry Group

The Commission has proposed the formation of a European Severe Accident Chemistry Group. The aim is to create a European forum for the free exchange of information on chemistry-related aspects of severe accidents. The first meeting of the group was held at the JRC-Ispra on May 23 and 24 1991, with the topic of: "Iodine Chemistry in the Reactor Containment Building during a LWR Severe Accident". The group will meet on a regular basis and possible future topics include: Primary Circuit Chemistry, Integral Experiments, Thermochemical Data. The Commission, through JRC-Ispra, acts as the coordinator of the group's activities.

7 Conclusions

The CEC is involved in a large number of severe reactor accident programmes, many of which are directly concerned with the behaviour of iodine throughout the reactor system. In the area of fundamental data acquisition and assessment there is a continuing programme to measure and assess thermochemical parameters to be added to the existing data bases of primary circuit modelling codes. Small-scale integral and separate-effects experiments have been conducted as part of the Falcon programme, and have examined phenomena such as vapour-aerosol interactions, the effects of organic paints and sump pH on containment iodine behaviour, and the characterisation of boric acid and control rod aerosols. The results of these experiments have also been used to test and develop certain severe accident modelling codes. Various experimental techniques have been implemented and assessed in the Falcon programme and the experience gained is being used in the large-scale Phebus-FP tests. Phebus-FP is a large-scale in-pile facility comprising a core region, reactor coolant system and containment. Integral tests will be conducted under representative accident conditions with studies of fuel bundle, primary circuit, and containment. Iodine behaviour in the containment will be of particular importance, with studies of the effects of temperature, aqueous sump pH, and organic paints.
Code modelling studies are concerned with fission product behaviour in the primary circuit (VICTORIA, RAFT), and iodine behaviour in the containment (IMPAIR-2, IODE, and INSPECT). The ultimate aim is to include many of these codes into a single European package (ESTER). The Commission has also formed the European Severe Accident Chemistry Group to provide a forum for the discussion of chemistry aspects of severe accidents analysis.

8 Acknowledgements

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References


### TABLE 1: FALCON TEST MATRIX (1989-90)

<table>
<thead>
<tr>
<th>Expt</th>
<th>Simulant Fuel</th>
<th>Irradiated Fuel</th>
<th>Control Rod</th>
<th>Boric Acid</th>
<th>Atmosphere</th>
<th>% Saturation</th>
<th>Paint</th>
<th>Sump (pH)</th>
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<td>-</td>
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<td>-</td>
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<td>He-27% H₂O</td>
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</tr>
<tr>
<td>FAL-HT7</td>
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<td>-</td>
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</tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>He-8% H₂O</td>
<td>68</td>
<td>-</td>
<td>-</td>
<td>24.10.89</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>He-16% H₂O</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>FAL-2</td>
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<td>-</td>
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<tr>
<td>FAL-3A</td>
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<td>✓</td>
<td>✓</td>
<td>He-16% H₂O</td>
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<td>-</td>
<td>-</td>
<td>28.02.90</td>
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<tr>
<td>FAL-3B</td>
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<td>-</td>
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<td>✓</td>
<td>He-16% H₂O</td>
<td>88</td>
<td>-</td>
<td>-</td>
<td>14.03.90</td>
</tr>
<tr>
<td>FAL-4</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>He-16% H₂O</td>
<td>61</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>FAL-5</td>
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<td>-</td>
<td>✓</td>
<td>✓</td>
<td>He-27% H₂O</td>
<td>92</td>
<td>-</td>
<td>-</td>
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<tr>
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<td>✓</td>
<td>He-16% H₂O</td>
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<td>✓</td>
<td>He-16% H₂O</td>
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<td>✓</td>
<td>✓ (8)</td>
<td>19.12.90</td>
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<td>✓</td>
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<td>95</td>
<td>✓</td>
<td>-</td>
<td>19.09.90</td>
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<tr>
<td>FAL-9</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>He-16% H₂O</td>
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<td>✓ (5)</td>
<td>31.10.90</td>
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<td>✓</td>
<td>✓</td>
<td>He-27% H₂O</td>
<td>95</td>
<td>✓</td>
<td>✓ (8)</td>
<td>09.10.90</td>
</tr>
<tr>
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<td>✓</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14.11.89</td>
</tr>
<tr>
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<td>✓</td>
<td>✓</td>
<td>He-16% H₂O</td>
<td>92</td>
<td>-</td>
<td>-</td>
<td>10.07.90</td>
</tr>
</tbody>
</table>

* Simulant fuel bundle experiment (6 fuel samples)
### TABLE 2 CURRENT PHEBUS-FP TEST MATRIX

<table>
<thead>
<tr>
<th>TEST</th>
<th>FUEL BUNDLE</th>
<th>REACTOR COOLANT SYSTEM</th>
<th>CONTAINMENT</th>
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</thead>
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<tr>
<td>FPT-0</td>
<td>LOW</td>
<td>LOW</td>
<td>✓</td>
</tr>
<tr>
<td>FPT-1</td>
<td>LOW</td>
<td>LOW</td>
<td>✓</td>
</tr>
<tr>
<td>FPT-2</td>
<td>HIGH</td>
<td>HIGH</td>
<td>✓</td>
</tr>
<tr>
<td>FPT-3</td>
<td>LOW</td>
<td>HIGH</td>
<td>✓</td>
</tr>
<tr>
<td>FPT-4</td>
<td>LOW</td>
<td>LOW/HIGH</td>
<td>✓</td>
</tr>
<tr>
<td>FPT-5</td>
<td>HIGH</td>
<td>HIGH</td>
<td>✓</td>
</tr>
</tbody>
</table>

1. one test may be performed without a control rod
2. point of injection may be before or after the bundle
3. one or two volumes (to be defined) containing water
4. to be performed after depressurisation
5. initial sump conditions
FIGURE 1: CsI - CdI₂ PHASE DIAGRAM
DISCUSSION

Vikis
You referred to the studies on Cs/I equilibration. Do those studies assume that Cs and I are released separately from fuel?

Drossinos
Yes, Cs and I were injected in different relative proportions.

Ritzman
Will the ESTER code contain mechanistic models or engineering correlations of phenomena? The choice will affect computer run times and costs.

Drossinos
ESTER provides an informatic structure for the coupling of independent codes. It provides a data base and a set of code of communication between different programs, which may be considered as independent ESTER modules. Thus, whether mechanistic models or correlations of phenomena will be included into ESTER depends on the codes incorporated. At the moment, most of the codes envisaged to be incorporated into ESTER consider mechanistic models.

Soda
Will ESTER consider ex-vessel phenomena?

Drossinos
As mentioned in the reply to Dr. Ritzman's question, ESTER provides the informatic structure for the coupling of initially independent computer codes. Thus, ESTER will be able to calculate nothing more, or, less, than what the initial program could. At the moment, it is not envisaged in that code that ex-vessel phenomena will be incorporated into ESTER.
2. Session II
HOMOGENEOUS PHASE CHEMISTRY
2.1 AQUEOUS SOLUTION OF IODIDE UNDER GAMMA RAY IRRADIATION
—FIXATION OF IODIDE BY ADDING SOLUBLE SILVER SALT—

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Department of fuel safety research
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Japan Atomic Energy Research Institute
Tokai-mura
Naka-gun
Ibaraki-ken
Japan

ABSTRACT

An experiment on the fixation of iodide by adding soluble silver salt in the aqueous solution under the gamma ray irradiation was performed to establish a method for confinement of methyl iodide formation during the severe accident of a LWR plant.

The formation of methyl iodide in the water phase of sump tank in the reactor pressure vessel containment building was presumed in this study by the reason of being of much obscure parts on the formation mechanism and transfer behavior of the methyl iodide under the severe accident conditions. And the separate effects tests on the chemical behavior of silver iodide and methyl iodide were performed under the gamma ray irradiation.

Though the high dependence on the accident events sequence or the plant construction for the formation and transfer behavior of the fission products iodine was inferred, it was shown from the experimental results as above that the method to confine the formation of the methyl iodide by adding the soluble silver salt into the sump tank water at the accident is desirable.
Introduction

The obscured points in the formation mechanism of volatile iodine species (in particular, methyl iodide) remain yet during the severe accident of LWR plant, and it is known that such instance as the methyl iodide is able to be insufficiently taken off by adsorbing on the charcoal bed with high humidity may occur. It is able to be predicted that the methyl iodide formation during the severe accident of LWR plant and the release of methyl iodide from the plant to it's circumstance in response to some accidental sequences may occur. Because of the increase of the complexity and the uncertainty on the risk evaluation of the severe accident with the probability of the methyl iodide release, the occurrence of the methyl iodide formation must be confined.

Now, the researches on the details of the phenomenon which may occur in the severe accident of LWR plant are in progress. Therefore, by using the method which choose the basically important phenomenon under the accident condition to constitute the accident events sequence which the methyl iodide may occur, an example of scenario of the accident as below was inferred;

a. primary coolant pipe breakage accident
b. primary coolant diminishing
c. reactor core damage, and FP release from damage fuels
d. transference of coolant leaked out from rupture part of primary coolant pipe into reactor pressure vessel containment building sump
e. formation of high level radiation field in sump tank (gaseous and water phases) with radioactive FPs. and maintaining integrity of reactor pressure vessel containment building
f. major parts of FPs iodine collect in sump tank, and then dissolve in water phase as iodide, and great parts of iodide form volatile iodine species (containing methyl iodide), and instant transferring of methyl iodide after forming from water phase to atmosphere.

Under the sequence inferred as above, in order to pursue the phenomena which confine the formation of methyl iodide via the precipitation of silver iodide by dissolving the soluble silver salt in the sump water, the experimentations as below were performed.
Experimental

a. When the methyl iodide was dissolved into the silver nitrate aqueous solution, the precipitation of silver iodide occurred. The data on the reaction as above are shown in the 1st table.

b. The potassium iodide or the cesium iodide aqueous solutions were added to a pair of silver nitrate aqueous solutions and the same solutions as above containing coexistent substances, respectively. One of the former (and the latter) above was irradiated by cobalt 60 gamma ray (1.3×10^6 R/h×2.75h), the other of the former (and the latter) was not. The experimental data on the samples as above are shown in the 2nd table.

The cesium iodide labeled with iodine-131 aqueous solutions were added to a pair of silver nitrate aqueous solutions and the same solutions above containing sodium acetate solutions, respectively. All of the solutions above were irradiated by the cobalt 60 gamma ray (1.3×10^6 R/h×2.75h), respectively. After the separation of the methyl iodide labeled with iodine-131 from each solution, the precipitates of the silver iodide labeled with iodine-131 were separated from each solution, respectively. Next, without the cobalt 60 gamma ray irradiation, the same experimentation as above were repeated. Both experimental data on the samples above are shown in the 3rd table.

On the sample a' in the 4th table, the cesium iodide labeled with iodine-131 aqueous solution was added to the silver nitrate solution containing cupric nitrate and sodium acetate, and then the air in the container was substituted by the nitrogen gas. And it's solution was irradiated by the cobalt 60 gamma ray (1.3×10^6 R/h×2.75h). After the finish of irradiation, the methyl iodide labeled with iodine-131 was separated from the sample solution, and then the precipitate of the silver iodide labeled with iodine-131 was separated from the same solution. On the sample b' in the same table, the cesium iodide labeled with iodine-131 aqueous solution was added to the silver nitrate solution containing cupric nitrate and sodium acetate. And the solution above was irradiated by the cobalt 60 gamma ray (1.3×10^6 R/h×2.75h). Then the sample was treated as the 1st one in the separation process. On the sample c' in the same table, the cesium iodide labeled with iodine-131 aqueous solution was added to the silver nitrate solution.
containing cupric nitrate. Then the air in the container containing the sample solution was substituted by the nitrogen gas. And then, the sample was treated as the 1st one in the following process. On the sample d' in the same table, the cesium iodide labeled with iodine-131 aqueous solution was added to the silver nitrate solution containing cupric nitrate. And the sample solution above was irradiated by the cobalt 60 gamma ray (1.3 x 10^6 R/h x 2.75h). Then the sample was treated as the 1st one in the following process.

c. The cesium iodide aqueous solutions were added to a pair of silver nitrate solutions and the same solutions containing cupric nitrate, respectively. All of the solutions above were irradiated by the cobalt 60 gamma ray (1.3 x 10^6 R/h x 2.75h). During the gamma ray irradiation, one of the silver nitrate solution and the same solution containing cupric nitrate were swept by the nitrogen gas stream, but the others were not. After the finish of irradiation, the precipitates of silver iodide in all solutions above were separated by filtrating, respectively. The copper in the all precipitates above were determined by the atomic absorption spectrochemical analysis, respectively. The experimental data above are shown in the 5th table.

d. The cesium iodide aqueous solution or the cesium iodide solutions containing the oxalic acid, the boric acid and the acetic acid, the oxalic acid and the ferric nitrate, or the cesium hydroxide and the acetic acid were shuttered up in the stainless steel bombs, respectively. All of the bombs above were irradiated by the gamma ray from the spent fuel assembly (6.6 x 10^5 or 6.9 x 10^5 R/h, 1 or 2 h), respectively. The methyl iodide in each bombs just after the finish of irradiation were swept through by the flow of herium gas, and collected into the trap cooled by the liquid nitrogen, respectively. Each methyl iodide in the traps were determined by the gas chromatography, respectively. The results of each methyl iodide determination and conversion rate (I -> CH3I) calculation are shown in the 6th table. The simplified flow diagram of the collection apparatus for the organic iodide is shown in the 1st figure, and the calibration curves of methyl iodide and methanol are shown in the 2nd figure.

e. The methyl iodide, the methyl iodide coexistent with the water, the methyl iodide coexistent with the air, and the methyl iodide coexistent with the air and the water were shuttered up in the stainless steel bombs, respectively. They were irradiated by the cobalt 60 gamma ray
(1.4x10^6 R/h=2h), respectively. After the finish of irradiations above, the formed amounts of the iodine or the same of the iodine and the iodide ion in their samples were measured, respectively. The data on the experiments above are shown in the 7th and 8th (CH4) in water in bombs) tables.

The data on the methyl iodide formations in the dimethyl sulfate—the sodium iodide labeled with iodine-131 aqueous solution and the dimethyl sulfate—the silver nitrate—the sodium iodide labeled with iodine-131 aqueous solutions (the one solution was irradiated by the cobalt 60 gamma ray, and the other three solutions were stood up for different times after mixing, respectively.) are shown in the 9th table. And the simplified flow diagram used for the experiments above is shown in the 3rd figure.

Results and Discussion

The occurrence of the iodide ion(I^-) by the hydrolysis of the methyl iodide dissolved in the water is shown in the results of the 1st table. The experimental data on the effects of gamma ray irradiation to the silver iodide in the water phase are shown in the results of the 2nd ~ 5th tables. The trend which the coexistent substances gave the effects to the stability of silver iodide precipitate was not authenticated (the 2nd table). The iodine-131 tracer was used for the confirmation of the stability of silver iodide precipitate in the aqueous solution (the 3rd and 4th tables). The silver iodide precipitate was stable in the aqueous solution under the cobalt 60 gamma ray irradiation at the relatively high dose rate (2nd ~ 5th). The amounts of methyl iodide formed in the solutions which were shutted up in the stainless steel bombs and then irradiated by the gamma ray from the JMTR spent fuel assembly were measured (the 6th table). As shown in the table, the fact upon the formation of methyl iodide in the samples was confirmed, but its formation mechanism is not resolved yet. In the 7th and 8th tables, the experimental results on the decomposition of methyl iodide by the gamma ray irradiation are shown. In the 7th table, it seemed that the methyl iodide in the bombs were present in both the gaseous and the liquid phases. In the 8th table, the methyl iodide dissolved in water was decomposed easier by the gamma ray irradiation. Under the experimental
condition, the decomposition rate of methyl iodide in the water phase by the cobalt 60 gamma ray irradiation was greater than that in the gaseous phase, apparently. The trend that the methyl iodide gas coexistent with the moisture was decomposed easier apparently by the gamma ray irradiation was found, also. The reason why the trends as described above occurred has not resolved yet, but may be elucidated by the decomposition accelerated with the reaction by the oxidation products formed from the water radiolysis. The results in the 9th table show the phenomena which the reactions between some methyl radical donors and the iodide ions(I⁻)(and the iodine) form the methyl iodide. As shown in the same table, the formation rate of methyl iodide in the aqueous solution diminished by the cobalt 60 gamma ray irradiation, apparently, and was confined by coexisting with the silver nitrate. In the experiment as shown in the table above, the iodide(I⁻) concentration was inferred to be approximately $10^{-16} \sim 10^{-9}$ mol/dm³, and only less than 1/30 of the iodide ions were used for the formation of methyl iodide by the coexistence with the silver nitrate($10^{-6}$ mol/dm³). If the all amounts of fission products iodine(hypothesized as CsI) in the reactor core were transferred and dissolved in the sump tank water in the reactor pressure vessel containment building, the concentration of the iodide(I⁻) in the water will be about 1 ppm, $8 \times 10^{-6}$ mol/dm³. The solubility of silver iodide is $3 \times 10^{-5}$/100 ml solution(from the reference). $1.1 \times 10^{-7}$ mol/dm³ at 373.15 K. By using these data above, it seems to be estimated that the amount of the iodide(I⁻) used for the formation of methyl iodide can be decreased at least to less than 1/10 of the initial amount by adding the soluble silver salt in the water. If the concentration of silver ion(Ag⁺) to be added in the sump tank water previously to the dissolution of fission products iodine is $1 \times 10^{-4}$ mol/dm³, it seems to be full for confining the formation and release of volatile iodine species. Forward, when the resolution of all phenomenon in the severe accident will be achieved, the accident scenario to which the method proposed in this paper can be applied and the limit to be effective application of the method above will be more clear by the results of many tests. Anyway, the contribution of the proposed method to the decrease of radiation impact brought to the circumstance around the LWR plant at the severe accident by the release of fission products iodine(mainly, the methyl iodide containing iodine-131, 129) will be expected reasonably.
Conclusion

1) The cobalt 60 gamma ray irradiation ($1.3 \times 10^6 \text{ R/h} \times 2.75 \text{ h}$) to the silver iodide just after the precipitation in the aqueous solution did not give the effect to the stability of the precipitate.

2) The aqueous solutions shuttled up in the stainless steel bombs as below were irradiated by the gamma ray from the spent fuel assembly (6.6 or 6.9 $\times 10^5 \text{ R/h}$, 1 or 2 h), respectively: CsI ($7.89 \times 10^{-4} \text{ H}$), CsI ($7.69 \times 10^{-5}$ to $7.89 \times 10^{-4} \text{ H}$) containing (COOH)2 ($5.56 \times 10^{-5} \text{ H} \sim 1.11 \times 10^{-3} \text{ H}$), H2SO3 (3.24 $\times 10^{-2} \text{ H}$) and CH3COOH ($1.67 \times 10^{-5} \text{ H} \sim 1.67 \times 10^{-3} \text{ H}$), Fe3+ ($1.79 \times 10^{-3} \text{ H}$) and (COOH)2 ($2.2 \times 10^{-4} \text{ H}$), or CsOH (3.2 $\times 10^{-6} \text{ H}$) and CH3COOH ($1.67 \times 10^{-5} \sim 1.67 \times 10^{-3} \text{ H}$), respectively. The methyl iodide occurred in each bomb just after the irradiation (max. $2.7 \times 10^{-7} \%$), but the formation mechanism of methyl iodide in each solution above were not resolved.

3) The methyl iodide dissolved in the aqueous solutions (6.44 $\times 10^{-6} \text{ H}$) were irradiated by the cobalt 60 gamma ray (1.4 $\times 10^6 \text{ R/h} \times 4 \text{ h}$), respectively. Thirty two % of the methyl iodide above (in average of 4 data) were decomposed to the iodine (I2) and the iodide (I-). The decomposition rate of methyl iodide dissolved in the aqueous solution was greater than that in the gaseous state, apparently.

4) In the aqueous solution shuttled up in the glass container, the methyl iodide was formed from the reaction between the methyl radical donor (dimethyl sulfate, 1 $\times 10^{-3} \text{ H}$ or 2 $\times 10^{-3} \text{ H}$) and the iodine-131 tracer (about 7 micro Ci) at the conversion rate of about 3.5 %. In the aqueous solution above, the formation of methyl iodide decreased distinctly by the cobalt 60 gamma ray irradiation ($7 \times 10^5 \text{ R/h} \times 1 \text{ h}$) or the addition of the silver nitrate ($1 \times 10^{-4} \text{ H}$).

5) Under the severe accident conditions of LWR, when the main source of methyl iodide formation is due to the reaction between the methyl radical donor and the soluble fission products iodide (containing the iodine formed from the reaction between the oxidation products by water radiolysis and the iodide ion), the addition of adequate amounts of silver nitrate to the water phase just before the dissolution of soluble fission products iodine can decrease distinctly the formation rate of methyl iodide by producing the silver iodide precipitate.
Acknowledgements

The author wishes to thank his laboratory's members for their cooperation: the gas chromatographic analysis of the methyl iodide by Mr. H. Naritomi, parts of the absorption spectrochemical analysis of the sample after gamma ray irradiation by Mr. H. Nagai and the experiment containing the iodine-131 tracer use by Mr. S. Okagawa.

The gamma ray source of the spent fuel assembly in the O-arai research institute and the cobalt 60 source in the Takasaki radiation chemistry research institute were used also.

References


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Fig. 1 Simplified flow diagram of apparatus for CH₄I collection
Fig. 2 Calibration curve of CH$_3$I or CH$_3$OH

Fig. 3 Simplified flow diagram of collector and counter for CH$_3$I labeled with Iodine-131
Table 1  Production of AgI by $^3$I from CH$_3$I Dissolved in AgNO$_3$ Soln.

<table>
<thead>
<tr>
<th>No.</th>
<th>Solution volume, ml</th>
<th>Amount of Ag, (M)</th>
<th>Amount of I, (M)</th>
<th>Recovered AgI (%)</th>
<th>Solution containing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>204</td>
<td>$1.15 \times 10^{-7}$</td>
<td>$3.95 \times 10^{-3}$</td>
<td>26</td>
<td>beaker</td>
</tr>
<tr>
<td>2</td>
<td>104</td>
<td>$2.26 \times 10^{-2}$</td>
<td>$8.82 \times 10^{-3}$</td>
<td>87</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>106</td>
<td>$5.55 \times 10^{-2}$</td>
<td>$6.36 \times 10^{-3}$</td>
<td>64</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>101</td>
<td>$5.83 \times 10^{-2}$</td>
<td>$1.05 \times 10^{-2}$</td>
<td>96</td>
<td>mees cylinder</td>
</tr>
<tr>
<td>5</td>
<td>1044</td>
<td>$5.64 \times 10^{-3}$</td>
<td>$7.74 \times 10^{-3}$</td>
<td>25</td>
<td>beaker</td>
</tr>
<tr>
<td>6</td>
<td>5000</td>
<td>$3.02 \times 10^{-3}$</td>
<td>$1.02 \times 10^{-3}$</td>
<td>about 13</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* No.1 ~ 5 as CH$_3$I, No.6 as KI

Table 2  AgI Precipitate under Irradiation of $^{60}$Co γ-Ray

<table>
<thead>
<tr>
<th>Solution volume, ml</th>
<th>Amount of Ag, (M)</th>
<th>Amount of I, (M)</th>
<th>Coexistent Substance, mg</th>
<th>Recovered AgI (%)</th>
</tr>
</thead>
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<tr>
<td>200</td>
<td>$1.88 \times 10^{-3}$</td>
<td>$3.93 \times 10^{-3}$</td>
<td>0</td>
<td>A$_1$ 71.7 A$_2$ 50</td>
</tr>
<tr>
<td></td>
<td>$4.87 \times 10^{-3}$</td>
<td>&quot;</td>
<td>0</td>
<td>B$_1$ 80.4 B$_2$ 34</td>
</tr>
<tr>
<td></td>
<td>$4.06 \times 10^{-3}$</td>
<td>&quot;</td>
<td>0</td>
<td>C$_1$ 50 C$_2$ 80.2</td>
</tr>
<tr>
<td>450</td>
<td>$8.24 \times 10^{-3}$</td>
<td>$8.73 \times 10^{-3}$</td>
<td>0</td>
<td>D$_1$ 28 D$_2$ 43</td>
</tr>
<tr>
<td>101</td>
<td>$3.69 \times 10^{-3}$</td>
<td>$7.84 \times 10^{-3}$</td>
<td>Fe$^{3+}$, 1°</td>
<td>E$_1$ 83.4 E$_2$ 80.2</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>Cu$^{2+}$, 1°</td>
<td>F$_1$ 92.2 F$_2$ 98.4</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>H$_2$BO$_3$, 2</td>
<td>G$_1$ 83.4 G$_2$ 90.4</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>Na$_2$CO$_3$, 1.78</td>
<td>H$_1$ 65.0 H$_2$ 96.3</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>acetone, $8 \times 10^{-3}$</td>
<td>I$_1$ 81.8 I$_2$ 81.3</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
<td>Na$_2$SO$_4$, 1.48</td>
<td>J$_1$ 83.2 J$_2$ 85.0</td>
</tr>
</tbody>
</table>

* as KL, b as C$^{60}$I, c as nitrate. No irradiation to sample A$_1$ ~ J$_1$; pH range of solution before γ irradiation: 5.1 ~ 5.8 to A$_1$ ~ D$_1$; and C$_1$ ~ J$_1$; 2.6 to E$_1$; and F$_1$. Gamma Ray Dose to sample A$_1$ ~ J$_1$: about $3.6 \times 10^5$ R (2.75 Hr $\times$ 1.3 $\times$ 10$^4$ R/hr).
### Table 3: AgI Precipitate Irradiated by $^{60}$Co Gamma Ray

<table>
<thead>
<tr>
<th>Sampling Bomb No.</th>
<th>Amount of Ag, (H)</th>
<th>Amount of $^{14}$(H)</th>
<th>Recovered AgI, %</th>
<th>Gross $\gamma$ Count, CPM</th>
<th>BKG $\gamma$ Count, CPM</th>
<th>Net $\gamma$ Count, CPM</th>
<th>Net $\gamma$ Count, CPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.88 \times 10^{-4}$</td>
<td>40</td>
<td>4198.0</td>
<td>270.5</td>
<td>3927.5</td>
<td>9818.8</td>
</tr>
<tr>
<td>b</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.88 \times 10^{-4}$</td>
<td>40</td>
<td>4585.7</td>
<td>270.5</td>
<td>4315.2</td>
<td>10788.0</td>
</tr>
<tr>
<td>c</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.88 \times 10^{-4}$</td>
<td>20</td>
<td>2622.0</td>
<td>270.5</td>
<td>2351.5</td>
<td>11757.5</td>
</tr>
<tr>
<td>d</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.88 \times 10^{-4}$</td>
<td>39</td>
<td>4271.0</td>
<td>270.5</td>
<td>4000.5</td>
<td>10257.7</td>
</tr>
<tr>
<td>Standard</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.93 \times 10^{-4}$</td>
<td>24.1</td>
<td>8104.5</td>
<td>270.5</td>
<td>7834.0</td>
<td>10572.2</td>
</tr>
<tr>
<td>Standard</td>
<td>$9.3 \times 10^{-4}$</td>
<td>$7.93 \times 10^{-4}$</td>
<td>24.1</td>
<td>8295.5</td>
<td>270.5</td>
<td>8025.0</td>
<td>10573.1</td>
</tr>
</tbody>
</table>

* Labeled with $^{131}$I  ** CH$_3$COONa - 3H$_2$O 1 mg added  † duplicate averaged  ‡ corrected on yield  ‡ not irradiated  All of solution's volume were 100 ml.

### Table 4: AgI Precipitate Irradiated by $^{60}$Co Gamma Ray

<table>
<thead>
<tr>
<th>Sampling Bomb No.</th>
<th>Amount of Ag, (H)</th>
<th>Amount of $^{14}$ (H)</th>
<th>Recovered AgI, %</th>
<th>Gross $\gamma$ Count, CPM</th>
<th>BKG $\gamma$ Count, CPM</th>
<th>Net $\gamma$ Count, CPM</th>
<th>Net $\gamma$ Count, CPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$2.4 \times 10^{-3}$</td>
<td>$2.0 \times 10^{-3}$</td>
<td>24.7</td>
<td>12428</td>
<td>161</td>
<td>12267</td>
<td>49664</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td></td>
<td>35.2</td>
<td>17452</td>
<td></td>
<td>17291</td>
<td>49122</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td></td>
<td>50.1</td>
<td>25740</td>
<td></td>
<td>25579</td>
<td>51056</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td></td>
<td>52.6</td>
<td>25937</td>
<td></td>
<td>25776</td>
<td>69004</td>
</tr>
<tr>
<td>Standard</td>
<td></td>
<td></td>
<td>97.2</td>
<td>50771</td>
<td></td>
<td>50610</td>
<td>52068</td>
</tr>
</tbody>
</table>

* Labeled with $^{131}$I  † One mg of CH$_3$COONa added  ‡ corrected on yield  ‡‡ Before irradiation, atmosphere in bombs were substituted with N$_2$ gas (100 ml/min in flow rate), through solution.

Three mg of Cu (as nitrate) were added to four AgNO$_3$ solutions, respectively.
Table 5: AgI Precipitate Irradiated by $^{60}$Co Gamma Ray

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amount of Ag (H)</th>
<th>Amount of I (H)</th>
<th>Added Cu$^{2+}$ (mg)</th>
<th>Sample (A)</th>
<th>Sample (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>AgI Recovery (%)</td>
<td>Cu in AgI (µg)</td>
</tr>
<tr>
<td>1</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>0</td>
<td>not weighed</td>
<td>— *</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>5</td>
<td>$1.2 \times 10^{-4}$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>0</td>
<td>85</td>
<td>— **</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1</td>
<td>91</td>
<td>1.1</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3</td>
<td>72</td>
<td>2.1</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9</td>
<td>87</td>
<td>3.8</td>
</tr>
<tr>
<td>9</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>0</td>
<td>91.9</td>
<td>— **</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1</td>
<td>93.4</td>
<td>2.2</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>&quot;</td>
<td>3</td>
<td>89.8</td>
<td>3.7</td>
</tr>
<tr>
<td>12</td>
<td>&quot;</td>
<td>&quot;</td>
<td>9</td>
<td>93.6</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Each sample solution's volume was 200ml. Sample solution (A) swept by N$_2$ gas, (B) not swept.

* no residue on filter paper. ** not measured
Table 6: Methyl iodide Produced by Irradiation of Gamma Ray

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Solute in water, ppm</th>
<th>Produced CH$_3$I, g</th>
<th>CH$_3$I/I$^-$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41ppm CsI, 20ppm (COOH)$_2$</td>
<td>$3 \times 10^{-4}$</td>
<td>$1.5 \times 10^{-3}$</td>
</tr>
<tr>
<td>2</td>
<td>41ppm CsI, 5ppm (COOH)$_2$</td>
<td>$2.5 \times 10^{-7}$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>3</td>
<td>20ppm CsI, 2000ppm H$_3$BO$_3$, 1ppm AcOH</td>
<td>$2.9 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>20ppm CsI, 2000ppm H$_3$BO$_3$, 10ppm AcOH</td>
<td>$2.0 \times 10^{-4}$</td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>5</td>
<td>20ppm CsI, 2000ppm H$_3$BO$_3$, 100ppm AcOH</td>
<td>$4.7 \times 10^{-7}$</td>
<td>$4.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>6</td>
<td>41ppm CsI, 100ppm Fe$^{3+}$*, 20ppm (COOH)$_2$</td>
<td>$8.2 \times 10^{-7}$</td>
<td>$4.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>7</td>
<td>20ppm CsI, 0.48ppm CsOH, 1ppm AcOH</td>
<td>$7.7 \times 10^{-7}$</td>
<td>$7.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>8</td>
<td>20ppm CsI, 0.48ppm CsOH, 10ppm AcOH</td>
<td>$7.7 \times 10^{-7}$</td>
<td>$7.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>9</td>
<td>20ppm CsI, 0.48ppm CsOH, 100ppm AcOH</td>
<td>$1.65 \times 10^{-6}$</td>
<td>$1.7 \times 10^{-1}$</td>
</tr>
<tr>
<td>10</td>
<td>205ppm CsI**</td>
<td>$1.3 \times 10^{-6}$</td>
<td>$1.3 \times 10^{-2}$</td>
</tr>
<tr>
<td>11</td>
<td>205ppm CsI, 100ppm (COOH)$_2$ (**)</td>
<td>$1.6 \times 10^{-6}$</td>
<td>$1.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>12</td>
<td>41ppm CsI, 5ppm (COOH)$_2$</td>
<td>$3.0 \times 10^{-7}$</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>13</td>
<td>41ppm CsI, 2000ppm H$_3$BO$_3$, 100ppm AcOH</td>
<td>$5.2 \times 10^{-7}$</td>
<td>$2.6 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

* Nitrate used.
** Distilled water not treated by potassium permanganate was used.

Sample 1 - 11 were irradiated for one hour, and the 12 and 13 for two hours.
† Sample No. 1 - 6 were irradiated at A location, sample No. 7 - 13 at B location. In JMTR canal, gamma ray dose rate at A location was evaluated as $6.9 \times 10^5$ R/hr, that at B location as $6.6 \times 10^5$ R/hr.
Table 7  Decomposition of Methyl Iodide by Irradiation of Gamma Ray from \( ^{60} \text{Co} \) Source at Takasaki Laboratory (1)

<table>
<thead>
<tr>
<th>Species No.</th>
<th>CH(_3)I, g</th>
<th>H(_2)O, g</th>
<th>Air, Pa</th>
<th>I(^-) in trap*</th>
<th>I(_2) in trap**</th>
<th>I(^-) in washing solution***</th>
<th>I(_2) in washing solution**</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>34.3</td>
<td>~0</td>
<td>&lt;133</td>
<td>336†</td>
<td>2.2</td>
<td>36</td>
<td>9.8</td>
</tr>
<tr>
<td>B</td>
<td>34.3</td>
<td>~0</td>
<td>1.01x10(^5)</td>
<td>140†</td>
<td>4.0</td>
<td>3.4</td>
<td>38.4</td>
</tr>
<tr>
<td>C</td>
<td>6.86</td>
<td>10.0</td>
<td>&lt;133</td>
<td>156†</td>
<td>&lt;0.1</td>
<td>10.2</td>
<td>1.42</td>
</tr>
<tr>
<td>D</td>
<td>6.86</td>
<td>10.0</td>
<td>1.01x10(^5)</td>
<td>208†</td>
<td>2.0</td>
<td>18.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

* 0.1N Na\(_2\)CO\(_3\) solution used.
** Carbon tetrachloride used.
*** Water used.
† Coexistence with CH\(_3\)I was presumable.

Table 8  Decomposition of Methyl Iodide by Irradiation of Gamma Ray from \( ^{60} \text{Co} \) Source at Takasaki Laboratory (2)

<table>
<thead>
<tr>
<th>No.</th>
<th>Recovered amount of sample solution after gamma irradiation, g</th>
<th>Found amount after gamma irradiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I(_2), g</td>
</tr>
<tr>
<td>A</td>
<td>475</td>
<td>1.26</td>
</tr>
<tr>
<td>B</td>
<td>460</td>
<td>1.32</td>
</tr>
<tr>
<td>C</td>
<td>475</td>
<td>1.28</td>
</tr>
<tr>
<td>D</td>
<td>495</td>
<td>1.60</td>
</tr>
<tr>
<td>Exp. No.</td>
<td>Solute</td>
<td>Time from mixing of soln. to gas sweeping (hr.)</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------------------------</td>
<td>-------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>$2 \times 10^{-2} \text{H (CH}_3\text{SO}_4}$  \  6.95 μCi $^{131}\text{I (as NaI)}$</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>2</td>
<td>$2 \times 10^{-3} \text{H (CH}_3\text{SO}_4}$  \  $10^{-4} \text{H AgNO}_3$  \  4.63 μCi $^{131}\text{I (as NaI)}$</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>3</td>
<td>$2 \times 10^{-3} \text{H (CH}_3\text{SO}_4}$  \  $10^{-4} \text{H AgNO}_3$  \  5.87 μCi $^{131}\text{I (as NaI)}$</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>4</td>
<td>$10^{-3} \text{H (CH}_3\text{SO}_4}$  \  $10^{-3} \text{H AgNO}_3$  \  3.55 μCi $^{131}\text{I (as NaI)}$</td>
<td>$7 \times 24$</td>
</tr>
<tr>
<td>5</td>
<td>$10^{-3} \text{H (CH}_3\text{SO}_4}$  \  $10^{-3} \text{H AgNO}_3$  \  1.79 μCi $^{131}\text{I (as NaI)}$</td>
<td>$14 \times 24$</td>
</tr>
</tbody>
</table>
DISCUSSION

Kupferschmidt
Did you detect forms of organic iodides other than CH$_3$I in your studies?

Ishiwatari
No other organic iodides were found in our experiments.
2.2 BATCH-TYPE TESTS ON FORMATIONS OF VOLATILE IODINE SPECIES FROM AQUEOUS IODIDE SOLUTION UNDER $^{60}$Co $\gamma$-RAYS IRRADIATION

M. Naritomi, H. Nagai, S. Okagawa, and N. Ishiwatari
Department of Fuel Safety Research
Japan Atomic Energy Research Institute,
Tokai-mura Ibaraki-ken

Abstract

Test programs with a dynamic flow type VITA (Volatile Iodine Test Apparatus) system are in progress in JAERI for elucidating the radiation-induced formations of volatile iodine species and their transport behavior under natural and/or forced convection conditions. In order to survey dominant factors affecting the radiation-induced reactions of volatile iodine formation in advance of the VITA programs, batch tests were carried out using closed pyrex-glass ampules (200ml), in which 100ml of aqueous iodide solution was filled with organic and various chemical additives. The test solutions were irradiated by $^{60}$Co $\gamma$-rays at 10 kGy/h (10$^6$ rad/h) for one hour. The formations of volatile iodine species ($I_2$, $CH_3I$ and so on) from aqueous iodide solution were measured.

We will describe the test results and discuss mechanisms of volatile iodine, especially methyl iodide, formations.
1. Introduction

In a late phase of a severe accident in a light water nuclear reactor (LWR), it will be expected that most of fission product iodine reside in the water pool of the containment. Chemical forms of the iodine resided will be mainly iodide ion species(I⁻), not volatile forms such as I₂ and CH₃I. However, exposure of β · γ - rays from fission products play an important role to convert some of the iodine to volatile forms. The volatile forms can be transported by natural and/or forced convections from the liquid to the gas phases, and then to the environment over a long period from days to months after the accident. Such a release may be important issues for a long time accident management which will include mitigations to the leakage and the venting of containment air.

In the iodine chemistry, there are still many problems remaining unsolved on radiation-induced formations of volatile iodine species and their revolatilizations from the aqueous I⁻ solution. A great deal of effort has been made for elucidating the reaction mechanisms of volatile iodine formations. However, the amount can not determine quantitatively because their reaction mechanisms are uncompleted. Organic iodide forms, especially methyl iodide, compose a significant part of airborne iodine resulting from the release of volatile iodine species. However, the source and the reaction mechanism of organic iodide formation have not been well characterized yet.

The test programs with VITA system are in progress for predicting the radiation-induced formations of volatile iodine species and their transport behaviors under natural and/or forced convection conditions. In advance of the VITA programs, batch tests were carried out using closed ampule(200ml) in order to survey dominant factors affecting the volatile iodine formations. Present paper will describe the results of the batch tests and will discuss on the mechanisms of volatile iodine, especially methyl iodide, formations.

2. Experimentals

The batch tests were carried out under a severe accident condition of an LWR plant such as radiation intensity, iodide concentration, solution pH and chemical additives.

2.1 Sample preparation and irradiation
Aqueous I⁻ solution were prepared by using redistilled water from potassium permanganate, reagent-grade chemicals and high grade gases because of eliminating organic and inorganic impurities from the test solution. 100 ml of aqueous I⁻ solution containing various additives was filled into a pyrex-glass ampule(200ml) and then 0.37 MBq(10 µ Ci) of radioactive ¹³¹I was added for analyzing radiolytically an extremely small quantity of iodine forms produced by the γ-irradiation. The solution prepared was deaerated by sweeping He gas at 80 ml/min during 30 min before sealing with gas-burner flame. Some were swept with air containing CH₄ in 2000 ppm at the same flow as He. The entire I⁻ solution samples were irradiated by ⁶⁰Co γ-rays. The dose rate was measured accurately by Fricke dosimetry. The test conditions are summed up as follows

1. Irradiation; 10 kGy/h(10⁶ rad/h) × 1h,
   (Some continue at 5.8 x 10² and 3.5 x 10³ Gy/h before 10 kGy in total dose)
2. Iodide(CsI) concentration; 10⁻⁷ to 10⁻⁵ mol/dm³
3. Additives
   (1) Organic materials
      (a) Methane(CH₄); 2000 ppm, corresponding to 3.2 x 10⁻⁵ mol/dm³ in liquid
      (b) Methyl ethyl ketone(CH₃COCH₃); 10⁻⁶ or 10⁻⁷ mol/dm³
      (c) Acetic acid(CH₃COOH); 10⁻⁷ to 10⁻³ mol/dm³
   (2) Boric acid(H₃BO₃); 0.032 mol/dm³
   (3) Cesium hydroxide(CsOH); added for pH control
4. Initial pH; 4 to 9.5
5. Temperature; ~ 25°C

2.2 Analytical method

Organic iodides formed were separated by sweeping He gas at 80 ml/min during 30 min from the irradiated solution. The separated gases were condensed in a liquid-N₂ cooled trap, made of pyrex-glass, through NaOH solution trap in which volatile inorganic iodine species such as I₂ were absorbed. The trap efficiency of methyl iodide was nearly 100 %. The cooled trap was directly connected to the supply of radio-gas chromatograph shown in Fig. 1-1, and then warmed to discharge the cooled gases from the trap. Organic iodides formed were separated by a glass column(4mm φ × 3m) packed with 5 % DOP impregnated chomosorb. Each organic iodide form separated was determined by counting the radioactivity.
Elemental iodine (I\textsubscript{2}), hypoiodous acid (HOI) and tri-iodide ion (I\textsubscript{3}\textsuperscript{-}) species react rapidly each other to be in equilibrium state in the irradiated solution. Therefore mixture of I\textsubscript{2}, HOI and I\textsubscript{3}\textsuperscript{-}, namely iodine forms (I\textsubscript{ox}), was extracted with carbon-tetrachloride (CCl\textsubscript{4}) solution from some of the irradiated sample, and then back-extracted with sodium thiosulfate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}) solution, in which only I\textsubscript{ox} forms were involved. The amount of I\textsubscript{ox} forms back-extracted was also determined by counting the radioactivity. Iodate form (IO\textsubscript{3}\textsuperscript{-}) was directly determined by radio-ionochromatograph shown in Fig.1-2. The detection limits were about 20Bq (5 \times 10\textsuperscript{-4} \mu Ci), corresponding to about 5 \times 10\textsuperscript{-3} % of the initial I\textsuperscript{-} inventory.

3. Results

Lots of studies\textsuperscript{(6, 7)} indicate that the exposure of 10 kGy allows the concentrations of I\textsubscript{ox}, iodate and organic iodide species to come almost to equilibrium. In the presented tests, therefore, their saturated formations can be expected because most of test solutions are irradiated at 10 kGy/h for one hour.

Fig.2 shows percent yields of I\textsubscript{ox} forms as a function of solution pH, with initial iodide (I\textsubscript{0}\textsuperscript{-}) concentration as parameters. In 10\textsuperscript{-4} mol/dm\textsuperscript{3} of I\textsubscript{0}\textsuperscript{-} concentration, the yields decreased from about 10 to 0.01% inversely proportion to increase of solution pH from 5 to 8. The yields also decreased with decreasing I\textsubscript{0}\textsuperscript{-} concentration. In 10\textsuperscript{-5} mol/dm\textsuperscript{3} or less, however, the relationship between the I\textsubscript{ox} yield and the I\textsubscript{0}\textsuperscript{-} concentration was little found. Above pH 8, the dependencies of solution pH and I\textsubscript{0}\textsuperscript{-} concentration on the I\textsubscript{ox} yields became smaller.

Fig.3 shows percent yields of IO\textsubscript{3}\textsuperscript{-} formation as a function of I\textsubscript{0}\textsuperscript{-} concentration with \gamma - rays exposure rate as parameters. The I\textsubscript{0}\textsuperscript{-} concentration was in a range from 10\textsuperscript{-5} to 10\textsuperscript{-4} mol/dm\textsuperscript{3}. Boric acid and CH\textsubscript{4} gas were added to all test solutions in 0.032 and 3.2 \times 10\textsuperscript{-5} mol/dm\textsuperscript{3}, respectively. The irradiation was continued at 5.8 \times 10\textsuperscript{2}, 3.5 \times 10\textsuperscript{3} or 1.15 \times 10\textsuperscript{4} Gy/h before 1.15 \times 10\textsuperscript{4} Gy in total dose. The pH values of 6 ~ 7.2 were measured after irradiation. The percent yields decreased from about 70(\pm 20) to 0.2(\pm 0.3) % inversely proportion to a cubic root of the I\textsubscript{0}\textsuperscript{-} concentration. Remarkable effects of \gamma - exposure rate on the yields were not found at a dose rate from 5.8 \times 10\textsuperscript{2} to 1.15 \times 10\textsuperscript{4} Gy/h.

Fig.4 shows effects of solution pH on the IO\textsubscript{3}\textsuperscript{-} yields with the I\textsubscript{0}\textsuperscript{-}
concentrations as parameters. Although experimental data obtained were rather widely scattered, the obvious relationships between IO₃⁻ yields and solution pH were observed; (i) the maximum yields were found in neutral solution at every I₀⁻ concentrations, (ii) the yields decreased in acidic and basic solutions. In the present tests, an excess of CH₃COOH was added to the test solution for pH control. The decrease in acidic solutions, therefore, may be partly due to the organic additive as shown in next figure.

Fig. 5 shows effect of CH₃COOH addition on IO₃⁻ yields. In both I₀⁻ concentrations of 10⁻⁶ and 10⁻⁵ mol/dm³, the IO₃⁻ yields decreased inversely proportion to a cubic root of CH₃COOH concentration. About 2 × 10⁻⁴ mol/dm³ of CH₃COOH additive, extrapolated from test results, may retard completely IO₃⁻ formation.

In the present tests, only methyl iodide was detected and other organic iodide species were below the detection limit. Fig.6 shows percent fractions of CH₃COOH additive utilized for CH₃I formation as a function of CH₃COOH concentration with I₀⁻ concentration as parameters. CH₃COOH was added to the test solutions in a range from 10⁻⁷ to 10⁻³ mol/dm³. The I₀⁻ concentration was in a range from 10⁻⁶ to 10⁻⁴ mol/dm³. In 10⁻⁴ mol/dm³ of I₀⁻ concentration, the fractions of CH₃COOH utilization decreased linearly from about 30 to 0.03 % inversely proportion to increase of CH₃COOH concentration from 10⁻⁷ to 10⁻⁴ mol/dm³. And also the utilization curves shifted down to the lower fraction sides with decreasing I₀⁻ concentration.

Fig.7 shows the utilizations of dissolved CH₄ gas and CH₃COC₂H₅ additives for CH₃I formation as a function of the respective concentrations in which CH₃COOH utilizations (Fig.6) are also shown by dotted lines. As is obvious from this figure, the utilizations of dissolved CH₄ gas and CH₃COC₂H₅ additives were in good agreement with those of CH₃COOH additive in spite of different types and chemical forms.

Fig.8 shows percent yields of CH₃I formation as a function of I₀⁻ concentration in a wide range from 10⁻⁷ to 10⁻⁴ mol/dm³. The CH₃I yields were nearly constant (0.015 to 0.05 %, 0.03% in average), almost independent of concentrations of I₀⁻ species and organic additives.
4. Discussion

The radiation-induced reaction sequence of I\(^-\) oxidation\(^{8-11}\) is given by

\[
\begin{align*}
\text{I} & \xrightarrow{\kappa_1} \text{·OH} \quad \text{I} & \xrightarrow{\kappa_2} \text{I}^- \quad \text{I} & \xrightarrow{2\kappa_4} \text{I}_2^- \quad \text{I}_3^- + \text{I}^- \\
\end{align*}
\]

The following rate coefficients were surveyed by Evans et al.\(^{12}\) for their LIRIC database/model.

\[
\begin{align*}
\kappa_1 &= 1.8 \times 10^{10}\text{(dm}^3\text{/mol sec)}, \quad \kappa_1' = 2.25 \times 10^6\text{ (sec}^{-1}\text{)}, \\
\kappa_2 &= 1.2 \times 10^8\text{ (sec}^{-1}\text{)}, \quad \kappa_2' = 1.2 \times 10^6\text{ (dm}^3\text{/mol sec)}, \\
\kappa_3 &= 1.2 \times 10^{10}\text{(dm}^3\text{/mol sec)}, \quad \kappa_3' = 6 \times 10^4\text{ (sec}^{-1}\text{)}, \\
2\kappa_4 &= 9 \times 10^9\text{ (sec}^{-1}\text{)}.
\end{align*}
\]

\(\text{I}_3^-\) species formed through the reaction sequence(1) decomposes to \(\text{I}_2^-\) and \(\text{I}^-\), and then \(\text{I}_2^-\) is further decomposed by base-catalytic hydrolysis to \(\text{HOI}\) and \(\text{I}^-\). It is natural to expect that some of \(\text{I}_3^-\), \(\text{I}_2^-\) and \(\text{HOI}\) species formed are reduced by radiation-induced reductants such as \(\text{e}_\text{s}^-\) and \(\text{H}\) atom. But their rates must be considered to be very small compared with those in the following successive reactions(2) because the intensities of reductants are probably very small at 10 kGy/h.

\[
\begin{align*}
\text{I}_3^- & \xrightarrow{\kappa_5} \text{I}_2^- \quad \text{I}_2^- \xrightarrow{\kappa_6} \text{HOI} \\
\kappa_5 &= 7.5 \times 10^6\text{(sec}^{-1}\text{)}^{12}, \quad \kappa_5' = 5.6 \times 10^6\text{(dm}^3\text{/mol sec)}^{12} \\
\kappa_6 &= 3.4 \times 10^6\text{(dm}^3\text{/mol sec)}^{13}, \quad \kappa_6' = 7.7 \times 10^7\text{(sec}^{-1}\text{)}^{13}
\end{align*}
\]

\(\text{HOI}\) species is gradually oxidized by radiation-induced oxidants. The reaction mechanisms are proposed by Buxton\(^{14}\) and Lin\(^{15}\), in the higher(\(10^{-4} \sim 10^{-2}\) mol/dm\(^3\)) and the lower(carrier free \(^{131}\text{I} \sim 10^{-3}\) mol/dm\(^3\)) \(\text{I}_0^-\) concentrations, respectively. Both mechanisms indicate that \(\text{HOI}\) is precursor of \(\text{IO}_3^-\) which is formed through intermediate \(\text{IO}_2^-\) radical.

\[
\begin{align*}
\text{HOI} & \xrightarrow{\kappa_7} \text{·OH} \quad \text{HOIOH} & \xrightarrow{\kappa_8} \text{IO}_2^- + \text{H}_2\text{O} \\
\kappa_7 &= 7 \times 10^9\text{(dm}^3\text{/mol sec)}^{12}, \quad \kappa_8 = 1.3 \times 10^6\text{(sec}^{-1}\text{)}^{12}
\end{align*}
\]

In the higher \(\text{I}_0^-\) concentration, the \(\text{·OH}\) radical may be effectively scavenged by \(\text{I}^-\) species. In the lower one, however, it may be scavenged dominantly by \(\text{H}_2\text{O}_2\) formed radiolytically, resulting in the formation of \(\text{HO}_2^-\) radical. In a dilute \(\text{I}^-\) solution, therefore, \(\text{HOI}\) may be mainly oxidized by \(\text{HO}_2^-\) radicals to form \(\text{IO}_2^-\) radical as proposed by Lin\(^{15}\). The mechanism and the rates, however, have not been characterized enough yet.

The \(\text{I}_0^-\) yields were inversely proportion to solution pH as shown in Fig.2. Only OH\(^-\) ion species in the successive reaction(2), therefore, can
be considered to take part in the reactions of $I_{Ox}$ formation. Thus the following successive reactions may be proposed for HOI oxidation in which another OH$^{-}$ ion does not take part.

$$\text{HOI} \xrightarrow{\kappa_{10}} \cdot \text{OH} + \kappa_{10} \left( \text{HO}_{2}^{-} \right) \xrightarrow{\kappa_{11}} 10^{-} \xrightarrow{\kappa_{12}} \text{HOI} \rightarrow \text{IO}_{3}^{-} + \text{H}^{+}$$

(4)

The solid and dotted curves in Fig. 2 were empirically obtained by calculation under assumptions that ① $I_{Ox}$ forms were produced by reaction sequences (1) and (2), ② radiation-induced reactions of HOI oxidation were in the rate determining step of $I_{Ox}$ formation, thus $I_{3}^{-}$, $I_{2}$ and HOI species formed were in a pseudo-equilibrium state, ③ the solution pH did not take part in radiation-induced reactions of HOI oxidation, and ④ $[I^{-}]_{a} = [I^{0}] + [I_{Ox}]$ could be approximated for an $I_{0}^{-}$ concentration above $10^{-5}$ mol/dm$^{3}$ in which $I_{0}^{-}$ formation could be approximately neglected.

Under above assumptions of ①, ② and ③ terms, the rate of $I_{Ox}$ formation can be expressed by

$$\frac{d [I_{Ox}]}{dt} = 2\kappa_{4} [I_{2}^{-}] + \kappa_{11} \left( \text{H}_{2}\text{O}_{2} \right) (\text{IO}^{\cdot})$$

$$- \left( \kappa_{9} \left( \cdot \text{OH} \right) + \kappa_{10} \left( \text{HO}_{2}^{-} \right) \right) \left( \text{HOI} \right)$$

(5)

Assuming a steady state to $\text{IO}^{\cdot}$ radical formation, the concentration can be derived from the reaction sequence (4);

$$[\text{IO}^{\cdot}] = \frac{\left( \kappa_{9} \left( \cdot \text{OH} \right) + \kappa_{10} \left( \text{HO}_{2}^{-} \right) \right) \left( \text{HOI} \right)}{\kappa_{11} \left( \text{H}_{2}\text{O}_{2} \right) + \kappa_{12} \left( \text{HO}_{2}^{-} \right)}$$

(6)

From the reaction sequence (2), the pseudo-equilibrium concentration of HOI form can be obtained; Using $I_{Ox}$ concentration to $[I_{Ox}]$, and also $I_{O^{-}}$ concentration to $[I_{O}]$,

$$[I_{Ox}] = 3 [I_{3}^{-}] + 2 [I_{2}] + [\text{HOI}]$$

(7)

$$[I^{-}]_{a} = [I_{Ox}] + [I^{-}] + [I_{0}^{-}]$$

(8)

$$K_{e} = \frac{\kappa_{9}}{\kappa_{9}^{\prime}} = \frac{[I^{-}] [I_{2}]}{[I_{3}^{-}]} , K_{e} = \frac{\kappa_{e}}{\kappa_{e}^{\prime}} = \frac{[\text{HOI}] [I^{-}]}{[I_{2}] [\text{OH}^{-}]}$$

$$= 1.3 \times 10^{-3} \text{mol/dm}^{3}$$

(9)

Substituting Eqs. (9) and (10) in Eq. (7),

$$[\text{HOI}] = \frac{[I_{Ox}]}{1 + \frac{2 [I^{-}]}{K_{e} [\text{OH}^{-}]}} + \frac{3 [I^{-}]^{2}}{K_{s} K_{e} [\text{OH}^{-}]}$$

(11)
Substituting Eqs. (6) and (11) in Eq. (5), the following equations can be approximately obtained.

\[
\frac{d (I_{\text{ox}})}{dt} = \alpha \left( I^- \right) - \frac{\beta K_s K_e (\text{OH}^-) (I_{\text{ox}})}{K_s K_e (\text{OH}^-) + 2K_e (I^-) + 3 (I^-)^2}
\]  

(12)

where

\[
\alpha = \frac{\kappa_1 \kappa_2 (\cdot \text{OH})}{\kappa_1' + \kappa_2}
\]

(13)

\[
\beta = \frac{\kappa_{11} (\text{HO}_2^-) (\kappa_9 (\cdot \text{OH}) + \kappa_{10} (\text{HO}_2^-))}{\kappa_{10'} (\text{HO}_2^-) + \kappa_{11} (\text{HO}_2^-)}
\]

(14)

Because the saturated formation of \( I_{\text{ox}} \) forms can be expected for the exposure of 10 kGy/h for one hour, the equilibrium concentration can be expressed by.

\[
(I_{\text{ox}}) = \left( \frac{\alpha}{\beta} \right) \frac{(I^-) (K_s K_e (\text{OH}^-) + 2K_e (I^-) + 3 (I^-)^2)}{K_s K_e (\text{OH}^-)}
\]

(15)

Substituting \( (I^-) = (I^-) + (I_{\text{ox}}) \) in Eq. (15)

\[
\{ K_s K_e (\text{OH}^-) + 2K_e [(I^-) - (I_{\text{ox}})] \}
\]

\[
(I_{\text{ox}}) = \left( \frac{\alpha}{\beta} \right) + 3 [(I^-) - (I_{\text{ox}})]^2 \times [(I^-) - (I_{\text{ox}})]
\]

(15')

Unknown constant of \( (\alpha / \beta) \) can be empirically determined to be \( 2.4 \times 10^{-5} \) by fitting averaged measurement of \( I_{\text{ox}} \) yield (10%) at \( I^- \) concentration \( (10^{-4} \text{mol/dm}^3) \) and solution pH (15) to the above equation. The solid and dotted curves in Fig. 2 were obtained by calculating Eq. (15') for \( I^- \) concentrations of \( 10^{-4} \) and \( 10^{-5} \) mol/dm\(^3\), respectively, based on the empirically determined \( (\alpha / \beta) \) value. The calculations of the \( I_{\text{ox}} \) yields under the above assumptions were in relative good agreement with the measurements over a wide pH range from 4 to 9.5 as shown in Fig. 2. However, the empirical equation (15') cannot apply to calculations of \( I_{\text{ox}} \) yields at an \( I^- \) concentration below \( 10^{-5} \) mol/dm\(^3\) because \( I_{\text{ox}} \) is dominantly formed. The theoretical determination of \( I_{\text{ox}} \) species, therefore, will be required for the estimation of \( I_{\text{ox}} \) yields in dilute \( I^- \) solutions.

As shown in Figs. 3, 4 and 5, the percent yields of \( I_{\text{ox}} \) formation depended considerably on \( I^- \) concentration, organic additives and solution pH. The similar results are obtained by Lin's experiments (15). However, the reaction mechanisms on radiation-induced formation and reduction of \( I_{\text{ox}} \) species are not characterized enough yet. The theoretical explanation, therefore, must await for further investigations.
The $\cdot$OH radical abstracts easily hydrogen from dissolved CH$_4$ to form $\cdot$CH$_3$ radical$^{(16)}$. On the other hand, it also abstracts readily an electron from CH$_3$COOH and CH$_3$COC$_2$H$_5$ species, resulting in the formation of $\cdot$CH$_3$ radical$^{(17)}$. In spite of such different formation mechanisms, the utilizations of their organic additives for CH$_3$I formation were nearly same as shown in Fig.7. These facts mean that there is an analogy between generation and decomposition of $\cdot$CH$_3$ radical, independent of chemical properties of organic additives such as oxidation states and forms. It may also support the utilization phenomena that alkoxyl radical(CH$_3$O$\cdot$) formed through reaction with O$_2$ is similar in strong oxidant to $\cdot$OH radical$^{(18)}$.

If accepted these assumptions, the following reaction sequence may be proposed for formation and decomposition of $\cdot$CH$_3$ radical.

$$\begin{align*}
RCH_3 & \xrightarrow{\kappa_{13}} (\cdot OH) \cdot CH_3 + ROH \\
2 \kappa_{14} (\cdot CH_3) & \rightarrow C_2H_6 \\
\kappa_{15} (RCH_3) & \rightarrow CH_4 + \cdot RCH_2 \\
\kappa_{16} (O_2) & \rightarrow CH_3O \xrightarrow{\kappa_{17} (O_2)}^{1/2} CH_3O \cdot \\
\kappa_{18} (RCH_3) & \rightarrow CH_3OH + RCH_2 \\
\kappa_{19} (HOI) + \kappa_{20} & \rightarrow CH_3I + I^{-} \cdot (or + \cdot OH) \\
\kappa_{21} (H) + \kappa_{22} (e^{-}) & \rightarrow \cdot CH_3 + I^{-} + H^+ 
\end{align*}$$

where R is functional group of organic compounds, corresponding to $\cdot$H, $\cdot$COC$_2$H$_5$ and $\cdot$COOH for CH$_4$, CH$_3$COC$_2$H$_5$ and CH$_3$COOH species, respectively.

$$\begin{align*}
\kappa_{13} & = 1.2 \times 10^{8} \text{ (dm}^3/\text{mol sec)} \text{ for CH}_4^{(12)} \\
2 \kappa_{14} & = 2 \times 1.2 \times 10^{8} \text{ (12)} \\
\kappa_{15} & = \sim 1 \times 10^{3} \text{ (12)} \\
\kappa_{16} & = 3.2 \times 10^{8} \text{ (12)} \\
\kappa_{17} & = 6 \times 10^{9} \text{ (12)} \\
\kappa_{18} & = 1 \times 10^{9} \text{ (12)} \\
\kappa_{19} & = 1.0 \times 10^{10} \text{ (12)} \\
\kappa_{20} & = 1.65 \times 10^{10} \text{ (12)} \\
\kappa_{21} & = 1.0 \times 10^{10} \text{ (12)} \\
\kappa_{22} & = 6 \times 10^{8} \text{ (12)} 
\end{align*}$$

The rate coefficients, $\kappa_{13}'$, $\kappa_{17}$, $\kappa_{17}'$ and $\kappa_{18}$ are unknown.

The rate of $\cdot$CH$_3$ formation will be expressed approximately by the above
reaction sequence;
\[
\frac{d (\cdot \text{CH}_3)}{dt} = 2.9 \times 10^{-13} G (\cdot \text{CH}_3) \cdot D - 2 \kappa_{14} (\cdot \text{CH}_3)^2
\]

\[\quad - (\kappa_{15} + \kappa_{18} K_{18} K_{17} (O_2)^{1/2}) (\text{RCH}_3) (\cdot \text{CH}_3) \quad (17)\]
where D is absorbed dose rate (rad/h), by which methyl radical is formed

at a rate of \(2.9 \times 10^{-13} G (\cdot \text{CH}_3) \cdot D \text{ (mol/dm}^3\text{sec)}\),

\(G (\cdot \text{CH}_3)\) is G-value for \(\cdot \text{CH}_3\) formation, expressed by

\[
G (\cdot \text{CH}_3) = \frac{G (\cdot \text{OH}) \kappa_{13} (\text{RCH}_3)}{\kappa_1 (I^-) + \kappa_{13} (\text{RCH}_3) + \kappa_{23} (\text{H}_2\text{O}_2) + \kappa_{24} (\text{H}_2)} \quad (18)
\]

where \(\kappa_{23} = 3.3 \times 10^7 \text{ (dm}^3\text{/mol sec)}^{(12)}\)

\(\kappa_{24} = 3.6 \times 10^7 \text{ (dm}^3\text{/mol sec)}^{(12)}\)

The following inequality can be assumed to the present test conditions such as radiation intensity and chemical additives.

\(\kappa_1 (I^-) \approx (\kappa_{13} (\text{RCH}_3) + \kappa_{23} (\text{H}_2\text{O}_2) + \kappa_{24} (\text{H}_2))\)

Therefore Eq.(18) will be rewritten approximately by

\[
G (\cdot \text{CH}_3) = \frac{\kappa_{13}}{\kappa_1} G (\cdot \text{OH}) \frac{(\text{RCH}_3)}{(I^-)} \quad (18')
\]

Assuming a steady state to \(\cdot \text{CH}_3\) radical formation in Eq.(17), the equilibrium concentration will be approximated as follows, because it can be considered for a dose rate of 10 Kgy/h that \(2 \kappa_{14} (\cdot \text{CH}_3) \approx (\kappa_{15} + \kappa_{18} K_{18} K_{17} (O_2)^{1/2}) (\text{RCH}_3\).

Thus

\[
(\cdot \text{CH}_3) = \frac{2.9 \times 10^{-13} G (\cdot \text{CH}_3) \cdot D}{(\kappa_{15} + \kappa_{18} K_{18} K_{17} (O_2)^{1/2}) (\text{RCH}_3)} \quad (19)
\]

Substituting Eq.(18') in Eq.(19),

\[
\frac{2.9 \times 10^{-13} \kappa_{13} G (\cdot \text{CH}_3) \cdot D}{\kappa_1 (\kappa_{15} + \kappa_{18} K_{18} K_{17} (O_2)^{1/2}) (I^-)} \quad (19')
\]

It is reported that \(\text{CH}_3\)I species are formed by the second-order reaction

with \(I_2\) and/or \(\text{HOI}\) species\(^{(16)}\). Therefore the formation rate can be expressed by

\[
\frac{d (\text{CH}_3\text{I})}{dt} = (\kappa_{19} (I_2) + \kappa_{20} (\text{HOI})) (\cdot \text{CH}_3)
\]

\[- (\kappa_{21} (H) + \kappa_{22} (\text{e}_-e^-)) (\text{CH}_3\text{I}) \quad (20)
\]

Because a steady state can be assumed to \(\text{CH}_3\)I formation at an exposure of

10 Kgy/h for one hour, the equilibrium concentration will be given by

\[
(\text{CH}_3\text{I}) = \frac{(\kappa_{19} (I_2) + \kappa_{20} (\text{HOI}))}{\kappa_{21} (H) + \kappa_{22} (\text{e}_-e^-)} (\cdot \text{CH}_3) \quad (21)
\]

And also assuming a steady state to the formation of reductants such as \(\text{e}_-e^-\) and \(H\) atom, the denominator of Eq.(21), i.e., the reducing rate of \(\text{CH}_3\)I
can be rewritten by
\[
\kappa_{21} \left[ \text{H} \right] + \kappa_{22} \left[ \text{e}^- \right] \\
= \frac{2.9 \times 10^{-13} \kappa_{21} \text{G} \left( \text{H} \right) \cdot D}{\kappa_{25} \left[ \text{OH}^- \right] + \kappa_{26} \left[ \text{O}_2 \right] + \kappa_{27} \left[ \text{H}_2\text{O}_2 \right]} \left\{ 1 + \left( \frac{\kappa_{22}}{\kappa_{21}} \right) \frac{K_{28}}{\left[ \text{H}^+ \right]} \right\} 
\]
(22)

where \( \kappa_{25} = 2.1 \times 10^7 \quad (\text{dm}^3/\text{mol sec})^{(12)} \)
\( \kappa_{26} = 1.3 \times 10^{10} \quad (\text{dm}^3/\text{mol sec})^{(12)} \)
\( \kappa_{27} = 9 \times 10^7 \quad (\text{dm}^3/\text{mol sec})^{(12)} \)

\( K_{28} = \frac{\left[ \text{H}^+ \right] \left[ \text{e}^- \right]}{[\text{H}]} = 1.8 \times 10^{-11} \quad \text{mol/dm}^3 \text{ at } 25^\circ \text{C}^{(21)} \)
(23)

From the above rate coefficients, Eq.(22) will be approximated by
\[
\approx 2.9 \times 10^{-13} \cdot \text{D} \left( \frac{\kappa_{21}}{\kappa_{26}} \right) \frac{\text{G} \left( \text{H} \right)}{\text{G} \left( \text{H} \right)} \left\{ 1 + \left( \frac{\kappa_{22}}{\kappa_{21}} \right) \frac{K_{28}}{\left[ \text{H}^+ \right]} \right\} 
\]
(22')

Substituting Eqs.(11), (19') and (22') in Eq.(21),
\[
\left[ \text{CH}_3\text{I} \right] = \Phi \cdot \frac{\text{G} \left( \text{OH} \right)}{\text{G} \left( \text{H} \right)} \left\{ 1 + \left( \frac{\kappa_{22}}{\kappa_{21}} \right) \frac{K_{28}}{\left[ \text{H}^+ \right]} \right\}^{-1} \\
\times \Psi \cdot \frac{\left[ \text{I}^- \right]}{\left[ \text{I}^- \right]} \quad 
\]
(24)

where \( \Phi = \frac{\kappa_{10} \kappa_{26} \left[ \text{O}_2 \right]}{\kappa_{21} \left( \kappa_{15} + \kappa_{18} \kappa_{17} \left[ \text{O}_2 \right] \right)^{1/2}} \)
(25)

\[ \Psi = \frac{K_5 \left( \left[ \text{I}^- \right] + K_6 \left( \frac{\kappa_{26}}{\kappa_{18}} \right) \left[ \text{OH}^- \right] \right)}{\left( 2 K_6 + 3 \left[ \text{I}^- \right] \right) \left[ \text{I}^- \right] + K_6 K_5 \left[ \text{OH}^- \right]} \]
(26)

The first term in the right side of Eq.(24) indicates a redox potential of the irradiation system. And the second is approximately the yield of I_{ox} forms.

The utilization of organic additives for CH_3I formation can be expressed by Eq.(24).
\[
\frac{\left[ \text{CH}_3\text{I} \right]}{\left[ \text{RCH}_3 \right]} = \Phi \cdot \frac{\text{G} \left( \text{OH} \right)}{\text{G} \left( \text{H} \right)} \left\{ 1 + \left( \frac{\kappa_{22}}{\kappa_{21}} \right) \frac{K_{28}}{\left[ \text{H}^+ \right]} \right\}^{-1} \\
\times \frac{\Psi}{\left[ \text{RCH}_3 \right]} \cdot \frac{\left[ \text{I}^- \right]}{\left[ \text{I}^- \right]} 
\]
(27)

As is obvious from the above equation, the utilization of organic additive is inversely proportion to the initial organic concentration and also nearly in proportion to the yield of I_{ox} forms. This equation may explain very well the measured utilizations of organic additives shown in Fig.7. These facts suggest that CH_3I may be formed by the pseudo-first order reaction with I_{ox} forms, i.e., the CH_3I concentration formed may be
independent of those of organic additives.

The yield of CH₃I formation also can be expressed by

\[
\frac{[\text{CH}_3\text{I}]}{[\text{I}^-]} = \Phi \cdot \frac{G(\text{OH})}{G(\text{H})} \left[ 1 + \left( \frac{\kappa_{2\text{a}}}{\kappa_{2\text{a}}'} \right) \frac{K_{2\text{b}}}{[\text{H}^+]} \right]^{-1} \\
\times \Psi \cdot \frac{\left( \frac{[\text{I}_{\text{ox}}]}{[\text{I}^-][\text{I}^-]} \right)}{[\text{I}^-]
\]

(28)

The second term indicates approximately the redox potential of I_{ox} forms/iodide system which has a fixed value at 25 °C. Therefore the CH₃I yield may be a nearly constant value which corresponds to both redox potentials of the irradiation and the iodine/iodide systems. This equation also explains very well the measured CH₃I yields shown in Fig.8.

5. Conclusion

From results of batch tests, the following conclusive remarks are derived on the radiation-induced formations of I_{ox} forms, iodate and methyl iodide species;

1. The mechanism and the rate coefficients will be considered to be established theoretically, at least 25 °C, on radiation-induced reaction of I_{ox} formation from aqueous I⁻ solution.

2. The empirical calculations of I_{ox} yield explain very well the measurements in an Iₐ⁻ concentration above 10⁻² mol/dm³, although radiation-induced oxidation of HOI is assumed to be in the rate determining step of I_{ox} formation.

3. In an Iₐ⁻ concentration below 10⁻⁵ mol/dm³, IO₃⁻ species is formed in higher yields. But the formation mechanism has not been characterized enough yet.

4. The utilization of organic additives for CH₃I formation may be independent of the chemical properties of organic additives such as types and forms.

5. The CH₃I yields may depend on redox potentials of γ-irradiation and the iodine/iodide systems, independent of concentrations of initial iodide and organic additive.

6. The following simple reaction sequence may be proposed for formations of volatile iodine species by using overall rate constants.

\[
\text{I}^- \xrightarrow{\kappa_1} \text{[Ox]} \quad (\text{I}_2 \quad \overset{\kappa_2}{\xrightarrow{[\text{OH}^-]}} \text{HOI}) \quad \overset{\kappa_3}{\xrightarrow{[\text{Ox}']}} \text{IO}_3^- \\
\overset{\kappa_1'}{\xrightarrow{[\text{Re}']}} \text{[Re']} \quad \overset{\kappa_2'}{\xrightarrow{[\text{I}^-]}} \text{[Re']} \quad \overset{\kappa_3'}{\xrightarrow{[\text{Re}''']}} \text{RI} \\
\]

RI \quad \overset{\kappa_5}{\xrightarrow{[\text{Re}''']}} \text{I}^-
6. Reference

(1) R.A.Lorenz, et al., Fission Product Release from High Irradiation LWR Fuel Heat to 1300 \textdegree{} 1600 \textdegree{}C in Steam, NUREG/CR1396, 1976


(3) Analysis and Evaluation of Crystal River-Unit 3 Incident, NSAC-3/INPO-1, EPRI, 1980


Fig. 1-2 Schematic Radio-Touch chromatography for the identification of $^{133}I$ species.

Fig. 1-1 Schematic Radio-Gas chromatography for the identification of organic iodide forms.
Fig. 2 Percent Yield of $I_{0x}$ forms
As a Function of Solution pH

Fig. 3 Percent Yield of $IO_3^-$ Formation
As a Function of Initial Iodide Concentration
Fig. 5: Effect of CH₃COO⁻ Addition on I⁻⁻⁻ Yields.

Fig. 4: Effect of Solution pH on I⁻⁻⁻ Yields.

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Fig. 6 Utilization of CH₃COOH Additive for CH₃I Formation

Fig. 7 Utilizations of Organic Additives for CH₃I Formation

Fig. 8 Percent Yields of CH₃I Formation As a Function of Initial Iodide Concentration
DISCUSSION

Evans
1) Did you plot your results against initial or final pH?
2) Since the yield of I_{2x} depended on initial iodine concentration, why is the same not true for the yield of CH_{3}I.

Naritomi
1) Plots are the yields in final pH.
2) CH_{3}I concentration depends on I_{2x} yield. Therefore the CH_{3}I yield is in nearly proportion to the redox potential of I_{2x}/iodide system, taking a constant value at 25°C.

Sims
Was your solution aerated or deaerated?

Naritomi
It was initially deaerated, but O_{2} is formed during irradiation.
2.3 STUDIES ON FORMATION AND TRANSPORT OF VOLATILE IODINE SPECIES IN RADIATION FIELD

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Abstract

In a late stage of a severe LWR accident, volatile iodine species are mainly formed by radiation-induced reactions in the water pool of reactor containment, and will be transported by natural and/or forced convection through gas/liquid interface into the gas phase, and then to the environment. The prediction of formation and transport models are examined in a late stage of a severe LWR accident. In order to direct our efforts to elucidate physical effects of natural and/or forced convection conditions on formation and transport of volatile iodine species, the test programs with a dynamic flow type VITA (Volatile Iodine Test Apparatus) system are in progress in JAERI.
1. Introduction

In a severe accident of a light water nuclear reactor (LWR), it will be expected that most of fission product iodine from the damaged fuels are released in the atmosphere of H$_2$/H$_2$O mixtures in the reactor vessel, chemical form of the iodine is non-volatile such as CsI which is easily dissolved in water to form I$^-$ ion species. In a post-accident, therefore, most of the iodine will be retained in the water pool of reactor containment. Although aqueous and/or thermal chemistry of inorganic and organic iodine have been fairly well understood by lots of researches, there are still remaining unsolved many problems such as radiation-induced formation of volatile iodine species and their revolatilization from the aqueous iodide solution ($^{11-22}$).

From results of batch tests under $^{60}$Co $\gamma$-rays irradiation ($^{33}$), the following simple reaction sequence was expected for radiation-induced formations of volatile iodine species (I$_2$, CH$_3$I and so on).

$$I^- \xrightarrow{\kappa_1 (\text{Ox})} I_2 \xrightarrow{\kappa_2 (\text{OH}^-)} \text{HOI} \xrightarrow{\kappa_3 (\text{Ox}')^+} IO_3^-$$

$$\kappa_4 (\text{R}^-) \xrightarrow{\kappa_5 (\text{Re}'^+)} I^-$$

where $\kappa_1 (\text{Ox})$ is overall rate constant for oxidation of I$^-$ ion species with radiation-induced oxidant and/or dissolved oxygen,

$\kappa_1' (\text{Re})$ is overall rate constant for reduction of I$_2$ and/or HOI with radiation-induced reductants,

$\kappa_2 (\text{OH}^-)$ is rate constant for base-catalytic hydrolysis of I$_2$ to form HOI,

$\kappa_2' (\text{I}^-)$ is rate constant for reducing HOI with I$^-$,

$\kappa_3 (\text{Ox}')$ is overall rate constant for oxidizing HOI to form IO$_3^-$ with radiation-induced oxidants,

$\kappa_3' (\text{Re}')$ is overall rate constant for reducing IO$_3^-$ with radiation-induced reductants,

$\kappa_4 (\text{R}^-)$ is overall rate constant for producing organic iodide by reaction between organic radicals and I$_2$ and/or HOI,

$\kappa_5 (\text{Re}'^+)$ is overall rate constant for decomposition of organic iodide with radiation-induced reductants and/or OH$^-$ ion.

The fate of volatile iodine species formed radiolytically in the liquid phase is the resultant of a complex array of chemical and transport degradation processes. Its prediction therefore will require knowledge of rates of their processes, at least of those which are dominant in the
Thus assuming an averaged concentration in the gaseous convection space to \((C_o')\), and also the space volume based on the liquid compositions to \(V_o\), the formation rate will be related by the following mass balance.

\[
\int \dot{m} \, dt = V_o \left( C_o \right) + V_o' \left( C_o' \right)
\]  
(25)

Differentiating the above equation with respect to time,

\[
\dot{m} = V_o \frac{d \left( C_o \right)}{dt} + V_o' \frac{d \left( C_o' \right)}{dt}
\]  
(26)

And also the following relation will be obtained for the mass balance in the gas phase based on the liquid compositions.

\[
\frac{V_o}{K_1} \left[ C_o \right] = V_o \left( C_o \right) + V_o' \left( C_o' \right), \text{ Thus}
\]

\[
\left[ C_o' \right] = \left( C_o \right) + \left( \frac{V_o'}{V_o} \right) \left( C_o' \right)
\]  
(27)

Substituting Eqs. (26) and (27) in Eq. (23) and also Eq. (27) in Eq. (24),

\[
\frac{1}{R_1 + R_2} \left\{ \int \dot{m} \, dt - \left( K_1 + \frac{V_o}{V_o'} \right) \left( C_o \right) - \left( \frac{K_1}{V_o} + \frac{1}{V_o'} \right) V_o' \left( C_o' \right) \right\}
\]

\[
= V_o \frac{d \left( C_o \right)}{dt} + V_o' \frac{d \left( C_o' \right)}{dt}
\]  
(28)

\[
\frac{1}{R_3} \left[ C_o' \right] = \left( \frac{1}{r_4} + \frac{1}{r_5} \right) \left( C_o \right) + V_o \frac{d \left( C_o \right)}{dt}
\]  
(29)

where \(R_3' = R_3 \left( \frac{V_o}{V_o'} \right)\)  
(29')

Solving the simultaneous equations (28) and (29) with respect to \([C_o]\),

\[
\frac{d^2 \left( C_o \right)}{dt^2} + \left( \alpha + \xi \right) \frac{d \left( C_o \right)}{dt} + \alpha \cdot \xi \left( C_o \right)
\]

\[
= \frac{\int \dot{m} \, dt}{R_3' (R_1 + R_2) V_o V_o' V_o}
\]  
(30)

where \(\alpha = \frac{1}{R_1 + R_2} \left( \frac{K_1}{V_o} + \frac{1}{V_o'} \right)\)  
(31)

\[\xi = \frac{1}{R_3' V_o'} + \left( \frac{1}{r_4} + \frac{1}{r_5} \right) \frac{1}{V_o}\]  
(32)

When the well mix is assumed to the bulk gas phase, the concentration of boundary layer, \((C_o')\), is equal to the bulk concentration, \((C_o)\). In this case, the mass transfer results in the expression of two film model accepted generally.
The batch test results on radiation-induced formation of volatile iodine species\(^\text{a}\) suggested that (1) I\(_2\) and HOI species reacted rapidly each other to be in the pseudo-equilibrium state. (2) the radiation-induced oxidation of HOI was in the rate-determining step of formation of oxidized iodine such as I\(_2\) and HOI. (3) only inorganic iodine reactions could be separated from the reaction sequence (1) because the formation of organic iodide species was minor.

Using mixture of I\(_2\) and HOI species to IO\(_x\) forms, the rates of inorganic iodine reactions will be expressed by the following differential equations:

\[
\begin{align*}
\frac{d [ I^- ]}{dt} &= \kappa_1 [ \text{Ox} ] [ I^- ] - \kappa_1' [ \text{Re} ] [ \text{IO}_x ] \quad (33) \\
\frac{d [ \text{IO}_x ]}{dt} &= \kappa_1 [ \text{Ox} ] [ I^- ] + \kappa_3 [ \text{Re}' ] [ \text{IO}_3^- ] \\
&\quad - ( \kappa_1' [ \text{Re} ] + \kappa_3 [ \text{Ox}' ] ) [ \text{IO}_x ] \quad (34) \\
\frac{d [ \text{IO}_3^- ]}{dt} &= \kappa_3 [ \text{Ox}' ] [ \text{IO}_x ] - \kappa_3' [ \text{Re}' ] [ \text{IO}_3^- ] \quad (35) \\
[ I^- ]_0 &= [ \text{IO}_x ] + [ I^- ] + [ \text{IO}_3^- ] \quad (36)
\end{align*}
\]

where \([ \text{IO}_x ] = 2 [ I_2 ] + [ \text{HOI} ], \quad K_2 = \frac{[ \text{HOI} ] [ I^- ]}{[ \text{OH}^- ] [ I_2 ]} \quad (37)\]

The batch tests\(^\text{a}\) also represented for an initial iodide concentration above \(10^{-5} \text{ mol/dm}^3\) that the formation of IO\(_3^-\) species might be ignore and the concentration of IO\(_x\) forms produced was \(10^{-6} \text{ mol/dm}^3\) or less. Therefore it may be assumed that \([ I^- ] \cong [ I^- ]_0\) at an initial iodide concentration above \(10^{-5} \text{ mol/dm}^3\). In this case, the overall rate constant of IO\(_x\) oxidation may be approximated by

\[
\kappa_3 [ \text{Ox}' ] = \frac{\kappa_3 K_2 [ \text{Ox}' ] [ \text{OH}^- ]}{2 [ I^- ]_0 + K_2 [ \text{OH}^- ]} \quad (38)
\]

Solving the differential equations (33) \(-\) (35) using the mass balance of Eq.(36), the concentration of IO\(_x\) forms will be expressed by

\[
[ \text{IO}_x ] = \frac{\int \dot{m} \, dt}{V \cdot \psi} = \kappa_1 \cdot \kappa_3' \cdot [ \text{Ox} ] \cdot [ \text{Re}' ] \cdot [ I^- ]_0
\]

\[
\times \left\{ 1 - \frac{\gamma_2 + \psi / \kappa_3' [ \text{Re}' ]}{\gamma_2 - \gamma_1} \exp( \gamma_1 t ) \right. \\
\left. + \frac{\gamma_1 + \psi / \kappa_3' [ \text{Re}' ]}{\gamma_2 - \gamma_1} \exp( \gamma_2 t ) \right\} \quad (39)
\]

where \(\gamma_1 = -\phi + ( \phi^2 - \psi )^{1/2}, \quad \gamma_2 = -\phi - ( \phi^2 - \psi )^{1/2}\) \quad (40)
\[ 2 \phi = \kappa \cdot [\text{Ox}] + \kappa' \cdot [\text{Re}] + \kappa_{3}' \cdot [\text{Re}'] \]
\[ + \frac{\kappa \cdot \kappa_{2} \cdot [\text{Ox}'] \cdot [\text{OH}^{-}]}{2 [\text{I}^{-}] \circ + \kappa_{2} \cdot [\text{OH}^{-}]} \]  \hspace{1cm} (41)

\[ \psi = \kappa \cdot \kappa_{3}' \cdot [\text{Ox}] \cdot [\text{Re}'] + \kappa' \cdot \kappa_{3}' \cdot [\text{Re}] \cdot [\text{Re}'] \]
\[ + \frac{\kappa \cdot \kappa_{3} \cdot \kappa_{2} \cdot [\text{Ox}] \cdot [\text{Ox}'] \cdot [\text{OH}^{-}]}{2 [\text{I}^{-}] \circ + \kappa_{2} \cdot [\text{OH}^{-}]} \]  \hspace{1cm} (42)

I\text{ Ox} forms are probably a source of I\text{2} release from the aqueous I\text{-} solution because I\text{3}^{-}, I\text{2}^{-} and HOI react rapidly each other to be in the pseudo-equilibrium state. Substituting Eq.(39) in Eq.(30) and then solving it to \([ C_{o} ]\), the concentration of I\text{2} species from the aqueous solution will be given by

\[ [ C_{o} ] = \frac{(\kappa \cdot \kappa_{3}' \cdot [\text{Ox}] \cdot [\text{Re}'] / \psi) \cdot [\text{I}^{-}] \circ}{(1 + \frac{K_{1} \cdot V_{t}}{V_{o}}) \{1 + R_{3} \left( \frac{1}{r_{a}} + \frac{1}{r_{b}} \right)\}} \]

\[ \times \left[ \left\{ 1 - \frac{\alpha \cdot \xi}{\gamma_{z} - \gamma_{s}} \right\} \left( \frac{\psi \cdot \kappa_{3}' \cdot [\text{Re}']}{(\gamma_{s} + \alpha) \cdot (\gamma_{s} + \xi)} - \frac{\psi}{(\gamma_{z} + \alpha) \cdot (\gamma_{z} + \xi)} \right) \right. \]
\[ \left. \times \left\{ 1 - \exp(-\alpha \cdot t) - \frac{\alpha}{\xi - \alpha} \left( \exp(-\alpha \cdot t) - \exp(-\xi \cdot t) \right) \right\} \right] \]

\[ + \frac{\alpha \cdot \xi}{\gamma_{z} - \gamma_{s}} \left\{ \frac{\gamma_{z} + \psi \cdot \kappa_{3}' \cdot [\text{Re}']}{(\gamma_{s} + \alpha) \cdot (\gamma_{s} + \xi)} \right. \]
\[ \left. \times \left\{ 1 - \exp(\gamma_{s} \cdot t) \right\} \right\} \]
\[ \times \left\{ \frac{1}{(\gamma_{z} + \alpha) \cdot (\gamma_{z} + \xi)} \right\} \]  \hspace{1cm} (43)

As described previously, reactions of organic iodide formation will treat separately from the reaction sequence (1) because the formation of organic iodide species is minor. In this case, the rate of organic iodide formation can be expressed by

\[ \frac{d [\text{RI}]}{dt} = \kappa_{4} \cdot [\text{R} \cdot ] \cdot [\text{I\text{ Ox}}] - \kappa_{5} \cdot [\text{Re}'' \cdot ] \cdot [\text{RI}] \]  \hspace{1cm} (44)

Substituting Eq.(39) in Eq.(44) and then solving it, the organic iodide concentration in the liquid phase will be expressed by

\[ [\text{RI}] = \frac{\int_{t}^{\infty} d t}{V_{t}} = \frac{\kappa_{1} \cdot \kappa_{3}' \cdot \kappa_{4} \cdot [\text{R} \cdot ] \cdot [\text{Ox}] \cdot [\text{Re}'] \cdot [\text{I}^{-}] \circ}{\kappa_{5} \cdot [\text{Re}'' \cdot ] \cdot \psi} \]
\[ \times \left\{ 1 + \frac{\gamma_{3} \cdot (\gamma_{z} + \psi / \kappa_{3}' \cdot [\text{Re}'])}{(\gamma_{z} - \gamma_{s}) \cdot (\gamma_{s} - \gamma_{3})} \right\} \exp(\gamma_{s} \cdot t) \]
\[
\begin{align*}
- \frac{\gamma_3 (\gamma_3 + \psi / \kappa_3 [Re')] \exp(\gamma_3 t)}{(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_3)} \\
- \frac{\gamma_3 \gamma_2 + \gamma_3 \psi / \kappa_3 [Re'] \exp(\gamma_3 t)}{(\gamma_1 - \gamma_3)(\gamma_2 - \gamma_3)}
\end{align*}
\]  

where \( \gamma_3 = -\kappa_3 \left( Re'' \right) \)

Substituting Eq. (45) in Eq. (30) and then solving it to \( (C_o) \), the concentration of organic iodide from the aqueous solution will be given by

\[
(C_o) = \frac{(\kappa_3 \kappa_3' \kappa_3 (B) (Ox) (Re') / \kappa_3 (Re'') \psi) (I^-)}{(1 + \frac{K_1 V \xi}{V_o}) \{1 + R_3 \left( \frac{1}{r_4} + \frac{1}{r_5} \right) \} \\
\alpha \cdot \xi \gamma_3 \left( \gamma_3 + \psi / \kappa_3' [Re'] \right) \\
(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_3)(\gamma_1 + \alpha)(\gamma_1 + \xi) \\
\alpha \cdot \xi \gamma_3 \left( \gamma_1 + \psi / \kappa_3' [Re'] \right) \\
(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_3)(\gamma_2 + \alpha)(\gamma_2 + \xi) \\
\alpha \cdot \xi \left( \gamma_3 + \gamma_3 + \psi / \kappa_3' [Re'] \right) \\
(\gamma_1 - \gamma_3)(\gamma_2 - \gamma_3)(\gamma_3 + \alpha)(\gamma_3 + \xi) \\
\times \{1 - \exp(-\alpha t) - \frac{\alpha}{\xi - \alpha} (\exp(-\alpha t) - \exp(-\xi t))\} \\
- \frac{\alpha \cdot \xi \gamma_3 (\gamma_2 + \psi / \kappa_3' [Re']) \{1 - \exp(\gamma_3 t)\}}{(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_3)(\gamma_2 + \alpha)(\gamma_2 + \xi)} \\
+ \frac{\alpha \cdot \xi \gamma_3 (\gamma_1 + \psi / \kappa_3' [Re']) \{1 - \exp(\gamma_2 t)\}}{(\gamma_2 - \gamma_1)(\gamma_2 - \gamma_3)(\gamma_2 + \alpha)(\gamma_2 + \xi)} \\
\times \{1 - \exp(\gamma_3 t)\}
\]

(46)

Substituting Eq. (3) in Eq. (2) and then the result obtained in Eq. (31), the rate constant, \( \alpha \), in Eq. (31) can be rewritten by

\[
\alpha = \frac{\beta \kappa_3 \kappa_3 \kappa_3 A}{\kappa_3 + \beta K_1 \kappa_3} \left( \frac{K_1}{V_o} + \frac{1}{V_l} \right) 
\]

(47)

It is estimated for the same friction velocity that \( \kappa_3 \gg \beta K_1 \kappa_3 \) for \( CH_3I \) and \( \kappa_3 < \beta K_1 \kappa_3 \) for \( I_2 \) because \( \beta \sim 1 \) for \( CH_3I \) and \( \beta > 1 \) for \( I_2 \) and also \( K_1 = 2.86 \) for \( CH_3I \) and \( K_1 = 65.4 \) for \( I_2 \) at 25°C. Therefore Eq. (47) may be rewritten approximately under conditions of a severe accident;

\[
= \beta \kappa_3 A \left( \frac{K_1}{V_o} + \frac{1}{V_l} \right) \text{ for } CH_3I
\]

(47')
\[ (\alpha_{\text{eq}}/K_1) A \left( \frac{K_1}{V_\alpha} + \frac{1}{V_t} \right) \text{ for } I_2 \]  

(47")

As is obvious from the above equations, the rate constant, \( \alpha \), is in proportion to sum of reciprocal of gas and liquid volumes based on the liquid phase compositions and also to the product of mass transfer coefficient and area of liquid/gas interface. The mass transfer coefficient may be represented approximately by \( \beta \, \alpha \) for CH₃I and by \( \alpha_{\text{eq}}/K_1 \) for I₂.

Substituting Eqs.(29') and (17) in Eq.(32), the rate constant, \( \xi \), in Eq.(32) can be rewritten by

\[ \xi = \frac{\kappa_{\text{eq}} A}{V_\alpha} + \left( \frac{1}{r_\text{eq}} + \frac{1}{r_\text{e}} \right) \frac{1}{V_\alpha} \]  

(48)

The rate constant, \( \xi \), is sum of those due to dispersion, wall deposition and leakage. The rate constant, \( \xi \), to the dispersion is in proportion to the product of dispersion coefficient and area of liquid/gas interface and also inversely proportion to gas phase volume. The dispersion coefficient due to natural convection were calculated by using Eqs.(18), (19) and (20). Fig.2 shows the calculated dispersion coefficients of Kr, I₂ and CH₃I as a function of temperature difference between wall and bulk gas with bulk gas temperature as parameters. As is obvious from this figure, the dispersion coefficient depends remarkably on the temperature difference between bulk gas and wall rather than the bulk temperature.

For an example, the rate constants, \( \alpha \) and \( \xi \), were estimated for the recoveries of CH₃I and I₂ after \(^{85}\text{Kr} \) venting of the TMI-2 reactor containment \(^{(17)} \), in which the thermohydraulics was estimated by the measurements of \(^{85}\text{Kr} \) recovery;

\[ \alpha = 1.53 \times 10^{-6} \text{ sec}^{-1} \left( = 0.132 \text{ day}^{-1} \right) \text{ for CH₃I and} \]

\[ = 3.95 \times 10^{-5} \text{ sec}^{-1} \left( = 3.41 \text{ day}^{-1} \right) \text{ for I₂} \]

\[ \xi = 4.91 \times 10^{-5} \text{ sec}^{-1} \left( = 0.424 \text{ day}^{-1} \right) \text{ for CH₃I and I₂.} \]

The following parameter values were used for the estimation of the above rate constants, \( \alpha \) and \( \xi \), and also natural convection was assumed;

\[ V_\alpha = 5.58 \times 10^{10} \text{cm}^3, \ V_t = 2.24 \times 10^8 \text{cm}^3, \ A = 9.2 \times 10^6 \text{cm}^2, \ K_1 = 2.86 \text{ for CH₃I, 65.4 for I₂, T = 26^\circ \text{C, pH = 8.5 and [I}^-] = 2.33 \times 10^{-7} \text{mol/dm}^3.} \]

Details of the parameter values will be referred in other paper.

Fig.3 shows the recoveries of CH₃I and I₂ as a function of time after \(^{85}\text{Kr} \) venting, in which a newly equilibrium concentration expected from the measurements of each species was used. The above rate constants explained
very well the recovery features of CH₃I and I₂ after ¹³¹Kr venting.

In a late stage of a severe LWR accident, therefore, a long term release of radiiodine may be considered to occur due to the natural convection. This examination suggests for natural convection that physical rate constants, α and ξ, are much less than chemical ones, γ₁, γ₂ and γ₃, resulting in the rate determining step of volatile iodine release. In this case, the concentration in the vessel will be expressed approximately by

\[
(C_{o}) = \frac{\Phi \cdot (I^-)_{o}}{(1 + \frac{K_1 V t}{V_o}) \{1 + R_3 \left( \frac{1}{r_s} + \frac{1}{r_o} \right) \} \times \{1 - \exp(-\alpha \ t) - \frac{\alpha}{\xi - \alpha} (\exp(-\alpha \ t) - \exp(-\xi \ t)) \}}
\]

(49)

where \(\Phi = \kappa : \kappa^{s'}(o_x)(Re') / \psi\) for I₂ release,

\(= \kappa : \kappa^{s'}(R *) (Ox) (Re'') / \kappa \circ (Re'') \psi\)

for organic iodide release.

As is obvious from Eq.(49), the physical and chemical processes are independent. The chemical effects contribute only to the concentration of volatile iodine species formed radiolytically and/or chemically in the aqueous solution, and the physical effects contribute only to the transport of volatile iodine species. Both processes may be treated separately for predicting the release of volatile iodine species.

In a forced convection condition, however, the chemical effects on the release of volatile iodine species may not be able to ignore because the physical mass transfer rate coefficients, α and ξ, increase relatively, resulting in the increase of chemical contribution to the release. In these cases, the concentration of I₂ and organic iodide species released from the aqueous solution may be estimated by Eqs.(43) and (46), respectively.

The above examinations suggest that a long term release of radiiodine may be governed by the natural and/or forced convection conditions following a severe LWR accident. In JAERI, therefore, the test programs with a dynamic flow type VITA (Volatile Iodine Test Apparatus) system are in progress for making efforts to elucidate the effectiveness of natural and/or forced convection conditions on the transport of volatile iodine species formed radiolytically.
3. VITA system

The VITA system is a small-scale apparatus designed to test the effectiveness of gas flow conditions on the formation and transport of volatile iodine species such as I$_2$ and organic iodide from the aqueous solution. It consists of about one litter of a main vessel (100mm $\phi \times 136$mm in high), made of pyrex glass, and two auxiliary loops as shown in Fig.4. The main vessel is placed in the GammaCell-220(Fig.5) with 430 TBq(11,630 Ci) in $^{60}$Co radioactivity, in which the maximum 800 ml of test solution can be filled. The solution is irradiated uniformly at an absorbed dose of about 10 kGy/h(10$^6$ rad/h). And also it can be heated by hot-water jacket system, resulting in the controlled temperature from ambient to 80 °C.

The aqueous loop provides for mixing the test solution and for on-line measurements of solution pH, redox potential(ORP), dissolved oxygen concentration(DO) and electrical conductivity(CD). The pH and ORP are intermittently measured by sampling automatically some loop solution because the loop solution is contaminated by the sensor's electrolytic solution. Aqueous iodine samples can be randomly extracted from the loop, and then iodine forms in the samples are analyzed radiolytically by extraction and ion-chromatograph techniques. So 3.7 MBq(100 $\mu$Ci) of $^{131}$I radioactivity is added to the test solution. The loop flow can be controlled at a rate from 20 to 200 ml/min.

The gas loop has 20 litter of a cylindrical gas storage vessel (300mm $\phi \times 300$mm in high) made of pyrex glass, in which gas mixer is installed. The loop provides for recirculating the gas phase between the main vessel and the gas storage one and for measurements of airborne iodine and hydrogen gas. Sampling systems of airborne iodine and hydrogen gas are installed in the gas storage vessel. The airborne iodine sampling system consists of 6 samplers in which 5% TEDA(triethylene-diamin) impregnated charcoal are packed, and 6 samplers are sequentially operated in order during the test. The hydrogen gas monitor consists of an automatic gas sampler and gaschromatograph with Molecular sieve-13X columns. The loop flow can be controlled at a flow rate from 50 to 2000 ml/min.

The following tests are planed with the above system;
(1) Phase 1; Effects of gas flow conditions on radiation-induced formations of volatile iodine species from the aqueous iodide solution,
(2) Phase 2; Effects of H$_2$/Steam/Air mixture atmosphere on radiation-induced formations of volatile iodine species from aqueous
iodide solution,

(3) Phase 3: Effects of wall painted surface on radiation-induced formation of volatile iodine species, and so on.

Expected results

(1) The transfer model described in the section 2 may be verified through the phase one tests. In which combination between chemical and physical effects will enable the estimation of volatile iodine release in a severe accident. Especially, the transfer model will clarify a long term release in a late stage of the accident.

(2) Lots of hydrogen gas are produced in a severe accident of LWR plant. Hydrogen gas reacts easily with $\cdot$OH radical by which iodide ion species is oxidized to form volatile iodine species. Therefore existence of hydrogen gas will suppresses the formations of volatile iodine species.

(3) Wall paints are a source of organic compounds following a severe accident. The mechanism of organic iodide formations may be clarified through the phase 3 tests.

4. Reference


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Airborne Iodine at TMI-2, Source and Filtration, Proc. 16th DOE Air
Fig. 1 Transfer Model of Volatile Iodine Species Formed Radiolytically from Aqueous Iodide Solution
Fig. 2 Mass transfer coefficients of Kr, I₂ and CH₃I to natural convection as a function of temperature difference between bulk and wall surface.

\[ k = 0.13 \frac{D_g}{l_{eff}} (Gr \cdot Sc)^{1/3} \]
Fig. 3 Recoveries of I$_2$ and CH$_3$I after $^{85}$Kr venting in the TMI-2
Fig. 4 New designed VITA (Volatile Iodine Test Apparatus) system
Fig. 5 GammaCell-220
DISCUSSION

Heuber
One of the objections of the VITA experiment seems to be the validation of a mass transfer model between the water and the gas phase. What do you think about the extrapolation of the results at the reactor scale?

Naritomi
A purpose of the VITA experiments is to elucidate effect of gas flow condition on radiation-induced formation of volatile iodine species and hydrogen gas. If the effect is small, the amount of volatile iodine formation may be estimated by redox potentials of the $\beta\gamma$-irradiation and the iodine/iodide systems, and also the release may be estimated by the mass transfer model for natural convection. I think that verification of the transfer model should be performed by chemical inert tracer such as Kr and Xe gases in other engineering scale system.

Ritzman
Do you expect to apply your mass transfer model to the RTF experiments done at AECL-Whiteshell?

Soda
If he comes up with good model, that will be incorporated into a computer code and used for RTF experiment prediction.
2.4 EFFECT OF BOILING UPON RADIOLYSIS OF IODIDE SOLUTION

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ABSTRACT

The effect of void fractions on oxidation of iodide ions was examined in \( \gamma \)-radiolysis of iodide solution. All hydrogen produced by radiolysis of water transferred to gas phase at void fractions of about 1 and 10% at 293 and 373K, respectively. At these void fractions, iodide ions were oxidized to iodate ions during irradiation with iodide concentration below \( 10^{-5} \) mol/L. This indicated that the fraction of OH radicals reacted with iodide ions was increased with the void fractions, because the reactivity between OH radicals and hydrogen was decreased. Analytical model was developed based on chemical reactions and mass transfer. The reaction scheme was composed of 35 reactions for pure water system and 89 reactions for iodide solution system. The analytical model could estimate the experimental results within ±20% of experimental values.

1. INTRODUCTION

The radiolysis of water produces such as hydrogen and OH radicals. If hydrogen remained in water, it reacted with OH radicals to produce water as a final product. In iodide solution, iodide ions also react with OH radicals. So the amount of hydrogen in the solution is important to evaluate oxidation of iodide ions. In some case, hydrogen in water is transferred to gas phase by boiling. In this study, the effect of void fractions on oxidation of iodide ions was examined in the \( \gamma \)-radiolysis of iodide solution. Boiling condition was simulated by bubbling of nitrogen gas. The experimental results were compared with analytical results obtained using a model that considered chemical reactions and mass transfer between the gas and liquid phases.

2. ANALYTICAL MODEL

2.1 Iodide Species

There are thirteen valencies for iodine species in aqueous solution\(^1\). In this study, nine valencies from I(-I) to I(V) were considered to simulate change of chemical forms from iodide to iodate in radiolysis of iodide solution. Fourteen iodine species, I\(^-\), I\(_2\)\(^-\), I\(_3\)\(^-\), I, I\(_2\), IO\(^-\), HOI, IO, I\(_2\)O\(_2\), IO\(_2\)\(^-\), HI\(_2\)O, IO\(_2\), HI\(_3\)O\(_3\) and I\(_{10}\)\(_3\)\(^-\), were chosen based on the following thermal hydrolysis assuming the temperature below 200°C and pH range from 4 to 8. The considered thermal hydrolysis are reported as follows\(^1\)~\(^6\):

\[
HI = H^+ + I^- \quad K = 1.9 \times 10^9
\]
\[
\begin{align*}
\text{IO}^- + \text{I}^- + \text{H}_2\text{O} & \rightleftharpoons \text{HI}_2\text{O}^- + \text{OH}^- & K = 0.13 \\
\text{HI}_2\text{O}^- & \rightleftharpoons \text{I}_2\text{O}_2^- + \text{H}^+ & K = 3.3 \times 10^{-15} \\
\text{I}^- + \text{OH}^- & \rightleftharpoons \text{IO}^- & K = 2 \times 10^2 \\
\text{H}_2\text{IO}^+ & \rightleftharpoons \text{H}^+ + \text{HIO}^- & K = 4.3 \times 10^{-2} \\
\text{HIO}_3^- & \rightleftharpoons \text{H}^+ + \text{IO}_3^- & K = 5 \times 10^{-14} \\
\text{HIO}_3^- & \rightleftharpoons \text{H}^+ + \text{IO}_3^- & K = 0.16
\end{align*}
\]

where \( K \) is an equilibrium constant at 25°C.

Although there is no necessity to consider \( \text{IO}^- \) from the point of the thermal hydrolysis of \( \text{HIO} \) (\( K = 2.3 \times 10^{-11} \)), the reaction rate constant of hydrogen peroxide with \( \text{IO}^- \) is about \( 10^8 \) times greater than that with \( \text{HIO}_3^- \). So \( \text{IO}^- \) was included in this model. As to \( \text{I}(\text{II}) \) and \( \text{I}(\text{III}) \), all possible species were considered because of inconsistency with reaction schemes.

2.2 Reaction Scheme

The following reaction scheme was considered in this model.

Under irradiation, main oxidizer is an OH radical produced by radiolysis of water. The reactions of oxidation of iodine ions are well known as follows.

\[ \text{I}^- + \text{OH}^- \rightarrow \text{I}^- + \text{OH}^- \]  
\[ \text{I}^- + \text{I}^- \rightarrow \text{I}_2^- \]  
\[ 2\text{I}_2^- \rightarrow \text{I}_3^- + \text{I}^- \]  
\[ \text{I}_3^- = \text{I}_2^- + \text{I}^- \]  
\[ \text{I}_2^- + \text{OH}^- \rightarrow \text{HOI}^- + \text{I}^- \]  

\( \text{HOI}^- \) is considered to be produced by hydrolysis of \( \text{I}_2^- \).

There is still uncertainty in reactions for iodine species with valency of between \( \text{II} \) and \( \text{V} \). We used the oxidizing reactions proposed by Buxton9) and Burns8). Although the production reaction for \( \text{IO}_2^- \) is proposed by Burns, this reaction is excluded in this model because the calculated amount of \( \text{IO}_3^- \) is increased too much by adding this reaction.

\[ \text{I}^- + \text{O}_2 \rightarrow \text{IO}_2^- \]

Hydrogen peroxide becomes important in long term irradiation because it accumulates in water. Hydrogen peroxide reacts as either oxidizing or reducing agent depend on iodine valency as follows10).

\[ \text{I}^- + \text{H}_2\text{O}_2 \rightarrow \text{HOI}^- + \text{OH}^- \]  
\[ \text{HOI}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{H}_2\text{O} + \text{O}_2 + \text{H}^+ \]  
\[ \text{IO}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{H}_2\text{O} + \text{O}_2 \]

Aqueous electrons, which are the radiolytic products of water, are converted to \( \text{O}_2^- \) in water containing air. So reducing reactions of \( \text{O}_2^- \) ions were included in this scheme in addition to reactions of \( \text{H} \) and \( \text{H}_2\text{O}_2 \).

The reaction scheme was consisted in 124 reactions, 35 reactions for pure water system and 89 reactions for iodine system, as shown in Table 1 and 2. Mass transfer of dissolved gases from liquid phase to gas phase through bubbles was modeled as follows,

\[ 
\phi = (\varepsilon C_1 - \varepsilon^* C_0) V/S 
\]

where \( \phi \): flux of gas transferred to bubbles, \( \varepsilon \): gas release coefficient,
gas absorption coefficient C: concentrations in the liquid and gas phase, S: contact area between the gas and liquid phases and V: volume of water. A set of reaction rate equation and mass transfer rate equations was integrated numerically by calculation code SIMPONY1), which had been developed for evaluation of water conditions in BWR primary system.

3. EXPERIMENTAL

Experimental apparatus is shown in Fig. 1. Test vessel with a volume of 11 l was made of stainless steel. Quartz glass tube with a volume of 1 l was also used in experiments for low iodide concentrations to reduce the effect of impurities. Deionized water was used for making CsI solution with concentrations up to $10^{-3}$ mol/l. Mixed gas of nitrogen and oxygen was circulated and discharged from the bottom of the vessel to simulate boiling condition. The void fraction was varied by changing the flow rate of gas bubbling.

The vessel was irradiated using Co-60 γ-ray source with a dose rate of 2.0 × 10³ Gy/h. Dose rate was measured using cerium chemical dosimeter with G( Ce⁴⁺) = 2.5.

The concentration of gases was measured periodically using a gas chromatograph with a silicon grease column. The concentrations of iodide and iodate ions were determined photometrically with absorbance coefficients of $1.3 \times 10^4$ l/mol/cm at 227 nm for iodide ions and $5.1 \times 10^3$ l/mol/cm at 194 nm for iodate ions.

4. RESULTS AND DISCUSSION

In boiling condition, or bubbling condition, hydrogen and oxygen were transferred to the gas phase via bubble surface. The concentrations of these gases were increased with void fraction because of increase of bubble surface areas. Almost all hydrogen and oxygen produced by radiolysis of water transferred to the gas phase at void fractions of about 1 and 10% at 293 and 373K, respectively.

The concentrations of hydrogen and oxygen in the gas phase were increased with dose although these concentrations in the liquid phase were nearly constant, as shown in Fig. 2 and 3. This indicated that equilibrium was attained for reactions of these gases between transfer to the gas phase and reaction with OH radicals. Hydrogen and oxygen were reacted via OH radicals to form water as follows,

\begin{align*}
H_2 + OH & \rightarrow H + H_2O \\
H + O_2 & \rightarrow HO_2 \\
2HO_2 & \rightarrow H_2O_2 + O_2
\end{align*}

As the calculated results are shown in Fig. 2 and 3, the analytical model can predict the experimental results fairly well. The discrepancy at high dose was considered to be due to uncertainty of reactions related to hydrogen peroxide, since hydrogen peroxide was accumulated with dose.

The effect of initial iodide concentration on the concentrations of hydrogen and oxygen transferred to the gas phase are shown in Fig. 4. The dose and void fraction were $10^4$ Gy and 1.5%, respectively. The gaseous concentrations increased with the initial iodide concentration. The fraction of the reaction for hydrogen and OH radicals was considered to be increased with decrease of the initial iodide concentration because of
competitive reactions for OH radicals. The calculated results agreed well with the experimental results within ±20% of experimental values.

After irradiation, the amounts of iodine and iodate ions were measured photometrically. The result are shown in Fig. 5. Almost all iodide ions were converted to iodate ions below initial concentration of iodide ions of $5 \times 10^{-6} \text{ mol/L}$. The calculated result was underestimated the turning point. This might be due to reaction of iodide ions with hydrogen peroxide after irradiation. As Buxton pointed out$^9$, this was considered to be due to the shift of the equilibrium reactions. The following equilibrium reactions are shifted to the left at low concentration of iodide ions.

$$I_2 + I^- \rightarrow I_3^-$$
$$\text{HOI} + I^- \rightarrow I_2 + OH^-$$

As the result, HOI is produced to form iodate ions by further oxidation. At high concentration of iodide ions, $I_3^-$ ions are formed to back to iodide ions. The effect of boiling is considered to shift the turning point for iodate conversion. If there was no boiling, the turning point for conversion to iodate ions could decrease because the amount of oxidizer such as OH radicals would be decreased by the reaction of hydrogen and OH radicals. This indicated that iodide ions were easier to convert to iodine and hence volatile iodine was easier to convert to HOI with boiling.

5. CONCLUSION

The effect of boiling on oxidation of iodide ions was examined in $\gamma$-radiolysis of iodide solution. The following conclusions were obtained for the radiolysis of iodide solution at temperature below 200°C and pH range from 4 to 8 under boiling condition.

(1) The following equilibriums are important to determine the oxidation state of iodide ions. At high iodide concentrations, the equilibriums are shifted to the right and then iodide ions are stable in near natural solution. At low iodide concentrations, iodate ions are formed via HOI under irradiation.

$$I_2 + I^- \rightarrow I_3^-$$
$$\text{HOI} + I^- \rightarrow I_2 + OH^-$$

(2) Under boiling conditions, the turning concentration of iodide ions is about $5 \times 10^{-6} \text{ mol/L}$. This turning concentration is lowered without boiling, because the amount of OH radicals is decreased by reaction of hydrogen and OH radical. This indicates that boiling makes it easier to convert iodine to iodate ions.

(3) All hydrogen and oxygen produced by radiolysis transfer to gas phase at void fractions of about 1 and 10% at 293 and 373K, respectively.

(4) Analytical model developed based on 124 chemical reactions and mass transfer. The analytical model can estimate the oxidation state of iodide ions and the amounts of hydrogen and oxygen produced by radiolysis of iodide solution.
REFERENCES

Fig. 1 Schematic Diagram of Experimental Apparatus
Fig. 2 Concentration of Hydrogen as Function of Dose

(Initial iodide concentration: $2 \times 10^{-5}$ mol/L)

(Void fraction: 1.6%)
Fig. 3 Concentration of Oxygen as Function of Dose

(Initial iodide concentration: $2 \times 10^{-5}$ mol/L)

(Void fraction: 1.6%)
Fig. 4 Dependence of Hydrogen and Oxygen Concentration in Gas Phase on Initial Iodide Ion Concentration

(Void fraction: 1.5%)
Fig. 5 Dependence of Iodate and Iodide Concentration on Initial Iodide Concentration

(Void fraction: 1.5%)
Table 1 Reaction Scheme for Pure Water System\textsuperscript{11})

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 $2e^- + 2H_2O \rightarrow H_2 + 2OH^-$</td>
<td>$1.64 \times 10^6$</td>
</tr>
<tr>
<td>2 $e^- + H + H_2O \rightarrow H_2 + OH^-$</td>
<td>$4.5 \times 10^8$</td>
</tr>
<tr>
<td>3 $e^- + OH \rightarrow OH^-$</td>
<td>$3.0 \times 10^{10}$</td>
</tr>
<tr>
<td>4 $e^- + O_2^- + H_2O \rightarrow HO_2^- + OH^-$</td>
<td>$3.3 \times 10^6$</td>
</tr>
<tr>
<td>5 $e^- + HO_2 \rightarrow HO_2^-$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>6 $e^- + H_2O \rightarrow H + OH^-$</td>
<td>$1.6 \times 10^7$</td>
</tr>
<tr>
<td>7 $e^- + H^+ \rightarrow H$</td>
<td>$2.4 \times 10^{10}$</td>
</tr>
<tr>
<td>8 $e^- + HO_2 \rightarrow OH + OH^-$</td>
<td>$1.3 \times 10^{10}$</td>
</tr>
<tr>
<td>9 $e^- + HO_2^- + H_2O \rightarrow OH + 2OH^-$</td>
<td>$6.3 \times 10^7$</td>
</tr>
<tr>
<td>10 $e^- + O_2 \rightarrow O_2^-$</td>
<td>$1.9 \times 10^7$</td>
</tr>
<tr>
<td>11 $H + H \rightarrow H_2$</td>
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</tr>
<tr>
<td>12 $H + OH \rightarrow H_2O$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>13 $H + HO_2 \rightarrow H_2O_2$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>14 $H + O_2^- \rightarrow HO_2^-$</td>
<td>$2.0 \times 10^{10}$</td>
</tr>
<tr>
<td>15 $H + OH^- \rightarrow e^- + H_2O$</td>
<td>$2.0 \times 10^7$</td>
</tr>
<tr>
<td>16 $H + H_2O_2 \rightarrow OH + H_2O$</td>
<td>$9.0 \times 10^7$</td>
</tr>
<tr>
<td>17 $H + O_2 \rightarrow HO_2$</td>
<td>$1.9 \times 10^7$</td>
</tr>
<tr>
<td>18 $OH + OH \rightarrow H_2O_2$</td>
<td>$5.0 \times 10^{9}$</td>
</tr>
<tr>
<td>19 $OH + HO_2 \rightarrow O_2 + H_2O$</td>
<td>$1.2 \times 10^{10}$</td>
</tr>
<tr>
<td>20 $OH + O_2^- \rightarrow O_2 + OH^-$</td>
<td>$1.2 \times 10^{10}$</td>
</tr>
<tr>
<td>21 $OH + H_2 \rightarrow H + H_2O$</td>
<td>$3.4 \times 10^7$</td>
</tr>
<tr>
<td>22 $OH + H_2O_2 \rightarrow HO_2 + H_2O$</td>
<td>$2.7 \times 10^7$</td>
</tr>
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<td>23 $OH + HO_2^- \rightarrow OH^- + HO_2$</td>
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<tr>
<td>24 $HO_2 + O_2^- \rightarrow HO_2^- + O_2$</td>
<td>$1.5 \times 10^7$</td>
</tr>
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<td>25 $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$</td>
<td>$2.7 \times 10^6$</td>
</tr>
<tr>
<td>26 $H^+ + O_2^- \rightarrow H_2O_2$</td>
<td>$5.0 \times 10^{10}$</td>
</tr>
<tr>
<td>27 $HO_2^- \rightarrow H^+ + O_2^-$</td>
<td>$8.0 \times 10^5$</td>
</tr>
<tr>
<td>28 $H^+ + OH^- \rightarrow H_2O$</td>
<td>$1.44 \times 10^{11}$</td>
</tr>
<tr>
<td>29 $H_2O \rightarrow H^+ + OH^-$</td>
<td>(\star)</td>
</tr>
<tr>
<td>30 $OH^- + H_2O_2 \rightarrow HO_2^- + H_2O$</td>
<td>$1.0 \times 10^8$</td>
</tr>
<tr>
<td>31 $H_2O + HO_2^- \rightarrow OH^- + H_2O_2$</td>
<td>$1.022 \times 10^4$</td>
</tr>
<tr>
<td>32 $H^+ + HO_2^- \rightarrow H_2O_2$</td>
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</tr>
<tr>
<td>33 $H_2O_2 \rightarrow H^+ + HO_2^-$</td>
<td>$3.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>34 $H_2O_2 \rightarrow OH + OH$</td>
<td>$7.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>35 $2O_2^- + 2H_2O \rightarrow O_2 + H_2O_2 + 2OH^-$</td>
<td>$5.6 \times 10^3$</td>
</tr>
</tbody>
</table>

\(1\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\) for second order reaction, at 25°C

\(\star\) Calculated with equilibrium constant
### Table 2 Reaction Scheme for Iodine System

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant *</th>
</tr>
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<tr>
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<tr>
<td>$I^- + OH$ $\rightarrow$ $I^- + OH^-$</td>
<td>$1.5 \times 10^{10}$</td>
</tr>
<tr>
<td>$I^- + H_2O_2$ $\rightarrow$ $HOI + OH^-$</td>
<td>$1.1 \times 10^{-2}$</td>
</tr>
<tr>
<td>$I^- + H + H^+$ $\rightarrow$ $I^- + H_2$</td>
<td>$5.3 \times 10^{6}$</td>
</tr>
<tr>
<td>$I^- + O^2^- + H_2O$ $\rightarrow$ $I^- + 2OH^-$</td>
<td>$4.7 \times 10^{7}$</td>
</tr>
<tr>
<td>$I_2^-$ $\rightarrow$ $I^- + I^-$</td>
<td>$1.0 \times 10^{5}$</td>
</tr>
<tr>
<td>$I_2^- + e^-$ $\rightarrow$ $2I^-$</td>
<td>$1.3 \times 10^{10}$</td>
</tr>
<tr>
<td>$I_2^- + H$ $\rightarrow$ $2I^- + H^+$</td>
<td>$1.0 \times 10^{6}$</td>
</tr>
<tr>
<td>$I_2^- + O_2^-$</td>
<td>$7.5 \times 10^{8}$</td>
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<td>$I_2^- + OH$ $\rightarrow$ $I_2 + OH^-$</td>
<td>$3.8 \times 10^{10}$</td>
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<td>$4.0 \times 10^{9}$</td>
</tr>
<tr>
<td>$I_2^- + H_2O_2$ $\rightarrow$ $2I^- + HO_2^- + H^+$</td>
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<td>$2I_2^-$ $\rightarrow$ $I^- + I_3^-$</td>
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</tr>
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<td>$I_2^- + H^+ + O_2$ $\rightarrow$ $I_2 + HO_2$</td>
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<td>$I_2^- + H$ $\rightarrow$ $I^- + H^+$</td>
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<td>$I + H_2O_2$ $\rightarrow$ $I^- + H^+ + HO_2$</td>
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<td>$I + I^-$ $\rightarrow$ $I_2^-$</td>
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<td>$2I$ $\rightarrow$ $I_2$</td>
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<td>$IO^- + e^- + H_2O$ $\rightarrow$ $I^- + 2OH^-$</td>
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<td>Reaction</td>
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<td>41</td>
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<td>64</td>
<td>IO₂⁻ + e⁻</td>
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<tr>
<td>65</td>
<td>IO₂⁻ + H⁺</td>
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<tr>
<td>66</td>
<td>IO₂⁻ + OH</td>
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<tr>
<td>67</td>
<td>IO₂⁻ + HO₂</td>
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<tr>
<td>68</td>
<td>IO₂⁻ + H₂O₂</td>
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<tr>
<td>69</td>
<td>IO₂⁻ + O₂⁻</td>
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<tr>
<td>70</td>
<td>IO⁻ + IO⁻</td>
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<tr>
<td>71</td>
<td>IO⁻ + HOI</td>
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<tr>
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<td>IO⁻ + IO</td>
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<td>HIO₂</td>
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<td>80</td>
<td>IO₂ + OH</td>
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<tr>
<td></td>
<td>Reaction</td>
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</tr>
<tr>
<td>81</td>
<td>( IO_2 + H_2O \rightarrow HIO_3^- + H^+ )</td>
</tr>
<tr>
<td>82</td>
<td>( IO_2 + H_2O_2 \rightarrow IO_3^- + H^+ + OH )</td>
</tr>
<tr>
<td>83</td>
<td>( IO_2 + I^- \rightarrow I_2 + O_2^- )</td>
</tr>
<tr>
<td>84</td>
<td>( IO_2 + I^- + H^+ \rightarrow IO + HOI )</td>
</tr>
<tr>
<td>85</td>
<td>( 2IO_2 + H_2O \rightarrow IO_3^- + HIO_2 + H^+ )</td>
</tr>
<tr>
<td>86</td>
<td>( 2HIO_3^- \rightarrow IO_3^- + HIO_2 + OH^- )</td>
</tr>
<tr>
<td>87</td>
<td>( IO_3^- + H \rightarrow HIO_3^- )</td>
</tr>
<tr>
<td>88</td>
<td>( IO_3^- + H^+ + OH \rightarrow IO_2 + H_2O_2 )</td>
</tr>
<tr>
<td>89</td>
<td>( IO_3^- + I^- + H^+ \rightarrow IO_2^- + HOI )</td>
</tr>
</tbody>
</table>

* (1·mol\(^{-1} \cdot \text{s}^{-1}) for second order reaction, at 25°C*
DISCUSSION

Sims
What was the pH of your solution.

Karasawa
There were no additives, so pH 6-7.

Ishigure
Did you do any calculation of the chemistry at 100°C? We don't have enough data base on the rate constant at high temperature especially for the reactions including the iodine species.

Karasawa
No, I didn't. This calculation was done at 25°C. We don't have activation energies for some iodine reactions.

Vikis
I agree with your decision not to consider the reaction of I+O2 -> IO2. For certain cases, the reaction does not occur in the gas phase. Is there experimental evidence for it?

Karasawa
No, there is no experimental evidence. But we omit this reaction from our reaction scheme because of too much production of iodate ions by calculation with this reaction.

Morell
Does it make sense in modelling to predict I3- as an intermediate iodine species? I3- doesn't exist in such low concentration (less than 10^-4 mol/l)?

Karasawa
Yes, it does. Although the concentration of I3- ions is small, the contribution of I3- ions cannot be ignored. I3- ions are produced by disproportionate reaction of I2- ions and the source of HOI. So we must include I3- ions in the oxidation reaction scheme for iodide ions.

Evans
Did you try varying the length of irradiation to see if the concentration of IO3- varied over time?

Karasawa
No, I didn't. I think the dose of 10 kGy is enough to get equilibrium for production of iodate ions.
2.5 MEASUREMENT ON THE RATE OF SOME REACTIONS RELEVANT TO IODINE CHEMISTRY IN THE AQUEOUS PHASE

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ABSTRACT

The equilibrium quotient for \( \text{HOI}^- + \text{OH}^- \rightleftharpoons 2 \text{OH}^- \) was measured to be about 0.2 mol dm\(^{-3}\) at 20 °C, which, combined with other thermodynamic data, led to an estimate that the rate constant \( k(\text{HOI}^- \rightarrow \text{OH}^- + \text{I}^-) \) must be smaller than 20 s\(^{-1}\) unlike previous evaluation by Büchler and Bühler. In near neutral conditions the reaction between \( \text{H}_2\text{O}_2 \) and the iodine species in the oxidation state between 0 and +1 was found to be explained in terms of two pathways, one via \( \text{O}^- \) with \( k(\text{O}^- + \text{H}_2\text{O}_2) \) of \( (6.6 \pm 2.0) \times 10^7 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) at 25 °C and another via \( \text{I}_2\text{OH}^- \) with \( k(\text{I}_2\text{OH}^- + \text{H}_2\text{O}_2)/Q_{12} \) of \( (2.0 \pm 0.6) \times 10^6 \) dm\(^6\) mol\(^{-2}\) s\(^{-1}\) at 25 °C, where \( Q_{12} \) stands for the equilibrium quotient for \( \text{I}_2\text{OH}^- \rightleftharpoons \text{HOI} + \text{I}^- \). The latter reaction has not been assigned previously. The rate constant \( k(\text{I}_2\text{OH}^- \rightarrow \text{I}_2\text{OH}^-) \) was estimated to be larger than \( 2 \times 10^9 \) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) in agreement with previous presumption by others.

1. INTRODUCTION

It has been recognized that kinetic aspect is important in analyzing the iodine chemistry in the containment after a severe accident. In particular the radiolytic effect in the aqueous phase has been considered to be a key factor which may influence the yield of volatile iodine species. \(^1\) Efforts have accordingly been devoted to experimental studies on the radiation chemistry of aqueous iodine system. \(^1\) Computational simulation of such an irradiated iodine system has also been undertaken to enable modeling of the situation after an accident. \(^1\) A large number of reactions are, however, involved to complicate the kinetics, and some of the rate constants are unknown or problematic.

In this paper experimental results are presented about some of the reactions relevant to an irradiated aqueous iodine system. One of them is concerning \( \text{HOI}^- \), which is an intermediate in the oxidation reaction:

\[
\text{I}^- + \text{OH}^- \rightarrow \text{HOI}^-
\]

\[
\text{HOI}^- \rightarrow \text{I}^- + \text{OH}^-
\]

Büchler and Bühler reported the rate constant \( k(\text{HOI}^- \rightarrow \text{I}^- + \text{OH}^-) \) to be \( (2.5 \pm 1.5) \times 10^6 \) s\(^{-1}\) on the bases of their pulse-radiolysis measurement on alkaline solutions. \(^2\) However, this value seemed to be inconsistent with the result of
our pulse-radiolysis study on neutral iodide solution, where there was no sign of absorption due to HOI" and rise of I atom signal was faster than that calculated assuming such rapid reverse dissociation of HOI" into I" and OH. 3 If the reaction HOI" → I" + OH" is really fast, it should affect product distribution in the cases where other reactants against OH" radical exist in the system. Reexamination was, therefore, undertaken about the stability of HOI".

In the analysis of our previous r-radiolysis experiments, reduction of free iodine, namely, the iodine species in the oxidation state between 0 and +1, by H₂O₂ has been assigned to be one of the most important reactions that determine the redox balance in relatively concentrated, i.e., 10⁻⁵-10⁻⁴ mol dm⁻³, iodide solutions. 4 However, the rate constants of the reactions:

\[
\begin{align*}
H₂O₂ + HOI & \rightarrow I^- + O_2 + H₃O^+ \\
H₂O₂ + OI^- & \rightarrow I^- + O_2 + H₂O
\end{align*}
\]

reported by Liebhafsky ⁵ did not seem to be compatible with the results of the r-radiolysis experiments. Measurements were, therefore, made about these reactions. Preliminary data were reported previously, which indicated that \( k(H₂O₂+OI^-) \) must be smaller than the Liebhafsky's value by two orders of magnitude. ³ Results of a newer series of experiments, made more carefully in defining the experimental conditions, are described in this paper.

Additional description is also given about an observation related to the kinetics of the reaction:

\[
I₂ + OH^- \rightarrow I^- + HOI
\]

The forward rate constant has often been assumed to be \( \approx 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \). So long as the value is very large it may not be counted as a crucial rate constant in the analysis of the radiolytic effect. Yet, since the hydrolysis of I₂ is a fundamental reaction, verification of its rate may be of some value.

2. EXPERIMENTAL

An optical pulse-radiolysis apparatus with µs time resolution was used for the experiments in sections 3.1 and 3.3. A Dynamitron accelerator of Research Center for Nuclear Science and Technology of the University of Tokyo was operated at 2.2 MV and with pulse width of 0.6 µs. Dose per pulse was limited less than 7 Gy to slow down radical decay due to recombination reactions. Dosimetry was made with a 1x10⁻² mol dm⁻³ KSCN solution, the product of the G value and the absorption coefficient of (SCN)₂ being taken to be 2.23x10⁻² dm⁻² J⁻¹.

A 300-W Xe lamp was used as an analyzing light source, and the optical path length of the sample cell was 1 cm. A glass flow system was used to refresh sample solution in the cell. In the experiment of section 3.3, two solutions, one containing I₂ and the other I⁻ and NaOH, were mixed a few seconds before pulsing. The purpose was to avoid change in the sample condi-
tions due to progress of hydrolysis toward $\text{HO}_3^-$ and $\text{I}^-$. In this experiment a spectrophotometer and a pH meter were especially connected downstream to the optical cell to monitor sample composition. Solutions for the experiments in section 3.1 were saturated with $\text{H}_2\text{O}_2$ after removing dissolved air by bubbling with Ar, while those for section 3.3 was saturated with $\text{O}_2$. All pulse radiolysis measurements were made at $20\pm2\,^\circ\text{C}$.

The experiments about the reduction of free iodine by $\text{H}_2\text{O}_2$, described in section 3.2, were made with a flow system comprising a glass reaction vessel, a spectrophotometer (Hitachi UV-330) and a pH meter (Horiba F-8). The reaction was first initiated by adding an aliquot of $\text{H}_2\text{O}_2$ solution to the reaction vessel containing $\text{I}^-$ and $\text{I}_2$ solution. Sample was then let flow intermittently at a programmed interval into the two measuring devices. In the spectrophotometer the rate of approach to a steady state, where reduction is balanced by oxidation, was observed by monitoring $\text{I}_3^-$ absorption at 287 or 353 nm. The $\text{H}_2\text{O}_2$ and $\text{I}^-$ concentrations were chosen high enough so that the kinetics of the approach to the plateau should be of the first order. The details of the kinetics are described later, but it is noted that the observed first-order rate ranged from $2.5\times10^{-4}$ to $1.7\times10^{-2}\,\text{s}^{-1}$ depending on the sample conditions. The reaction vessel was thermostatted at $25\,^\circ\text{C}$.

The rate of reaction between free iodine and $\text{H}_2\text{O}_2$ depends strongly on pH of the solution. The previous experiment suggested that phosphate buffer catalyzes the reaction, while citrate buffer is inert in this regard. For this reason the present sample solutions were buffered with disodium citrate and NaOH at $1\times10^{-2}\,\text{mol dm}^{-3}$ in the sum of citrate and hydrogen citrate concentrations. The ionic strength was adjusted throughout to $0.2\,\text{mol dm}^{-3}$ with NaClO$_4$. The use of the automated flow system and control of the ionic strength as well as the buffer concentration are the points improved over the previous preliminary experiment.

All chemicals used were of GR grade except for suprapur NaOH from Merck. Triply distilled or mili-Q water was used to make sample solutions.

3. RESULTS AND DISCUSSION

3.1 Stability of HOI$^-$

Although a nanosecond pulse-radiolysis study by Ellison et al suggested the presence of HOI$^-$ as an intermediate in the oxidation of $\text{I}^-$ in a near neutral solution, the results of our previous measurements in the $\mu$s region could well be described without taking into account of very short-lived HOI$^-$, viz., by a reaction scheme in which atomic iodine is assumed to be produced immediately upon the reaction between $\text{I}^-$ and OH$^-$. The situation is different in an alkaline solution, where HOI$^-$ can be a kinetically significant species. Behar et al first made a brief note on the absorption spectrum of HOI$^-$ in an alkaline solution, which was later studied in more detail by Büchler and Bühler.

Fig. 1 shows an absorption spectrum measured in the present pulse radiolysis experiment on a solution $2\times10^{-4}$ and $10\,\text{mol dm}^{-3}$, respectively, in
[KI] and [NaOH]. The solution also contained N_2O to convert hydrated electron into 0. Time dependence of the absorption in Fig. 1 varied significantly with wavelength, the initial rise being faster at the shorter wavelength. It was clear that two intermediate species are involved and that one of them is the well known I_2^- 8.9 The contribution of I_2^- absorption to the band in Fig. 1 could readily be estimated from a separate measurement on another I_2^- band at 725 nm. The spectrum obtained after subtracting the I_2^- component, shown as a broken-lined spectrum having a maximum at 340 nm, agrees reasonably with that assigned to HOI^- by others.2,7

The reactions leading to I_2^- formation may be written as follows.

\[
1^- + 0^- + H_2O \rightleftharpoons 10H^- + OH^- \quad (1) \\
HOI^- \rightleftharpoons 1^- + OH^- \quad (2) \\
HOI^- \rightleftharpoons 1^- + OH^- \quad (3) \\
HOI^- + 1^- \rightleftharpoons I_2^- + OH^- \quad (4) \\
1^- + 1^- \rightleftharpoons I_2^- \quad (5)
\]

These reactions are followed by recombination reactions to produce free iodine.

The molar absorption coefficient of HOI^- was estimated assuming that
$G(0^-) = 0.56 \mu$ mol j$^{-1}$ and that all 0$^-$ radicals are converted into iodine radicals, i.e., HOI$^-$, I$^-$ and I$_2^{2-}$, by 25 $\mu$s. The latter assumption is equivalent to regard that $k_2$(HOI$^-$→OH$^+$+I$^-$) is so small that neither O$^-$ nor OH$^+$ is present in significant amount at 25 $\mu$s. This view is consistent with the later discussion. The coefficient at 340 nm was calculated to be $3000 \pm 500$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ after correcting for loss of iodine radicals due to recombination reactions. This value is somewhat smaller than (4.5±2.0)$\times$10$^3$ dm$^{-3}$ mol$^{-1}$ cm$^{-1}$ obtained by Büchler and Bühler, who used a different method of analysis. However, this degree of discrepancy does not affect the later discussion.

It is straightforward to estimate the equilibrium quotient $Q_3$ and analysis at various delay times led to a value $(2.3 \pm 0.8)\times10^4$, which happens to agree very well with that reported by Büchler and Bühler. One can then calculate $Q_3$ to be 0.2 mol dm$^{-3}$, making use of the well known $Q_5$ of 1.1$\times$10$^5$ dm$^{-3}$ mol$^{-1}$. This $Q_3$ is considerably smaller than an estimate made by Schwarz and Bielski on the bases of the reported stability of BrOH$^-$ and ClOH$^-$.

Büchler and Bühler made detailed analysis on the time dependence of the absorption to evaluate various rate constants and equilibrium quotients. Their result on equilibrium (2), however, seems suspicious when one considers the following thermodynamic relationship. Since $Q_3$ is obtained above, one may estimate free energy of formation $\Delta G_f^\infty$ of HOI$^-$ by use of $\Delta G_f^\infty$ (I$^-$) and $\Delta G_f^\infty$ (OH$^-$). The latter two free energies are known, respectively, to be 26.6±2.1 and -157.3 kJ mol$^{-1}$. The result is $\Delta G_f^\infty$(HOI$^-$) = -84.7±3.1 kJ mol$^{-1}$. Free energy difference of equilibrium (2) is then calculated to be $58.1 \pm 5.9$ kJ mol$^{-1}$, $\Delta G_f^\infty$ (I$^-$) and $\Delta G_f^\infty$ (OH$^-$) being given to be -51.7±0.2 and 25.1±2.0 kJ mol$^{-1}$ respectively. This $\Delta G^\circ$ (2) corresponds to $Q_2$ of 6.5$\times$10$^{-11}$ mol dm$^{-3}$. Since the rate constant $k_2$ is known to be 1.5$\times$10$^{10}$ dm$^{3}$ mol$^{-1}$ s$^{-1}$, the forward $k_2$ is estimated to be 1 s$^{-1}$ or less than 20 s$^{-1}$ with due allowance made for uncertainties in $\Delta G_f^\infty$'s and in $Q_2$. The value of $k_2$ reported by Büchler and Bühler is $(2.25 \pm 1.50)\times10^6$ s$^{-1}$, which must have been seriously overestimated.

### 3.2 Reduction of Free Iodine by H$_2$O$_2$

Although H$_2$O$_2$ is capable of oxidizing I$^-$ ion, the rate constant of reaction (6):

$$I^- + H_2O_2 \rightarrow HOI + OH^- \quad \text{(6)}$$

is small, $1.2\times10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 25 °C, so that in a neutral to alkaline solution reducing reaction (7):

$$OI^- + H_2O_2 \rightarrow I^- + H_2O + O_2 \quad \text{(7)}$$

plays a much important role. In fact it was confirmed from a simulational analysis of our $\gamma$-radiolysis experiments that contribution of reaction (7) is essential to prevent accumulation of I$_2$ in those solutions whose initial I$^-$ concentration is $10^{-5}$ or $10^{-4}$ mol dm$^{-3}$. 

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The reduction of free iodine by $H_2O_2$ has been analyzed by Liebhafsky in terms of reactions (7) and (8):

$$HIO + H_2O_2 \rightarrow I^- + H_3O^+ + O_2 \quad (8)$$

He obtained $3.3 \times 10^9$ and $37 \text{ dm}^2 \text{ mol}^{-1} \text{ s}^{-1}$ respectively, for $k_7$ and $k_8$. As mentioned in the Introduction, our preliminary measurements suggested that his $k_7$ might have been overestimated due probably to some catalytic effect of additives used in his experiment. Our tentative values were $1.4 \times 10^7$ and $2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, for $k_7$ and $k_8$.

For convenience a kinetic equation for the first-order rate $\alpha$, at which the observed $I_3^-$ absorption changes to reach plateau, is derived here. The reactions involved in addition to (6), (7) and (8) are

$$I_2 + H_2O \rightarrow \rightarrow I^- + H_3O^+ + H^+ \quad (9)$$

$$HOI \rightarrow OI^- + H^+ \quad (10)$$

$$I_2 + I^- \rightarrow I_3^- \quad (11)$$

$$I_2OH^- \rightarrow I^- + HOI \quad (12)$$

$$I_2OH^- + H_2O_2 \rightarrow 2I^- + H_3O^+ + O_2 \quad (13)$$

$$I_2 + H_2O_2 \rightarrow 2I^- + 2H^+ + O_2 \quad (14)$$

$$I_3^- + H_2O_2 \rightarrow 3I^- + 2H^+ + O_2 \quad (15)$$

The species $I_2OH^-$ and its reaction with $H_2O_2$ are included here, and this point is different from the formulation in the previous analysis. At 0.2 mol dm$^{-3}$ ionic strength the equilibrium quotient for $Q_9$, $Q_{10}$ and $Q_{11}$ are, respectively, estimated to be $8.4 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$, $3.8 \times 10^{-11} \text{ mol} \text{ dm}^{-3}$ and 700 dm$^3$ mol$^{-1}$ from the literature equilibrium constants. 15,16,17 In connection with $Q_{12}$, different values from 0.03 to 0.15 have been reported for the equilibrium $O_1^- + I^- = I_2OH^- + OH^-$. 16,18,19

Since the present experiments were made in such conditions that [HOI], [OI$^-$] and [I$_2$OH$^-$] are much less than the sum of [I$_2$] and [I$_3^-$], differential change in free iodine concentration may be equated with $d/dt(\text{[I}_2\text{]+[I}_3^-\text{])}$, and hence.

$$\frac{d}{dt}(\text{[I}_2\text{]+[I}_3^-\text{])} = -(k_7[OI^-] + k_8[HIO]) + k_{13}[I_2OH^-] +$$

$$k_{14}[H_2O_2] + k_{15}[I_3^-] - k_8[1^{-}] [H_2O_2] \quad (16)$$

Both $[I^-]$ and $[H_2O_2]$ were kept large enough to be regarded approximately constant during the reaction. Further, in the time scale of the present measurements any deviation from equilibrium concentration is expected to be small in regard to all equilibria, including (10) and (12). The solution for equation (16) can then be derived as

$$[I_3^-] = ([I_3^-]_0 - [I_3^-]_s) \exp(-\alpha \cdot t) + [I_3^-]_s \quad (17)$$

where

$$\alpha = (1 + Q_{11}[I^-]^{-1}(k_7Q_{10}[H^+]^{-2}([I^-]^{-1} + k_8Q_9[H^+]^{-1}[I^-]^{-1})$$
\[ + k_{13}Q_{9}\cdot Q_{12}^{-1}\cdot [H^+]^{-1} + k_{14} + k_{15}Q_{11}[I^-]\cdot [H_2O_2] \]

\[ [I_3^-]_s = k_6Q_{11}\cdot (1 + Q_{11}[I^-])^{-1}\cdot [I^-]^2\cdot [H_2O_2] \cdot \alpha^{-1} \]

and \([I_3^-]_0\) is initial \(I_3^-\) concentration.

The dependence of \(\alpha\) on \([H^+]\) was measured first. Though the graph is not shown here, it was confirmed by plotting experimental \(\alpha/[H_2O_2]\) against \([H^+]^{-1}\) at constant \([I^-]\) that both \(k_{14}\) and \(k_{15}\) are negligible. The result of another plotting, \(\alpha/[H^+]\cdot [H_2O_2]^{-1}\) versus \([I^-]^{-1}\), is shown in Fig. 2, where two sets of data taken, respectively, at \(5\times10^{-4}\) and \(1.5\times10^{-3}\) mol dm\(^{-3}\) in \([I^-]\) are plotted. Each set may be regarded to be on a straight line. The slope and the intercept of which should correspond to \(k_7Q_9Q_{10}(1+Q_{11}[I^-])^{-1}\cdot [I^-]^{-1}\) and \((1+Q_{11}[I^-])^{-1}(k_8Q_9\cdot [I^-])^{-1}+k_{13}Q_9\cdot Q_{12}^{-1}\). The two slopes can be assigned to give a ratio of 4.5 expected from the \([I^-]\) dependence. and \(k_7\) was estimated to be \((6.6\pm2.0)\times10^{-7}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\).

The data in Fig. 2 certainly show presence of significant intercept component, but determination of \(k_8\) and \(k_{13}\) is difficult because of the scatter in the data. Another series of experiments were made to examine \([I^-]\) dependence of \(\alpha\) at constant \([H^+]\) of \(1.2\times10^{-7}\) mol dm\(^{-3}\). The result is shown in Fig. 3, where \(\alpha/(1+Q_{11}[I^-])\cdot [H_2O_2]^{-1}\) is plotted against \([I^-]^{-1}\). Here the slope and the intercept should represent, respectively, \(k_7Q_9Q_{10}[H^+]^{-2}+k_8Q_9[H^+]^{-1}\) and \(k_{13}Q_9\cdot Q_{12}^{-1}\cdot [H^+]^{-1}\). The presence of a significant intercept component indicate that there is a previously unknown reaction pathway through \(I_2OH\). Determination of \(k_8\) is still difficult, and the line in Fig. 3 is drawn tentatively by neglecting \(k_8\). The intercept gives \(k_{13}Q_{12}^{-1}\) of \((2.0\pm0.6)\times10^{-6}\) dm\(^3\) mol\(^{-2}\) s\(^{-1}\), from which \(k_{13}\) may be calculated to be \(5.8\times10^{-3}\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\). if one uses \(Q_{12}\) calculated from the equilibrium constant for \(O^1 + I^1 \rightarrow 2OH^- + OH^-\) as reported by Wren et al.\(^{19}\)

One notices on returning to Fig. 2 that the both intercepts of the two lines in Fig. 2 may almost entirely be explained by the \(I_2OH^-\) component calculated from the above \(k_{13}Q_{12}^{-1}\). Hence, it seems most likely that the HOI path. reaction (8), is relatively unimportant in the present conditions and that our previous estimate for \(k_{13}\) made from an intercept component in a plot similar to Fig. 2. was overestimated. This view is rather consistent with a small \(k_8\) of \(37\) dm\(^3\) mol\(^{-1}\) s\(^{-1}\) as reported by Liebhafoisky.\(^5\)

3.3 Reaction between \(I_2\) and \(OH^-\)

Though it was only very brief description, experimental data on the kinetics of the primary step of \(I_2\) hydrolysis have once been presented.\(^{13}\) A short summary will, therefore, suffice here.

In an attempt to measure the rate constant of the reaction between HOI and \(O_2^-\), pulse-radiolysis measurements were made on \(O_2^-\)-saturated alkaline solution of \(I_2\), HOI and \(I^-\). While HOI was found unreactive toward \(O_2^-\), it was noticed simultaneously that the observed time profile of \(I_3^-\) absorption, used as a monitor for \(I_2\) as well here, was difficult to be explained when only radical reactions were taken into account. It was soon realized that pulse-
Fig. 2. Plot of \( \alpha [H^+] [H_2O_2]^{-1} \) against \([H^+]^{-1}\), showing \([H^+]\) dependence of the overall reaction rate at constant \([I^-]\). ○: \([I^-]= 5 \times 10^{-4} \text{ mol dm}^{-3}\); ●: \([I^-]= 1.5 \times 10^{-3} \text{ mol dm}^{-3}\). 25°C.

Fig. 3. Plot of \( \alpha (1 + Q_{11}[I^-]) [H_2O_2]^{-1} \) against \([I^-]^{-1}\), showing \([I^-]\) dependence of the overall reaction rate at constant \([H^+]\) of \(1.2 \times 10^{-7} \text{ mol dm}^{-3}\). 25°C.
induced rapid depletion of \( I_2 \) due to reaction (20):

\[
O_2^{\cdot -} + I_2 \rightarrow O_2 + I_2^{\cdot -}
\]  

(20)

is followed not only by recombination of \( I_2^{\cdot -} \) but also by reactions (21) and (22):

\[
\begin{align*}
I_2 + OH^- & \rightleftharpoons I_2OH^- \\
I_2OH^- & \rightleftharpoons HOI + I^-
\end{align*}
\]  

(21)  

(22)

The experiment was thus like that of the relaxation method. Analysis disregarding the presence of \( I_2OH^- \), being equivalent to assume very fast equilibration of (22), led to an estimate that \( k(I_2 + OH^-) = (6 \pm 4) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

The kinetics of \( I_2 \) hydrolysis was first studied by Eigen and Kustin.\textsuperscript{20} and recently reexamination was made by Palmer and van Eldik.\textsuperscript{21} In both of these studies the forward reaction of (21) was assumed to be nearly diffusion-controlled. The above finding confirms this view, since the true \( k_{21} \) has to be larger than the above estimate neglecting the intermediate \( I_2OH^- \). It is, however, noted that the experimental results by Palmer and van Eldik indicated, as they stressed in their paper, faster equilibration of (22) relative to (21).\textsuperscript{21} Since this point appears to be inconsistent with the assignment of large \( k_{21} \), some problem remains in the kinetics of \( I_2 \) hydrolysis.

4. CONCLUDING REMARKS

From the measurement on \( HOI^{\cdot -} \) the rate constant \( k_2(\text{HOI}^{\cdot -} \rightarrow \text{OH}^- + I^-) \) was estimated to be less than 20 \text{s}^{-1} at 25 °C. There is little need to take this \( k_2 \) into account in the analysis of continuously irradiated system even in the case of dilute \( I^- \) solution.

The result about the reaction between \( HO_2^+ \) and free iodine confirmed on one hand that \( k_7(OI^{\cdot -} + HO_2) \), being \( (6.6 \pm 2.0) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 25 °C, is much smaller than the value by Liebhafsky. On the other hand the result also suggested the presence of reaction between \( I_2OH^- \) and \( HO_2^+ \). In neutral to alkaline solution, however, the former reaction via \( OI^{\cdot -} \) will dominate at low \( I^- \) concentration.

The reaction between \( I_2 \) and \( OH^- \) was confirmed to be a nearly diffusion-controlled reaction, but it was pointed out that detailed kinetics of the primary step of \( I_2 \) hydrolysis is not completely clear yet.

5. REFERENCES

DISCUSSION

Sims
What are the reasons for the difference between your results and those of Liebhafsky? Do you see any evidence of catalysis?

Shiraishi
In the previous study we certainly observed significant catalytic effect of phosphate or borate buffer on reaction (7). Citrate buffer was found inert in this regard, though it appears to accelerate acid-base equilibration.

Kupferschmidt
Have you considered the possibility that the reaction of OI⁻ with H₂O₂ may actually proceed by reaction of HOI with HO₂⁻? In both cases, identical acid dependencies would be expected.

Shiraishi
I agree and, we are aware of that possibility. In the present experimental conditions it is impossible to distinguish whether the reaction is between OI⁻ and H₂O₂ or between HOI and HO₂⁻.
3. Session III
IODINE CHEMISTRY AT SURFACES
3.1 THE KINETICS OF REACTION BETWEEN IODINE VAPOUR AND BULK-MATERIAL AEROSOLS

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ABSTRACT

Bulk materials within the reactor core such as Ag-In-Cd control rod and boric acid could generate an aerosol concentration greater than 1 g m^{-3} during a severe accident. The surface area of these aerosols could be approximately 500 x greater than the total internal surface area of the primary circuit, implying that vapour-aerosol interaction mechanisms could dominate the transport of the fission products released from the damaged fuel. However, only limited studies have been undertaken to quantify such interactions, and models to describe all potential interactions are not currently available within the relevant computer programs (eg VICTORIA).

Thermogravimetric experiments have been conducted to follow the interaction of iodine vapour with aerosol substrates as functions of temperature, flow velocity and vapour pressure. The reaction of iodine vapour with silver or cadmium substrates is limited by either mass transfer of iodine molecules from the gas phase (resulting in linear reaction rates) or diffusion through the product layer (resulting in parabolic reaction kinetics).

1. INTRODUCTION

The release of fission products from a severe nuclear reactor accident could be accompanied by the generation of copious quantities of aerosol originating from the bulk materials within the reactor core (1). Subsequent interactions between the fission product vapours and aerosol would have an important effect on the transport and attenuation of the radioactive species in the damaged reactor system (2).

Bulk materials within the reactor core such as Ag-In-Cd control rod and boric acid could generate an aerosol concentration greater than 1 g m^{-3} during a severe accident (2, 3). The surface area of these aerosols could be approximately 500 x greater than the total surface area of the primary circuit, implying that vapour-aerosol interactions could dominate the transport of the fission products released from the degraded fuel. In particular, the interaction between the fission products and aerosols will define the physicochemical forms of the source term from the primary circuit to the containment building. Although the importance of this phenomenon has been recognised in sensitivity studies conducted within the UK, only limited studies have been undertaken to quantify such interactions, and suitable models are not included in the relevant computer programs (eg VICTORIA).
Although chemical reactions are modelled in VICTORIA, such as the reaction of iodine vapour with cadmium aerosol to produce cadmium iodide, only thermodynamic considerations are taken into account. The reactions are assumed to be limited only by the rate of mass transfer of vapour molecules from the gas phase to the aerosol surface. However, this approach does not take account of the role of chemical kinetics in modifying the rate of reaction. The object of this study was to assess the uncertainties in this assumption and determine the factors that can influence specific chemical reactions so that more realistic models can be developed to describe vapour-aerosol interactions. Further details of this work are given in reference 4.

2. EXPERIMENTAL DETAILS

Thermogravimetric experiments have been conducted to follow the interaction of iodine vapour with aerosol substrates as a function of temperature, flow velocities and vapour pressures. The apparatus is shown in Figure 1 (Stanton Redcroft model STA1500). The main module of the apparatus is mounted on a marble bench to ensure freedom from vibration that would interfere with the measurements. The balance control unit is linked to the electronic microbalance system which displays the weight, and provides an analogue signal proportional to the weight (connected to a chart recorder), thus enabling a continuous measurement of the sample weight to be recorded. The furnace is precisely controlled to a maximum temperature of 1500°C by the temperature programmer. The temperature of the sample is monitored by a Pt-Rh thermocouple plate under the sample crucible, and recorded on the same chart as the weight measurement.

The system is purged with pure argon before an experiment is initiated. The gas containing iodine vapour and argon diluent enters the apparatus through the base of the furnace, and passes over the sample via an alumina capillary. The exhaust gas is then transported through the micro environment cup baffles and exits from the furnace base (Figure 1). Control of diluent gas flow (10 to 100 cm$^3$ min$^{-1}$) is achieved using a needle valve in conjunction with a calibrated flow meter.

As a consequence of the geometry (in particular the position of the sample in the reaction zone), only a small proportion of the vapour/crrier gas was expected to come in direct contact with the sample surface. A series of calibration experiments were conducted so that this effect could be quantified and hence enable standard mass transfer equations to be adapted to characterise the furnace (for subsequent analysis of the main experiments). The water vapour-magnesium perchlorate system was chosen to accomplish the calibration; magnesium perchlorate is a very powerful desiccant and will rapidly take up water (only limited by the supply of water molecules from the vapour phase). Thus, the mass transfer from vapour to sample can be determined (4).

Experiments were conducted to study the following systems:

(i)  $I_2$/MnO,
(ii) $I_2$/Ag,
(iii) $I_2$/Cd.

Manganese (II) oxide is a structural material aerosol expected to be generated under accident conditions (1). It can also be regarded as a
representative oxide aerosol and has been used in a number of large-scale experimental studies. Cadmium is used as a neutron absorber within Ag-In-Cd control rods and is likely to be one of the major components of any bulk-material aerosol generated in a reactor accident (1). Data from this system are relevant to the interpretation of the Falcon experiments in which significant releases of both iodine and cadmium occurred (5). This system is also representative of a volatile reactive vapour and a metallic aerosol. Silver is the major constituent of the control rods and could generate significant quantities of aerosol in a severe accident (1). The kinetics of the iodine-silver system are well established (6, 7), thus enabling the results from the current studies to be compared with those in the literature. Iodine vapour was generated directly before entry to the furnace by passing the argon carrier gas at preset rates through an all-glass column packed with iodine crystals contained in a water bath of controlled temperature. The iodine partial pressure was controlled by setting the water bath to the required temperature.

3. RESULTS

The rate of uptake of water by magnesium perchlorate was used to characterise the mass transfer characteristics of the system. As expected, the rate was independent of time at 20°C and could be expressed simply as a function of the flow rate.

No mass gain or reaction was observed when manganese monoxide was exposed to iodine over a range of conditions (iodine pressure from 4 to 30 Pa and sample temperature from 100 to 400°C). Sorption of iodine onto the sample surface may have occurred, but because of the small mass of iodine involved with this type of interaction (maximum of a monolayer on the sample surface), it proved impossible to quantify using the balance.

Both cadmium and silver increased in mass when exposed to iodine vapour, indicating reaction to form the appropriate iodide. The rate of mass gain was always below that calculated assuming complete reaction (see Figure 2) and followed one of two forms. The first resulted in a constant or linear rate of reaction as observed in the water-magnesium perchlorate experiments (Figure 2a), the second followed a decreasing rate of reaction with time (see Figure 2b). Linear rates of reaction were always observed when the sample temperature was above the melting point of the metal substrate (321°C for cadmium) or the reaction product (552°C for silver iodide). At lower temperatures either parabolic or linear rates of reaction were observed depending on the experimental conditions.

4. DISCUSSION

4.1 Calibration Studies

The reaction of water vapour with magnesium perchlorate was so fast that the rate of uptake of water vapour was only dependent on the mass transfer of the water molecules from the gaseous phase. The rate of mass gain was also a function of the gas velocity which indicates mass transfer limitations. These variations in the rate of uptake of water were used to obtain mass transfer coefficients for the apparatus. The following equation was used to calculate the mass transfer rate (dm/dt) of water from the vapour phase:
\[
\frac{dm}{dt} = A h c_{H_2O}
\]

where \( A \) is the exposed area of the perchlorate sample, \( h \) is the mass transfer coefficient, and \( c_{H_2O} \) is the vapour concentration of water. This equation assumes that little vaporisation takes place (confirmed by experiments where water revaporation from hydrated samples was studied). The mass transfer coefficient is given by

\[ h = 0.5 f \nu Sc^{-2/3} \]

where \( f \) is the fanning friction factor, \( \nu \) is the gas flow velocity, and \( Sc \) is the Schmidt number defined by

\[ Sc = \frac{\mu}{\rho \nu} \]

in which \( \mu \) is the viscosity of argon \((20 \times 10^{-6} \text{ kg m}^{-1}\text{s}^{-1})\), \( \rho \) is the density of argon \((1.64 \text{ kg m}^{-3} \text{ at STP})\) and \( D \) is the diffusion constant of water in argon. The following equation was used to calculate this diffusion constant \((8)\):

\[
D = \frac{0.001 T^{1.75}}{p} \left\{ \frac{1/M_1 + 1/M_2}{\sqrt{(\Sigma v_1)^{1/3} + (\Sigma v_2)^{1/3}}} \right\}^2
\]

where \( M_1 \) and \( M_2 \) are the molecular weights of argon and water, and \( \Sigma v_1 \) and \( \Sigma v_2 \) are their respective molecular diffusion volumes. The friction factor \((f)\) is usually expressed in terms of the Reynolds number \((Re)\) for the system,

\[ f = C Re^{-n} \]

The values of the constants \( C \) and \( n \) depend on the particular range of Reynolds numbers being considered, which is given by

\[ Re = \frac{vd\rho}{\mu} \]

where \( d \) is a characteristic length for the particular geometry under consideration. The geometry of the experiment is rather complex, making it difficult to define this factor. Two options are the diameter of the cup holding the sample or the diameter of the micro-environment cup of the thermogravimetric balance (the latter is approximately four times the size of the former). The diameter of the cup was used to estimate the Reynolds number in the present work. A Reynolds number of 2 can be calculated on the basis of the following experimental parameters: density \( \rho \) of 1.6 kg m\(^{-3}\), viscosity of \( 20.0 \times 10^{-6} \text{ kg m}^{-1}\text{ s}^{-1} \), cup diameter of \( 5.0 \times 10^{-3} \text{ m} \) and a typical flow velocity of \( 5.0 \times 10^{-3} \text{ m s}^{-1} \). It proved impossible to find a correlation for the friction factor that was valid at these low Reynolds numbers. Therefore, the data obtained for magnesium perchlorate were fitted
by adjusting the constants $C$ and $n$ for the fanning friction factor (Table 1). This correlation was then used to describe mass transfer processes for the other systems being considered.

### 4.2 Main Experiments

The reaction of a vapour with an aerosol is limited by thermodynamic and kinetic factors. If it is not thermodynamically favourable, the reaction will not occur. This limitation was shown in experiments conducted with MnO, where no reaction was observed experimentally as predicted by the thermodynamic parameters (sorption of I$_2$ onto the MnO surface may have occurred but would not have been detected because of balance sensitivity). The characteristic thermodynamics can be modelled using computer codes providing a data base is available that contains the thermodynamic quantities of the relevant species.

However, even if favoured thermodynamically, a reaction may not proceed or will be limited by kinetic restrictions placed upon the rate by the reaction mechanism. Thus, in the experiments conducted to study the reactions of iodine vapour with silver and cadmium to form metal iodides, only a small proportion of the maximum reaction was observed (see Figure 2).

When the thickness of the reaction product is greater than 100Å (as observed in the current experiments), the degree of reaction follows either a linear or parabolic time dependancy law. Parabolic rates are the most common, particularly for reactions occurring at high temperatures. The mechanism associated with the parabolic law relies on the formation of a coherent product between the reactants. The reaction rate is then limited by transport across this film by either the outward diffusion of cations or the inward diffusion of anions when the product exhibits electronic conduction, or alternatively by electron transport when the product is an ionic conductor (6). The driving force for the diffusion process is a concentration and electrical gradient across the film arising from the free energy change associated with the reaction. As a result the chemical potential across the film is inversely proportional to the film thickness. Likewise, the rate of increase in the film thickness is inversely proportional to the film thickness, and this relationship can be integrated to give the parabolic law in the usual form:

$$\Delta m_x^2 = 2kt$$

where $k$ is the parabolic rate constant. A detailed theoretical derivation of this expression has been given by Wagner (6).

The extents of the Cd-I$_2$ and Ag-I$_2$ reactions were measured at various points ($\Delta m_{x_0}, \Delta m_{x_1}$ etc.) at times ($t_0, t_1$ etc.), and the value of the rate constant were obtained using the equation,

$$\Delta m_{x_2}^2 - \Delta m_{x_1}^2 = 2k (t_2 - t_1)$$

A plot of $\Delta m_{x_2}^2 - \Delta m_{x_1}^2$ versus $\Delta t$ will be a straight line of gradient $2k$ if the parabolic law applies. Such plots are shown for the cadmium and silver experiments in Figure 3, indicating compliance with the parabolic law under the defined conditions. Variations in the rate constants at varying sample temperatures are shown in Figures 4 and 5 for cadmium and silver, respectively.
An important assumption of the parabolic model is that thermodynamic equilibrium is maintained at the vapour-product interface and through the product layer. The equilibrium at the vapour-product layer interface follows the general equation

$$\frac{\partial nX_2}{\partial t} = MX^n + [M^{n^+}] + n[e_h]$$

where $X_2$ is the vapour phase reactant, $[M^{n^+}]$ is a cation vacancy generated by the reaction of $X_2$ with the $MX^n$ lattice, and $[e_h]$ is an electron hole. As the rate of diffusion through the product layer is determined by either ion migration in electronic conductors or electron transport in ionic conductors, the overall rate will be governed by the position of the surface equilibrium. For example, when $I_2$ is the vapour species and $AgI$ is the reaction product:

$$\frac{1}{2} I_2 = AgI + [Ag^+] + [e_h]$$

for which the equilibrium constant $K$ is given by:

$$K = \frac{[Ag^+][e_h]}{[P(I_2)]^{1/2}}$$

As silver iodide is an ionic conductor the rate of reaction will be determined by the electron hole concentration, and the parabolic rate constant ($k$) will have the following dependencies

$$k \propto \frac{K[P(I_2)]^{1/2}}{[Ag^+]}$$

The inverse proportionality of the rate with respect to the concentration of the cation vacancies explains the unexpected increase in the rate of reaction of $I_2$ with silver below 140°C (Figure 5). The solubility of the impurities in the $AgI$ product is reduced at lower temperatures; hence, the concentration of cation vacancy defects is reduced and the rate of reaction increases. At much higher temperatures the concentration of cation vacancies is only limited by the amount of impurities in the foil and not by their solubility limit, therefore the rate of reaction increases with temperature. A step in the rate-temperature curve is clearly detected at 146°C where the $\alpha$-$AgI$ lattice converts to the $\beta$ form, with an associated change in the diffusion characteristics. The results obtained for the iodine-silver system are in good agreement with a previous study conducted over the range 20 to 140°C (9), when a similar dependence of reaction rates with temperatures was observed and the pressure dependency of the rate constant was also demonstrated.

Cadmium iodide is an electronic conductor; hence, the rate constant in the iodine-cadmium system will be proportional to the number of ionic vacancies and the rate will always increase with temperature (Figure 4). The rate of change of the parabolic rate constant alters rapidly in the region of 250°C, although there is no documented phase change for cadmium iodide in
this temperature range. One possibility is that the predominant charge-
carrying species changes in this region; another is that the mutual
solubility of the reactants and products increases to an extent that
influences the rate of reaction on approaching the melting point of cadmium.

The agreement between the predicted mass gain calculated using mass
transfer considerations and that observed experimentally for silver and
cadmium under various conditions of flow and temperature suggests that the
mass transfer of iodine molecules from the vapour phase was the limiting
process when the linear law was observed. Furthermore, the independence of
the linear law to the nature of the condensed phase was demonstrated in
experiments under the same conditions that resulted in linear rates of
reaction of approximately equal magnitude for iodine deposited on both
cadmium and silver (see Table 2).

The rate predicted at the beginning of the reaction using parabolic
kinetics would be extremely large and greater than that which could be
accommodated by the mass transfer of iodine molecules from the gas phase. It
therefore would be expected that linear laws would be initially obeyed until
a product film has grown to a critical thickness above which diffusion
through this barrier becomes the rate determining process and a parabolic law
is followed. In most of the experiments where parabolic kinetics was
observed, this point occurred almost instantly on exposure to iodine,
although it was possible to delay the change so that it could be readily
observed by a suitable choice of reaction conditions (see Figure 2c).

5. APPLICATIONS TO SEVERE ACCIDENT ANALYSES

It is clear from these studies that at least three types of information
are required to calculate the behaviour of vapour/aerosol interactions during
severe accidents:

(1) phase of the aerosol substrate (solid or liquid),
(2) product phases produced by the reaction with the aerosol,
(3) mass transfer rate and parabolic rate constants for the surface
    reactions.

The deposition behaviour will be governed by mass transfer processes under
relatively stagnant conditions at high temperatures when the aerosols are in
the molten state. However, in areas of the reactor at relatively low
temperatures with relatively rapid fluxes of vapour, the deposition behaviour
will be governed by parabolic kinetics at the aerosol interface.

Experiments are required that consider a range of representative vapour
mixtures and metal surface components that simulate reactor conditions more
closely. For example, cadmium aerosol particles generated in a severe
accident may not be pure, but contain significant proportions of other metals
resulting in an increased defect concentration in any product lattice and
hence increasing the diffusion and reaction rates.

An equation of the following general form should be used in severe
accident codes such as VICTORIA:
\[ \frac{dm}{dt} = \frac{k_1}{k_2 + m} - k_3 \]

in which \( k_1/k_2 \) is equal to the mass transfer rate, and \( k_3 \) is a vaporisation rate. At early times, \( m \) will be close to zero, and the rate of mass increase is simply \( k_1/k_2 - k_3 \), reflecting a gas-phase mass transfer limited process. However, as \( m \) increases, the equation starts to reflect parabolic kinetics of the form \( \frac{dm}{dt} = k_1/m \). Further work is required to acquire the rate constants for a variety of prototypic systems.

6. CONCLUSIONS

Thermogravimetric studies have been undertaken at Winfrith to study the interaction of molecular iodine vapour with specific aerosol materials over a wide range of conditions. This work has shown the necessity to characterise the extent of reaction as a function of time so that rate laws and mechanisms can be identified and quantified. The main conclusion of this work are summarised below.

(1) The reaction of iodine vapour with cadmium and silver was limited by one of two processes: mass transfer of iodine molecules from the gas phase to the metal surface, or passivation of the cadmium by a film of CdI\(_2\), or AgI reaction product through which diffusion must occur to sustain further reaction.

(2) When the reactions were limited by mass transfer of iodine molecules from the gas phase, the extent of reaction was in good agreement with that predicted using adapted mass transfer equations and independent of the nature of the condensed phase. Such conditions are identified with low iodine pressure and low flow rates or when the formation of a stable product layer was not possible, for example at temperatures above the melting point of the metal.

(3) When the reactions were limited by the passivation of a coherent film of reaction product(s), rates were found to be inversely proportional to the extent of reaction and obeyed a parabolic law. Rate constants were determined over a range of temperatures for both silver and cadmium over the expected experimental conditions. A general formula has been derived:

\[ \frac{dm}{dt} = \frac{k_1}{k_2 + m} - k_3 \]

where \( \frac{dm}{dt} \) is the rate of mass increase with time, \( k_1/k_2 \) is the mass transfer rate, and \( k_3 \) is a vaporisation term. Further work is required to measure the rate constants of other representative systems to produce a general model.
ACKNOWLEDGEMENTS

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REFERENCES


### TABLE 1

**COMPARISON OF EXPERIMENTAL DATA AND THEORETICAL CALCULATIONS FOR THE REACTION OF WATER VAPOUR WITH MAGNESIUM PERCHLORATE AT 20°C**

<table>
<thead>
<tr>
<th>Flow Velocity (cm³ min⁻¹)</th>
<th>Experimental Mass Gain Rate* (mg min⁻¹)</th>
<th>Calculated Mass Gain Rate (mg min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.041</td>
<td>0.041</td>
</tr>
<tr>
<td>30</td>
<td>0.061</td>
<td>0.057</td>
</tr>
<tr>
<td>50</td>
<td>0.073</td>
<td>0.085</td>
</tr>
<tr>
<td>70</td>
<td>0.12</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Uncertainties in data ± 2%

### TABLE 2

**LINEAR RATE LAW DATA FOR THE REACTION OF IODINE VAPOUR WITH CADMIUM AND SILVER UNDER IDENTICAL EXPERIMENTAL CONDITIONS***

(Flow rate 50 ml min⁻¹, iodine pressure 4 Pa, temperature 240°C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Mass Gain (mg min⁻¹)</th>
<th>Iodine Deposition Rate (mol I₂ min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver</td>
<td>1.47 x 10⁻³</td>
<td>5.8 x 10⁻⁹</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.40 x 10⁻³</td>
<td>5.5 x 10⁻⁹</td>
</tr>
</tbody>
</table>

* Uncertainties in data ± 2%
Figure 1  Thermogravimetric Apparatus
(a) Linear Rate Law \( (p(I_2) = 4 \text{ Pa}, \text{ Ar flow} = 50 \text{ cm}^3\text{min}^{-1}) \)

(b) Parabolic Rate Law \( (p(I_2) = 30 \text{ Pa}, \text{ Ar flow} = 50 \text{ cm}^3\text{min}^{-1}) \)

(c) Initial Linear Dependance followed by Parabolic Rate of Reaction \( (p(I_2) = 4 \text{ Pa}, \text{ Ar flow} = 40 \text{ cm}^3\text{min}^{-1}) \)

---

Observed

---

Calculated assuming complete reaction of the Iodine vapour

---

Figure 2  Thermogravimetric Data for the Reaction of Cadmium with Iodine at 513K
Figure 3  Interaction of Iodine Vapour with Silver and Cadmium
Iodine Vapour Pressure 30pa, Silver (right hand axis) at 252°C
and Cadmium (left hand axis) at 240°C
Figure 4  Interaction of Iodine Vapour with Cadmium
Iodine Pressure 30 Pa
Figure 5  Interaction of Iodine Vapour with Silver
Iodine Pressure 30Pa
DISCUSSION

Tennankore

What size distribution did you assume to arrive at surface area estimates of bulk material aerosol?

Bowsher

The surface area of bulk-materials aerosols of \( \sim 10^6 \text{ m}^2 \) was based on the assumption of aerosols with an average geometric diameter of 0.3 \( \text{ m} \).

Evans

1) Under accident conditions, would you expect more than monolayer coverage?
2) Could a layer of I\(_2\) accumulate on the CdI\(_2\) surface?
3) Have you tried to relate your rates of reaction with diffusion coefficients for CdI\(_2\)?

Bowsher

1) Whilst monolayer coverage might be expected if the iodine vapors was allowed to interact with all the aerosol this is probably an unrealistic scenario. It is more probable that the fission product iodine could interact event with the more volatile aerosol released at the same time. Calculations based on the cadmium inventory indicate a surface coverage of between 100 and 1000 monolayers.

2) I believe that would be possible for accidents with high flow rates of iodine, resulting in saturation at the surface and heterogeneous nucleation. This would give a complex aerosol with a surface coating of I\(_2\) on top of a CdI\(_2\) layer with a Cd kernel.

3) It is not certain what the dominant diffusion process is for the case of CdI\(_2\) formation; either diffusion of iodine through CdI\(_2\), or diffusion of vacancies through the product layer. Whilst data are available in the literature for AgI formation, very little is known for CdI\(_2\).

Tennankore

The overall resistance to reaction in your system could be written as the sum of three contributions: Mass transfer resistance, diffusional resistance and the inverse of kinetic rate constant (for a 1st order reaction) with a fast reaction (fast kinetics and fast diffusion). You can characterize mass transfer resistance, \((1/kA)\), where \(k\) is the mass transfer coefficient and \(A\) is the surface area. Using this, one may estimate the combination of the other two resistances, \((1/kA + 1/DA)\), for the reaction of interest. However, unless the surface area is independently characterized, it would not be possible to apply this data to a real system where the surface area could be widely different. Could you comment on the applicability of your kinetic rate data to such practical systems (say the primary circuit with foaming aerosol)?

Bowsher

The kinetic studies were based on initial mass transfer experiments to follow the interaction of water vapor with a well-defined surface of Mg(C1O4)\(_2\) of area 100 mm\(^2\). These data were then used to assess the diffusion direction of iodine with other materials (MnO, Ag and Cd) with the same surface area. We have confidence in the data as the results are consistent with experiments in flowing systems where the surface area of the aerosols was higher (\( \sim 2 \text{ m}^2 \)).
3.2 VOLATILE ORGANIC IODINE FORMATION BY SURFACE PROCESSES

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ABSTRACT

In order to predict the contribution to iodine release following a reactor fault, measurements of volatile organic iodine formation from adsorbed I⁻ ions have been made on a number of surfaces over a wide range of concentrations. The results have been used to develop a semi-mechanistic computer model based on surface reactions, with which the formation of volatile organic iodine species can be predicted. The surface reactions chosen were all reasonable reactions, known to occur on catalyst surfaces which have been studied elsewhere.

A second volatile species, identified as inorganic iodine, was also produced by surface reactions.

1. INTRODUCTION

An estimate of volatile organic iodine species formation, typified by CH₃I formation, is necessary in assessing the consequences of nuclear reactor faults and accidents. In an early review, Postma and Zavidoski[1] proposed an algorithm for estimating organic iodide formation in severe accidents which was implicitly based on homogeneous radiolytic processes. However, their review contained clear evidence that, under less severe conditions, surface formation reactions may dominate. Evidence of a relation between vessel surface to volume ratio and organic iodine formation, typical of surface processes, was presented.

It was known that other workers were studying homogeneous organic iodine formation processes.[2, 3, 4] Moreover, many reported incidents at nuclear reactors have resulted in only small releases of iodine from the reactor circuit; in this type of fault radiation levels are low and surface processes would be expected to be dominant. For those reasons, the AEA programme of organic iodine formation studies has concentrated on formation by surface processes.

Laboratory experiments have established the validity of the hypothesis that surface processes involving iodine absorbed from an iodide solution lead to significant volatile iodine production; both inorganic and organic species were identified. A semi-mechanistic computer model has been developed which predicts formation rates in reasonable agreement with the experimental results over a wide range of concentrations and pH. The model has been applied to the conditions of the first two ACE/RTF tests;[5] differences from the measured gaseous organic iodine concentrations could be due to the different surface materials involved.

2. PROCEDURE

2.1 Basis for the experimental procedure

Starting from a review of the relevant chemistry, including catalyst chemistry,[6] and from the premise that CH₃I was a likely major volatile iodide component and that analogous reactions would be possible for other iodides, a reaction scheme was hypothesised:
\[(CH_3OH)_s + MOH \rightleftharpoons CH_3OM + H_2O \quad (1)\]
\[(HI)_s + MOH \rightleftharpoons IM + H_2O \quad (2)\]
\[IM + CH_3OM \rightarrow (CH_3I)_s + M_2O \quad (3)\]
\[(CH_3I)_s \rightleftharpoons (CH_3I)_g \quad (4)\]
\[M_2O + H_2O \rightarrow 2MOH \quad (5)\]
\[(CH_3I)_g \rightarrow \text{Inorganic iodine} \quad (6)\]

where the subscripts "s" and "g" denote adsorbed (surface) and gaseous species, respectively. Reactions (1) and (2) represent the dissociative and competitive reaction of adsorbed organic material and iodine species at reactive surface (hydroxyl) sites to form surface compounds. These surface compounds react to form adsorbed organic iodide \((CH_3I)_s\) (Reaction (3)), which then equilibrates with the gas phase (Reaction (4)). Reaction (5) represents the re-activation of de-activated sites and reaction (6) represents an unspecified mechanism for removal of gaseous organic iodide. The last reaction was needed because experimental data in the literature indicated that an equilibrium atmospheric concentration is reached in a closed system. An interesting consequence of this reaction set is that an excess of either iodide or the organic adsorbant will swamp the surface and suppress the formation of organic iodide.

Surfaces studied included an epoxy-phenolic paint (Type M253, supplied by W. and J. Leigh, Ltd.), crushed concrete identical to that used in the construction of the Sizewell B reactor containment and type 304 stainless steel. In addition, scoping studies and a number of other experiments were made on a soda glass surface (glass ballotini). Although concrete was an important structural material, its porosity and uncertainty regarding the extent of water penetration and gas diffusion out meant that its surface area was undefined. Because the reactions were hypothesised to take place at surface hydroxyl sites, glass was selected as a convenient material with a reproducible surface and a defined surface area.

2.2 Experimental technique and results

A full description of the experimental technique and some of the measured data on volatile inorganic and organic iodine formation as a function of time have been published.[7] Briefly, a suitable area (15 to 50dm\(^2\)) of an experimental surface was immersed in a solution of I\(^-\) ions traced with \(^{131}\)I and allowed to equilibrate. The solution was then drained away and the surface burden of iodine estimated from the loss of iodine in solution. The sample surface was then placed in a vessel through which water-saturated air (or an air/N\(_2\) mixture) was passed. For elevated temperature measurements, the air was subsequently cooled and surplus water (and some inorganic iodide) removed in a condenser. The gas flow then passed through a "Maypack" selective filter [8] where iodine species were absorbed for analysis. The Maypack filters were replaced at intervals during each experiment. A typical experiment was run for 216 hours (9 days) with \(\gamma\)-radiation on for 144 hours.

In a small number of measurements with painted surfaces, the iodine-loaded paint was suspended in a large sealed vessel (40dm\(^3\)); the gaseous contents of the vessel were purged through a Maypack at intervals.
Table 1
Experimental data for measurements on a glass surface.

Experiment 49, 25°C, 16/11/90.
Glass beads, surface 16.2 dm².
Radiation on after 48 hours 0.6 kGy.hr⁻¹.
Radiation off after 192 hours.
Final adsorbate I⁺ concentration: 1.5 x 10⁻⁶ M.
Surface I⁺ concentration: 4.7 x 10⁻¹³ g.atoms.dm⁻².
Iodine burdens in table: g.atoms.
Iodine in condenser during Maypack 2: 1.8 x 10⁻₁³ g. atom.
Iodine in condenser during Maypack 3: 1.0 x 10⁻₁³ g. atom.
Iodine in condenser during Maypack 4: 1.3 x 10⁻¹³ g. atom.
Iodine in condenser during Maypack 5: 2.9 x 10⁻¹³ g. atom.
Iodine in condenser during Maypack 6: 1.0 x 10⁻¹³ g. atom.
Iodine in condenser during Maypack 7: 2.3 x 10⁻¹⁴ g. atom.

<table>
<thead>
<tr>
<th>Elapsed Time (hrs)</th>
<th>Glass fibre filter</th>
<th>Carbon filter 1</th>
<th>Carbon filter 2</th>
<th>Carbon bed</th>
<th>Inorganic deposition rate (g.atoms.hr⁻¹)</th>
<th>Inorganic penetration rate (hr⁻¹)</th>
<th>Charcoal bed inorganic</th>
<th>Corrected organic</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>5.3 x 10⁻¹⁴</td>
<td>2.2 x 10⁻¹²</td>
<td>1.8 x 10⁻¹²</td>
<td>3.9 x 10⁻¹³</td>
<td>1.3 x 10⁻¹⁰</td>
<td>3.3 x 10⁻¹⁰</td>
<td>2.3 x 10⁻¹³</td>
<td>1.6 x 10⁻¹³</td>
</tr>
<tr>
<td>48</td>
<td>4.4 x 10⁻¹⁴</td>
<td>1.3 x 10⁻¹²</td>
<td>3.3 x 10⁻¹²</td>
<td>1.8 x 10⁻¹³</td>
<td>7.0 x 10⁻¹⁰</td>
<td>2.3 x 10⁻¹⁰</td>
<td>6.7 x 10⁻¹⁴</td>
<td>1.1 x 10⁻¹³</td>
</tr>
<tr>
<td>72</td>
<td>3.1 x 10⁻¹³</td>
<td>9.1 x 10⁻¹²</td>
<td>2.5 x 10⁻¹²</td>
<td>2.5 x 10⁻¹³</td>
<td>5.0 x 10⁻¹⁰</td>
<td>2.5 x 10⁻¹⁰</td>
<td>5.6 x 10⁻¹³</td>
<td>1.9 x 10⁻¹³</td>
</tr>
<tr>
<td>96</td>
<td>3.5 x 10⁻¹³</td>
<td>1.1 x 10⁻¹¹</td>
<td>2.9 x 10⁻¹²</td>
<td>3.3 x 10⁻¹³</td>
<td>6.0 x 10⁻¹⁰</td>
<td>2.4 x 10⁻¹⁰</td>
<td>6.2 x 10⁻¹³</td>
<td>2.7 x 10⁻¹³</td>
</tr>
<tr>
<td>168</td>
<td>5.9 x 10⁻¹³</td>
<td>1.1 x 10⁻¹¹</td>
<td>2.9 x 10⁻¹²</td>
<td>9.3 x 10⁻¹³</td>
<td>3.5 x 10⁻¹⁰</td>
<td>7.3 x 10⁻¹⁰</td>
<td>9.2 x 10⁻¹³</td>
<td>8.4 x 10⁻¹³</td>
</tr>
<tr>
<td>192</td>
<td>2.7 x 10⁻¹⁵</td>
<td>6.1 x 10⁻¹²</td>
<td>9.0 x 10⁻¹³</td>
<td>1.6 x 10⁻¹²</td>
<td>2.9 x 10⁻¹⁰</td>
<td>1.3 x 10⁻¹⁰</td>
<td>9.8 x 10⁻¹⁴</td>
<td>1.5 x 10⁻¹⁵</td>
</tr>
<tr>
<td>216</td>
<td>2.4 x 10⁻¹³</td>
<td>1.5 x 10⁻¹²</td>
<td>9.7 x 10⁻¹³</td>
<td>7.9 x 10⁻¹³</td>
<td>1.3 x 10⁻¹⁰</td>
<td>7.5 x 10⁻¹⁰</td>
<td>7.8 x 10⁻¹³</td>
<td>9.1 x 10⁻¹³</td>
</tr>
</tbody>
</table>

The iodine burdens on the Maypack components, determined by the radioactivity of tracer I¹³¹, were analysed in terms of inorganic and organic volatile iodine components. The varying proportions of the inorganic and organic contributions to the total volatile iodine, over the whole range of experiments, support the view that (at least) two volatile species were present. The identity of one of those species as inorganic iodine (I₂) is inferred from the retention behaviour on the Maypack absorbers. The proportion of volatile inorganic iodine on the Maypack was typically in the range from comparable with to an order of magnitude greater than the organic iodine in experiments with the flowing gas system. In the static vessel, the proportion of inorganic iodine was always reduced, indicating that important but relatively slow removal processes operated.

A typical set of results from one experiment (Table 1) shows the increase of volatile species formation when γ-radiation was turned on after 48 hours and the subsequent decrease when the radiation was turned off. The data from all the experiments was analysed in an empirical way to provide a simple linear algorithm which could be used to estimate volatile organic iodine formation following a reactor fault [8]. This had the form:

\[ f = (k + k_{rad} \times D) \times a \times c \]

where:
- \( f \) = formation rate ("mass".hr⁻¹)
- \( D \) = dose rate at the surface (β + γ) (Gy.hr⁻¹)
- \( a \) = area of wetted surface (dm²)
\[ c = \text{iodine concentration in solution in contact with the surface ("mass".dm}^{-3}) \]

The concentration of iodine in solution wetting the surface was used in the algorithm for convenience of use; a pH-dependent distribution coefficient between solution and surface was implicit in the pH-dependent values of the formation rates in the algorithm. The suggested rates for use in the algorithm (\( k \) and \( k_{\text{rad}} \), Table 2) were based on the upper bound of the experimental data, rather than on the regression line, because it was considered desirable to avoid underestimating the rate of formation of volatile iodine.

**Table 2**

<table>
<thead>
<tr>
<th>Surface</th>
<th>Conditions</th>
<th>( k(\text{dm.hr}^{-1}) ) (no radiation)</th>
<th>( k_{\text{rad}}(\text{dm.Gy}^{-1}) ) (radiation part)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paint</td>
<td>Acidic</td>
<td>( 4.2 \times 10^{-07} )</td>
<td>( 1.7 \times 10^{-09} )</td>
</tr>
<tr>
<td>Paint</td>
<td>Alkaline</td>
<td>( 1.4 \times 10^{-07} )</td>
<td>( 6.4 \times 10^{-10} )</td>
</tr>
<tr>
<td>Concrete</td>
<td>Any</td>
<td>( 8.1 \times 10^{-09} )</td>
<td>( 5.0 \times 10^{-11} )</td>
</tr>
<tr>
<td>Concrete dust-proofed</td>
<td>Any</td>
<td>( 3.7 \times 10^{-08} )</td>
<td>( 1.9 \times 10^{-10} )</td>
</tr>
</tbody>
</table>

In order to obtain a more precise estimate of volatile organic iodine formation including taking account of small effects, such as an influence of iodine concentration on the formation rate, a computer code was developed to model the experimental data.

3. THE COMPUTER MODEL

The code was based on the FACSIMILE package for solving simultaneous differential equations,[10] which will solve a set of equations written in the form of chemical reactions. A basic equation for a chemical reaction would have the form:

\[ \text{F1} \% \text{KF} \% \text{FR} : \quad A + B = C + D ; \]

which is equivalent to the chemical formulation:

\[ \frac{k_r}{k_i} \quad A + B \rightleftharpoons C + D \]

\( \text{F1} \) is a label for a parameter which carries the value of the instantaneous difference between the rate of the forward and reverse reactions; it also forms a convenient label for the equation. The value of \( \text{F1} \) at any instant is given by:

\[ \text{F1} = (\text{KF} \times A \times B) - (\text{KR} \times C \times D) \]

In some cases equations may be split as a convenient way to take account of other factors:

\[ \text{F1} \% \text{KF} : \quad \text{AG} = ; \]

\[ \text{F1A} \% \text{F1} / \text{SV} : \quad = \text{AS} ; \]
where SV is a surface/volume ratio. These two equations represent removal of $A_*$ from a gas phase and its deposition as $A_*$ onto a surface. Division by SV of the quantity of material leaving the gas phase correctly represents material added to the surface phase. The mass balance is maintained when allowance is made for the areas and volumes involved.

The basic units used through the code were seconds, moles and dm. Thus volume concentrations were expressed as mol.dm$^{-3}$ and surface concentrations as mol.dm$^{-2}$.

The equations used in the code to represent chemical reactions are shown (Figure 1). The additional coding needed to define parameters, variables and the time sequence of the experiments has been omitted. A typical input data set, needed to run the final model, is also shown (Figure 2). The surface iodine burden, HIS, is calculated within the code from input solution concentration and distribution coefficient data. The rate constants for each equation, the number of active surface sites (MOH) and the effective concentration of surface organic material (CH3OHS) were unknown. These unknowns were fitted iteratively in an early, simplified version of the programme to match the experimental data for a paint surface at ambient temperature.[7] A reverse rate constant was only included in those equations where it was required to fit the experimental observations. Only those equations which include both the forward and reverse rate constants can lead to equilibrium distribution of the reactants. In addition to equations F1 to F8 for organic iodide formation (reactions (1) to (5)) and the corresponding radiolytic reactions (F17, F18), which had a basis in known reactions, it was necessary to add reactions which formed volatile inorganic iodine species. These were needed to maintain the correct surface loading of iodine in face of the known losses of inorganic iodine into the Maypack filters. Equations F21 to F25 were added on a purely empirical basis to remove the appropriate quantities of inorganic iodine and are not intended to be mechanistic.

The derived value of MOH ($3 \times 10^{-8}$ mol.dm$^{-2}$ or $55 \AA^2$.MOH$^{-1}$) was in good agreement with the number of surface nitrogen atoms or secondary alcohol groups on the surface of the epoxy-phenolic paint, as measured by photoelectron spectroscopy. The optimised initial value of CH3OHS ($5.0 \times 10^{-11}$ mol.dm$^{-2}$) was held constant throughout the simulation. In physical terms, this implies that mechanisms exist to replenish absorbed (CH$_3$OH)$_n$ from sources of organic material as it is consumed and that the rate of replenishment is not a rate-determining step.

Having determined the parameters for a basic programme, measurements on other surfaces were considered and additional reactions were added to extend the range of applicability.

(i) "Surface efficiency factors" were added to the input data set and used to scale the reaction rates for different surfaces. It was found that different factors were needed for organic and for inorganic formation reactions and also for radiolytic and non-radiolytic
FIGURE 1

Equations to model organic iodine formation at surfaces.

\[
\begin{align*}
F1\&.E10 & \times 0.051 : \\
F2\&.0E10 & \times 6.3.7E05 : \\
F3\&.KFACT & \times (0.230 + 77 \times 02) \times OFACT : \\
F4\&.1E01 & : \\
\text{***** ADSORPTION/DESORPTION OF CHI ***** :} \\
F5\&.5E-5 & : \\
F5A\&F3 & / SV : \\
F6\&.1E-03 & : \\
F6A\&F6 & * SV : \\
F7\&.KBUFFER & / KBUFFER / CH3OH : \\
F8\&.KPURGE & : \\
\text{***** TEMPERATURE DEPENDENT REACTIVITY LOSS ***** :} \\
F9\&.K9 & : \\
F10\&.K9 & : \\
\text{***** EQUILIBRATION OF GASEOUS AND AQUEOUS ORGANIC ***** :} \\
F1\&.KPART & : \\
F1A\&F1 & * LOG : \\
F12\&.KPART & * PV + LOG : \\
F12A\&F2 & / LOG : \\
\text{***** ORGANIC IODINE DESTRUCTION IN SOLUTION. ***** :} \\
F13\&.HYD & : \\
F14\&.0E-3 & * DR : \\
\text{***** ORGANIC IODINE DESTRUCTION IN ATMOSPHERE. ***** :} \\
F15\&.2E-05 & : \\
F15A\&F5 & / SV : \\
F16\&.1E-3 & * DR + 0.0012 : \\
F16A\&F6 & / SV : \\
\text{***** RADIATION FORMATION REACTION ***** :} \\
F17\&.KRAD & * (359 + 3.03e05 * 02) * ROFACT : \\
F17A\&F17 & / : \\
\text{***** SURFACE PARTITIONING REACTION OF I (HIAQ) ***** :} \\
F18\&.K19 & : \\
F19A\&F19 & * LV / AREA : \\
F20\&.K19 & * LV (DIST \times AREA) : \\
F20A\&F20 & * AREA / LV : \\
\text{***** INORGANIC FORMATION REACTION ***** :} \\
\text{***** THIS SECTION IS NOT MECHANISTIC ***** :} \\
F21\&.0E14 & + 97 \times 02 \times IFACT : \\
F21A\&F21 & / SV : \\
F22\&.0E14 & + 97 \times 02 \times IFACT : \\
F22A\&F22 & / SV : \\
F23\&.KRAD & * (359 + 1.65e05 \times 02) * RIFACT : \\
F23A\&F23 & / SV : \\
F24\&.KPURGE & : \\
F25\&.0E-04 & : \\
F25A\&F25 & / SV : \\
\text{***** EMPIRICAL INCLUSION OF RADIONUCLIDIC I ***** :} \\
\text{***** PRODUCTION AND UPTAKE BY PAINT ***** :} \\
F19\&.KIX & : \\
F31A\&F31 & * LV / AREA :
\end{align*}
\]

reactions. (OFAC, ROFACT, IFACT, RIFACT, scaling factors in F3, F17, F18, F21, F22, F23) The scaling factors were unity for the painted surface because the rates in the code were derived for that surface (Table 3).

(ii) A decomposition rate for gaseous CH₃I (F15) was determined from measurements in a static atmosphere.[7] No component due to radiolysis could be detected.
(iii) A temperature scaling factor was determined for a glass surface and found to be unity over the temperature range 25°C to 75°C, i.e. zero temperature coefficient. (KFACT in F3)
The data for the painted surface was not consistent with a zero temperature coefficient.
(KFACT = 1 at 25°C and 4.0 at 75°C)

(iv) A temperature-dependent diffusion factor was determined for the epoxy-painted surface, corresponding to loss of iodine into the bulk paint. (F9, F10)

(v) Partitioning of iodide from solution to replace the original absorbed layer was included to accommodate iodine in the capillary film on the sample surface, or contact with bulk solutions. (F19, F20)

(vi) Partitioning of CH$_3$I between gas and liquid phases was added (F11, F12) using a temperature-dependent partition coefficient calculated from data given in the review by Borkowski.[11, 6]

(vii) On the basis of measurements in the ACE/RTF tests,[5] the hydrolysis of CH$_3$I in the
aqueous phase was added, using a temperature-dependent hydrolysis rate constant taken from
the review by Borkowski.[11, 6] (F13) An additional radiolytic destructive reaction in
solution was also added. (F14)

(viii) No gas phase radiolytic decomposition of organic iodine could be detected in the RTF
experiments but, for consistency, the reaction was added (F16). The rate constant used was
that for the reaction in solution; the dose rate is reduced in the ratio of the densities of liquid
and gas and the overall effect is negligible in all conditions tested.

(ix) In the ACE/RTF tests, substantial quantities of radiolytically formed oxidised inorganic
iodine were taken up by the paint. There is no inorganic iodine solution chemistry in the
current organic iodine code. The uptake by the paint was modelled by a first order transfer of
iodine from solution to the surface (F31), using a rate constant determined empirically from
the analytical data for each test. A conditional switch was included in the code to suppress the
partitioning of iodine between the surface and solution (F19, F20) when the rate used in F31
was non-zero.

Not all reactions are used in all simulations. With the exception of the switch between
partitioning and addition of radiolytic iodine to the surface, other unwanted reactions are
eliminated by setting appropriate parameters (gas flow rate, liquid volume, dose rate, etc.) to
zero in the input data set.

<table>
<thead>
<tr>
<th></th>
<th>M253 paint</th>
<th>RTF paint</th>
<th>Glass (i)</th>
<th>Glass (ii)</th>
<th>Concrete</th>
<th>Stainless steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>OFACT</td>
<td>1.0</td>
<td>1.0</td>
<td>3.0</td>
<td>0.7</td>
<td>0.14</td>
<td>1.2</td>
</tr>
<tr>
<td>ROFACT</td>
<td>1.0</td>
<td>120</td>
<td>3.0</td>
<td>2.0</td>
<td>0.14</td>
<td>1.5</td>
</tr>
<tr>
<td>IFACT</td>
<td>1.0</td>
<td>0.25</td>
<td>30</td>
<td>2.0</td>
<td>0.01</td>
<td>3.0</td>
</tr>
<tr>
<td>RIFACT</td>
<td>1.0</td>
<td>0.25</td>
<td>30</td>
<td>4.0</td>
<td>0.01</td>
<td>0.2</td>
</tr>
</tbody>
</table>

4. PERFORMANCE OF THE MODEL

4.1 Comparison with laboratory data

A full comparison of predictions from the model with the experimental data on which it was
based has been made elsewhere.[7, 12] A convenient method of showing the deviations
between the modelled and measured values for volatile iodine species release from the surface
was a graphical comparison (Figure 3). The comparison shows a scatter of points on both
sides of the unit ratio line which represents perfect modelling. The results for other
experiments are similar, indicating that there are not systematic deviations between the model
and experiment.
4.2 Comparison with ACE/RTF tests

The organic iodine data from the ACE/RTF tests [5] was used both to provide parameters for the code (CH$_3$I phases, see Section 3) and for a test of the code (CsI and I$_2$ phases). Because the configuration of the RTF tests included a liquid pool and "unwetted" containment walls above the liquid, it was expected that two sets of surface reaction equations would be needed to model the different iodine burdens on wetted and dry walls. When the experimental data from the tests became available, the measurements indicated that the difference of iodine burden on submerged and unwetted walls was comparable to the measuring accuracy. The standard set of equations (Figure 1) was therefore used to model the ACE/RTF tests. Except for the CsI test without radiolysis, which was treated identically to the laboratory experiments, the surface burden of iodine was taken to be equal to the experimentally measured mass deficit of iodine during the test. The surface iodine burden was uniformly distributed over the total containment surface. Values of the two adjustable parameters, OFACT and ROFACT, were adjusted to suit the measured data (Table 3). The corresponding inorganic iodine factors, IFACT and RIFACT, were adjusted only using Test 1A, (CsI). The code contains no reactions to model the volatility and hydrolysis of I$_2$ in solution and it would not be expected that the code would model inorganic iodine volatility correctly.

**FIGURE 3**

Comparison of modelled and experimental volatile iodine species formation on M253 paint.

- Organic Iodine formation on M253 paint
- Inorganic Iodine formation on M253 paint

- Log (g. atoms.) Calculated values vs. Log (g. atoms.) Experimental values.

- * Air, ambient temperature.
- + Nitrogen, ambient temperature.
- Δ Air, elevated temperature.
FIGURE 4

ACE/RTP test results and simulations.

(A)
Test 1, CsI, no radiation.

(B)
Test 1, I_3, no radiation.

FIGURE 5

ACE/RTP test results and simulations.

(A)
Test 2, CsI, radiation, alkaline.

(B)
Test 2, I_3, radiation, alkaline.
When the model was applied to Tests 1A and 1C (CsI and I₂), the calculated gaseous organic iodine values were reasonably close to the experimentally measured values (Figure 4A and B). For Test 2A (Figure 5A) the calculated results were a factor of two lower than the measured values. The measured solution iodine deficit was at the limit of the analytical accuracy,[13] so this error is probably reasonable. The calculated results for Test 2C were in good agreement with the measured results (Figure 5B).

The calculated results for Tests 3B and 3E (CsI and I₂) showed the correct time dependence but were a factor of two to three low (Figure 6A and B). Inspection of the values of species concentrations within the code output showed that the high surface iodine concentrations were displacing organic species from the reactive surface sites and reducing the yield of volatile iodine. In the code, iodine is lost from the surface by diffusion into the bulk paint at a rate determined for the UK epoxy paint. Paradoxically, increasing the rate of diffusion of iodine into the paint would increase the rate of volatile organic iodine production. This was confirmed by one test run with an arbitrarily increased diffusion rate.

No attempt was made to adjust the iodine diffusion rate to match the results for Test 3. An alternative explanation of the low calculated results is possible. If "ROFACT" was artificially high because, in the RTF tests, a significant contribution came from a homogeneous liquid phase radiolytic formation of volatile organic iodine, discrepancies between Tests 2 and 3 could be expected. For this reason, it was felt that altering the diffusion term would not be justified without "separate effect" tests on the Canadian paint.
5. CONCLUSIONS

The initial hypothesis, that volatile organic iodine species are produced in significant quantities by surface reactions, has been validated by experiment. Comparable, or larger quantities of a second volatile iodine species were also found; the behaviour of this species is consistent with inorganic iodine I$_2$ but the identification is based only on absorption behaviour in Maypack detectors.

A computer code, based on known surface reactions, has been developed which gives a reasonable simulation of the experimental results for a range of surfaces and a wide range of concentration and pH. It was necessary to include four adjustable rate parameters in the code, which need to be determined for each surface type. The four parameters control the rate of formation of organic and inorganic volatile species by non-radiolytic and radiolytic processes.

The code was developed from measurements based on absorption of I$^-$ ions from solution. It would be anticipated that the same code would be applicable to volatile species formation following absorption from I$_2$ in solution, with due allowance for the different distribution coefficients between a surface and I$^-$ or I$_2$ in solution. This has not been experimentally validated and has been tested only using results from the ACE/RTF tests, where both I$^-$ and I$_2$ were included in different phases of the tests. The epoxy-phenolic paint on the surface of the containment vessel was not identical to that used to develop the model. In the absence of radiation, modelled results are close to the measured values of gaseous organic iodine. In the presence of radiation, the modelled results are good for alkaline solutions but low for acidic solutions. Two possible reasons have been identified for low calculated values of organic iodine production in radiolysed acid solutions. One is that a diffusion term for surface iodine into the paint, where it is no longer reactive, was underestimated by the use of a value determined for UK paint. The second is that no homogeneous aqueous radiolytic formation reactions are included in the code.

The code, in its present form, cannot be used predictively because it lacks the inorganic iodine reactions needed to describe the radiolytic oxidation of I$^-$ and the uptake of oxidised iodine species by surfaces. At present, the surface burden of iodine must be input empirically.

ACKNOWLEDGEMENTS

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Valuable suggestions have been made by Drs. W.G.Burns and H.E.Sims and Mr.C.P.Davies has contributed to the experimental programme.
REFERENCES


   (ii) Evans, G.J., Preliminary results from ACE/RTF Test 2.
   (iii) Jobe, D.J., Preliminary results from ACE/RTF Test 3.


DISCUSSION

Karasawa
Have you studied the pH dependence of organic iodide production?

Sims
I think the pH dependence was such that organic iodide production increases with decreasing pH.

Ritzman
What was the effect of radiation in your measurements of organic iodide?

Sims
The effect of radiation was always to increase the rate of organic iodide production.

Evans
In these experiments the organic iodides were produced from surfaces that were not in contact with water, have you performed experiments with submerged paints?

Sims
We have not yet done submerged surfaces but experiments are underway.
3.3 THE EFFECTS OF ZINC PRIMER SURFACES ON IODINE BEHAVIOUR WITHIN CONTAINMENT


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ABSTRACT

The effects of zinc-primer-coated containment surfaces on iodine chemistry have been investigated. Intermediate-scale tests in the Radioiodine Test Facility (RTF) involving such a surface and $10^{-5}$ mol dm$^{-3}$ CsI aqueous solutions show remarkably low iodine volatility ($<2.4 \times 10^{-11}$ mol dm$^{-3}$). This is in part due to the reductive properties of the surface and its appreciable affinity for iodine. Up to 66% of the initial iodine inventory was found on the zinc primer surfaces at the end of each RTF test, with most of the retained iodine on surfaces in contact with the aqueous phase. Separate-effects experiments have shown that surface adsorption of iodine is greatest under aerobic alkaline conditions. The results are rationalized in terms of I$^-$ incorporation into zinc corrosion products.

1. INTRODUCTION

It is generally recognized that radioiodine is one of the most hazardous fission products that can escape from irradiated fuel in a reactor accident. This is due to the combination of its large inventory in fuel, short half-life and biological activity. Furthermore, iodine has volatile chemical forms, which increases the probability of its release to the environment. One way that potential iodine releases can be reduced is by deposition onto containment surfaces. Indeed, previous studies [1-5] have shown that surface deposition may be an important process for reducing gas phase iodine concentrations. However, the extent of iodine mitigation is dependent on the conditions within containment and the nature of the surface. As a result, the performance of each containment surface should be assessed under conditions expected during an accident.

One of the surfaces present in several CANDU reactor containment buildings is an inorganic zinc primer coating. This coating, which is used to protect containment carbon steel liners from corrosion [6], has been shown to be an effective sink for gas phase elemental iodine and methyl iodide [1]. Little is known, however, about the performance of this coating under simulated accident conditions and its overall effect on iodine chemistry within containment.

* CANada Deuterium Uranium. Registered trademark of AECL.
This paper summarizes recent results from intermediate-scale experiments with zinc primer surfaces in the Radioiodine Test Facility (RTF). In addition, separate-effects tests are described that rationalize the unexpected interactions between this surface and aqueous iodine species.

2. EXPERIMENTAL

2.1 Radioiodine Test Facility Experiments

The RTF is an intermediate-scale facility designed to test the behaviour of iodine under simulated reactor accident conditions. Details of the design and operation of the RTF have been described previously [7-9]. A schematic of this facility is shown in Figure 1.

The zinc primer coating used in the current study was Carbo Zinc 11, a self-curing, inorganic-based coating (Carboline Co., St. Louis, MO). It consists of two parts: Carboline Zinc Filler, which is composed of elemental zinc dust, and Carbo Zinc 11 Base, which contains crystalline silica, hydrated aluminum silicate (kaolin), mica, tetramethoxysilane and several alcohols, including methanol, ethanol, isopropanol and 2-ethoxybutanol. When the two components are mixed, reaction of hydrolyzed tetramethoxysilane with the elemental zinc results in the formation of a zinc silicate matrix in which unreacted zinc particles are embedded [10]. The manufacturers of this coating indicate that zinc constitutes 85 ± 1 wt% of the dry film. This zinc-based coating was applied to a 340 dm³ carbon steel vessel within 4 h of sandblasting. The vessel was then aged for at least 8 weeks before use in the RTF. The vessel was subsequently placed in the lead canister (see Figure 2) and connected to the piping manifold. For radiation tests, the 315-TBq cobalt-60 irradiation source was secured within the vessel. This operation was undertaken in a hot cell because of the high dose rates associated with the irradiation source. The vessel was then pressure tested and the lead canister transported to the RTF, where it was connected to the various process loops.

Prior to the start of a test, the vessel was thoroughly purged with ultra-high-purity air (Matheson), followed by the addition of distilled water. The pH was adjusted to 10 using LiOH and 100 to 300 mL of a concentrated solution of CsI was then added. The injected CsI solution, which was prepared the night before and purged with high-purity argon to remove any volatile iodine species or organics, was routinely labelled with 370 MBq of carrier-free iodine-131 (ICN Biomedicals). This enabled the use of γ-counting techniques for the determination of total gas and aqueous phase iodine concentrations. Samples were analyzed using a LKB Compugamma automatic γ-counting system equipped with a well-type 3 x 3 NaI detector. Iodine speciation of gas and aqueous phase samples was achieved through the use of species-selective adsorbents [11] and solvent extraction techniques [12], respectively; the adsorbents and extracted fractions were analyzed using γ-counting techniques. Organic iodide speciation of gas and aqueous phase samples was determined by gas chromatography (GC) and high-performance liquid chromatography (HPLC), respectively.

Experimental conditions for the RTF test program are listed in Table 2.1.
Table 2.1

RTF Test Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Iodine</td>
<td>$10^{-5}$ mol.$\cdot$dm$^{-3}$ CsI</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Aqueous Volume</td>
<td>25 dm$^3$</td>
</tr>
<tr>
<td>Gas Volume</td>
<td>315 dm$^3$</td>
</tr>
<tr>
<td>Initial pH</td>
<td>10 (unbuffered)</td>
</tr>
<tr>
<td>Gas Recirculation Rate</td>
<td>30 dm$^3$$\cdot$min$^{-1}$</td>
</tr>
<tr>
<td>Aqueous Recirculation Rate</td>
<td>11 dm$^3$$\cdot$min$^{-1}$</td>
</tr>
<tr>
<td>Gas Venting Rate - on/off</td>
<td>0/7-10 dm$^3$$\cdot$min$^{-1}$</td>
</tr>
<tr>
<td>Dose Rate - without/with cobalt-60</td>
<td>0/2 kGy.$\cdot$h$^{-1}$</td>
</tr>
<tr>
<td>irradiation source</td>
<td></td>
</tr>
</tbody>
</table>

After injection of the CsI, which constitutes initiation of the test, the gas and aqueous phase concentrations of iodine were continuously monitored, as were gas and aqueous phase temperatures, pH and the dissolved oxygen concentration. Whenever steady-state conditions became apparent, an intentional perturbation of the system was undertaken and changes in gas and aqueous phase properties were monitored. Perturbations that were studied include venting and the addition of organic material (methyl ethyl ketone), redox reagent ($N_2H_4$) or base (LiOH). Since for each test several deliberate perturbations were made, the duration of each test was approximately 25 d.

At the end of a test, the aqueous phase was sampled, the remainder discarded and the zinc-primer-coated vessel washed several times with water and dilute hydrazine solutions to remove any weakly adsorbed iodine. The vessel was then treated with Nalclean 66 (Alchem Inc., Burlington, ON), a commercially available scale remover. The water, aqueous hydrazine and Nalclean 66 solutions were subsequently analyzed for total iodine.

As the treatment of the vessel with Nalclean 66 destroys the original zinc primer coating, the carbon steel vessel was freshly sandblasted, repainted and aged prior to the second RTF test.
2.2 Bench-Scale Program

2.2.1 Preparation of Zinc Primer Pellets

Attempts to coat carbon steel coupons with zinc primer were unsuccessful because of the difficulty in obtaining reproducible coupon surfaces. Also, the zinc primer did not adhere well to the corners of these coupons, thereby exposing the carbon steel substrate. As a result, the iodine surface adsorption tests were conducted using pressed pellets of the coating. Aliquots of the paint base and filler were mixed and allowed to dry for several days. The zinc primer mixture was then ground with a SPEX 8000 mixer and the resulting material passed through a 140-mesh sieve. One-gram portions were then pressed into small discs (12.9-mm diameter x 1.4 mm) using a Specac pellet press (Spectrex Ltd., Montreal, PQ). Immediately prior to use, the coupons were polished to a 1200-grit finish. The geometric surface area of the coupons was routinely 3.3 cm².

2.2.2 Adsorption Studies

Sodium hydrogen sulfate, sodium acetate, boric acid and hydrazine sulfate were obtained from the Fisher Scientific Company and were ACS- or reagent-grade quality. Argon (ultra-high-purity) was from Matheson. Test solutions were prepared by dissolving Aldrich "Gold Label" CsI or I₂ into water previously purified by distillation and deionization using a Barnstead Nanopure System. The test solutions were then labelled with iodine-131 (ICN Biomedicals), appropriate quantities of buffer and other reagents were added as required, and the solution was diluted to the desired concentration. The pH was then adjusted with either H₂SO₄ or LiOH.

Iodine deposition studies were undertaken in two different apparatus. Tests designed to determine iodine deposition from aqueous I⁻ solutions were conducted in a 0.5-dm³ glass vessel in which up to 16 coupons were placed. The test solution was mixed using a magnetic stirrer and Teflon-coated stirring bar. Tests in this apparatus could be conducted in an air environment or anaerobically, using a continuous argon purge of the test solution. At selected times, test coupons were removed for γ-counting. Prior to analysis, samples were thoroughly rinsed twice with distilled water to remove entrained solution. Separate tests showed that additional washings were unnecessary.

Because of the volatility of elemental iodine, tests with I₂ could not be undertaken with the previously described apparatus. Rather, they were conducted in sealed 20-ml glass vials in which a single test coupon was placed. Agitation of the test vials was achieved using a wrist-shaker. Test coupons were analyzed as described above.

3. RESULTS

3.1 Radiiodine Test Facility

Figures 3 and 4 illustrate the effects of radiation, zinc primer surfaces and systematic perturbations to RTF operating conditions on iodine behaviour in the RTF. For each test, the initially added aqueous CsI solution (10⁻⁵ mol.dm⁻³) was allowed to equilibrate with the gas phase and surfaces prior to changing experimental conditions. These changes in condition included (i) direct venting (DV) of the gas phase during which the gas phase in the RTF is replaced with ultra-high-purity air, (ii) use
of a charcoal filter (CF) venting procedure where the RTF gas phase is recirculated through a TEDA (triethylenediamine)-impregnated charcoal bed to remove airborne iodine species, and (iii) addition of methyl ethyl ketone (MEK), (iv) hydrazine (N₂H₄) or (v) base (LiOH) to determine their influence on iodine behaviour. As Figures 3 and 4 show, these perturbations impact on iodine behaviour and a rationalization of their effect is described elsewhere [7,13]; this paper focusses primarily on the surface effect phenomena observed in these tests.

Figure 3 depicts gas and aqueous phase iodine concentrations in the RTF with the cobalt-60 irradiation sources installed, whereas Figure 4 represents the results of a similar test conducted without the irradiation source. Comparison of these figures for the first 100 h of the test shows that the airborne iodine concentration increases quickly within the first few hours and then either reaches a steady state concentration (1.6 x 10⁻¹² mol.dm⁻³) in the test with the cobalt-60 irradiation source or continues to increase slowly without the irradiation source, reaching a value of 2.4 x 10⁻¹¹ mol.dm⁻³. It should be noted that the modest increase in gas phase iodine concentration at 22.6 h coincides with activation of trace heaters on the Gas Recirculation Loop, although the reason for this correlation is unclear.

Figures 3 and 4 also illustrate that aqueous phase iodine concentrations, in general, decrease with time. In the test with radiation, approximately 45% of the original iodine inventory cannot be accounted for in the gas and aqueous phases; for the non-radiation test, this increases to about 66%. As shown in Table 3.1, post-test mass balance analysis revealed that most of the missing iodine was retained on the zinc primer surface. Indeed, washing of the surfaces with distilled water and hydrazine solutions removed only a small fraction of the retained iodine. The remaining surface iodine was removed with Nalclean 66 decontamination solution.

Prior to vessel decontamination, the reaction vessel was monitored for iodine-131. It was found that the zinc primer surfaces in contact with the aqueous phase retained most of the iodine. As shown in Table 3.2, analysis of coupons placed in the RTP supports this observation. A visual inspection of the vessel also revealed the presence of white deposits on portions of the vessel surface that had been in contact with the aqueous phase. These deposits were found to contain higher levels of iodine-131 than did surrounding surfaces.

### 3.2 Iodine Adsorption onto Zinc Primer Surfaces from CsI Solutions

Figure 5 shows the results of a radiotracer study examining iodine adsorption onto zinc primer surfaces from an aerated 10⁻⁵ mol.dm⁻³ CsI solution (pH 9; 0.001 mol.dm⁻³ H₂BO₃; 0.001 mol.dm⁻³ N₂H₄); hydrazine was added to reduce any I₂ or IO₃⁻ present in the iodine-131 radiotracer. The extent of surface loading was initially linear, with a deposition velocity of 1 x 10⁻⁵ cm.s⁻¹. The iodine loading continued to increase, even after equilibration for one week, reaching a value of approximately 5 µg.cm⁻². Similar results were also obtained with pellets made from high-purity metallic zinc (Aldrich, Milwaukee).

Dramatically different behaviour was observed when the test was repeated in an argon atmosphere, as also shown in Figure 5. Under these conditions, negligible quantities of iodine (<0.01 µg.cm⁻²) were deposited on the zinc primer surfaces.

To substantiate these observations, a test with 10⁻³ mol.dm⁻³ CsI was
conducted under anaerobic conditions. Adsorption of iodine was initially minimal (0.1 \( \mu g \cdot cm^{-2} \)) over a three-day period, but, upon the introduction of air into the test apparatus, iodine retention rapidly increased to approximately 80 \( \mu g \cdot cm^{-2} \).

Tests in the absence of hydrazine were also conducted to ensure that hydrazine was not involved in the iodine sorption process. Similar results to those already described were obtained.

Table 3.1

Mass Balance Measurements for RTF Zinc Primer Experiments

<table>
<thead>
<tr>
<th></th>
<th>Radiation Test % Recovery</th>
<th>Non-Radiation Test % Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Phase</td>
<td>39.4</td>
<td>20.6</td>
</tr>
<tr>
<td>Gas Phase</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Surfaces - H(_2)O/N(_2)H(_4) Wash</td>
<td>10.7</td>
<td>4.4</td>
</tr>
<tr>
<td>- Nalclean 66</td>
<td>34.2</td>
<td>61.7</td>
</tr>
<tr>
<td>Sampling</td>
<td>12.5</td>
<td>11.4</td>
</tr>
<tr>
<td>Venting</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Coupons</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>98.7</strong></td>
<td><strong>98.4</strong></td>
</tr>
</tbody>
</table>

Table 3.2

Surface Loadings of Iodine on RTF Surfaces

<table>
<thead>
<tr>
<th></th>
<th>Gas Phase (ng \cdot cm(^{-2}))</th>
<th>Aqueous Phase (ng \cdot cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation Test</td>
<td>870</td>
<td>5300</td>
</tr>
<tr>
<td>Non-Radiation Test</td>
<td>5.5</td>
<td>2100</td>
</tr>
</tbody>
</table>

* As determined by analysis of coupons in RTF.
3.3 Iodine Adsorption onto Zinc Primer Surfaces from I₂ Solutions

Tests were conducted with initial I₂ concentrations of 5 \times 10^{-5} \ mol\cdot dm^{-3}. The results obtained at pH 1.7 (0.05 mol\cdot dm^{-3} sulfate buffer) are shown in Figure 6. Iodine loading onto the zinc primer pellets increased over the first 5 h of equilibration, reaching a maximum of approximately 0.21 µg\cdot cm^{-2}. This was followed by a slow decrease in iodine loading. Similar behaviour was also observed at pH 4.8 (0.05 mol\cdot dm^{-3} acetate buffer), except iodine loadings did not change appreciably at longer equilibration times.

Product analysis studies were conducted under anaerobic conditions to determine the chemical form and quantity of iodine remaining in solution after reaction. Spectrophotometric analysis of reaction mixtures revealed I⁻ as the only detectable form of iodine in solution, comprising more than 97% of the initially added I₂.

4. DISCUSSION

As illustrated in Figures 3 and 4, very low iodine volatilities are observed in both the presence and absence of high radiation fields when CsI solutions are added to the RTP and allowed to equilibrate with the gas phase and surfaces. There are several reasons for this behaviour. Firstly, the zinc primer coating used in these tests contains elemental zinc, a powerful reductant (E° = 0.763 V) that reacts with oxidized forms of iodine. Indeed, previous work has shown that zinc primer coatings readily reduce both aqueous and gas phase I₂ [1,14]. Since the I⁻ product formed is involatile under RTP operating conditions, minimal iodine volatility would be expected. Secondly, the primer is predominantly inorganic in nature, except for various volatile alcohols that readily evaporate during the aging period. Therefore, formation of volatile organic iodides should be limited because of the modest quantity of organic material available for reaction.

The higher gas phase iodine concentrations observed in the non-radiation test may be due to the formation of organic iodides by thermal reaction of iodine with trace organics. In support of this suggestion, gas speciation analysis with species-selective adsorbents revealed that, prior to the direct vent (DV), all but 2% of the gas phase iodine was in the form of organic iodides; this was confirmed by gas chromatography, which demonstrated that gas phase iodine was almost exclusively in the form of CH₃I. By comparison, lower gas phase organic iodide concentrations in the RTP radiation test may arise because of radiolytic decomposition of the organic iodides formed [15].

Despite the very modest volatilization of iodine in the RTP experiments, Figures 3 and 4 reveal a dramatic decrease in the aqueous phase concentration of iodine. This can only be explained by surface deposition of iodine, as was substantiated by post-test analysis of the reaction vessel. Furthermore, as shown in Table 3.2, iodine retention occurred predominantly on surfaces in contact with the aqueous phase. This was unexpected based on the nature of the surface and the iodine species in solution. Speciation analysis revealed that I⁻ was the predominant aqueous iodine species throughout both RTP experiments. Iodide ion does not have any known adsorption affinity for elemental zinc, nor does it adsorb appreciably onto various clay minerals, including the aluminum silicate kaolinite [16], which is contained in the zinc primer coating. Indeed, the latter class of compounds have permanent negative surface charges arising.
from isomorphous substitution of $\text{Si}^{4+}$ with lower valent cations, such as $\text{Al}^{3+}$, within the silicate structure. This results in cationic, not anionic, exchange properties [17,18]. Nevertheless, as shown in Figure 5, confirmation of the RTF results was obtained in separate-effects tests in which aerated CsI solutions were equilibrated with zinc primer pellets.

A rationalization of this phenomenon is possible based on the dramatically different results obtained under anaerobic conditions. As shown in Figure 5, negligible retention of iodine on zinc primer surfaces occurs in the absence of air. This suggests that oxygen and oxidation processes play a key role in determining the extent of iodine deposition. The nature of the oxidation reaction controlling iodine deposition is not immediately clear, however. For example, oxidation of $\text{I}^-$ to $\text{I}_2$ and subsequent disproportionation to iodate could be responsible for surface deposition of iodine since these products would be expected to have higher affinities for surfaces. However, the oxidation of $\text{I}^-$ by dissolved oxygen under these test conditions (i.e., pH 9 to 10) is extremely slow [19,20]. Furthermore, these oxidized species are readily reduced back to $\text{I}^-$ by the zinc component of the coating, which, as already noted, has minimal affinity for $\text{I}^-$. This was confirmed for the case of $\text{I}_2$ in a separate-effects test (see Figure 6). Another argument against $\text{I}^-$ oxidation as the reaction responsible for iodine surface retention is the presence of aqueous hydrogen peroxide. Hydrogen peroxide is not only a product of water radiolysis, it is also formed in the reaction of zinc metal with dissolved oxygen [21,22]:

$$
\text{Zn}_{(s)} + \text{O}_2^{(aq)} + 2\text{H}^+_{(aq)} = \text{Zn}^{2+}_{(aq)} + \text{H}_2\text{O}_2^{(aq)}
$$

As a result, $\text{H}_2\text{O}_2$ is present in solution in both the presence and absence of high radiation fields. Under the alkaline conditions of these tests, therefore, any reaction leading to oxidation of $\text{I}^-$ to $\text{I}_2$, and its hydrolysis product HOI, would be countered by reactions (2) and (3).

$$
\text{H}_2\text{O}_2^{(aq)} + \text{HOI}_{(aq)} = \text{I}_2^{(aq)} + \text{H}^+_{(aq)} + \text{O}_2^{(aq)} + \text{H}_2\text{O}
$$

$$
\text{H}_2\text{O}_2^{(aq)} + \text{OI}^-_{(aq)} = \text{I}_2^{(aq)} + \text{O}_2^{(aq)} + \text{H}_2\text{O}
$$

Although there is some uncertainty as to the actual mechanism and rate constant for reaction (3) [23,24], reduction of HOI and $\text{OI}^-$ is much faster than $\text{I}^-$ oxidation. Therefore, iodine will be maintained predominantly in $\text{I}^-$ form, suggesting that an alternative oxidation process must be responsible for iodine adsorption.

We believe this process involves the corrosion of the zinc component of the primer coating. Indeed, similar iodine sorption behaviour was observed whether test surfaces were prepared with zinc primer or high-purity elemental zinc. As already noted, zinc metal is a powerful reductant that is readily oxidized to $\text{Zn}^{2+}_{(aq)}$ by dissolved oxygen. However, under the alkaline conditions of the RTF and separate-effects tests, zinc(II) has a very limited solubility and would precipitate on the corroding surface. The precipitated zinc can have various forms, depending on the experimental conditions: zinc hydroxide (probably as $\epsilon$-$\text{Zn(OH)}_2$), hydrated zinc oxide, or a basic carbonate if carbon dioxide is available [25].

Shown in Figure 7 are scanning electron microscopy (SEM) micrographs of zinc primer pellets before and after equilibration with a pH 9 buffered (10^{-3} \text{ mol dm}^{-3} \text{ borate}) solution. The equilibrated samples reveal formation
of a deposit that contains zinc, according to SEM energy-dispersive x-ray analysis. X-ray diffraction analysis also suggests the presence of minor amounts of a basic zinc carbonate, Zn₄CO₃(OH)₆•H₂O. Finally, x-ray photoelectron spectroscopy (XPS) results reveal that the deposit contains divalent zinc; it also confirms the presence of carbonate. Preliminary results for coupons equilibrated with 10⁻⁵ mol·dm⁻³ CsI solutions suggest similar corrosion behaviour.

These results, combined with the known corrosion chemistry of zinc, are consistent with the assignment of the deposited material as a mixture of various zinc hydroxides (α-, β-, γ-, ε-Zn(OH)₂), zinc oxide (ZnO), and one or more basic zinc carbonates. Iodine retention on these surfaces may arise from I⁻ incorporation into the oxidized zinc product as it precipitates [26]. Alternatively, Blok and De Bruyn [27-29] have suggested that, during precipitation of ZnO, anions that are present in solution may be incorporated onto the surface as a layer of Zn(OH)₁₋₆X₀.₆ (X = NO₃, halides). This would also be consistent with our findings.

Indirect evidence supporting a direct relationship between zinc corrosion and I⁻ surface retention is obtained from the RTF experiments. Firstly, the highest iodine loadings in the zinc primer-coated vessel occurred at sites of greatest zinc primer corrosion. Secondly, small variations in pH apparently influence iodine surface loadings significantly. This is illustrated in Figure 8, which depicts the time-dependent variation of pH and total aqueous iodine concentration in the non-radiation RTF experiment. Total aqueous phase iodine concentrations declined steadily when the pH was greater than approximately 9.8, but, when the pH fell below 9.8, the total aqueous phase iodine concentration remained constant or increased. These results suggest that the extent of iodine deposition increases with increasing pH and that desorption of previously sorbed iodine occurs when the pH is lowered. Such behaviour could be explained by equilibria involving either pH-dependent precipitation of an insoluble iodide or I⁻ adsorption onto a surface component whose solubility or absorption properties are dependent on pH. Various forms of zinc hydroxide and zinc oxide are reported to have minimum solubilities in the pH range 9.3 to 9.7 [26,28], thereby supporting the possibility of their involvement in iodine adsorption.

5. CONCLUSIONS

Results from RTF experiments have demonstrated that low steady-state gas phase iodine concentrations (<2.4 x 10⁻¹¹ mol·dm⁻³) are obtained in the presence of zinc primer surfaces. This is partly due to the strongly reducing nature of this surface, which favours I⁻ formation, and its low content of organic material. The latter should result in decreased organic iodide formation.

The RTF experiments have also shown that zinc primer surfaces have a significant affinity for iodine, in particular, those surfaces in contact with the aqueous phase. Up to 66% of the initially added I⁻ was retained on RTF zinc primer surfaces.

Separate effects tests have demonstrated that surface retention occurs only under oxidizing conditions and suggest that oxidation of the zinc surface, not aqueous I⁻, is responsible for this behaviour. Iodine retention may result from incorporation of I⁻ into oxidized zinc(II) products, such as zinc hydroxides, oxides and basic carbonates, which exhibit minimal solubility in the pH range 9 to 10.
Finally, it should be noted that the conditions that favour iodine retention on zinc primer surfaces, namely aerobic and alkaline conditions, are also those that are expected to be maintained within CANDU containment buildings after a reactor accident.

ACKNOWLEDGEMENTS

The authors thank S. Sunder and N.H. Miller for performing the XPS work, L.C. Brown for the SEM/EDX analyses and A.M. Duclos for the XRD studies. We also thank P. Taylor, J.C. Wren, J. Edward and R.J. Fluke for reviewing the manuscript. This work was funded jointly by AECL Research and Ontario Hydro, Hydro Quebec and the New Brunswick Electric Power Commission under the CANDU Owner's Group (COG) program, Working Party 06, Work Package 425.

REFERENCES


Figure 1. Schematic diagram of Radioiodine Test Facility (RTF).

Figure 2. Cross-sectional view of RTF lead canister.
Figure 3. Changes in gas and aqueous phase iodine concentrations as a function of time in radiation RTF test. (DV: direct vent; CF: charcoal vent; see text for details).

Figure 4. Changes in gas and aqueous phase iodine concentrations as a function of time in non-radiation RTF test. (DV: direct vent; CF: charcoal vent, see text for details).
Figure 5. Iodine retention on zinc primer pellets from solutions containing $1 \times 10^{-5}$ mol.dm$^{-3}$ CsI and $1 \times 10^{-3}$ mol.dm$^{-3}$ $\text{N}_2\text{H}_4$ at pH 9.

Figure 6. Iodine retention on zinc primer pellets from solutions containing $5 \times 10^{-5}$ mol.dm$^{-3}$ $\text{I}_2$ at pH 1.7 and 4.8.
Figure 7. SEM micrographs of zinc primer pellet before (a) and after (b) equilibration with $10^{-3}$ mol dm$^{-3}$ $\text{H}_3\text{BO}_3$ at pH 9.
Figure 8. Time-dependent changes in pH (—) and total aqueous phase iodine concentration (---) in non-radiation RTF test with zinc primer surface.
DISCUSSION

Bowsher
The retention of iodine at zinc surfaces under oxidizing, alkaline conditions is very interesting. Could you speculate on whether similar processes would occur for stainless steel surfaces where Fe(OH)₃ may be formed at the surface?

Kupferschmidt
In principle, yes, however, stainless steel surfaces would not be expected to corrode as readily as zinc-based surfaces. It is interesting to note that other experiments have revealed that significant retention of iodine occurs on corroding carbon steel surfaces.

Vikis
Why did you see about twice or much iodine deposited on surfaces in the absence of radiation than in the presence of radiation?

Kupferschmidt
This behaviour arises primarily from differences in pH. Overall, the pH in the non-radiation test was higher than in the radiation test. As described in this paper, alkaline conditions favour I⁻ retention on zinc primer surfaces in contact with the aqueous phase.

Weber
You have focussed on the aqueous phase deposition. Does this experimental effort give any insight into gas phase deposition?

Kupferschmidt
Significant retention of iodine on gas phase surfaces was observed in the RTF radiation test i.e., 870 ng.cm⁻². This is consistent with earlier work (Rosenberg et al., BMI-1865 (1969)) that showed that I₂ and CH₃I are retained on zinc primer surfaces.

Sims (Comment)
I think the difference between steel and zinc is that steel corrode much less. I think you have inadvertently created an ion exchange material. Is the effect poisoned by other anions?
3.4 IODINE CHEMISTRY IN THE PRESENCE OF VINYL SURFACES

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A.S. Palson, R. Portman and G.G. Sanipelli

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ABSTRACT

The effects of vinyl surfaces on iodine chemistry have been studied in both small-scale separate-effects tests and intermediate-scale integral experiments in the Radiiodine Test Facility (RTF). In an RTF experiment conducted without radiation in a vinyl-coated vessel, low gas phase iodine concentrations were measured (<3.5 x 10^{-11} mol.dm^{-3}) and little deposition of iodine on surfaces was observed. In a similar test conducted with radiation, gas phase iodine concentrations as large as 3.5 x 10^{-9} mol.dm^{-3} were observed. This coincided with dramatic decreases in pH and dissolved oxygen concentration. In addition, at least 67% of the iodine inventory was retained on surfaces, primarily those exposed to the gas phase. The separate-effects studies suggest that the pH, dissolved oxygen and iodine volatility behaviour in the RTF radiation test can be attributed to radiolytic decomposition of organics originating from the organic-based coating. Additional experiments indicate that iodine volatility can be minimized, even in the presence of vinyl surfaces and aqueous phase organics, if alkaline pH conditions are maintained.

1. INTRODUCTION

In a reactor accident, radiiodine behaviour within the containment building would be a complex function of many variables. One potentially important variable that is not yet adequately understood is the effect of surfaces on iodine chemistry. Various types of surfaces are present within reactor containment buildings - indeed, containment surfaces vary significantly from reactor to reactor. In the preceding paper [1], an inorganic-based zinc primer coating was shown to be an excellent sink for iodine, with iodine volatility remarkably low in a radiation environment. However, organic-based coatings, which may influence iodine behaviour differently, are encountered more frequently within containment. For example, the containment buildings of several operating CANDU reactors have been painted with a vinyl-based coating. Since vinyl coatings are known to degrade more rapidly in radiation environments than other commonly used coatings [2,3], it is important that their performance under simulated accident conditions be tested and their effect on iodine behaviour assessed.

* CANada Deuterium Uranium. Registered trademark of AECL.
This paper presents results from small-scale separate-effects experiments and intermediate-scale tests conducted in the Radioiodine Test Facility (RTF) in the presence of vinyl-coated surfaces. The findings are rationalized in terms of organic radiolysis reactions and aqueous phase iodine chemistry.

2. EXPERIMENTAL

2.1 Radioiodine Test Facility Experiments

Details of the design and operation of the RTF have been described previously [1,4-6]. The vinyl coating used in this study was Amercoat 99R (Ameron Inc., Protective Coating Division, Brea, CA). Based on the manufacturer's analysis, the coating's resin is polyvinyl chloride, copolymerized with about 13% vinyl acetate. The coating also contains kaolin, titanium dioxide, carbon black and chlorinated paraffins (primarily C_{12}'s to C_{24}'s), which serve as plasticizers for the brittle vinyl film. The solvent system used to apply the coating was a mixture of toluene, xylene and methyl isobutyl ketone.

Prior to application of the vinyl coating to the 340-dm³ carbon steel reaction vessel, the vessel was freshly sandblasted and a base coat of Carbo Zinc 11 zinc primer (Carboline Co., St. Louis, MO) was applied. The vinyl topcoat was then added in two separate applications to ensure complete coverage of the zinc primer base. The vessel was allowed to age naturally for three months at ambient temperature.

Experimental conditions are shown in Table 2.1 and are similar to those described in the previous paper of this Proceedings [1]. In summary, two tests with 10^{-5} mol.dm^{-3} CsI solutions (pH 10) were conducted in the RTF: one with and the other without a 280-TBq cobalt-60 irradiation source. The duration of each test was approximately 650 h, with each test divided into several stages to investigate the effects of venting and the addition of organic materials, hydrazine and LiOH. This paper addresses only the early stages (i.e., initial 150 h) of each test.

At the end of the first test, the vessel was washed with 10^{-3} mol.dm^{-3} N\textsubscript{2}H\textsubscript{4} and Nalclean 66 (Alchem Inc., Burlington, ON), and then sandblasted. The vessel was recoated with the zinc primer and vinyl paints and aged three months before undertaking the second test.

2.2 Separate-Effects Experiments

Coupons were prepared from carbon steel rod that was freshly sandblasted prior to application of the zinc primer coating. Two topcoats of the vinyl paint were then applied and the coupons were aged for approximately three months before use. Coupon surface areas were routinely 5 cm².

In a typical test, 5-mL aliquots of 1 x 10^{-5} mol.dm^{-3} iodine-131-labelled CsI solution were placed in 55 mL glass irradiation vessels. The apparatus is depicted in Figure 1. In some tests, the CsI-containing solution was unbuffered but adjusted initially to pH 9 with LiOH. In other cases, a 0.1 mol.dm^{-3} H\textsubscript{3}BO\textsubscript{3} medium, adjusted to either pH 9 or 6, was used. Two coupons were placed in each flask, one in the gas phase, the other in the aqueous phase; the flask was then purged with ultra high purity air. The flasks were placed in a Gammacell 220 (AECL, Ottawa, ON) and irradiated for various lengths of time (0.9 kGy.h^{-1}). After irradiation, the gas phase was passed through a sampling tube containing CdI\textsubscript{2}, iodophenol and
Table 2.1
RTF Test Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Iodine Concentration</td>
<td>$10^{-5}$ mol.dm$^{-3}$ CsI</td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Aqueous Volume</td>
<td>25 dm$^3$</td>
</tr>
<tr>
<td>Gas Volume</td>
<td>315 dm$^3$</td>
</tr>
<tr>
<td>Initial pH</td>
<td>10 (unbuffered)</td>
</tr>
<tr>
<td>Gas Recirculation Rate</td>
<td>30 dm$^3$.min$^{-1}$</td>
</tr>
<tr>
<td>Aqueous Recirculation Rate</td>
<td>11 dm$^3$.min$^{-1}$</td>
</tr>
<tr>
<td>Gas Venting Rate - off/on</td>
<td>0/7-10 dm$^3$.min$^{-1}$</td>
</tr>
<tr>
<td>Dose Rate - without/with cobalt-60 irradiation source</td>
<td>0/2 kGy.h$^{-1}$</td>
</tr>
<tr>
<td>Surface Type</td>
<td>Zinc primer base/ Vinyl topcoat</td>
</tr>
</tbody>
</table>

Triethylenediamine-(TEDA)-impregnated charcoal. These have been shown to be effective species-selective adsorbents for I$_2$, high-molecular-weight organic iodides (e.g., butyl iodide) and low-molecular-weight organic iodides (e.g., methyl iodide) respectively [7]. Aqueous phase samples were subjected to radiochemical solvent extraction to estimate the concentration of aqueous phase iodine species [7]. The coupons were rinsed with distilled water to remove residual iodine solution. The resulting adsorbents, solutions and coupons were analyzed for iodine using a LKB Compugamma automatic $\gamma$-counting system equipped with a 3 x 3 well-type NaI detector.

Separate-effects experiments were also conducted using methyl ethyl ketone (MEK) in place of the vinyl coupons. Solutions (5 mL) containing $1 \times 10^{-3}$ mol.dm$^{-3}$ MEK and $1 \times 10^{-5}$ mol.dm$^{-3}$ CsI were added to the irradiation flasks, which were placed in the Gammacell for up to 4 d. As for the vinyl coupon study, the test solutions were initially adjusted to pH 9 with LiOH; some solutions were buffered at this pH (0.1 mol.dm$^{-3}$ H$_3$BO$_3$), others were not. Gas phase iodine concentrations and gas and aqueous phase iodine speciation were determined using the procedures already described.
Additional tests with MEK were undertaken in a special irradiation loop installed in the Gammacell. A schematic of this facility is shown in Figure 2. The glass irradiation flask has a volume of 2 dm³ and is connected to gas and aqueous phase recirculation loops. The aqueous recirculation loop contains on-line pH and dissolved oxygen sensors. In addition, both loops have sampling ports that facilitate gas and aqueous phase analysis by gas chromatography and high-performance liquid chromatography, respectively. In a typical experiment, 0.2 dm³ of water was added to the flask, recirculation of the gas (1.5 dm³.min⁻¹) and aqueous (0.05 dm³.min⁻¹) phases initiated and the solution adjusted to the desired pH. The flask was then lowered into the Gammacell, and after reaching stable measurements of pH and dissolved oxygen concentration, MEK was added. The pH and dissolved oxygen and MEK concentrations were subsequently monitored for several hours.

Throughout this paper, the term "iodine" is defined as the sum of all iodine-containing species in a given phase, unless otherwise noted.

3. RESULTS

3.1 RTF Tests

Figure 3 shows the gas and aqueous phase iodine concentrations for the initial 150 h of the RTF test conducted without radiation. During this period, the total aqueous phase iodine concentration remained essentially constant. More complex behaviour was observed in the gas phase, however. For the first 21 h of the test, the gas phase was continuously recirculated through a filter containing TEDA-impregnated charcoal. Such filters have high radiiodine removal efficiencies [8], thereby accounting for the very low gas phase iodine concentration (<5 x 10⁻¹³ mol.dm⁻³) observed in the early stages of this test. When recirculation was stopped, the total gas phase iodine concentration gradually increased to 3.5 x 10⁻¹¹ mol.dm⁻³. Gas phase iodine speciation analysis revealed that the predominant airborne iodine species was low-molecular-weight organic iodides (>80%). This was substantiated by gas chromatography, which showed CH₃I as the primary volatile iodine species.

Dramatically different behaviour was observed with radiation. As illustrated in Figure 4, the total gas phase iodine concentration increased to 3.5 x 10⁻⁹ mol.dm⁻³ within the first 20 h, after which it decreased exponentially. As Figure 5 shows, the rapid initial increase in iodine volatility did not occur until about 6 h, by which time the pH and dissolved oxygen concentration had decreased substantially. Gas phase speciation analyses within the first 150 h suggested that most of the airborne iodine (>60%) was in I₂ form; however, at longer times, low-molecular-weight organic iodides dominated the gas phase (>80%). The total aqueous phase iodine concentration remained constant for the first 8 h, after which it decreased dramatically; only 10% of the initial iodine inventory was in solution at 150 h. This was followed by a gradual increase in the aqueous phase iodine concentration over the remainder of the test. Approximately 25% of the initial iodine inventory was in solution at the end of the test (620 h).

Iodine mass balances were determined at the end of each test and are summarized in Table 3.1. Good total recoveries were obtained, with surface adsorption accounting for most of the initial iodine inventory not present in either the gas or aqueous phases; approximately 11% of the initial
iodine inventory was associated with surfaces in the non-radiation test, whereas surfaces accounted for approximately 67% of the iodine in the radiation test. Washing the vessel with water and hydrazine was ineffective in removing the adsorbed iodine. However, most of the retained iodine was removed when the vessel was treated with Nalclean 66, a strong surface decontaminating agent. In the radiation test, approximately 7.5% of the iodine inventory remained with the surface, even after rigorous decontamination. Considerable deposition of iodine onto the gas phase sampling and recirculation lines also occurred; this was not observed in the non-radiation test.

Table 3.1
Mass Balance Results for RTF Vinyl Experiments

<table>
<thead>
<tr>
<th></th>
<th>Radiation Test % Recovery</th>
<th>Non-Radiation Test % Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous Phase</td>
<td>25.3</td>
<td>85.3</td>
</tr>
<tr>
<td>Gas Phase</td>
<td>0.03</td>
<td>0.001</td>
</tr>
<tr>
<td>Surface Adsorption</td>
<td></td>
<td></td>
</tr>
<tr>
<td>- H2O/N2H4 washes</td>
<td>4.0</td>
<td>0.5</td>
</tr>
<tr>
<td>- Nalclean 66</td>
<td>40.1</td>
<td>10.9</td>
</tr>
<tr>
<td>- Residual I</td>
<td>7.5*</td>
<td>-</td>
</tr>
<tr>
<td>- Stainless steel</td>
<td>15.*</td>
<td>-</td>
</tr>
<tr>
<td>sampling lines</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas and Aqueous Samples</td>
<td>0.5</td>
<td>0.03</td>
</tr>
<tr>
<td>Venting</td>
<td>5.4</td>
<td>0.02</td>
</tr>
<tr>
<td>Coupons</td>
<td>0.01</td>
<td>0.0013</td>
</tr>
<tr>
<td>Total</td>
<td>97.9</td>
<td>96.8</td>
</tr>
</tbody>
</table>

* Estimated by γ-counting

Analysis of vinyl-coated coupons placed in the RTF during these experiments further demonstrated the differing surface adsorption behaviour with and without radiation. In the non-radiation test, modest retention of iodine was measured on coupons exposed to the gas phase (5 ng·cm⁻²) and aqueous phase (32 ng·cm⁻²). In the radiation test, iodine surface loadings of approximately 100 and 10 ng·cm⁻² were measured on coupons exposed to the gas and aqueous phases, respectively. However, the latter surface loadings (i.e., for the radiation test) are underestimated since these coupons were treated with Nalclean 66 prior to analysis.

Post-test monitoring of the vinyl-painted vessel from the radiation test, after treatment with Nalclean 66, also revealed higher iodine loadings on surfaces in contact with the gas phase. Interestingly, the greatest adsorption was observed just above the water-air interface, with
progressively less adsorption as distance from the interface increased. Physical inspection of the vessel also revealed that the vinyl paint had become brittle, with formation of numerous blisters. This surface deterioration was greatest on those portions of the vessel nearest the cobalt-60 irradiation source. No such deterioration was observed in the non-irradiation test.

3.2 Separate-Effects Experiments

Table 3.2 summarizes the results of separate-effects experiments investigating the influence of radiation and vinyl surfaces on iodine chemistry. Results from the two RTF experiments are also tabulated for comparative purposes. For simplicity, only the 40-kGy absorbed dose results are reported; this dose represents the point at which the maximum gas phase iodine concentration was observed in the RTF radiation test. When flasks containing unbuffered pH 9 solutions of CsI (1 x 10^{-5} mol.dm^{-3}) and vinyl coupons were irradiated, similar decreases in pH and increases in gas phase iodine concentration were observed as during the RTF radiation test; the gas phase iodine speciation was also comparable. High loadings of iodine on the coupons were also observed. Similar gas phase iodine concentrations were measured when pH 6 solutions (0.1 mol.dm^{-3} H_{3}BO_{3}) were irradiated, both with and without vinyl coupons. Alternatively, tests with buffered pH 9 solutions showed dramatically lower retention of iodine on

<table>
<thead>
<tr>
<th>Surface</th>
<th>Dose (kGy)</th>
<th>pH</th>
<th>Surface Loading gas aqueous (ng·cm^{-2})</th>
<th>Total Gas Phase Iodine Concentration (mol.dm^{-3})</th>
<th>Airborne Fraction as ( I_{2} ) RI (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTF</td>
<td>0</td>
<td>9.8 to 8.1 (^{c})</td>
<td>5</td>
<td>32</td>
<td>3.5 \times 10^{-11}</td>
</tr>
<tr>
<td>RTF</td>
<td>40</td>
<td>9.8 to 6.6 (^{c})</td>
<td>&gt;100</td>
<td>&gt;10</td>
<td>3.5 \times 10^{-9}</td>
</tr>
<tr>
<td>Vinyl</td>
<td>40</td>
<td>9.6 to 5.2 (^{c})</td>
<td>70</td>
<td>8</td>
<td>3 \times 10^{-9}</td>
</tr>
<tr>
<td>Vinyl</td>
<td>40</td>
<td>6 (^{d})</td>
<td>110</td>
<td>10</td>
<td>1 \times 10^{-8}</td>
</tr>
<tr>
<td>Vinyl</td>
<td>40</td>
<td>6 (^{d})</td>
<td>-</td>
<td>-</td>
<td>5 \times 10^{-9}</td>
</tr>
<tr>
<td>Vinyl</td>
<td>40</td>
<td>6 (^{d})</td>
<td>9</td>
<td>4</td>
<td>3 \times 10^{-10}</td>
</tr>
<tr>
<td>Vinyl</td>
<td>40</td>
<td>9.3 (^{d})</td>
<td>-</td>
<td>-</td>
<td>5 \times 10^{-11}</td>
</tr>
</tbody>
</table>

\(^{a}\) Initial aqueous CsI concentration - 1 x 10^{-5} mol.dm^{-3}

\(^{b}\) RI - organic iodide fraction

\(^{c}\) Initial and final pH values; unbuffered solution.

\(^{d}\) 0.1 mol.dm^{-3} H_{3}BO_{3}; pH adjusted with LiOH.

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vinyl coupons and reduced iodine volatilities. Gas phase iodine speciation analysis revealed organic iodides as the predominant volatile form of iodine. Control tests at pH 9 without vinyl coupons exhibited lower gas phase iodine concentrations, primarily because of lower yields of volatile organic iodides.

Tests using MEK instead of vinyl coupons exhibited similar behaviour. These results are summarized in Table 3.3. The pH of the unbuffered solutions was found to decrease significantly after receiving a dose of only 10 kGy. Under these conditions, the total gas phase iodine concentration reached $1.6 \times 10^{-8}$ mol·dm$^{-3}$, with most of the iodine in the form of organic iodides. With additional irradiation, the gas phase iodine concentration decreased, primarily because of a reduction in the concentration of organic iodides. Much lower iodine volatilities were observed when the pH was maintained at pH 9 (0.1 mol·dm$^{-3}$ H$_3$BO$_3$).

Figure 6 illustrates the changes in pH and dissolved oxygen concentration observed in the Gammacell irradiation facility after the addition of $10^{-3}$ mol·dm$^{-3}$ MEK. The dissolved oxygen concentration decreased almost immediately to 6 ppm, where it remained until about 10 h, after which it began to increase slowly. The pH fell more slowly, reaching 3.8 after 22 h. These changes coincided with the disappearance of MEK and formation of numerous intermediate products, as determined by high-performance liquid chromatography.

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>pH</th>
<th>$[I_{(g)}]$ (mol·dm$^{-3}$)</th>
<th>$I_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>9 to 5.4$^c$</td>
<td>$1.6 \times 10^{-8}$</td>
<td>20 80</td>
</tr>
<tr>
<td>20</td>
<td>9 to 4.2$^c$</td>
<td>$4.5 \times 10^{-9}$</td>
<td>15 85</td>
</tr>
<tr>
<td>40</td>
<td>9 to 4.2$^c$</td>
<td>$1.3 \times 10^{-9}$</td>
<td>75 25</td>
</tr>
<tr>
<td>10</td>
<td>9$^d$</td>
<td>$8.3 \times 10^{-10}$</td>
<td>5 95</td>
</tr>
<tr>
<td>20</td>
<td>9$^d$</td>
<td>$2.3 \times 10^{-10}$</td>
<td>30 70</td>
</tr>
<tr>
<td>40</td>
<td>9$^d$</td>
<td>$7.7 \times 10^{-11}$</td>
<td>30 7</td>
</tr>
</tbody>
</table>

* Aqueous phase initially contains $1 \times 10^{-5}$ mol·dm$^{-3}$ CsI and $1 \times 10^{-3}$ MEK.

* Total gas phase iodine concentration.

* Percent gas phase $I_2$ and organic iodides (RI).

* Initial and final pH values; unbuffered solution.

* 0.1 mol·dm$^{-3}$ H$_3$BO$_3$; pH adjusted with LiOH.

Table 3.3

Effect of MEK on Iodine Volatility

4. DISCUSSION

The importance of surfaces on iodine chemistry is demonstrated by comparing iodine behaviour in this study with that described in the
previous paper [1]. For example, RTF tests conducted with zinc primer surfaces exhibited low gas phase iodine concentrations whether or not high radiation fields were present. Also, the zinc primer surface in contact with the aqueous phase was found to be a good "sink" for iodine, with radiation only modestly influencing surface adsorption. On the other hand, with vinyl surfaces, iodine volatility was enhanced greatly with radiation. Radiation also influenced the extent of surface adsorption, which occurred primarily on gas-phase-exposed surfaces. The contrasting behaviour of iodine in these two studies can be attributed to the differing chemical nature of the two surfaces.

The low volatility of iodine in the non-radiation RTF experiments is not surprising because the thermal oxidation of $I^-$,

$$2I^- + 1/2 O_2 + 2H^+ \rightarrow I_2 + H_2O$$  \hspace{1cm} (1)

is slow [9] under the alkaline conditions of these tests. As such, low concentrations of gas phase $I_2$ and organic iodides would be expected, the latter being formed in solution or on surfaces by reaction of organic material with $I_2$ or its hydrolysis products HOI and OI$^-$. Even with radiation, however, high gas phase iodine concentrations would not be expected under alkaline conditions. This is supported by the bench-scale results shown in Table 3.2. When pH 9 buffered solutions of CsI were irradiated in the presence of vinyl coupons, modest gas phase iodine concentrations were measured ($3 \times 10^{-10}$ mol dm$^{-3}$). Although higher than in similar tests conducted without vinyl coupons, the volatility of iodine was appreciably less than that observed in the RTF radiation test and in separate-effects tests with unbuffered solutions of CsI containing vinyl coupons. For the latter two, enhanced iodine volatility was observed only after the pH had decreased dramatically. This correlation between pH decrease and enhanced iodine volatility for the RTF radiation test is illustrated in Figure 5. This figure also suggests the involvement of dissolved oxygen in the volatilization process.

One possible cause for the decrease in pH and dissolved oxygen concentration in the presence of radiation is the oxidative degradation of the vinyl coating, which is a vinyl chloride - vinyl acetate copolymer. A physical examination of the coating after the RTF radiation test did reveal extensive deterioration of the vinyl surface. Previous work has shown that oxygen is consumed and HCl is formed when poly(vinyl chloride) (PVC) is irradiated in an oxygen atmosphere [10,11]. However, oxygen consumption and HCl production are dependent on a number of factors, including temperature, dose and PVC formulation (i.e., presence of plasticizers and stabilizers). $G(-O_2)$ and $G(HCl)$ values (μmol J$^{-1}$) of 0.7 to 3.9 and 0.002 to 2.4, respectively, have been reported for PVC [10,11]; the corresponding G values are unknown for the vinyl-based coating used in this study. However, when coupons prepared from this vinyl coating were placed in both the gas phase and aqueous phase of a sealed glass vessel and irradiated to a dose of up to 50 kGy, insufficient Cl$^-$ was detected to account for the observed pH decrease. As such, radiolytic decomposition of the vinyl copolymer cannot by itself account for the changes in pH (and, presumably, dissolved oxygen concentration).

Interestingly, similar decreases in pH and dissolved oxygen concentration have been observed when aqueous solutions of MEK were irradiated in the Gammacell, as shown in Figure 6. As for the vinyl RTF test program, such changes were not observed without radiation.
Furthermore, remarkably similar correlations between volatility, pH and dissolved oxygen concentration were noted in the zinc primer RTF radiation test upon addition of MEK [12]. These observations suggest that a common mechanism may be operative.

With the high doses encountered in the RTF radiation tests, radiolytic decomposition of organic compounds, such as MEK, would readily occur. In aqueous solution, reactions of organic compounds (RH) with water radiolysis products like OH· would result in the formation of organic radicals

$$\text{RH} + \text{OH}\. \rightarrow \text{R}\. + \text{H}_2\text{O}$$

that subsequently react with dissolved oxygen to form peroxo radicals,

$$\text{R}\. + \text{O}_2 \rightarrow \text{RO}_2\. \text{.}$$

These can undergo further reaction, with ultimate formation of carboxylic acids (RO₂H). This explanation would then account not only for the decrease in dissolved oxygen concentration, since under the conditions of this test oxygen consumption in the aqueous phase is likely faster than gas-to-liquid mass transfer of oxygen, but also for the relatively rapid decrease in pH, because of organic acid formation. The pH drop may also arise in part from the further oxidation of the organic acids to CO₂, which in aqueous solution, forms carbonic acid (pKₐ 6.38). A more detailed discussion of the radiolysis of aqueous phase organics is presented elsewhere in these Proceedings [13].

Similar reactions may account for the results of the vinyl RTF tests. This surface, unlike the zinc primer coating used in the previous paper [1], is predominantly organic in nature. Indeed, the solvent system used to apply the vinyl coating includes methyl isobutyl ketone (MIBK), which should react similarly to MEK. Accelerated aging tests have shown that traces of MIBK, toluene and xylene are still present after heating vinyl-coated coupons to 40°C for 1 week; treatment of this coating for one week at 40°C temperatures is believed to be equivalent to natural aging for 1 to 2 a at room temperature [14]. In any event, release of organic materials from the paint to the aqueous phase, with subsequent radiolytic oxidation to carboxylic and carboxylic acids, would be consistent with our findings.

The increase in the total gas phase iodine concentration in the RTF radiation test is a natural consequence of the decrease in pH and dissolved oxygen concentration. Elemental iodine is formed radiolytically from I⁻ according to the reaction scheme [15]

$$\text{I}⁻ + \text{OH}\. \rightarrow \text{I}_2 + \text{OH}\. \text{.} \quad \text{(4)}$$

$$2\text{I}⁻ \rightarrow \text{I}_3 + \text{I}⁻ \quad \text{(5)}$$

$$\text{I}_3 = \text{I}⁻ + \text{I}_2 \quad \text{(6)}$$

However, I₂ is rapidly reduced by the solvated electron [16],

$$\text{e}⁻ + \text{I}_2 \rightarrow \text{I}_2 \quad \text{(7)}$$

and under aerobic conditions, by O₂ [17].
\[ \text{e}^- + \text{O}_2 \rightarrow \text{O}_2 \] (8)
\[ \text{O}_2^+ + \text{I}_2 \rightarrow \text{O}_2 + \text{I}_2 \] (9)

The net result is a low steady-state concentration of \( \text{I}_2 \). However, as the dissolved oxygen concentration decreases, the rates of reactions (8) and (9) decrease. Furthermore, instead of reacting with dissolved oxygen, the solvated electron reacts with \( \text{H}_2\text{O}_2 \) [18], formed during water radiolysis, to produce \( \text{OH}^- \).

\[ \text{e}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH}^- + \text{OH}^- \] (10)

This results in enhanced oxidation of \( \text{I}^- \) to \( \text{I}_2 \) (reactions (4)-(6)). Alternatively, the enhanced volatility of iodine in the RTP and separate-effects radiation experiments can be rationalized in terms of pH phenomena. The increase in iodine volatility may in part arise from the reaction of \( \text{H}_2\text{O}_2 \) with free iodine, which is reported to proceed primarily through reduction of \( \text{OI}^- \) [19,20],

\[ \text{H}_2\text{O}_2 + \text{OI}^- \rightarrow \text{I}^- + \text{O}_2 + \text{H}_2\text{O} \] (11)

Although there are uncertainties regarding the rate constant and mechanism of this reaction, the reaction is undoubtedly rapid under alkaline pH conditions. Because of its strong inverse acid dependency, however, reaction (11) becomes slow under mildly acidic conditions. Since \( \text{OI}^- \) is in equilibrium with \( \text{I}_2 \),

\[ \text{I}_2 + \text{H}_2\text{O} = \text{HOI} + \text{H}^+ + \text{I}^- \] (12)
\[ \text{HOI} = \text{OI}^- + \text{H}^+ \] (13)

the decreasing rate of destruction of \( \text{OI}^- \) with decreasing pH results in higher aqueous \( \text{I}_2 \) concentrations. This in turn brings about enhanced iodine volatility, consistent with the results of this study.

The increased formation of \( \text{I}_2 \) with radiation may also account for the surface adsorption behaviour of iodine in the RTP and separate-effects tests. Little surface adsorption of iodine was observed without radiation, where \( \text{I}_2 \) concentrations were low, and no detectable loss of iodine to surfaces occurred with radiation until conditions favouring \( \text{I}_2 \) formation (i.e., near-neutral pH) were obtained. Furthermore, surface adsorption of iodine occurred primarily on gas-phase-exposed surfaces, indicating that the sorbed iodine was volatilized from solution prior to adsorption on surfaces. Since organic iodides, such as methyl iodide, have less affinity for most surfaces than does \( \text{I}_2 \) [21], it is likely that interaction of gas phase \( \text{I}_2 \) with the vinyl surfaces was responsible for most of the adsorption. Gas phase iodine speciation analysis supports this suggestion; \( \text{I}_2 \) was the dominant airborne iodine species during the first 150 h of the RTP radiation test.

From a reactor safety perspective, the principal finding of this study is that high gas phase iodine concentrations within containment are possible under accident conditions if appreciable quantities of organics or organic-based surfaces are present. Indeed, recent intermediate-scale and separate-effects experiments with other organic-based coatings and organics have shown that this phenomenon is generic in nature and not limited to
vinyl coatings or to MEK [22]. Since in each case large increases in iodine volatility occurred only after appreciable decreases in pH, this suggests that iodine volatility can be reduced if alkaline conditions within containment are maintained. The separate-effects test results of Tables 3.2 and 3.3 support this suggestion. When solutions containing vinyl coupons or MEK were held at pH 9 and irradiated, iodine volatilities were 10- to 20-fold lower than when the pH was allowed to fall.

Although a hypothesis for the effect of organics and organic-based coatings on iodine volatility has been formulated in this paper, additional study is required to validate it and to determine the nature of the radiolytic reaction products as a function of dose and class of organic. In this way, a better understanding of iodine chemistry under accident conditions will be obtained and appropriate mitigation and abatement strategies can be developed to minimize iodine volatility.

CONCLUSIONS

RTP experiments with vinyl-coated surfaces have shown that low gas phase iodine concentrations are obtained in the absence of radiation. However, with radiation, gas phase iodine concentrations of up to $3.5 \times 10^{-9}$ mol·dm$^{-3}$ were observed. The increase in iodine volatility coincided with decreases in pH and dissolved oxygen concentration. Similar trends were observed in separate-effects experiments with addition of organics. This behaviour is consistent with radiolytic oxidation of organic compounds to carboxylic acids, or possibly carbonic acid. The resulting decrease in pH favours formation of volatile I$_2$ and organic iodides.

Little retention of iodine occurred on the vinyl surfaces in the absence of radiation, but with radiation, at least 67% of the iodine inventory was retained on surfaces. This is attributed to adsorption of I$_2$, which is formed under the conditions of the radiation test.

Separate-effects experiments indicated that maintaining alkaline pH conditions may be an effective accident management strategy to minimize iodine volatility in the presence of organics and organic-based coatings.

ACKNOWLEDGEMENTS

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REFERENCES


Figure 1. Glass irradiation flask and gas sampling system used in separate-effects experimental program. (HMWt RI: high-molecular-weight organic iodides; LMWt RI: low-molecular-weight organic iodides)

Figure 2. Gammacell irradiation loop used in separate-effects experimental program.
Figure 3. Total gas and aqueous phase iodine concentrations during the initial 150 h of the RTP non-radiation experiment. (CF: charcoal filter; see text for details)

Figure 4. Total gas and aqueous phase iodine concentrations during the initial 150 h of the RTP radiation experiment. (HB denotes the times when the hydrogen recombiner was activated to remove H₂ produced by water radiolysis).
Figure 5. Plot of the gas phase iodine concentration, pH and dissolved oxygen concentration during the initial 20 h of the RTF radiation experiment.

Figure 6. Changes in the dissolved oxygen concentration and pH in the Gammeacell irradiation loop after addition of $10^{-3}$ mol·dm$^{-3}$ methyl ethyl ketone.
DISCUSSION

Morell
To what extent in CANDU-Reactors are used polyvinyl chloride copolymerized vinyl coatings?

Kupferschmidt
Vinyl coatings were used for coating containment surfaces only in early CANDU reactors. Newer reactors use zinc primer-, epoxy- or polyurethane based coatings.

Fluke (Comment)
The use of vinyl paint was halved at Ontario Hydro in 1978, halfway through construction of the Pickering "B" nuclear generating stations. Vinyl paints have not been used since.

Sims (Comment)
The effects on pH observed with vinyl paint would be expected with other organic coatings. It was observed in the ACE RTF tests where pH had to be kept high. There are many organic polymers in containment as it is important to maintain high pH.
3.5 ACE BENCH-SCALE STUDIES OF IODINE VOLATILITY AND INTERACTION WITH EPOXY PAINTED SURFACES

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AECL Research
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ABSTRACT

The effects of pH, temperature, gamma irradiation, initial speciation and epoxy paint on iodine behaviour were studied in bench-scale experiments in support of the Advanced Containment Experiments (ACE) Phase B research program. The water/air partition coefficient and the retention of iodine on submerged epoxy painted coupons were evaluated. Additional information was obtained through radiochemical measurements of the aqueous and gas phase iodine speciation.

Following irradiation, the overall iodine volatility depended strongly on pH, however, it did not differ significantly between solutions prepared with I₂ and I⁻. At 80°C, extensive organic iodide formation occurred in unirradiated basic-solutions containing epoxy painted coupons, resulting in up to 10% of the liquid phase iodine being converted to higher molecular weight organic iodides of low volatility.

In a related study, the adsorption of I₂(g) on epoxy painted coupons at 80°C was investigated. Although the initial rate of deposition appeared to be limited by gas phase mass transfer, the rate over the longer term was suggestive of a slower chemical reaction. Desorption of the deposited iodine was extremely slow, indicating that the majority of the iodine on the epoxy was irreversibly bound. A semi-empirical model was developed and found to represent reasonably both the present results and those of other studies.

1. INTRODUCTION

To improve the existing understanding of post-accident iodine behaviour, a variety of studies were initiated within the Advanced Containment Experiments (ACE) Phase B research program. These studies included experiments in the large-scale Containment Systems Test Facility (CSTF) [1] located at Hanford, Washington, and in the Radioiodine Test Facility (RTF) [2] at the Whiteshell Laboratories. In support of these experiments, a bench-scale research program was undertaken to study the behaviour of iodine under a variety of conditions [3]. The objectives of the bench-scale program was to assess the separate effects of epoxy-painted surfaces, pH, gamma irradiation and initial speciation on iodine behaviour, in order to assist in rationalizing the trends observed in the larger-scale tests.

The original bench scale program consisted of three phases. In the first phase, 10⁻³ M solutions prepared with either I₂ or CsI, were studied at 25°C: both acidic (pH = 5) and basic (pH = 9) conditions and the presence of
epoxy-painted carbon-steel coupon were assessed. The second phase was similar to the first phase except that the experiments were performed at 80°C. In the third phase, effects of gamma irradiation were investigated. The pH values used were selected to be consistent with those used in the RTF and CSTF experiments, that is values expected following reactor accidents. A similar criterion led to the use of $10^{-5}$ M solutions. The study emphasized measurements of iodine volatility and deposition, although insight into the speciation was also provided.

During the execution of the ACE Phase B experiments it became apparent that a greater understanding of the interaction of iodine with epoxy paint would be of great value in interpreting the observed behaviour and in simulating this behaviour using iodine codes. Consequently, a limited investigation of the interaction of iodine with epoxy-painted surfaces was undertaken following the completion of the original bench-scale program. The emphasis of this investigation was on the adsorption of I$_2$(g) onto epoxy paint at 80°C, although a small number of experiments relating to aqueous phase interactions were also performed. In this paper, the findings of the original bench-scale program are summarised along with results from the subsequent study of the interaction of iodine with epoxy paint.

2. METHODOLOGY

The majority of the experiments were performed using 50 mL glass flasks. For each of the 24 experimental condition, 5 mL of solution was added to 8 to 10 of these flasks, which were then sealed using ground-glass connections. After being exposed to the desired environment, for periods ranging from 15 min to 2 weeks, gas and aqueous phase samples were collected. By sampling different flasks after various periods of exposure, time-related variations in iodine behaviour were determined.

The solutions were prepared by dissolving Aldrich "Gold Label" CsI or I$_2$ in water previously purified by distillation and filtration/deionization using a Barnstead Nanopure system. These solutions were labelled with $^{131}$I before being diluted to $10^{-5}$ M using a 0.1 M boric acid solution of the desired pH; the pH was adjusted using H$_2$SO$_4$ and LiOH. Before being added to the flasks, the CsI-containing solutions were purged with purified air to remove any volatile species present. After the addition of 5 mL of the test solution, the gas phase of each flask was swept with purified air. In the case of the I$_2$ solutions, the boric acid solution was purged with purified air prior to adding the labelled I$_2$ solution but sweeping of the gas space in the flasks was foregone to avoid loss of I$_2$. When the condition being studied involved epoxy surfaces, an epoxy-painted carbon-steel coupon was submerged in each of the flasks. These coupons were made from 2-cm-long pieces of 0.6-cm carbon-steel rod having a painted surface area of $\approx$5 cm$^2$. The coupons were sandblasted and immediately painted using Keeler and Long No. 4500 epoxy paint. They were cured at room temperature for at least several weeks before use. This procedure was chosen to be consistent with the RTF painted carbon steel vessel.

The experiments in Phases 1 and 2 were performed using a shaker/water bath, which could accommodate up to 20 flasks. In Phase 3 the solutions were irradiated in a $^{60}$Co gamma irradiation cell that provided a dose rate of 1 kGy/h. Because of the limited size of the cell, only 5 flasks could be irradiated simultaneously. Analysis of a solution was initiated within 5 to 10 min of a
flask being removed from the irradiation cell.

Sampling of the iodine involved determining the $^{131}\text{I}$ activity in known volumes of the liquid and gas phases. The gas phase activity was determined by drawing air for 20 s through gaseous iodine adsorbents at a measured flow rate of about 100 mL/min. After sampling the gas phase iodine, the pH of the solution was measured using a temperature-compensated combination electrode. The extent of iodine sorption on the submerged and dry paint was determined by counting the entire coupon after rinsing it twice with water, in order to remove any entrained solution. The relatively low activity in these rinses indicated that the rinsing had a negligible impact on the amount of adsorbed iodine.

The liquid and gas phase iodine speciation was determined using radiochemical separation procedures in order to provide further insight into the behaviour of iodine. The gas phase iodine speciation was assessed through species-selective adsorbents: CdI$_2$ on chromosorb, iodophenol on alumina, and TEDA-impregnated charcoal. In previous studies [4,5], it was found that, under the given flow conditions, the CdI$_2$ was effective in the retention of $\text{I}_2$; and that the iodophenol effectively adsorbed higher-molecular-weight organic iodides, such as butyl iodide, and a species present above HOI solutions. The TEDA-impregnated charcoal was effective in retaining more-penetrating lower-molecular-weight organic iodides, such as methyl and ethyl iodide. The adsorbents, approximately 4 mL of each, were placed in series in a piece of 8-mm-ID Teflon tubing separated by glass wool. Aqueous iodine speciation was assessed using a radiochemical solvent extraction procedure developed from the procedures used by Lin [6] and Burns et al. [7]. This procedure, described elsewhere [3,5] allowed the relative fractions of $I^-$, $IO_3^-$ total organic iodide, and in some cases $I_2^-$ and "free iodine" (a measure of the sum of the $I_2$, HOI and $OI^-$ concentrations) to be determined. This procedure proved to be valuable in determining trends relating to the relative magnitude of these fractions, although when the fractions were small the results were likely accurate only to within a factor of two. However, when the measured fractions constituted more than 1% of the total iodine, as was often the case for the $IO_3^-$ and organic iodide fractions, the results were generally reliable to within 25%. Overall, the precision was sufficient to resolve important trends in the aqueous iodine speciation.

Samples were counted using a well-type 3 x 3 NaI detector in a LKB Compgamma system. The small size of all the samples ensured that they could fit into the well of this detector system. The amount of $^{131}\text{I}$ added to each flask varied from 0.5 to 50 $\mu$Ci, depending on the volatility expected under the given experimental condition. This $^{131}\text{I}$ tracer was purchased (ICN Biomedical) in 10-mCi allotments as "Carrier-Free" and reducing-agent-free dissolved NaI and contained no more than 1 $\mu$g stable $^{137}\text{I}/20$ mCi $^{131}\text{I}$ when received.

The deposition of $I_2$(g) from dry air at 80°C onto 5 cm$^2$ carbon steel coupons painted with Keeler®Long 4500 epoxy paint, was investigated using an apparatus constructed with teflon tubing. Purified compressed air was heated to 80°C in a furnace and divided into two streams. One stream was passed through a trap containing $^{131}\text{I}_2$(s) (ICN Biomedical) before recombining with the second stream. The flow of air was then passed through a length of 8 mm 1D teflon tubing containing an epoxy coated coupon. The coupon was in close proximity to a shielded 3 x 3 NaI detector, allowing the rate of deposition of $^{131}\text{I}_2$ onto the epoxy to be monitored continuously. The system was trace-heated and properly instrumented to insure that the air and the coupon remained at 80°C. The
concentration of I$_2$(g) was set by varying, using needle valves and rotameters, the fraction of the air that flowed through the trap containing the I$_2$(s) while maintaining the total flow near 800 mL/min. The concentration of I$_2$(g) was measured by sampling known volumes of air through septums installed at various locations in the system. Concentrations of I$_2$(g) ranging from 6 x 10$^{-9}$ to 8 x 10$^{-7}$ were investigated. Following some experiments, the coupon was placed in a heated teflon tube system, with a known flow of dry air (=800 mL/min), in order to evaluate the rate of desorption. No rinsing of was performed as these coupons were never in contact with any aqueous iodine.

3. RESULTS AND DISCUSSION

3.1) Iodine behaviour in the absence of paint

The volatility and speciation of iodine in the absence of paint was investigated over a range of conditions within the original ACE bench scale program. Presented in Table 1 are mean values of the iodine partition coefficient (H, the ratio of the aqueous to gas phase iodine concentrations) and the associated standard deviation, for a variety of 10$^{-5}$ M CsI solutions. These values were calculated by averaging four to six longer term measurements in order to facilitate comparisons. In some cases, significant time-related behaviour was observed even after the first few days, resulting in uncertainty of up to a factor of two in these mean values. However, this spread was much smaller than the order-of-magnitude differences of interest in this scoping study and hence important trends could still be readily resolved.

![Table 1](image)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Partition Coefficient (x10$^{-5}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Dose Rate (kGy/h)</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
</tr>
</tbody>
</table>

The partition coefficient was always lower under acidic conditions than under basic conditions, typically by more than an order of magnitude. This difference likely was due to slower I$^-$ oxidation in conjunction with less extensive organic iodide formation under basic conditions; generally, the concentration of organic iodides in the aqueous phase was approximately ten times...
higher at pH 5 than at pH 9. For the irradiated solutions, the effect of pH on volatility was found to be most pronounced between pH 5 and 6. The effects of pH on iodide oxidation and iodine volatility has been discussed elsewhere for both irradiated [8] and unirradiated [9] solutions.

The partition coefficient appeared to be higher at the higher temperature although this difference was only marginally significant. Lower overall volatility at higher temperature may appear inconsistent since the volatility of most iodine species and the rate of iodide oxidation would be expected to be greater at higher temperatures. However, at both temperatures, organic iodides made a significant contribution to the gas phase iodine. The rate of hydrolysis of organic iodides increases greatly with increasing temperature; for methyl iodide, for example, increasing the temperature from 25 to 80°C causes the rate of hydrolysis to increase by about three orders of magnitude while the volatility of CH₃I increases by less than a factor of four [10].

Irradiation of iodide solutions caused an increase in the overall iodine volatility, particularly under acidic conditions. This effect was consistent with the reasonably well understood interaction of iodine with the products of water radiolysis, such as the oxidizing OH radical or the reducing O₂⁻ radical. In the liquid phase, irradiation had a significant effect on speciation. The fraction of I₂ rose to 20% after a dose of 40 kGy and then decreased to values near 10%. Free iodine fractions as high as 10% were also observed. In the gas phase above the acidic solutions, both lower-molecular-weight organic iodides and I₂ were the dominant forms. This was surprising as in other work, I₂ has been found typically to dominate over acidic CsI solutions following irradiation and lower values of the partition coefficient have been determined [11,12]. Under basic conditions, irradiation had less effect on the volatility. The gas phase was dominated by lower-molecular-weight organic iodides that accumulated during the early stages of the irradiation, reaching a constant value near 3x10⁻¹¹ M within the first day of irradiation.

### TABLE 2

**AVERAGE VALUES OF THE PARTITION COEFFICIENT FOR 10⁻⁵ M "I₂" SOLUTIONS**

<table>
<thead>
<tr>
<th>Condition</th>
<th>Partition Coefficient (x10⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Dose Rate (kGy/h)</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>1</td>
</tr>
</tbody>
</table>
Presented in Table 2 are mean values of the iodine partition coefficient for a variety of solutions prepared with $10^{-9}$ M I$_2$. At 25°C, the partition coefficient was almost 100 times lower under acidic than under basic conditions. The reason for the deviation between the value of 290 in Table 2, and the expected value of 80 is uncertain but may have been partially due to extensive adsorption of I$_2$ onto the glass surfaces of the flasks. The pH dependence was attributed to the pH dependence of I$_2$ disproportionation to HOI:

$$I_2 + H_2O \rightarrow HOI + I^- + H^+$$  \hspace{1cm} (1)

Under basic conditions, most of the initial I$_2$ undergoes rapid disproportionation to far less volatile HOI and I$. In these experiments I$_2$ was the predominant species in the gas phase under both acidic and basic conditions. However, the gas phase concentration was 100 times lower above the basic solutions. The predominance of I$_2$ above the basic solutions was not surprising in view of the apparent low volatility of HOI. In contrast, the absence of a significant reduction in the gas phase I$_2$ concentration over the long-term was unexpected in view of the anticipated disproportionation of I$_2$ to IO$_3$^-.

Closer examination of the mechanism of I$_2$ disproportionation proposed by Furrow [13] revealed a possible explanation for this lack of time dependence. According to Furrow's mechanism the disproportionation of I$_2$ to IO$_3$^- occurs through HOI, with HIO$_3$ as an intermediate:

$$HOI + HOI \rightarrow HIO_3 + I^+ + H^+$$  \hspace{1cm} (2)

$$HOI + HIO_3 \rightarrow IO_3^- + I^- + H^+ + H^+$$  \hspace{1cm} (3)

Reaction (3) is in competition with the reverse of Reaction (2):

$$HIO_3 + I^- + H^+ \rightarrow HOI + HOI.$$  \hspace{1cm} (4)

Furrow suggests that Reaction (4) is very rapid, although the rate and pH dependence have not yet been established. At higher HOI concentrations, Reaction (4) is not significant and Reaction (2) is the rate-limiting step. As the concentration of HOI decreases, Reaction (4) becomes more significant, and the rate of HOI elimination and IO$_3$^- formation becomes limited by Reaction (3) and consequently is very slow. Thus, this mechanism suggests that after a period, which is dictated by the rate of Reaction (4), the rate of I$_2$ disproportionation, and hence disappearance in the gas phase, should be insignificant. This is in agreement with the trend that was observed experimentally.

At 80°C, no significant dependence of the partition coefficient on pH was observed and this was not as expected. This may have been due partially to the disproportionation of I$_2$ to HOI (Reaction (1)): at 80°C over a quarter of the initial I$_2$ should have rapidly disproportionated to HOI at pH 5.5. Only under basic conditions however, did the extent of IO$_3$^- formation approach the expected 10 to 15%. In the case of the acidic solutions, IO$_3$^- constituted only a few percent of the total iodine, indicating that another pathway for I$_2$ elimination must also have existed.

The effect of irradiation on the I$_2$ solution was the opposite of that observed for the I$^-$ solutions: irradiation caused the volatility to decrease. As a result, the long-term partition coefficient for the irradiated I$_2$ solutions was similar to that observed for the irradiated CsI solutions. This result
suggests that over the long term, the partition coefficient is independent of the chemical form of iodine released into a reactor containment. This trend was also evident in ACE RTF tests 2 and 3: the long term volatility was similar for irradiated solutions initially containing I⁺, I₂, or CH₃I.

3.2) The interaction of iodine with epoxy surfaces

Measurements of the retention of iodine by submerged epoxy paint revealed that I⁻ could become irreversibly bound to this paint. At 25°C, the rate of adsorption was very slow, much slower than that typical of aqueous phase mass transfer, and the distribution coefficient (Kd, the ratio of the surface to fluid concentration) was higher under acidic conditions (Kd ≤ 4 x 10⁻¹ cm⁻¹) than under basic conditions (Kd ≤ 10⁻² cm⁻¹). At 80°C, the paint rapidly attained a maximum loading (mass of iodine per unit area) that depended only weakly on pH. The value of the distribution coefficient (Kd ≤ 4 x 10⁻² cm⁻¹) was lower than that observed under acidic conditions at 25°C.

Measurement of the deposition of I₂(aq) onto the paint was complicated by the apparent chemical reduction of the I₂ to I⁻. Following the addition of I₂ to solutions containing samples of the epoxy paint, a rapid loss of I₂ was observed followed by a slower appearance of I⁻. This phenomena was investigated in a few preliminary experiments using a customized cell that allowed UV absorbence in 70 mL of stirred solution at 80°C, containing a suspended coupon, to be measured continuously. In an experiment involving a 5 x 10⁻⁶ M I₂/0.1 M H₃BO₃ solution, it was found that as I₂ was removed from the solution, apparently through deposition on the epoxy paint, I⁻ appeared. Unfortunately, it is not yet known whether this was due to an aqueous phase or surface reaction and further work in this area is required.

The presence of the epoxy paint produced a second important chemical effect: at 80°C it caused up to 10% of the iodine to be converted to organic form(s) in basic solutions prepared with I₁ or I⁻. This effect did not occur in acidic solutions nor basic solutions at 25°C. Through a potentially related mechanism, the epoxy paint also caused the rapid elimination of free iodine and hence suppressed the expected formation of IO₃⁻. This epoxy-related formation of organic iodides affected the overall volatility. In the case of the solutions prepared with I₁, the effect of the epoxy was so severe that the partition coefficient was slightly lower under basic conditions than under acidic conditions (8 x 10⁻⁴ vs 1 x 10⁻⁴). It is interesting to note that most of the gas phase iodine above the basic 80°C solutions, prepared using either I₂ or I⁻, was in a form retained by iodophenol. The high abundance of organic iodides in the liquid phase in addition to the retention of most of the gas phase iodine by iodophenol strongly suggests that the gas phase iodine was predominantly in the form of higher-molecular-weight organic iodides.

In the ACE Phase B experiments performed under similar conditions in the RTF using an epoxy-painted vessel [14], extensive organic iodide formation was also observed, but there were some important differences. In RTF test 1A, in which CsI was added to the solution, the fraction of organic iodides in the aqueous phase increased exponentially throughout the test. However, this fraction reached only 1.5% after seven days compared with the 10% observed in the bench-scale tests after six days. In RTF test 1C, involving a solution prepared with I₁, the organic iodide fraction jumped almost instantly to 10%, whereas in
the comparable bench-scale experiments, it rose steadily for over a week before reaching a similar value. It was speculated that these differences were due to experimental differences between the two programs. Specifically, in the RTF, iodine was added to 80°C water in contact with the epoxy whereas in the bench-scale experiments epoxy-coated coupons were added to solutions containing iodine, which were subsequently heated to 80°C.

Further insight into the epoxy-paint-induced formation of organic iodides was provided through a separate set of experiments summarized in Table 3. These experiments involved contacting pH 9 solutions at 80°C with epoxy painted coupons for various periods and, in some cases then removing the coupons prior to adding I\(_2\). Samples were collected at 20-min intervals following the addition of the I\(_2\), and analyzed using the radiochemical solvent extraction procedure. It was found that when a solution had been in contact with the epoxy coated coupons for 10 minutes or more before adding any I\(_2\), the rate of organic iodide formation was extremely rapid. As was observed in RTF test 1C, formation of organic iodides occurred within minutes and little further change occurred over the remainder of the experiment. Unfortunately, the rate of this conversion was too rapid to be evaluated quantitatively using the given methodology. The very rapid nature of the organic iodide formation suggested that the reaction(s) involved was occurring in the aqueous phase as opposed to on the epoxy surface. This hypothesis was confirmed by the equally extensive organic iodide formation that occurred when the epoxy was removed from the solution prior to adding the I\(_2\). As is indicated in Table 3, the extent of conversion to organic iodide depended on the duration of contact between the epoxy and the solution, and on the iodine concentration of the solution. These dependencies suggested that the extent of conversion possibly was limited by the availability of organic reactant.

**TABLE 3**

**ORGANIC IODIDE FORMATION IN BASIC SOLUTIONS AT 80°C**

<table>
<thead>
<tr>
<th>Contact Time Prior to I(_2) addition</th>
<th>Coupon removed</th>
<th>Initial [I(_2)/M0I]</th>
<th>Percent Organic Iodide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 h</td>
<td>No</td>
<td>10(^{-5}) M</td>
<td>10%</td>
</tr>
<tr>
<td>1 h</td>
<td>No</td>
<td>10(^{-4}) M</td>
<td>2%</td>
</tr>
<tr>
<td>1 h</td>
<td>Yes</td>
<td>10(^{-5}) M</td>
<td>11%</td>
</tr>
<tr>
<td>18 h</td>
<td>Yes</td>
<td>10(^{-5}) M</td>
<td>12%</td>
</tr>
<tr>
<td>10 min</td>
<td>Yes</td>
<td>10(^{-5}) M</td>
<td>6%</td>
</tr>
<tr>
<td>10 s</td>
<td>Yes</td>
<td>10(^{-5}) M</td>
<td>3%</td>
</tr>
<tr>
<td>no coupon</td>
<td></td>
<td>10(^{-5}) M</td>
<td>3%</td>
</tr>
</tbody>
</table>

Extensive production of organic iodides only occurred at higher temperatures and under basic pH conditions. It can be speculated that the elevated temperature was required to enhanced the release of organic components.
from the paint while the basic pH contributed to either the rate of release or
the occurrence of the subsequent chemical reaction. Further experiments in this
area evidently are required in order to gain a satisfactory understanding of
this potentially important phenomena. However, it is evident that investigation
of the effect of submerged surfaces on iodine behaviour should consider the
effect on solution chemistry of components released from paints, in addition to
potential surface reactions.

For irradiated solutions, the adsorption of iodine onto the epoxy paint was
similar for both I\textsuperscript{-} or I\textsubscript{2}, as initial species. This was consistent with the
observed independence on the initial speciation of the partition coefficient.
The distribution coefficient depended substantially on pH, ranging from 2x10\textsuperscript{-3}
cm under basic pH conditions to 1 cm under acidic conditions. In the case of the
acidic solutions, the distribution coefficient did not appear to have attained a
maximum value when the experiment was terminated. In separate sets of
experiments, epoxy-painted coupons were also suspended in the gas phase of a few
flasks. After two days of irradiation under basic pH conditions, the loading on a
gas phase coupon was about a factor of two lower than that on an aqueous phase
coupon. In a set of experiments performed under acidic conditions, the iodine
loading on gas phase coupons was one hundred times higher than that on aqueous
phase coupons. However in a second set, the loading in the gas phase coupons was
comparable to that on the aqueous phase coupons. The divergence likely was
related to the gas phase speciation: in the first set about a third of the gas
phase iodine was in the form of I\textsubscript{2}, whereas in the second set lower-molecular-
weight organic iodides dominated the gas phase and the contribution of I\textsubscript{2} was not
significant.

3.3) The adsorption of I\textsubscript{2}(g) by epoxy paint

Measurement of the adsorption of I\textsubscript{2}(g) onto epoxy at 80°C confirmed that
this paint could act as a significant sink for gas phase iodine. The loading of
iodine ranged from 0.14 to 0.65 mg/cm\textsuperscript{2}, depending on the I\textsubscript{2}(g) concentration.
This loading was equivalent to a coverage of hundreds of monolayers, although the
majority of the iodine on the surface was found to be essentially irreversibly
bound. The initial deposition velocity, the initial rate of deposition divided by the
I\textsubscript{2}(g) concentration, was relatively independent of the I\textsubscript{2}(g)
concentration. The average for four experiments was 0.19 ± 0.05 cm/s. A similar
value was obtained for a silver coupon, indicating that the rate of deposition
onto both the epoxy and the silver was governed by the rate of gas phase mass
transfer rather than by the nature of these surfaces. The long-term deposition
velocity was much smaller than the initial value.

It is interesting to note that Rosenberg et al. [15] reported an initial
deposition velocity for I\textsubscript{2}(g) in 115°C air/steam to epoxy paint similar to the
measured gas phase mass transfer coefficient for his apparatus (0.39 cm/s).
More recently Dufresne [16] has reported an initial deposition velocity for I\textsubscript{2}(g)
in 90°C air/steam onto the epoxy paint used in the present study of 0.9 cm/s.
The differences between these initial deposition velocities suggests that at
least in the present work and that of Rosenberg et al. [15], the initial
deposition velocity was dictated by the rate of gas phase mass transfer, a
property of the apparatus rather than of the paint. It is clear that once I\textsubscript{2}(g)
reaches epoxy paint, adsorption can be extremely rapid.

Over the long term, the distribution coefficient did not vary significantly
with the gas phase iodine concentration, the apparent scatter was within the estimated experimental uncertainty. In most cases the distribution coefficient (Kd) appeared to increase continuously over time achieving values as high as 9000 cm. The only exception occurred for the highest gas phase iodine concentration studied (8 x 10^-3 M I) for which the coupon appeared to saturate after about 40 hours at a Kd value near 4000 cm. This corresponded to a surface loading of approximately 0.65 mg/cm². The apparent independence of Kd on the gas phase iodine concentration suggests that the deposited iodine was in "equilibrium" with the gas phase iodine and, consequently, that describing the surface loading in terms of a distribution coefficient (i.e. a multiple of the gas phase concentration) is appropriate. However, such an approach implies that the surface has an infinite capacity to absorb I₂. This may well not be realistic as is indicated by the apparent saturation of the surface in the case of the 8 x 10^-3 M I, experiment. In addition, an "equilibrium" interpretation also implies that the iodine is reversibly bound which was not the case. Iodine was found to desorb from the paint at a very slow rate. Less than 20% of the iodine was removed during 600 hours of exposure, at 80°C, to dry air flowing at 800 mL/min. This very slow desorption demonstrated that the majority of the iodine on the coupon was well bound, indicating that it had reacted with some component of the paint. During these experiments, particularly tests involving higher I₂(g) concentrations, the white epoxy paint developed a orange/yellow discoloration. Visual inspection revealed that this discoloration was limited to the surface of the paint. There was no evidence that any of the iodine reached the carbon steel substrate however, this possibility cannot be dismissed completely and therefore should be considered in any future studies.

The trends observed in relation to the adsorption of I₂(g) on epoxy paint can be summarised of follows:

1) The initial deposition velocity was dictated by the rate of gas phase mass transfer;

2) The amount of iodine retained over the long term depended on the gas phase concentration;

3) The rate of desorption was extremely slow;

4) The paint had a finite capacity to absorb I₂.

3.4) Modelling the adsorption of I₂(g) on epoxy paint

A model of iodine adsorption onto paint has been created in order to develop a quantitative description of the behaviour observed in this research. The model involves iodine on the surface in two different forms. The I₂(g) deposits onto the painted surface at a rate limited by the gas phase mass transfer coefficient and the number of available sites. The balance between the rates of deposition and desorption of this reversibly bound I₂ results in a constant distribution between airborne and surface I₂. However, while on the surface, the I₂ can react with the paint to become chemically bound. The rate of this reaction is proportional to the concentration of I₂ on the surface and the extent is limited by the number of available sites. After reacting, the chemically-bound iodine can be desorbed from the surface at a very slow rate. The model was found to describe the experimental results obtained at all of the I₂(g) concentrations investigated, as can be seen in Figure 1. Some divergence
between the model and the experimental results occurred for the experiment performed using $6 \times 10^{-9}$ M $\text{I}_2(\text{g})$. This may have been partially due to the experimental uncertainty in the $\text{I}_2(\text{g})$ concentrations.

The adsorption behaviour dictated by the model is best illustrated by the results for the $8 \times 10^{-7}$ M $\text{I}_2(\text{g})$ concentration. The loading of iodine on the paint initially increases at a rate governed by the gas phase mass transfer coefficient. Once the ratio of the loading to gas phase concentration approaches the distribution coefficient, the rate of increase of the loading (ie the deposition velocity) decreases substantially as the rate of loading becomes governed by the rate of chemical reaction. Eventually, all the sites for deposition are filled and the loading achieves a maximum value. At somewhat lower $\text{I}_2(\text{g})$ concentrations, the long-term rate of loading is still governed by the rate of chemical reaction, but since the reversibly bound concentration is lower, a longer time is required to achieve saturation. At very low $\text{I}_2(\text{g})$ concentrations, saturation will never be achieved, although a steady state balance between the rates of the forward and reverse surface chemical reactions will occur. At much higher $\text{I}_2(\text{g})$ concentrations, the surface can become rapidly saturated if all the sites are filled prior to the ratio of the loading to gas phase concentration achieving the distribution coefficient.

The model was found also to represent the data of Dufresne [16] and Rosenberg [15] reasonably well (Figure 2), although changes in the gas phase mass transfer coefficient and the distribution coefficient were required. Higher values of the distribution coefficient were rationalized in terms of the use of 50 to 60% steam in these other studies as compared with dry air in the present study. Recent data from CEA/IPSN indicate that the presence of steam can increase the deposition of $\text{I}_2(\text{g})$ on paint by a factor of 4 to 8 [17]. However, further study of the effect of steam on iodine deposition is required. The changes in the gas phase mass transfer coefficients were rationalized in terms of the differences in the experimental systems. As indicated in Figure 2, the model represented experimentally observed trends quite well. Furthermore, in the case of Rosenberg's results, approximately 55% of the surface iodine was calculated to be reversibly bound, whereas 45% was observed experimentally. A report is being prepared in which in which the experimental results and the model are described in more detail [18].

3.5) Comparison with results from the RTF

Presented in Table 4 is a comparison of the partition coefficients measured in this research with the values observed in equivalent RTF tests [2, 14, 19]. It should be noted that all the RTF test were performed at elevated temperatures (60 or 80°C) whereas the bench scale tests with radiation were performed made at 25°C.

The consistency between the results from the two programs provides support for the trends discussed in this paper. For example, in both programs the long term volatility did not differ between irradiated solutions prepared with I$^-$ and I$_2$. In addition, it appears, based on these static measurements of volatility, that the great difference in scale had no significant impact. However, caution should be exercised as differences in mass transfer related phenomena, such as the adsorption on surfaces, were observed.

Examination of these results also allows insight into the significant
impact of the epoxy paint at elevated temperature on the volatility observed in
the RTF. For example, for unirradiated basic-solutions, the paint likely
enhanced iodine volatility when I\(^-\) was added to the RTF whereas the opposite was
the case when I\(_2\) was the initial species. These trends are consistent with the
reaction of iodine with compound(s) released by the paint at elevated
temperature, described in section 3.2. For the irradiated-basic solutions, the
volatility in the RTF experiments, performed at 60°C, was higher than that
observed in the bench scale tests, performed at 25°C, likely due to the release
of compounds from the paint at the higher temperature. It appears that for
acidic-irradiated solutions, the presence of the epoxy paint had a small, if any,
effect the partition coefficient and hence that any reduction of I\(_2\) by the paint
did not contribute greatly to the volatility relative to the aqueous phase
chemistry. However, this hypothesis requires further study as the epoxy paint
may well have played an important role in suppressing iodine volatility in RTF
test 3A [2].

**TABLE 4**

**A COMPARISON OF THE BENCH SCALE AND RTF MEASUREMENTS**

<table>
<thead>
<tr>
<th>CONDITION</th>
<th>PARTITION COEFFICIENT ((\times 10^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bench no paint</td>
</tr>
<tr>
<td>Species</td>
<td>Radiation</td>
</tr>
<tr>
<td>I(^-)</td>
<td>No</td>
</tr>
<tr>
<td>I(_2)</td>
<td>No</td>
</tr>
<tr>
<td>I(^-)</td>
<td>Yes</td>
</tr>
<tr>
<td>I(_2)</td>
<td>Yes</td>
</tr>
<tr>
<td>I(^-)</td>
<td>Yes</td>
</tr>
<tr>
<td>I(_2)</td>
<td>Yes</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS

The volatility of iodine generally decreases with increasing pH, although
this trend can be reversed for solutions in contact with epoxy paint at higher
temperatures. This reversal is at least partially due to the extensive formation
of organic iodides under basic pH conditions, through aqueous phase reaction(s)
with material released from the epoxy paint. Furthermore, under acidic
conditions, interaction with the epoxy paint results in the reduction of I\(_2\) to
I\(^-\). Under irradiation, the long-term partition coefficient does not differ
between buffered solutions prepared with I\(_2\) instead of I\(^-\) but does depend
strongly on pH, particularly between pH 5 and 6.

The initial rate of deposition onto epoxy paint of gas phase I\(_2\) in dry air
at 80°C may be dictated by the rate of gas phase mass transfer. Over the long
term, the rate is much slower, likely limited by a slow chemical reaction. The 
rate of desorption is extremely slow, also indicative of chemical bonding. 
However, the amount of iodine retained by the epoxy paint over the long term 
depends on the gas phase concentration, suggesting that an equilibrium is 
achieved. These apparently conflicting trends have been resolved through a model 
that reasonably represents both the current experimental results and data from 
other studies.

This research, although quite fruitful, has raised as many questions as it 
has answered. Considerable further work is required in order to attain a 
satisfactory understanding of the interaction of iodine with epoxy painted 
surfaces. Specifically, the effects of steam, substrate and temperature on the 
adsorption of I$_2$(g) on epoxy paint should be investigated in order to evaluate 
the validity of the assumptions used to extent the proposed model to the results 
of other laboratories. Attempts should be made apply the model to other paints 
although this may require further experimental measurements. Further work on the 
reduction of I$_2$(aq) by epoxy paint could prove valuable to rationalizing the 
distribution of iodine between submerged and dry surfaces. Also the component(s) 
of epoxy paint involved in the production of organic iodides in hot, basic 
solutions should be identified as this may contribute or suppress long term 
iodine volatility.

ACKNOWLEDGEMENTS

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express their gratitude to the staff at Whiteshell Laboratories, Ontario Hydro 
and EPRI for their valuable suggestions.

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Nucl. Chem. 43(12), 3229-3238, 1981


16) J. Dufresne, personal communication.

17) G. Hueber, personal communication.

18) G.J. Evans and A.S. Palson, "The Adsorption of I$_2$ Vapours by Epoxy Paint at 80°C", To be released as ACE-TR-B11.

Figure 1. The retention of I$_2$(g) on epoxy paint at 80°C for various I$_2$(g) concentrations. The lines are derived from a semi-empirical model (see text).

Figure 2. Application of a model of I$_2$(g) retention on epoxy paint to the experimental results of Rosenberg et al. (15) and Dufresne (16).
DISCUSSION

Bowsher
You indicated that a "worst-case" could exist with highest iodine volatility at pH 4. What is the mechanism for decreasing volatility at very acidic pH (pH < 4)?

Evans
Although the mechanism is still uncertain, simulation using LIRIC indicates that at pH less than 4 the concentration of OH decreases and that of H increases hence the net rate of radiolytic I⁻ oxidation likely was slower.

Weber
Please Comment on the uncertainty in the mass transfer models (adsorption/desorption). Using similar data and similar models, I find it impossible to narrow the individual adsorption/desorption coefficients very precisely, although the ratio (representing equilibration) is more easily determined.

Evans
I assumed that the rate of deposition during the initial part of each experiment was indicative of the rate of gas phase mass transfer since the loading on the paint was still low and hence the rate of desorption was negligible. The rate of gas phase mass transfer also was evaluated using a silver coupon and the result was similar to that obtained for the epoxy paint.
3.6 DISCUSSION ON SESSION III

Fluke
Since painted surfaces were seen to be important in experiments, and were also seen to be the least well modelled. How would you summarize the current state-of-the-art and general R&D priorities for painted surfaces?

Ritzman
Presently we have data and experience on some coatings that are or have been in NPP's at simulated severe accident conditions and a range of effectiveness as iodine sinks seems to show in the data. Depending on coating character and environmental conditions. Other important coatings which have relatively wide use in the nuclear power industry may also require examination in integral tests like those at the RTF but this should probably not be done until an orderly process of categorizing/grouping candidate materials having common properties or expected performance is attempted. Assuming this can be done, and I suspect it can, the resulting classes of coatings should be screened further with small lab scale evaluation experiments before proceeding directly to integral testing. To be valid screening experiments the test conditions should approximate severe accident environments as closely as possible. The role of surfaces as sources of organic iodides or organics which might be released to react with iodine in the liquid or gas phase is equally important. A method to categorize paints in terms of their reactivity and types of organic compound releases, and conduct of small screening experiments before doing limited integral tests for confirmation is needed here too.

Evans
We heard about three points in this session and saw different phenomena on surface adsorption in particular, for each. Are we going to have to study every paint used in reactors? In relation to pH control, it appears that high pH may well be adequate to suppress iodine volatility. I hope a more finer answer will be possible by the time of the next workshop. However, there are two other questions that are related: how hard will it be to keep the pH high? and what pH? I hope better answers to these will also be available by the next workshop.

Kupferschmidt
I must disagree with my colleague's suggestion that "every possible surface found within confinement must be studied in detail since data presented at this meeting revealed that iodine behaviour differed dramatically with various surface". Although iodine chemistry did differ from surface to surface, remarkably similar behaviour was observed for the epoxy and vinyl studies discussed yesterday. Indeed, we have additional unpublished data that shows polyurethane exhibits the same general behaviour. Therefore, although differences between different types of coatings would be expected, it is unlikely that detailed studies of similar classes of surfaces will be required to obtain a reasonable estimate of their effect on iodine chemistry.
4. Session IV

INTEGRAL EXPERIMENTS
4.1 THE ADVANCED CONTAINMENT EXPERIMENTS (ACE) RADIOIODINE TEST FACILITY EXPERIMENTAL PROGRAM


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ABSTRACT

Results of the Advanced Containment Experiments (ACE) Radioiodine Test Facility (RTF) program are reported. This study consisted of four intermediate-scale experiments that investigated the effects of radiation, pH, surfaces and initial iodine speciation on iodine behaviour. The tests revealed that, in high radiation fields, the long-term volatility of iodine is independent of the initial iodine speciation (CsI, I₂, CH₃I). This is presumably because radiolytic reactions interconvert aqueous iodine species; I⁻ was the predominant aqueous iodine species after an absorbed dose of about 30-40 kGy. Tests at pH 9 and 5.5 demonstrated that iodine volatility increased significantly with decreasing pH. In addition, this study demonstrated that containment surfaces can play an important role in determining iodine volatility, gas and aqueous phase iodine speciation, and surface adsorption.

1. INTRODUCTION

In the event of an accident in a water-cooled reactor, iodine would be released to containment from failed fuel primarily in the form of CsI. Because CsI is involatile and highly soluble in water, it is readily contained and, therefore, does not pose a significant radiobiological hazard. However, subsequent reactions within the containment could produce volatile forms of iodine that are more readily released to the environment. For example, if acidic pH conditions arise within containment, radiolytic oxidation of I⁻ to volatile I₂ would occur. It is also possible that volatile organic iodides would be formed from reaction of iodine species with surfaces or organic compounds present in the containment building.

To address these and other uncertainties of iodine behaviour under accident conditions, a series of intermediate-scale experiments were conducted in the Radioiodine Test Facility (RTF) as part of the Advanced Containment Experiments (ACE) iodine project. This program specifically addressed questions of the role of radiation, pH and initial iodine speciation on iodine behaviour in a painted containment vessel. A follow-up reference test in an unpainted stainless steel vessel also was undertaken. Finally, the integral "all-effects" data from these tests have been used as a benchmark to develop and validate computer codes that predict iodine behaviour under conditions relevant to reactor accidents [1].
This paper describes the ACE/RTF experimental program and includes a preliminary assessment of the results.

2. EXPERIMENTAL

The design and operation of the RTF have been described previously [2,3]. Table 2.1 lists the ACE/RTF test matrix and Table 2.2 is a summary of the experimental conditions. Tests 1, 2, and 3 were undertaken in a 387-dm$^3$ epoxy-painted carbon steel vessel. The vessel coating was allowed to age for at least 15 d prior to the start of a test. Each test was composed of three separate stages in which 10$^{-5}$ mol·dm$^{-3}$ solutions (35 dm$^3$) of iodine-131-labelled CsI, I$_2$ and CH$_3$I were sequentially added to the RTF. Each stage was typically of 5-d duration, after which the vessel was thoroughly rinsed with distilled water and 1 x 10$^{-3}$ mol·dm$^{-3}$ aqueous hydrazine solution to minimize iodine carry-over between stages. After the final stage of each test, the old paint was removed by sandblasting and a fresh coat of the epoxy paint was applied to the vessel.

Test 4 was conducted in a 350-dm$^3$ vessel fabricated from 316 stainless steel. Unlike the earlier tests, only CsI was used. Because of the smaller size of this vessel, the volume of the test solution was only 27 dm$^3$. Due to the long duration of this test, H$_2$ gas, produced from the radiolysis of water, had to be removed from the vessel to avoid reaching explosive limits. This was achieved by opening an exhaust valve and applying a slight positive pressure to the RTF main vessel using ultra-high-purity air.

Table 2.1

ACE/RTF Test Matrix

<table>
<thead>
<tr>
<th>Test</th>
<th>Radiation</th>
<th>Surface</th>
<th>pH</th>
<th>Initial Iodine Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>Epoxy**</td>
<td>9</td>
<td>CH$_3$I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I$_2$, CsI</td>
</tr>
<tr>
<td>2</td>
<td>Yes</td>
<td>Epoxy**</td>
<td>9</td>
<td>CH$_3$I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I$_2$, CsI</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>Epoxy**</td>
<td>5.5 → 9</td>
<td>CH$_3$I</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I$_2$, CsI</td>
</tr>
<tr>
<td>4</td>
<td>Yes</td>
<td>Stainless Steel</td>
<td>9 → 5.2</td>
<td>CsI</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>5.2 → 9</td>
</tr>
</tbody>
</table>

* Cobalt-60 irradiation source. Average dose rate approximately 2 kGy·h$^{-1}$.

** Keeler & Long self-priming epoxy-amine enamel #4500.
Same vessel used for all three stages.
Table 2.2
ACE/RTP Test Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Iodine Concentration</td>
<td>$10^{-5}$ mol dm$^{-3}$ I</td>
</tr>
<tr>
<td>Temperature</td>
<td>80°C, 60°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>Atmospheric</td>
</tr>
<tr>
<td>Aqueous Volume</td>
<td>35 dm$^3$</td>
</tr>
<tr>
<td>Gas Volume</td>
<td>350 dm$^3$</td>
</tr>
<tr>
<td>Initial pH</td>
<td>9, 5.5 (controlled)</td>
</tr>
<tr>
<td>Gas Recirculation Rate</td>
<td>23 dm$^3$.min$^{-1}$</td>
</tr>
<tr>
<td>Aqueous Recirculation Rate</td>
<td>3 dm$^3$.min$^{-1}$</td>
</tr>
<tr>
<td>Dose Rate - without/with cobalt-60 irradiation source</td>
<td>0/2 kGy.h$^{-1}$</td>
</tr>
<tr>
<td>Surface Type</td>
<td>- Self-priming epoxy on carbon steel - 316L stainless steel</td>
</tr>
<tr>
<td>Stage Duration</td>
<td>4-5 d</td>
</tr>
</tbody>
</table>

Test 1 was conducted at 80°C, the intended operating temperature for the entire series of tests. However, prior to the start of Test 2, "chalking" (i.e., release of solids from the coating) was observed. This phenomenon is common to many paints when heated to elevated temperatures. As a result, subsequent tests were conducted at 60°C. No further difficulties were encountered.

The pH was carefully controlled at either 5.5 or 9.0 by repeated additions of H$_2$SO$_4$ and/or LiOH. The total gas phase iodine concentration was monitored throughout each test using an on-line $\gamma$-counting device that automatically collected and analyzed the concentration of airborne iodine [4]. The relative fractions of gas phase iodine species were determined using species-selective adsorbents [5]: CdI$_2$ on Chromosorb P for I$_2$, iodophenol on alumina for high-molecular-weight organic iodides (e.g., butyl iodide) and triethylenediamine (TEDA)-impregnated charcoal for low-molecular-weight organic iodides (e.g., methyl iodide). Gas chromatography on selected samples was also undertaken. Total aqueous phase iodine concentrations were determined using an on-line 3 x 3 NaI $\gamma$-detector that was calibrated daily. Aqueous phase iodine speciation was estimated using a radiochemical solvent extraction procedure [5].

Throughout this paper, unless speciation is specifically identified,
the term "iodine" includes the sum of all iodine species present in the phase being considered.

3. RESULTS

3.1 Gas Phase Iodine Behaviour

Figures 1 through 4 show the gas phase iodine concentration as a function of time and initial iodine speciation for Tests 1 to 4, respectively. In Test 1, performed at pH 9 without radiation, the gas phase iodine concentration depended strongly on the initial form of iodine added to the RTF, with the highest volatility measured in the CH₃I stage and the lowest during the I⁻ stage. In each stage, following the introduction of the iodine, the total gas phase iodine concentration increased rapidly, going through a maximum at about 2 h. In the I⁻ case, this initial rise may have been due to the presence of a small quantity of a volatile iodine species in the radiotracer, although efforts were made to purge the tracer solutions of volatile forms of iodine. Over the longer term, gas phase iodine concentrations increased during the I⁻ stage and decreased during the I₂ and CH₃I stages. As a result of these opposing trends, the importance of initial speciation on iodine volatility decreased with time.

Under similar pH conditions but with radiation (Test 2), dramatically different results were obtained. As shown in Figure 2, iodine volatility became independent of the initial chemical form of iodine within 40 h of its addition. This also was reflected in the aqueous phase, which, within a few hours, was almost exclusively I⁻ (i.e., 99%).

In Test 3 (Figure 3), the pH was initially held constant at 5.5 and then abruptly increased to 9. As for Test 2, similar iodine volatilities were observed after approximately 40 h, regardless of initial iodine speciation. A comparison of Figure 2 with the pH 5.5 portion of Figure 3 also reveals that iodine volatility was approximately an order of magnitude greater at pH 5.5 than 9. Increasing the pH from 5.5 to 9.0 did not result in a rapid decrease in iodine volatility. Rather, for the I⁻ and I₂ stages, gas phase iodine concentrations decreased only slowly, whereas for the CH₃I stage, the total gas phase iodine concentration did not change appreciably with the increase in pH.

Figure 4 depicts the gas phase iodine concentration as a function of time in Test 4. Unlike the previous experiments, Test 4 was conducted in a stainless steel vessel. The gas phase iodine concentration remained very small (<3.5 x 10⁻¹¹ mol·dm⁻³) while the pH was maintained at pH 9.0. Decreasing the pH from 9.0 to 5.1, however, resulted in a rapid increase in the total gas phase iodine concentration to 3.2 x 10⁻⁸ mol·dm⁻³. The gas phase iodine concentration subsequently decreased to a steady-state concentration of 6.5 x 10⁻⁹ mol·dm⁻³. The pH then was increased rapidly to pH 9.1 and a resulting decrease in the total gas phase iodine concentration was observed. However, even after almost 50 h, the airborne iodine concentration did not decrease to the level measured during the initial pH 9 stage.

In almost all the tests conducted in the epoxy-coated vessel, low-molecular-weight organic iodides dominated the gas phase (60-80%). One important exception was the CsI stage of Test 1, where high-molecular-weight organic iodides predominated (65%). Also, the relative fraction of gaseous I₂ was higher in the pH 5.5 CsI and I₂ stages of Test 3 (30-40%) than for the pH 9 stages of Test 3 (10%) or for Tests 1 or 2 (10-15%).
fraction of gas phase I₂ was also higher in Test 4 with the stainless steel vessel. In Test 4, equivalent quantities of I₂ and low- and high-molecular-weight organic iodides were observed in the gas phase during the initial pH 9 stage. However, when the pH was decreased to 5.1, approximately 95% of the airborne iodine was in the form of I₂. This decreased to about 50%, with the remainder present equally as low- and high-molecular-weight organic iodides, when the pH was increased to 9.

3.2 Aqueous Phase Iodine Behaviour

Figures 5 and 6 show the total aqueous phase iodine concentration for solutions initially containing I₂ and I⁻, respectively. The figures illustrate that, when the pH was held at 9, both in the presence and absence of the cobalt-60 irradiation source, the total aqueous phase iodine concentration remained constant at the initial concentration of 10⁻⁵ mol.dm⁻³. However, for Test 3, with pH initially set to 5.5, the aqueous phase iodine concentration decreased approximately 65%. The subsequent increase in pH to 9 had no effect on the concentration of iodine in solution.

In the presence of the stainless steel surface, the total aqueous phase iodine concentration also varied with pH (Figure 7). While the pH was initially held at 9.0, the aqueous phase iodine concentration remained constant at 1.2 x 10⁻⁵ mol.dm⁻³. Following the decrease in pH from 9.0 to 5.1, the aqueous phase iodine concentration decreased sharply and continued to decrease until the pH was increased to 9.1. The aqueous phase iodine concentration subsequently increased, although it had not returned to its original concentration when the test was terminated. A water rinse of the gas phase surfaces resulted in the further recovery of 28% of the initially added iodine.

The concentrations of the aqueous phase iodine species were also observed to be pH-dependent. In all tests except Test 1, I⁻ became the dominant species within the first few minutes of an experiment; in the CH₃I stage of Test 1, organic iodides dominated the aqueous phase for approximately the first hour. In the I₂ stage of Test 1, approximately 10% of the iodine was rapidly converted to organic iodides, whereas in the CsI stage, slow conversion to organic iodides of only 1% of the initial iodine inventory was observed. In the corresponding I₂ and CsI stages of Test 2, less than 1% of the initial iodine inventory was rapidly converted to organic iodides. In Test 4, the concentrations of I₂, "free iodine" (i.e., combination of I₂, HOI and OI⁻) and organic iodides increased by an order of magnitude with the pH decrease from 9.0 to 5.1. When the pH was subsequently increased, the I₂ and "free iodine" concentrations dropped quickly to their original levels; the organic iodide concentration decreased more slowly. For the Test 3 series, higher concentrations of these potentially volatile forms of iodine were also observed during the pH 5.5 portion of each test stage.

4. DISCUSSION

The ACE RTF experimental program has demonstrated that numerous factors may influence iodine behaviour under accident conditions within containment. One of the most interesting findings is the effect of radiation on iodine speciation and volatility. In the Test 1 series of experiments, conducted without irradiation, iodine volatility was very dependent on initial iodine speciation. In fact, even after 30 h, iodine
volatility for the CsI and CH$_3$I stages differed by more than four orders of magnitude. On the other hand, in Tests 2 and 3, which were conducted in the presence of a cobalt-60 irradiation source, iodine volatility differed by less than a factor of 10 after 30 h. This influence of radiation on iodine behaviour can be attributed primarily to aqueous phase radiolysis reactions.

In the absence of radiation, interconversion of I$^-$, I$_2$ and organic iodides is relatively slow. For example, under the conditions of Test 1, the pseudo-first-order rate constant for aqueous phase CH$_3$I hydrolysis

$$\text{CH}_3\text{I} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{I}^- + \text{H}^+$$  (1)

is reported to be only $8 \times 10^{-5}$ s$^{-1}$ [6,7]. Although the measured disappearance of CH$_3$I in the RTP was somewhat larger, suggesting that an additional CH$_3$I removal mechanism may have been operative in the RTP, the conversion to I$^-$ is nevertheless slow. Similarly, thermal oxidation of I$^-$ to elemental iodine,

$$2\text{I}^- + 1/2 \text{O}_2 + 2\text{H}^+ \rightarrow \text{I}_2 + \text{H}_2\text{O}$$  (2)

proceeds slowly under the alkaline conditions of Test 1 [8]. At pH 9, formation of I$_2$ would be followed by disproportionation,

$$\text{I}_2 + \text{H}_2\text{O} \rightarrow \text{HOI} + \text{I}^- + \text{H}^+$$  (3)

$$3\text{HOI} \rightarrow \text{IO}_3^- + 2\text{I}^- + 3\text{H}^+$$  (4)

and/or reaction with organics in aqueous solution,

$$\text{I}_2/\text{HOI/IO}^- + \text{RH} \rightarrow \text{RI}$$  (5)

to generate organic iodides. Indeed, reactions (2) and (5) may account for the slow but significant conversion of I$^-$ to organic iodides (12%) noted in the CsI stage of Test 1. They may also be responsible for the gradual increase in the airborne iodine concentration since organic iodides dominated the gas phase. However, the yield of organic iodides is higher than would be expected based on the known rate of reaction (2) [8]. This may indicate that the epoxy coating is directly involved in the enhanced conversion of I$^-$ to organic iodides.

Faster and more extensive formation of organic iodides was observed in the I$_2$ stage of Test 1. Approximately 10% of the iodine was converted to organic iodides within a few minutes, with the remainder of the iodine in the form of I$^-$. Reaction of free iodine with aqueous phase organics originating from the epoxy coating (reaction (5)) is likely responsible for the high yield of organic iodides, as suggested by related bench-scale experiments [9]. The subsequent slow decrease in iodine volatility may be attributed to the hydrolysis of these organic iodides. In any event, the lengthy period required to attain comparable iodine volatilities from the CH$_3$I, I$_2$ and CsI Test 1 stages is qualitatively consistent with the relatively slow rates of thermal oxidation of I$^-$, with subsequent reaction of the formed I$_2$, and organic iodide hydrolysis.

With radiation, iodine volatility is a delicate balance between opposing oxidizing and reducing radiolytic reactions. Previous work has shown that CH$_3$I(aq) readily undergoes decomposition by reaction with water radiolysis products [10],
$\text{CH}_3\text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{OH} + \text{I}^-$ \hfill (6)

$\text{CH}_3\text{I} + \cdot\text{e}^- \rightarrow \text{CH}_3\cdot + \text{I}^-$ \hfill (7)

$\text{CH}_3\text{I} + \text{H}^- \rightarrow \text{CH}_3\cdot + \text{I}^- + \text{H}^+$ \hfill (8)

and in aerated solution may react with the perhydroxyl ion ($\text{O}_2^-$) or radical ($\text{HO}_2^-$),

$\text{CH}_3\text{I} + \text{O}_2^- \rightarrow \text{CH}_3\cdot + \text{I}^- + \text{O}_2^-$ \hfill (9)

Similarly, $I_2$ is readily scavenged by $O_2^-$, leading to $I^-$ formation. Alternatively, oxidation of $I^-$ can also occur,

$I^- + \text{OH}^- \rightarrow \text{I}^- + \text{OH}^-$ \hfill (10)

ultimately forming elemental iodine [11]. In turn, these oxidized iodine species may react with organic radicals,

$I_2 + \text{R}^- \rightarrow \text{RI} + \text{I}^-$ \hfill (11)

$I^- + \text{R}^- \rightarrow \text{RI}$ \hfill (12)

to form organic iodides. Hence, radiolytic reactions would be expected to result in rapid interconversion of iodine species, with iodine volatility independent of initial iodine speciation in the longer term. The results depicted in Figures 2 and 3 support this suggestion.

The increase in the gas phase iodine concentration observed in Test 4 when the pH was decreased from 9 to 5.1 is consistent with our general understanding of the dependence of iodine volatility on pH. Several reactions may play an important role in this phenomenon. For example, the reaction of $\text{H}_2\text{O}_2$ with free iodine exhibits an inverse-second-order dependence on $[\text{H}^+]$ [12,13]. As a result, the rate of iodine reduction, presumably via the reaction

$\text{H}_2\text{O}_2 + \text{OI}^- \rightarrow \text{I}^- + \text{O}_2 + \text{H}_2\text{O}$ \hfill (13)

is drastically reduced by a decrease in pH. Elemental iodine, which is in equilibrium with $\text{OI}^-$, can then accumulate. Alternatively, $O_2$, formed in irradiated aerated solution, is an effective reductant for $I_2$ [14]. At pH 5.1, however, the quantity of $O_2$ is reduced through protonation to form $\text{HO}_2^-$ ($\text{pK}_a = 4.8$), which is a less effective reductant for elemental iodine; rather, it readily oxidizes $I_2$ [15]. This, in turn, would also account for an increase in the $I_2$ concentration with decreasing pH.

Several interesting features become apparent when the results of Tests 2 and 3 are compared with those of Test 4. The steady-state airborne iodine concentration was much smaller in the initial pH 9 stage of Test 4 as compared with Test 2 and appears to arise primarily from a lower concentration of airborne organic iodides. This can be attributed to the reduced quantity of organic material available in Test 4 and the resulting minor role of reactions (11) and (12). Alternatively, a comparison of the acidic stages of Test 3 and 4 reveals that the total airborne iodine concentration in Test 4 is higher than that observed in Test 3. This may be due in part to the small difference in pH between these tests (5.1 vs
5.5), but, it is unlikely that such a small pH difference could account for the dramatically different gas phase iodine speciation; most of the airborne iodine in Test 4 was in the form of elemental iodine (95%), whereas the gas phase in Test 3 was dominated by organic iodides (70%). Although the speciation results are consistent with the presence or absence of organics, other factors (see below) are likely responsible for the speciation and volatility dependence observed in these tests.

The increase in gas phase iodine concentration in the stainless steel test when the pH was decreased to 5.1 and the high iodine volatility observed in the Test 3 series at pH 5.5 also coincide with dramatic decreases in the aqueous phase iodine concentration (see Figures 5, 6 and 7). The latter is much more extensive, however, than can be accounted for by the increase in the gas phase iodine concentration; rather, such behaviour is indicative of iodine surface deposition. Indeed, scanning of the vessel after both tests revealed appreciable adsorption of iodine, predominantly on gas phase surfaces. This was further verified by analysis of coupons placed within the reaction vessel. Direct surface loading measurements of the vessel for each stage were not possible, however, because of the multi-stage nature of Tests 1 through 3. Nevertheless, approximately 65% of the initial iodine inventory is believed to have deposited on surfaces during the CsI and I₂ stages of Test 3, based on the quantity of iodine unaccounted for in the gas and aqueous phases. Interestingly, approximately 85% of the initial iodine inventory was apparently deposited on surfaces in the stainless steel test. Further evidence of surface adsorption on stainless steel is provided by the observation that rinsing of the stainless steel vessel with water resulted in a significant recovery (28%) of iodine. These results differ dramatically from those observed for the comparable stages of Tests 1 and 2 at pH 9; no significant surface adsorption was observed in the latter tests.

These results can be rationalized on the basis of radiolytic formation of aqueous phase I₂, with subsequent volatilization and deposition on gas phase surfaces. Certainly, significant deposition only occurred under conditions favouring I₂ formation (i.e., low pH, high dose rate). As well, deposition of elemental iodine onto epoxy and stainless steel surfaces has been observed previously [16,17]. Similar findings were also obtained in experiments conducted with a vinyl-based coating in the RTP [18].

A review of Figures 5 and 6 reveals that no significant change in aqueous iodine concentration occurred when the pH was increased to 9 in the presence of epoxy surfaces. This differs considerably from Test 4 (Figure 7), which revealed a significant increase in the aqueous phase iodine concentration when the pH was increased to 9. This observation is best rationalized in terms of reversible iodine adsorption/desorption on stainless steel and irreversible retention of iodine on epoxy surfaces. Indeed, bench-scale experiments with the identical epoxy coating under similar experimental conditions have verified the near irreversibility of iodine adsorption on this surface [9]. On the other hand, desorption from stainless steel is dependent on experimental conditions. Desorption studies by Rosenberg et al. [16] at 115°C revealed that appreciable desorption (65%) of iodine from 304 stainless steel occurs in dry air. Under non-condensing steam conditions, however, little desorption was observed. Modest desorption was also noted in studies conducted by Parker et al. [19] in the Confinement Mockup Facility. These results suggest that more than one adsorption mechanism may be involved in the retention of iodine on stainless steel surfaces.
The increase in the aqueous phase iodine concentration in Test 4 after addition of alkali is consistent with the chemistry of elemental iodine. As noted earlier, under acidic conditions, aqueous I\textsubscript{2} formation occurs and an equilibrium involving I\textsubscript{2} is established amongst the aqueous phase, the gas phase and the stainless steel surfaces. When the pH is subsequently increased, the I\textsubscript{2} concentration drops dramatically because of disproportionation (reactions (3) and (4)) and reduction by H\textsubscript{2}O\textsubscript{2} (reaction (13)). Subsequent mass transfer reactions of I\textsubscript{2} from the gas phase to the aqueous phase and from the stainless steel surfaces to the fluids with which they are in contact occur to maintain equilibrium conditions amongst the phases. The net effect is an increase in the total aqueous phase iodine concentration, as was observed.

Such a process involving surface desorption to the gas phase could result in higher gas phase iodine concentrations than would otherwise be expected. Indeed, higher gas phase iodine concentrations were observed in the latter pH 9 stage of Test 4 than during the initial pH 9 stage. It should be noted that higher fractions of organic iodides (50%) were observed than would be expected if only I\textsubscript{2} desorption occurred. This may indicate that sorbed I\textsubscript{2} reacted with organic impurities on the surface to form volatile organic iodides.

It is unlikely, however, that all of the adsorbed iodine in Test 4 is in I\textsubscript{2} or organic iodide form. Studies by Deane and Marsh [17] have revealed that reduction of I\textsubscript{2} can occur on stainless steel surfaces at 100°C to form metal iodides (MX\textsubscript{3}, M = Fe, Cr), which are readily soluble in water. This may explain the removal with a water spray of a large fraction of the initial iodine inventory (28%) from RTF stainless steel surfaces.

5. SUMMARY

The ACE/RTF experiments have demonstrated the importance of several factors on iodine behaviour within containment under reactor accident conditions. One of the most important factors was radiation. Without radiation, the volatility of iodine was dependent on the initial speciation of iodine, presumably because interconversion of iodine species by non-radiolytic reactions is relatively slow. In contrast, in the presence of radiation, the long-term volatility of iodine was independent of initial speciation. This is attributed to aqueous phase radiolytic reactions that result in rapid interconversion of iodine species.

Iodine volatility was shown to increase significantly with decreasing pH. However, changing the pH from acidic to alkaline conditions did not result in rapid decreases in iodine volatility. This may have been due to desorption of volatile iodine species from surfaces, in the case of stainless steel, and the influence of organics in the epoxy tests.

Surfaces were shown to influence iodine volatility and speciation. Higher gas phase iodine concentrations were observed under alkaline pH conditions with epoxy surfaces than with stainless steel and are believed to arise from reaction of iodine species with organic compounds originating from the epoxy coating. Under acidic conditions, organic iodides dominated the gas phase in the presence of epoxy surfaces, whereas I\textsubscript{2} was the principal airborne iodine species in the presence of stainless steel surfaces.

Both the stainless steel and epoxy surfaces exhibited appreciable affinity for iodine but only under conditions favouring I\textsubscript{2} formation (i.e., low pH, high dose rate). Deposition occurred primarily on surfaces in
contact with the gas phase. However, different adsorption processes are involved since retention on this epoxy is essentially irreversible, whereas adsorption on stainless steel is in part reversible.

The ACE/RTF program also demonstrated on an intermediate-scale that iodine volatility is strongly dependent on pH, increasing significantly with decreasing pH. However, changing the pH from acidic to alkaline conditions did not result in rapid decreases in iodine volatility. This may be due to desorption of volatile iodine species from surfaces, in the case of stainless steel, and competing radiolytic processes for the formation and destruction of organic iodides, for the epoxy tests.

This paper has offered some analysis and interpretation of the ACE/RTF results. Some mechanisms have been proposed, however, many of the results are not yet fully understood. Ongoing analysis of these tests, in conjunction with modeling efforts and laboratory separate-effects experiments, will be required if a more thorough mechanistic understanding of iodine behavior under accident conditions is to be obtained.

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REFERENCES


Figure 1. Total gas phase iodine concentration as a function of time in ACE/RTF Test 1 (pH 9, 0 kGy·h⁻¹, epoxy-coated vessel).

Figure 2. Total gas phase iodine concentration as a function of time in ACE/RTF Test 2 (pH 9, 2 kGy·h⁻¹, epoxy-coated vessel).
Figure 3. Total gas phase iodine concentration as a function of time in ACE/RTF Test 3 (pH 5.5 → 9, 2 kGy·h⁻¹, epoxy-coated vessel).

Figure 4. Total gas phase iodine concentration as a function of time in ACE/RTF Test 4 (pH 9 → 5.1 → 9, 2 kGy·h⁻¹, stainless steel vessel).
Figure 5. Total aqueous phase iodine concentration as a function of time for the $I_2$ stages of the ACE/RTF tests.

Figure 6. Total aqueous phase iodine concentration as a function of time for the CsI stages of the ACE/RTF tests.
Figure 7. Total aqueous phase iodine concentration as a function of time for ACE/RTP Test 4 (CsI, pH 9 + 5.1 + 9, 2 kGy·h⁻¹, stainless steel vessel).

DISCUSSION

Bowsher
Your results indicate significant differences between the interaction of iodine with epoxy and stainless steel surfaces. In particular, you see release of gaseous iodine from the steel surface and ready dissolution of the product. Is it possible that these observations can be interpreted in terms of iron iodide formation as this decomposes to release gaseous iodine and water-soluble?

Kupferschmidt
It is probable that a significant fraction of the iodine retained on the stainless steel surfaces is as solvable iron iodide. However, the results also show that a small fraction of the surface iodine is irreversibly adsorbed. Also, the high gas phase iodine concentrations observed after the pH increase to 9 suggest the presence of reversibly adsorbed volatile iodine species, such as I₂ and possibly organic iodines.

Dutton
In the presence of epoxy surfaces, is the conclusion that the gas phase iodine was predominantly in organic form independent of the initial iodine species?

Kupferschmidt
Yes. Regardless of whether the pH was alkaline or acidic gas phase iodine was primarily in organic form.
4.2 THE ACE LARGE SCALE IODINE EXPERIMENT AT THE CONTAINMENT SYSTEMS TEST FACILITY (CSTF)

R. L. Ritzman(a), J. D. McCormack(b),
D. R. Dickinson(b), and R. T. Allemann(c)

ABSTRACT

The behavior of iodine was studied under conditions simulating its release into a nuclear reactor containment vessel during a possible severe accident. The vessel atmosphere included gram/m$^3$ range concentrations of mixed CsOH/MnO aerosols. Measurements showed that HI, I$_2$ and Cs were removed from the gas phase at similar rates, primarily by gravitational settling, indicating that the iodine vapor species had become associated with aerosol particles. About 0.2% of the total iodine was converted to organic species in the test.

1. INTRODUCTION

Many experimental studies have been done in a variety of vessels to examine radioiodine behavior under anticipated reactor accident conditions (1,2,3). However, these studies have included only limited investigation of severe accident phenomena. The goal of the present work was to develop data for some of the processes that are important to describe iodine transport and deposition in containment during severe LWR accidents so iodine models can be more thoroughly evaluated and improved.

The key process to be addressed was the interaction between vapor iodine species (specifically, hydrogen iodide and elemental iodine) and bulk aerosol material at expected severe accident concentrations. Other processes occurring in the test would include iodine deposition on and possible desorption from painted surfaces and iodine accumulation and reaction in a buffered water pool. This paper will focus on the vapor-aerosol interaction aspects of the work although general data on iodine behavior will be discussed. The experiment was conducted at the CSTF which is located at the Hanford site near Richland, Washington.

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2. EXPERIMENTAL

2.1 Facility Description

The CSTF, consists of a containment vessel, aerosol generating facilities, office space, chemical laboratory space, maintenance facilities, effluent disposal facilities, and normal utility services. Figure 2-1 is a schematic diagram showing the containment vessel and the principal supplementary equipment used in the present experiment. The containment vessel is a vertical cylinder with standard dished top and bottom heads. The inner diameter is 7.62m, the overall height is 20.33m, and the vessel has an enclosed volume of 852m$^3$. The vessel is fabricated of carbon steel plate and the interior surfaces were coated for this experiment with a design-basis-accident qualified paint which is similar to that used in commercial nuclear power plants. Specifically, the paint used was Keeler and Long No. 4500 epoxyamine self-priming surfacing enamel and was applied by airless spray to the sandblasted surfaces.

The exterior of the containment vessel contains a 25mm thick layer of thermal insulation with an outer aluminum foil protective layer. Miscellaneous steel structures consisting of I-beams, grating, railing, and piping are located within the containment space. The surface areas for heat transfer and/or material deposition are as follows: top and bottom head, 63m$^2$ each; cylinder wall, 394m$^2$; internal components, 221m$^2$. The horizontal areas for aerosol settling are bottom head, 45.5m$^2$ and internal components, 42.3m$^2$.

2.2 Aerosol and Iodine Generation Systems

A mixed aerosol of CsOH (water soluble) and MnO (insoluble) was generated and introduced to the containment vessel independently of iodine. The CsOH aerosol was generated by reaction of cesium vapor with steam while the MnO aerosol was generated by reaction of manganese vapor (produced by plasma torch heating of metallic manganese powder) with steam. The reactions and mixing of the resulting aerosols took place in a 5.2m$^3$ steel vessel which was connected to the containment vessel by a 6.4m long delivery pipe (see Figure 2-1). The mixing vessel and delivery pipe were insulated and heated to prevent steam condensation.

The hydrogen iodide and the elemental iodine were introduced into the containment vessel at separate times using a delivery system which was independent from the aerosol delivery system. For hydrogen iodide the anhydrous gas was metered from a pressurized gas bottle through a 11-mm bore stainless steel line which terminated near the center of the containment vessel. The mass of hydrogen iodide delivered was determined by measuring the weight loss of the gas bottle. Elemental iodine vapor was delivered by passing hot
nitrogen gas over a weighed amount of iodine crystals in a stainless steel chamber which was connected to the same stainless steel line used for delivering hydrogen iodide. Previous calibration determined the flow rate needed to transfer the full iodine charge to the containment vessel within a period of five minutes.

2.3 Instrumentation and Sampling Equipment

Various types of instrumentation and sampling devices were used to measure conditions and determine the time dependent behavior of the injected aerosol and iodine forms in the containment vessel. Temperature mapping of the containment vessel was done with a large number of conventional thermocouples connected to a programmed data acquisition system. This system also recorded the output from various pressure transducers, steam and gas flow meters, and gas composition analysis meters. The volume of the water in the sump pool at the bottom of the containment vessel was periodically measured using a calibrated level gauge which was also connected to the data acquisition system.

Through-the-wall sampling stations exist at the CSTF (four within the vessel, one on the inlet pipe) to permit extraction of samples from inside the apparatus. These samples can be any combination of glass-fiber filters (for aerosol concentration measurement), Maypacks® (for airborne iodine species separation/measurement), cascade impactors (for aerosol particle size determination), deposition coupons (for measuring deposition rates on surfaces), and scanning electron microscope samples (for particle morphology determination). The frequency and duration of these samples during an experiment are adjusted according to the anticipated lifetime of the airborne materials. In the present case, past experience and simple pretest model calculations were used to guide specification of the sampling protocol.

The remaining sampling equipment used during the experiment consisted of wall condensate collectors (for measuring local condensation rates), deposition trays (for aerosol collection), and coating deposition racks (for measuring paint uptake) Periodic sampling of the water pool at the bottom of the vessel was also performed.

2.4 Chemical Analyses

The various types of samples described in the previous section had to be analyzed for manganese, cesium and iodine content so the time dependent

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1* The sampling media in the order of flow were (a) Teflon filter for capturing particulate iodine; (b) two silver membrane filters for capture of elemental iodine vapor (and hydrogen iodide gas also); (c) two activated carbon-impregnated filters to retain "heavy organic" iodine species, and (d) a 60g bed of charcoal impregnated with 5 weight percent triethylene-diamine for retention of light organic compounds such as methyl iodide.
distribution of these source materials in the containment vessel could be determined. This was accomplished, in most cases, using simple wet chemistry and instrumental analysis procedures. Aliquots of liquid samples (pool water or condensate) or of dissolved solid samples (deposits on filters, impactor stages, or deposition coupons) were analyzed for manganese using atomic absorption spectrometry and for cesium using flame emission spectroscopy. Further details of these procedures can be found in Reference (4). Some cesium analyses were made directly on surface deposits using the method of energy dispersive X-ray fluorescence (EDXRF). This was applied to paint coupons and, in some cases, to Maypack components.

Analysis for iodine required special care and the development of new procedures that would extend the lower limit of measurement sensitivity. All liquid samples were made alkaline when taken. Aliquots were subsequently treated with alkaline sulfite and analyzed by specific ion electrode if sufficient iodine (greater than one microgram) was expected to be present for measurement. Otherwise, analyses for iodine were performed using the more sensitive (about 0.1 microgram/sample) induction coupled plasma/mass spectrometer (ICP/MS) method (5). All reagents used in these analyses were checked to assure low inherent iodine levels and matrix-matched calibration standards were employed. The ICP/MS technique was also used where necessary to measure iodine on Maypack components and other deposition samples. This required use of established combustion and volatilization procedures to free the iodine from the component and to collect and process it for final measurement (6). A special study with pilot samples was done to refine these procedures for our particular application and to demonstrate the method would provide the required sensitivity and accuracy. It was possible to analyze some Maypack components (Teflon filters, silver membranes, carbon filters, or charcoal beds) and some paint coupons for iodine using the EDXRF method (i.e., if iodine loadings were greater than about 5 micrograms). Again, special effort was spent in calibrating the technique and developing sample self-absorption correction factors for the different types of samples. Altogether, hundreds of elemental analyses were performed using this and the other methods outlined above.

2.5 Test Sequence and General Conditions

The experiment was performed over a period of about four days in the closed containment vessel. The vessel was brought to a temperature of about 100°C and a pressure of about 240kPa by steam addition at the vessel centerline (see Figure 2-1). Steam addition was continued throughout the experiment to make up for heat losses. This addition provided a constant condensation of water on the wall which flowed into the pool at the bottom of the vessel. Prior to vessel closure, the pool had been filled with 3870kg of water and the pH had been adjusted to 5.2 by addition of 41kg of KH₂PO₄ and 120g of NaOH as a buffer. The pool was heated by direct steam sparging to match the temperature of the atmosphere and thus eliminate thermal stratification near the pool surface. No
venting of the containment vessel occurred during the experiment. Nitrogen was added as needed to keep constant noncondensable gas pressure in the vessel.

The important test conditions are summarized in Table 2-1. Each iodine release was immediately preceded by the introduction of fresh CsOH and MnO aerosol. Following the release of HI (Test B1), one day was allowed to pass for aerosol decay to occur. The I₂ release (Test B2), was then made and followed with two days of decay allowance. At this point, the pH of the water pool at the bottom of the vessel was changed from 5.6 to above 8.5 (addition of 12.1 kg of NaOH) and the test continued another day to study changes in iodine distribution with pH (Test B3). Time zero for the experiment was designated as the beginning of the first aerosol injection. The HI release was started at \( t = 35 \text{ min} \) or 5 minutes after the aerosol input had ended. The second aerosol injection was started at \( t = 1440 \text{ min} (1.00 \text{ day}) \) and the I₂ release began at \( t = 1475 \text{ min} \). The pool pH change was initiated at \( t = 4275 \text{ min} (2.97 \text{ days}) \) and the experiment ended at \( t = 6000 \text{ min} (4.17 \text{ days}) \).

3. RESULTS

3.1 General Observations

Extensive data on temperature differentials within the vessel were recorded. Inspection of the data points for the bulk gas showed radial \( \Delta T \) values were less than 0.2°C and vertical \( \Delta T \) values were less than 1.6°C. This relative uniformity in temperature within the atmosphere suggests a well-mixed, unstratified system existed throughout the experiment. Other thermal-hydraulic parameters were nearly uniform and, thus, close to the average conditions in Table 2-1. The water in the containment vessel pool was circulated with an external pump at an estimated rate of one liter per second. The final pool surface area occupied 75% of the cross sectional area of the containment vessel. A water mass balance was performed by comparing the measured steam input to the measured increase in pool mass. The two values agreed within 2%.

3.2 Aerosol and Iodine Behavior

The containment atmosphere was sampled periodically for suspended masses of these materials using Maypacks, as outlined earlier. Sampling and analytical errors for airborne concentrations derived from these measurements are estimated at ±40% for manganese and cesium and +100%, -50% for individual iodine species. Determination of iodine on many, but not all, of the Maypack components used EDXRF. This method can also measure cesium which was unexpectedly found on some of the silver and charcoal filters. It was noted that high levels of iodine on these silver or charcoal filters often were accompanied by high levels of cesium, indicating that some cesium and iodine containing aerosol
had penetrated the Teflon filters, presumably as solution droplets. To correct for iodine transfer by this process, the ratio of iodine to cesium on the Teflon filter was used to adjust the iodine amount found on the silver and charcoal filters by setting the net cesium on the silver or charcoal filter to zero. The results of the adjusted Maypack data, expressed in terms of suspended mass concentrations, are plotted in Figures 3-1, 3-2, and 3-3 for manganese, cesium, and total iodine for the entire test sequence. The maximum concentrations occurred at the end of the injection periods and the concentrations then decreased exponentially for several orders of magnitude. For manganese and cesium, the behavior after each release (0-30 min and 1440-1470 min) was very similar, as would be expected, considering the containment conditions were similar for both test intervals. The manganese decreased at a slightly slower rate ($t_{1/2} = 45$ min) than the cesium ($t_{1/2} = 40$ min). The manganese and cesium both reached low concentration levels; near the sensitivity limits of the chemical analysis.

The iodine behavior is more complex since data are available from the different Maypack sampling media; i.e., the Teflon filter (interpreted as particulate), the silver (interpreted as I$_2$ or HI), and charcoals (interpreted as organic iodine). The data in Figure 3-3 shows the total iodine (sum of iodine on all Maypack components) and just the particulate iodine (that on the Teflon filter alone). Some similarities as well as differences can be seen between the first release (iodine as HI) and the second release (iodine as I$_2$). In both cases, the initial iodine concentrations decrease with a $t_{1/2}$ of about 40 min which is the same as that for cesium in Figure 3-2. Also, in both tests, the particulate iodine concentration continued to drop with the 40 min half-life to very low levels, but the total iodine concentration declined much more slowly at later times. This indicates that effects of other species or processes are important at these times and it can be seen that they are at least a factor of 10 more significant in the I$_2$ release compared to the HI release.

Plots of airborne iodine concentrations obtained from the cesium adjusted iodine measurements on the other Maypack sampling components are given in Figure 3-4 (silver), 3-5 (charcoal paper), and 3-6 (charcoal bed). It is evident that iodine caught by silver and by charcoal bed components dominate the later time behavior. This would suggest I$_2$ (or HI) species and methyl iodide species, respectively. The charcoal paper species, normally interpreted as higher molecular weight organic iodine, represent minor contributors throughout. These three figures also show that the pool pH change at 4275 min (71.25 hr) did not produce any significant change in airborne iodine species distribution or concentration.

As noted earlier, the water pool was recirculated and samples were taken periodically. The samples were analyzed for cesium and iodine (sampling and analysis of manganese were not reliable due to its insoluble nature) and the concentrations multiplied by the total liquid volume in the pool at the time of sampling to determine the mass of each element in the pool. The results of these measurements are shown in Figure 3-7. The figure also shows the mass of cesium and iodine that was injected to the containment vessel for reference. It can be seen
that a large fraction of the total cesium and iodine mass added to the vessel was soon found in the pool water. The only other repository for these materials other than the atmosphere were the internal surfaces in the vessel.

3.3 Aerosol Size Distributions

Cascade impactor samples were taken directly from the vessel atmosphere during the experiment which after analysis provided a measure of how the mass collected by the impactor was distributed as a function of particle size for each chemical element (i.e., Mn, Cs, and I). The data were expressed as log-normal distributions and the results in terms of AMMD (Aerodynamic Mass Median Diameter), GSD (Geometric Standard Deviation), values are given in Table 3-1. The AMMD values generally increased with time from initial values to maxima at the 133 min sample and then decreased. Samples were taken at longer times but insufficient masses were collected to yield useful results. The impactor measurements were made in a manner such that the aerosol particles were collected on the impactor stages according to their actual size; i.e., according to their total mass/volume including any absorbed water (7).

Aerosol size estimates were also obtained from stainless steel deposition coupons which were inserted into the vessel atmosphere for short periods to collect aerosol by gravitational settling. This allowed calculation of aerodynamic settling mean diameter (ASMD) values. The results were similar to the cascade impactor measurements; i.e., they indicated a general trend for particles sizes to rise to a peak at about 130 min and then decline. The ASMD values at the peak were in the range of 9-12 μm.

4. DISCUSSION

The concentration-time plots in Figures 3-1, 3-2, and 3-3 indicate very similar behavior of vapor iodine species and aerosol material for several hours after their injection to the vessel. The same removal half-time for iodine and cesium in each test would suggest that the cesium aerosol was particularly effective in absorbing each iodine charge (HI or I₂). That is the iodine very quickly began to behave as particulate species even though it was injected in vapor form.

It is interesting to compare the aerosol and iodine behavior in this experiment to what was observed in a similar experiment that was conducted about 20 years ago in the same facility (8). At that time it was called the Containment Systems Experiment (CSE) and the experiment of interest was identified as CSE Run A-5. This was a natural effects containment experiment performed at a slightly higher temperature and pressure than the ACE experiment. The vessel had the same external insulation (although newer) and the interior was painted (although with a phenolic rather than an epoxy paint). The fission product simulant, which was injected over a 10 min period after the vessel had reached steady conditions, consisted of a mass of I₂ similar to that used in the ACE-B2 test along with a small
amount of cesium aerosol. Several hours of sampling with Maypacks, etc. were used to follow the airborne concentrations and ultimate distribution of the simulant materials.

Table 4-1 summarizes the principal conditions and some key results obtained in the two experiments. The conditions are very similar except for the mass of cesium aerosol used and consequently the cesium to iodine mass ratio in the two systems. It can be seen that this difference had no significant effect on cesium removal half-times but it did substantially affect the iodine removal half-times. It appears that cesium aerosol removal occurred mostly by gravitational settling in both experiments. The equivalent half-times, similar fractions of cesium held on vertical surfaces, and similar ASMD estimates all support this interpretation. The same process appears to have dominated iodine removal in ACE/B2 but not in CSE/A-5 since there was insufficient cesium aerosol in that experiment to absorb most of the available I$_2$ vapor. Thus in CSE/A-5 the dominant mechanism of iodine removal was determined to be boundary-layer vapor diffusion and sorption at internal surfaces. This accounts for the high fraction of iodine held by the vertical surfaces in that experiment.

Table 4-1 also contains estimated total surface areas for the cesium aerosols and estimated rate constants for the key iodine mass transfer processes in the two experiments. The aerosol surface areas were calculated assuming the particles were solution droplets and using particle size distribution data from the experiments. The rate constants were calculated assuming the vessel atmosphere was well stirred and using standard expressions for mass transfer to suspended particles (9), stirred aerosol settling (10), and natural convection driven boundary layer diffusion (11). The gas phase mass transfer step was assumed rate controlling for aerosol uptake and for wall deposition. It is evident that the rate constant for aerosol uptake is dominant and this should preferentially occur as long as the capacity of the aerosol to absorb iodine is not approached. In both experiments the vapor-aerosol interaction process probably was complete within the time scale of the atmosphere mixing process (a few minutes) and the iodine removal rate (half-time) that was recorded by samplers depended on how much iodine vapor had been captured by the cesium aerosol in the brief early transient. Note that the estimated rate constants for I$_2$ wall deposition are about 2.7 times those for aerosol settling. This difference is quite consistent with the measured difference in early iodine removal half-time in the two experiments.

With respect to long term airborne iodine in the ACE experiment, the results in Figures 3-4, 3-5, and 3-6 show that this involves less than 2 percent of the initial mass charge. As noted earlier, nearly all of this appeared to be a result of the second iodine release (I$_2$) and for a few hours it was primarily I$_2$ with t$_{1/2}$ ~ 11 hours while near the end of the experiment it was primarily CH$_3$I with t$_{1/2}$ ~ 47 hours. Now I$_2$ would not be expected to have such a long t$_{1/2}$ if its behavior were due simply to irreversible wall deposition. (The estimated rate constant for wall
deposition in Table 4-1 corresponds to a t 1/2 of 16 min.). More complicated kinetics were surely occurring, probably involving a source-sink competition whose net effect was the observed t 1/2, but insufficient data are available to determine the exact nature of the interaction(s). The amount of methyl iodide measured in the experiment was only about 0.2% of the total iodine mass introduced and the observed t 1/2 was similar to that measured in other iodine experiments in the CSTF/CSE vessel (8).

5. CONCLUSION

The principal conclusion of this work is that high concentrations of reactive aerosol will affect the dominant mechanism and rate of removal of iodine introduced in vapor form to a large containment vessel. This has important implications when formulating models which may be used to analyze and/or predict the behavior of iodine in reactor containments during severe accidents.

ACKNOWLEDGEMENT

The work reported in this paper was supported by the ACE Project which is a consortium of organizations from 19 countries in Asia, Europe, and North America.

The authors wish to acknowledge the efforts of the many Battelle Pacific Northwest Laboratory and Westinghouse Hanford Company staff who contributed to the planning and successful execution of the experiment.

REFERENCES


Figure 3-2  Cesium Concentration in the Containment Vessel Atmosphere

Figure 3-3  Total and Particulate Iodine Concentrations in the Containment Vessel Atmosphere
Figure 3-7 Aerosol Mass Suspended in the Containment Vessel Sump Water

Table 2-1
Average Test Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Test B1</th>
<th>Test B2</th>
<th>Test B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV pressure (kPa)</td>
<td>242.0</td>
<td>250.0</td>
<td>247.0</td>
</tr>
<tr>
<td>CV gas temperature (°C)</td>
<td>102.1</td>
<td>101.3</td>
<td>100.9</td>
</tr>
<tr>
<td>CV wall temperature (°C)</td>
<td>101.3</td>
<td>100.5</td>
<td>100.1</td>
</tr>
<tr>
<td>CV pool temperature (°C)</td>
<td>101.7</td>
<td>101.3</td>
<td>100.8</td>
</tr>
<tr>
<td>CV steam fraction</td>
<td>0.45</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Pool pH</td>
<td>5.5</td>
<td>5.6</td>
<td>8.5</td>
</tr>
<tr>
<td>Steam flow to CV (g/s)</td>
<td>28.0</td>
<td>28.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Condensation rate on wall (g/m²s)</td>
<td>0.057</td>
<td>0.057</td>
<td>0.057</td>
</tr>
<tr>
<td>Pool mass at start of test period (kg)*</td>
<td>6000</td>
<td>8320</td>
<td>13240</td>
</tr>
<tr>
<td>Aerosol introduced to CV (g)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>307.0</td>
<td>266.0</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>743.0</td>
<td>373.0</td>
<td></td>
</tr>
<tr>
<td>Duration of aerosol release (min)</td>
<td>30.0</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Iodine release:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical form</td>
<td>H I</td>
<td>I₂</td>
<td></td>
</tr>
<tr>
<td>Mass I added (g)</td>
<td>110.0</td>
<td>101.0</td>
<td></td>
</tr>
<tr>
<td>Duration of release (min)</td>
<td>5.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>Initial concentrations in CV (g/m³)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>0.13</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>0.36</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.88</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>Aerosol decay time (days)</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

CV = containment vessel.
*Ending pool mass = 16270 kg.
*Calculated from mass added with no removal.
Table 3-1
Particle Size Distributions From Cascade Impactors

<table>
<thead>
<tr>
<th>Sample Time, min&lt;sup&gt;(a)&lt;/sup&gt;</th>
<th>AMMD, μm</th>
<th></th>
<th>GSD</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mn</td>
<td>Cs</td>
<td>I</td>
<td>Mn</td>
<td>Cs</td>
</tr>
<tr>
<td>30</td>
<td>3.1</td>
<td>2.5</td>
<td>-</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>46</td>
<td>3.1</td>
<td>1.9</td>
<td>1.8</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td>133</td>
<td>10.1</td>
<td>8.9</td>
<td>9.2</td>
<td>2.6</td>
<td>2.7</td>
</tr>
<tr>
<td>410</td>
<td>3.4</td>
<td>4.1</td>
<td>3.9</td>
<td>2.6</td>
<td>2.9</td>
</tr>
<tr>
<td>1470 (30)</td>
<td>5.6</td>
<td>3.9</td>
<td>-</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>1486 (46)</td>
<td>2.9</td>
<td>2.4</td>
<td>2.6</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>1573 (133)</td>
<td>8.0</td>
<td>3.1</td>
<td>lost</td>
<td>3.5</td>
<td>4.3</td>
</tr>
<tr>
<td>1828 (388)&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>1.7</td>
<td>0.9</td>
<td>1.4</td>
<td>5.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> The times in parenthesis indicate elapsed time after start of the second aerosol injection.
<sup>(b)</sup> Low mass with questionable results.

Table 4-1
Comparison Data For The ACE/B2 and CSE/A-5 Experiments

<table>
<thead>
<tr>
<th>Test Conditions/Data</th>
<th>ACE/B2</th>
<th>CSE/A-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel Volume, m&lt;sup&gt;3&lt;/sup&gt;</td>
<td>852</td>
<td>594</td>
</tr>
<tr>
<td>Internal Area, m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>741</td>
<td>571</td>
</tr>
<tr>
<td>Wall Area Only, m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>520</td>
<td>418</td>
</tr>
<tr>
<td>Cross Section Area, m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>Bulk Gas Temp., °C</td>
<td>101</td>
<td>123</td>
</tr>
<tr>
<td>Gas Pressure, kPa</td>
<td>250</td>
<td>319</td>
</tr>
<tr>
<td>Cs Input Mass, g</td>
<td>266</td>
<td>11.1</td>
</tr>
<tr>
<td>I Input Mass, g</td>
<td>101</td>
<td>85.5</td>
</tr>
<tr>
<td>Cs Removal Half-Time, min.</td>
<td>40</td>
<td>38</td>
</tr>
<tr>
<td>I Removal Half-Time, min&lt;sup&gt;(a)&lt;/sup&gt;</td>
<td>40</td>
<td>17</td>
</tr>
<tr>
<td>Cs on Vertical Surfaces, %</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>I on Vertical Surfaces, %</td>
<td>20</td>
<td>75</td>
</tr>
<tr>
<td>ASMD for Cs Aerosol, μm&lt;sup&gt;(b)&lt;/sup&gt;</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>Estimated Surface Area of Aerosol, m&lt;sup&gt;2&lt;/sup&gt;</td>
<td>840</td>
<td>4</td>
</tr>
<tr>
<td>Estimated Rate Constants:</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aerosol Uptake, min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Aerosol Settling, min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>I&lt;sub&gt;2&lt;/sub&gt; Deposition on Wall, min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.044</td>
</tr>
</tbody>
</table>

<sup>(a)</sup> During early times involving most of the iodine mass
<sup>(b)</sup> Aerodynamic settling mean diameter
DISCUSSION

Tennankore
Was there any variation in iodine content (concentration) as a function of aerosol size? For instance, did the mass fraction of iodine in the different stages of the cascade impactor show any correlation with the mean size for the stage?

Ritzman
I personally have not inspected the raw data from the aerosol impactor samples to give a specific answer but this was not an item that the experimental team made any mention of in the draft final report of the experiment.
4.3 LARGE-SCALE EXPERIMENTS ON IODINE RELEASE ASSOCIATED WITH COOLANT FLASHING DUE TO RUPTURED HIGH-PRESSURE TUBES

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ABSTRACT

Large-scale experiments were performed in order to study the radionuclide release especially of iodine associated with coolant flashing in the case of a ruptured high-pressure tube. It was investigated how radionuclides such as non-volatile iodide I\(^{-}\), cesium Cs\(^{+}\) and volatile iodine I\(_{2}\) dissolved in a coolant at pH 6 distribute in the water and steam phases and to what extent they are released from a compartment.

Experimental parameter studies include
- the effect of discharge geometry on the release of droplet-borne radionuclides (Li\(^{+}\)-tracer),
- the influence of volatile and non-volatile iodine fractions on iodine release (I\(^{-}\)/I\(_{2}\)-tests using radio-iodine tracer I123).

Additionally, some essential aspects of long-term behaviour of iodine (release from sumps) were covered.

The experimental results show that the release is in any case below 1\(_{2}\). The highest values are obtained when the discharged two-phase jet impacts directly on an impingement plate. In the case of non-volatile iodide (I\(^{-}\)) the same release as with Li\(^{+}\)-tracer is obtained, leading to the conclusion that release of iodide takes place only by droplet carry-over. The use of volatile iodine (I\(_{2}\)) does not significantly raise the release compared to a purely droplet-borne iodide release. This can be explained by the chemical behaviour of I\(_{2}\) under the prevailing conditions. Thus the overall release is clearly dominated by the droplet-borne fraction.

The long-term release of iodine from sumps at pH 6 - 6.5 is also negligibly small: a theoretical treatment based on measured partition coefficients yielded a release < 0.1 \(\%\) within 10 hours.

1. INTRODUCTION

In the event of ruptured high-pressure tubes containing primary coolant both non-volatile and volatile fission products are released during the flashing process. The evaluation of the radiological consequences requires a conclusive knowledge of fission product behaviour under these specific conditions.

One example for radionuclide release associated with coolant flashing is the rupture of a pressure sensing line in German Power Plants (design base accident [1]). Of major importance in this case is how radionuclides such as non-volatile I\(^{-}\), Cs\(^{+}\) and volatile I\(_{2}\) dissolved in the coolant distribute in the water and steam phases and to which extent they are released from the measuring transducer compartment in the annulus. The main
aim of the experiments thus is to compare measured release ratios with the calculatory basis outlined in the guidelines of the Federal Ministry of the Interior [1].

Two types of release paths have to be considered:
- droplet-borne release of non-volatile fission products such as Cs⁺ and I⁻ (relevant in short-term period 0-30 min, i.e. until high-pressure line has been shut off [1])
- release of volatile fission products, especially I131 (relevant both in short-term period of 0-30 min and in long-term period of up to several hours where revolatilization from sumps takes place)

Thus experiments in an approx. 1:1 scale test facility [2] were designed to yield information on
- the short-term release of non-volatile fission products where, in addition, the effect of jet orientation and impingement was studied (Li⁺-tracer)
- the short-term release of volatile (I₂) and non-volatile (I⁻) iodine with I123-tracer
- the long-term behaviour of iodine (release from sumps).

Additionally, the droplets which act as a carrier for especially non-volatile fission products are characterized by a light scattering probe during the short-term period. The resulting water mass fraction from these size and concentration data is compared with the tracer release.

These large-scale experiments complement previous tests [3,4] where only the short-term release of non-volatile fission products was measured (Cs⁺-tracer) at one discharge geometry.

2. EXPERIMENTAL

The loss of primary coolant from a ruptured pressure-sensing line as well as the release of radionuclides from the measuring transducer compartment is simulated by the experimental set-up in Fig. 1. The cross-sectional area of the ruptured line, the volume of the measuring transducer compartment and the cross-sectional area of the exhaust air duct are simulated on an approximately 1:1 scale. The main components are the high-pressure vessel, the blow-down line, the low-pressure vessel, the exhaust pipe and the spray condenser.

The high-pressure vessel (8.7 m³, 310 °C, 100 bar) simulates the primary coolant system. Up to 4000 kg saturated water can be discharged in one test run resulting in test durations of up to 60 min. The blow-down line (ID 15 mm) simulates the ruptured pressure-sensing line leading into the measuring transducer compartment. The discharge geometry is tubular (ID 15 mm), i.e. no additional nozzle is used. The discharge area and the area of the flow delimiter (contraction ID 5 mm) are 1:1-related to actual pressurized water reactor (PWR) geometries.

The liquid phase resulting from depressurization of the saturated water is collected in a sump tank. The steam phase, with droplet fractions due to coolant flashing, exits the low-pressure vessel via an outlet at the top. Its area of 0.14 m² is equal to vent areas in the measuring transducer compartment. The exhaust pipe consists of 6 m long vertical and 5.8 m long horizontal parts. The steam phase is then condensed and collected in a tank.

Parameters such as temperature, pressure, mass, steam velocity at several positions are recorded on-line in order to monitor the thermodynamic conditions during the test. Li⁺-tracer is dissolved in the high-pressure vessel (approx. 150 ppm Li⁺ as LiNO₃). Iodine solution (I⁻ or 10 × I₂/90 × I⁻) is injected upstream of the flow delimiter (ID 5 mm) into
the blow-down line. 1.7 l of iodine solutions at $8 \times 10^{-4}$ g I/l, with radiiodine tracer (NaI/Il23, Amersham), is used leading to a final iodine concentration of $4 \times 10^{-7}$ g I/l in the blow-down line.

No I$^-$ is retained at the walls of the feed solution unit. In 10 I I$_2$/90 I$^-$-solutions, kept at pH 3 with HCl to avoid I$_2$-hydrolysis, retention of the I$_2$-fraction at walls is less than 10-20 % of all I$_2$. The pH in the blow-down line is maintained at pH 6 - 6.3 by injecting a NaH$_2$PO$_4$/Na$_2$HPO$_4$-buffer upstream of the iodine injection.

A light-scattering probe was used for the measurement of the droplet size distribution and the water mass fraction in the exhaust pipe.

Liquid and steam samples for tracer analysis are collected at locations indicated in Fig. 1. Additional isokinetic sampling (Kurz, Model 1275, USA) of a partial flow for tracer analysis in the exhaust pipe is done in tests with Li$^+$-tracer. In tests with iodine steam samples are passed through discriminating filter units which contain DSM 11 and AC 6120 (Sudchemie, Munich, FRG) for I$_2$ and organic iodide analysis, respectively.

Tracer analysis is done either by AAS for Li$^+$ (detection limit 0.1 ppb, tracer concentration range 10 ppb - 300 ppm) or by γ-spectrometry for Il23 using NaI(Tl)- or Ge/Li-detectors.

The discharge geometries in the short-term tests with Li$^+$-tracer are as follows (Fig. 2):
- free horizontal discharge
- free vertical discharge (jet directed upwards)
- horizontal discharge against a rectangular impingement plate (500x500 mm), distance plate-outlet = 2 x ID or 10 x ID (ID = 15 mm).
In all short-term tests with iodine the impingement plate at a distance of 10 x ID was used.

3. RESULTS

3.1 Evaluation of Results

In all tests an initial transient phase of 0-10 min, during which heating-up of the low-pressure vessel and the exhaust pipe takes place, is followed by a quasi-stationary phase. The tracer release per time is significantly lower in the transient phase than in the quasi-stationary phase > 10 min. This is caused by partial condensation of steam at walls which diminishes the velocity of carrier medium for droplets. For reasons of conservatism only tracer releases during the stationary phase are presented in this paper.

The release $\varnothing$ is defined as the quotient of the tracer released ($M_{Tr(A)}$), for example from the low pressure vessel, and the tracer input ($M_{Tr(E)}$) in the blow-down line during the same time span:

$$\varnothing = \frac{M_{Tr(A)}}{M_{Tr(E)}} = \frac{\text{mass of tracer released}}{\text{mass of tracer input}}$$  \hspace{1cm} (1)

In the German calculatory basis [1] a different release definition is used. Here the release, $f$, resembles formally a partition coefficient and is defined as the quotient of the tracer concentration in the flowing two-phase mixture and the tracer concentration in the sump, both of which are mass-related:

$$f = \frac{C_{Tr(A)}}{C_{Tr(S)}} = \frac{\text{tracer concentration in exhaust pipe}}{\text{tracer concentration in sump}}$$  \hspace{1cm} (2)
The releases $\varnothing$ and $f$, as defined by (1) and (2), are related by

$$f = \varnothing \cdot \frac{1 - x}{x}$$  \hspace{1cm} (3)

$x$: steam quality.

It follows from equation (3) that the release $f$, contrary to the release $\varnothing$, depends on the steam quality $x$ and thus on pressure and temperature. When release results of different authors are compared $\varnothing$ has to be used.

3.2 Results of Short-Term Tests

The results are presented in the order given by the test matrix in Table 1. The thermodynamic and thermohydraulic conditions during all tests are summarized in Table 2. All tests were carried out under very similar conditions.

The release results of tests with Li$^+$-tracer are shown in Fig. 3. The release $\varnothing$ is practically the same for free horizontal and free vertical discharge geometries. The total release (in condenser tank and in wall condensate) is $0.20-0.22$ %. Introducing an impingement plate at a distance of $2 \times$ ID = 30 mm raises the total release to 0.59 %. No significant difference is observed when the distance is changed to $10 \times$ ID = 150 mm during the test.

Parallel to monitoring the tracer releases the droplets were characterized by means of a light scattering probe. From these measurements it can be clearly inferred that the higher release in the case of an impingement plate stems from an increase of, especially, fine droplets (Fig. 4). The droplet mass flow in the exhaust pipe, $m_A$, can be calculated from the droplet size distribution. Relating $m_A$ to the mass flow in the blow-down line, $m_E$, yields the droplet release $\varnothing_{Dr}$:

$$\varnothing_{Dr} = \frac{m_A}{m_E}$$  \hspace{1cm} (4)

On average the tracer concentration in the droplets should be higher by a factor of $1/1-x$ which takes into account the evaporation during flashing. Therefore, a so-called "theoretical" release $\varnothing_{Li^+,theor.}$ of droplet-borne tracer can be determined from droplet measurements:

$$\varnothing_{Li^+,theor.} = \varnothing_{Dr} \cdot \frac{1}{1 - x}$$  \hspace{1cm} (5)

The "theoretical" Li$^+$-tracer releases $\varnothing_{Li^+,theor.}$ are contrastingly shown together with the experimentally determined tracer releases $\varnothing_{Li^+,exp.}$ in Table 3.

Both values change with the discharge geometry in the same way. However, the experimentally determined tracer releases, $\varnothing_{Li^+,exp.}$ (here: in condenser tank), are lower by a factor of 3 than the tracer releases to be expected from droplet measurements alone, i.e. according to equation (5). This implies that the tracer concentration in the droplets is on average lower than the tracer concentration postulated in equation (5) ($< 1/1-x$). The reason for this discrepancy is that the droplets contain - as can be expected - steam condensate which is tracer-free.

The release results of the tests with iodine, where an impingement plate at a distance of $10 \times$ ID was employed in all cases, are summarized in Fig. 5. Test Iod-II is a purely iodide test ($100 \%$ I$^-\$). In tests Iod-III and Iod-IV also volatile elementary iodine ($10 \%$ I$_2$/$90 \%$ I$^-\$) was dosed into the blow-down line. However, all tests yielded comparable release results
of $\varnothing = 0.51 - 0.63 \%$ (sum of release in condenser tank and in wall condensate). Thus the iodine release is not significantly different to the purely droplet-borne Li\textsuperscript{+}-release of $\varnothing = 0.59 \%$ which was obtained in test Li-III using an impingement plate (cf. Fig. 5). In accordance with this finding the organic iodide measured in the exhaust pipe ($\varnothing \leq 0.02 \%$) was very low, too.

3.3 Long-Term Release From Sumps

Contrary to the droplet-borne release which plays a role only during the short-term period (0-30 min) when using iodine the long-term period has to be taken into consideration, too. Here "long-term period" denotes the time-span 30 min - 10 h after shutting off the broken pressure-sensing line. By way of I\textsubscript{2} revolatilization iodine, which is predominantly contained in the liquid phase, can be liberated from sumps which may have formed especially in the measuring transducer compartment. This subsequent release from the sump into the gas phase is mainly effected by the normal ventilation of the room which leads to an air-flow passing continuously over the sump surface. Chemically, the reversion of the I\textsubscript{2} hydrolysis reaction (the so-called Dushman-reaction) in the sump constitutes a source for volatile I\textsubscript{2}. It has to be emphasized, however, that the long-term iodine release from sumps can only lead to an iodine release via the exhaust air of a power station if it is conservatively assumed that the exhaust air from the annulus is not filtered (in reality the filtration starts within 10 min after the beginning of this design base accident [1]).

The long-term release (30 min-10 h) can suitably be inferred from a theoretical treatment which can be found in the literature [5, 6, 7] and will be dispensed with here. The main characteristic of this theoretical treatment is a boundary layer at the interface sump-gas phase which is saturated with iodine according to the partition coefficient R. This means that the establishment of the I\textsubscript{2} equilibrium in the gas phase moving parallel to the phase boundary applies only for a boundary layer limited by the flow and not for the whole moving gas phase. Contrary to the assumption of an instantaneous establishment of equilibrium for the whole gas phase the iodine release from the sump is reduced.

The main parameter for iodine revolatilization is the I\textsubscript{2} partition coefficient R. R was experimentally determined in test Iod-IV, i.e. under realistic large-scale conditions where the sump was dammed up in the low-pressure vessel during and up to 10 hours after the blow-down phase. From the iodine analysis of the gas phase in the low-pressure vessel and in the sump an I\textsubscript{2} partition coefficient $R = 1.5 - 3.4 \times 10^5$ at 61 - 84 °C is induced. For the calculation of the long-term release (30 min-10 h) a conservative $R = 1 \times 10^5$ and conservative boundary conditions pertinent to German FWR [1] are used. The total release $\varnothing$ from sumps is calculated to be at the most 0.06 % of the total iodine discharged.

4. DISCUSSION

4.1 Results of Short-Term Tests

With the present large-scale tests the standard deviation for both the Li\textsuperscript{+} and the iodine release was $\pm 15 \%$. Thus the relative error $\Delta \varnothing/\varnothing$ could be lowered by a factor of about 3 compared to the previous tests [3,4].

The former droplet-borne release $\varnothing = 0.13 - 0.22 \%$, which was measured only with a free horizontal discharge geometry, agrees well with the present release $\varnothing = 0.14 - 0.16 \%$ obtained with the same geometry (release
in condenser tank is compared).

The essential information gained from the new tests as regards droplet-borne release is a marked influence of discharge geometry. Changing the discharge geometry from 'free horizontal' to 'free vertical' does not significantly alter the release whereas introducing an impingement plate - which simulates a wall onto which the discharged jet may impact in reality - markedly increases the release by a factor of 3. One can assume that the maximum impingement effect was covered at the chosen distances of 2 x ID to 10 x ID [8,9]. The increase in the tracer release \( \Omega \) is qualitatively related to an increase in, especially fine, droplets. However, the release \( \Omega \) cannot be quantitatively calculated from the droplet mass flux alone. Without the tracer measurements, i.e. based solely on the droplet release \( \Omega_{\text{Dr}} \), the droplet-borne radionuclide release \( \Omega \) would be overestimated. The droplet measurements are, however, indispensable for a more profound understanding of the measured tracer release as well as retention in exhaust pipes etc.

The release of non-volatile iodide (I\(^-\)) corresponds very well to the purely droplet-borne release of Li\(^+\)-tracer. This proves that no iodide is oxidized to volatile iodine species by initially present oxygen. The main result of the iodine tests is, however, that the addition of volatile elemental iodine (I\(_2\)) leads to the same release within the experimental error as with only non-volatile iodide. Besides, the contribution of volatile organic iodide (0.01 - 0.02 I) to the release can be neglected.

From the experimental results it has to be assumed that elemental iodine (I\(_2\)) is hydrolysed in the blow-down line in spite of the very short residence time of approx. 7 ms. In principle, the hydrolysis of I\(_2\) to produce I\(^-\) and HOI can be kinetically described. Formal computation of the hydrolysis reaction at high temperatures (200-300 °C), for example with the iodine code IMPAIR2 [10], leads to believe that no more I\(_2\) is present at the flashing.

It has to be pointed out, however, that in this case kinetic calculations are based on rate constants which have to be extrapolated to very high temperatures. Thus a large error and, in addition, a change in reaction mechanism cannot be ruled out. Even a volatility of HOI would have to be considered under the high-temperature conditions. All these reasons emphasize the importance of experimental investigations.

No iodine tests comparable to the present ones have been carried out elsewhere so far. However, the release results with droplet-borne tracer (Li\(^+\)) can be compared with results of the Canadian Water Aerosol Leakage Experiments (WALE) [8]. In the WALE-tests the droplet-borne tracer release (Cs\(^+\)-tracer), also due to a flashing process, was studied with a similar experimental set-up. Considering the differences of the experimental conditions the results from both projects show a good agreement. The higher tracer release of the WALE-tests (up to a factor of 1.5-2) may be due both to the use of a nozzle and to the lack of a contraction in the blow-down line (no pre-flashing). Accordingly, WALE-experiments without a nozzle, that is with a tubular discharge outlet, show a reduced release.

From our point of view a discussion of the calculated long-term release results can be dispensed with as the long-term iodine release from sumps under the specific conditions in German PWR's can be neglected compared to the short-term release.

The main objective of the investigations is a comparison of the experimentally determined release results with the assumptions in the German Calculatory Basis [1]. For this aim the releases f used in [1] are calculated from the measured releases \( \Omega \) (for definitions of f and \( \Omega \) cf. chapter 3.1) and are presented for all tests in Table 4. For all tests the
measured releases are < 1 % and hence at least one order of magnitude lower than the value of 10 % assumed in the German Calculatory Basis [1].

5. CONCLUSIONS

New large-scale experiments were performed with Li\(^+\)- and radiiodine I\(_{123}\)-tracer in order to investigate the release from a compartment of non-volatile (Cs\(^+\), I\(^-\)) and volatile (I\(_2\)) radionuclides associated with coolant flashing in the case of a ruptured high-pressure tube (design base accident: rupture of pressure-sensing line).

The main results can be summarized as follows:
- The total release of radionuclides in the short-term period 0-30 min (time span for shutting off the broken line) is unequivocally governed by the droplet-borne release. The release is highest when the two-phase jet impinges near the orifice at close distance in which case 0.6 % of the total tracer is released from the compartment (\(\phi = 0.6 \%\)). The measured release agrees well with results of Canadian tests [8] considering the differences in experimental conditions.
- Fractions of volatile I\(_2\) (10 % I\(_2\) and 90 % I\(^-\)) do not significantly increase the release; even in this case the droplet-borne release is dominant.
- The iodine release in the long-term period (30 min to 10 h) as a result of I\(_2\)-revolatilisation from sumps formed in the compartment is negligibly small.
- The release of radionuclides in the case of a ruptured pressure-sensing line is overestimated by at least one order of magnitude in the German Calculatory Basis.

ACKNOWLEDGEMENTS

The authors wish to thank their colleagues H. Lochner, G.-U. Greger, W. Zech, Mrs. M. Beuerle, Mrs. D. Bauer, R. Sendelbeck, K. Grabetz, H. Schnabel and G. Röbig for their collaboration, B. Casper and H. Friederichs from the Gesellschaft für Reaktorsicherheit, GRS, for their support and availability for discussion and the Bundesministerium für Forschung und Technologie (Government Department of Research and Technology) for sponsoring this project.

REFERENCES

Bekanntmachung von Empfehlungen der Reaktor-Sicherheitskommission und der Strahlenschutzkommission vom Oktober 1983


Table 1: Test Matrix For Short-Term Release Tests

<table>
<thead>
<tr>
<th>test</th>
<th>discharge geometry(^1)</th>
<th>test</th>
<th>discharge geometry(^1)</th>
<th>iodine species</th>
<th>remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li-Ia (commissioning)</td>
<td>←→</td>
<td>Iod-I</td>
<td>←→</td>
<td>100 % I(^-)</td>
<td>no conclusive release results</td>
</tr>
<tr>
<td>Li-Ib</td>
<td>←→</td>
<td>Iod-II</td>
<td>←→</td>
<td>100 % I(^-)</td>
<td></td>
</tr>
<tr>
<td>Li-II</td>
<td>←↑</td>
<td>Iod-III</td>
<td>←→</td>
<td>10 % I(_2)</td>
<td></td>
</tr>
<tr>
<td>Li-III</td>
<td>←↑</td>
<td>Iod-IV</td>
<td>←→</td>
<td>10 % I(_2)</td>
<td>sump water stored in low-pressure vessel</td>
</tr>
</tbody>
</table>

\(^1\): free horizontal discharge  
↑: free vertical discharge  
|: horizontal discharge against an impingement plate
Table 2: Thermohydraulic Conditions During Stationary Phase Of All Tests

<table>
<thead>
<tr>
<th>location</th>
<th>data</th>
<th>unit</th>
<th>Li-Ia</th>
<th>Li-Ib</th>
<th>Li-II</th>
<th>Li-III</th>
<th>Iod-I</th>
<th>Iod-II</th>
<th>Iod-III</th>
<th>Iod-IV</th>
</tr>
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<tbody>
<tr>
<td>high-pressure vessel</td>
<td>pressure</td>
<td>bar</td>
<td>92</td>
<td>93</td>
<td>94</td>
<td>94</td>
<td>97</td>
<td>97</td>
<td>97</td>
<td>97</td>
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<tr>
<td></td>
<td>°C</td>
<td>305</td>
<td>305</td>
<td>305</td>
<td>306</td>
<td>307</td>
<td>308</td>
<td>307</td>
<td>307</td>
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<tr>
<td></td>
<td>concentration (initial value)</td>
<td>ppm</td>
<td>137</td>
<td>176</td>
<td>139</td>
<td>146</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>mass flow</td>
<td>kg/min</td>
<td>67.3</td>
<td>65.3</td>
<td>65.0</td>
<td>66.0</td>
<td>69.0</td>
<td>70.2</td>
<td>70.8</td>
<td>70.3</td>
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<td>blow-down line (ID 15 mm)</td>
<td>pressure</td>
<td>bar</td>
<td>13</td>
<td>13</td>
<td>26</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>26</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td>195</td>
<td>195</td>
<td>226</td>
<td>224</td>
<td>223</td>
<td>222</td>
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<tr>
<td>low-pressure vessel</td>
<td>temperature</td>
<td>°C</td>
<td>100</td>
<td>99</td>
<td>99</td>
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<td>97</td>
<td>100</td>
<td>99</td>
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<tr>
<td></td>
<td>pressure, relative</td>
<td>mbar</td>
<td>17</td>
<td>24</td>
<td>18</td>
<td>17</td>
<td>18</td>
<td>35</td>
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<td>0.426</td>
<td>0.428</td>
<td>0.428</td>
<td>0.428</td>
<td>0.428</td>
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<tr>
<td>exhaust pipe (ID 414 mm)</td>
<td>temperature</td>
<td>°C</td>
<td>98</td>
<td>98</td>
<td>99</td>
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<tr>
<td></td>
<td>pressure, relative</td>
<td>mbar</td>
<td>17</td>
<td>20</td>
<td>18</td>
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<td>18</td>
<td>34</td>
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<td>10</td>
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<tr>
<td></td>
<td>velocity</td>
<td>m/s</td>
<td>5.6</td>
<td>5.8</td>
<td>5.9</td>
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<td>5.5</td>
<td>5.6</td>
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<td>wall condensate</td>
<td>mass flow, vertical part</td>
<td>g/min</td>
<td>100</td>
<td>90</td>
<td>120</td>
<td>130</td>
<td>150</td>
<td>148</td>
<td>162</td>
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<tr>
<td></td>
<td>concentration, vertical part</td>
<td>ppm</td>
<td>71</td>
<td>98</td>
<td>176</td>
<td>176</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>mass flow, horizontal part</td>
<td>g/min</td>
<td>17</td>
<td>7</td>
<td>8</td>
<td>13</td>
<td>15</td>
<td>15</td>
<td>18</td>
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<tr>
<td></td>
<td>concentration, horizontal part</td>
<td>ppm</td>
<td>2</td>
<td>15</td>
<td>5</td>
<td>58</td>
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<td>-</td>
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<td>condenser</td>
<td>mass flow</td>
<td>kg/min</td>
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<td>29.8</td>
<td>34.6</td>
<td>28.5</td>
<td>22.0</td>
<td>24.7</td>
<td>21.7</td>
<td>18.5</td>
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<tr>
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<td>mass flow</td>
<td>kg/min</td>
<td>38.6</td>
<td>39.0</td>
<td>39.2</td>
<td>39.4</td>
<td>45.1</td>
<td>45.6</td>
<td>45.8</td>
<td>-</td>
</tr>
<tr>
<td>test</td>
<td>Li-Ib</td>
<td>Li-II</td>
<td>Li-III</td>
<td></td>
<td></td>
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<tr>
<td>discharge geometry (schematically)</td>
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</tr>
<tr>
<td>steam quality (x) (after expansion)</td>
<td>0.423</td>
<td>0.423</td>
<td>0.426</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>water mass fraction (y) (of vent gas) ([%])</td>
<td>0.6</td>
<td>0.4</td>
<td>1.6</td>
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<td></td>
<td></td>
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<tr>
<td>droplet mass flow in exhaust pipe ([g/s])</td>
<td>2.6</td>
<td>1.8</td>
<td>7.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>mass flow in blow-down line ([kg/s])</td>
<td>1.09</td>
<td>1.08</td>
<td>1.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>droplet release ([%])</td>
<td>0.24</td>
<td>0.17</td>
<td>0.67</td>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>&quot;theoretical&quot; Li-release (\phi_{Li, theor.}) (cf. equation 5) ([%])</td>
<td>0.41</td>
<td>0.29</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>measured Li(^+)-release (\phi_{Li^+, exp.}) in condenser tank ([%])</td>
<td>0.16</td>
<td>0.12</td>
<td>0.41</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>test</td>
<td>Li-Ia</td>
<td>Li-Ib</td>
<td>Li-II</td>
<td>Li-III</td>
<td>Iod-II</td>
<td>Iod-III</td>
<td>Iod-IV</td>
<td></td>
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<td>-------------------------------------------</td>
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<td></td>
</tr>
<tr>
<td>$\phi_{\text{condenser tank}}$ [^2]</td>
<td>0.14</td>
<td>0.16</td>
<td>0.12</td>
<td>0.41</td>
<td>0.37</td>
<td>0.45</td>
<td>0.38</td>
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<tr>
<td>$\phi_{\text{vertical wall condensate}}$[^2]</td>
<td>0.061</td>
<td>0.066</td>
<td>0.095</td>
<td>0.177</td>
<td>0.14</td>
<td>0.17</td>
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<td>$\phi_{\text{horizontal wall condensate}}$[^2]</td>
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<td>0.001</td>
<td>0.001</td>
<td>0.006</td>
<td>0.002</td>
<td>0.005</td>
<td>0.002</td>
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<td>$\phi_{\text{total}}$ [^2]</td>
<td>0.20</td>
<td>0.23</td>
<td>0.22</td>
<td>0.59</td>
<td>0.51</td>
<td>0.63</td>
<td>0.54</td>
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<tr>
<td>steam quality $x$</td>
<td>0.423</td>
<td>0.423</td>
<td>0.423</td>
<td>0.426</td>
<td>0.428</td>
<td>0.428</td>
<td>0.428</td>
<td></td>
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<tr>
<td>water to steam ratio (1 - $x$)/$x$</td>
<td>1.36</td>
<td>1.36</td>
<td>1.36</td>
<td>1.35</td>
<td>1.34</td>
<td>1.34</td>
<td>1.34</td>
<td></td>
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<tr>
<td>$f$ (cf. equations 2 and 3) [^2]</td>
<td>0.28</td>
<td>0.31</td>
<td>0.30</td>
<td>0.80</td>
<td>0.68</td>
<td>0.84</td>
<td>0.72</td>
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</tbody>
</table>

$\phi$: tracer release, cf. equation (1)
f: release as defined in Calculatory Basis [1], cf. equations (2) and (3)
free horizontal discharge:
tests Li-1a, Li-1b

free vertical discharge:
test Li-II

horizontal discharge against
an impingement plate:
test Li-III: 2 x ID = 30 and 10 x ID = 150
tests Iod-I, Iod-II, Iod-III, Iod-IV: 10 x ID

Fig. 2: Arrangements of Different Discharge Geometries
(all units are in mm)
Fig. 3: Droplet-Borne Tracer Release During Stationary Phase at Different Discharge Geometries (Li⁺-Tracer)
Fig. 4: Mass-Related Droplet Size Distribution During Stationary Phase

a) Test Li-Ib: free horizontal discharge (→)

b) Test Li-III: horizontal discharge against an impingement plate at the distance of 2 x ID = 30 mm (→ |)
Fig. 5: Tracer Release During Stationary Phase For Li⁺- And Iodine-Tests
(each test with impingement plate)
DISCUSSION

Soffer

1) What is the applicability of these results to a steam generator tube rupture accident in a PWR?
2) Low iodine volatility at a sump pH of 6 to 6.5 seems at odds with other discussions at this meeting. What is your comment?

Morell

1) In our opinion, these results can be applied to SG tube rupture in a PWR. As an additional retention mechanism, you have the droplet separator and the steam dryer in the dome of a SG.
2) You are talking about a different situation: the higher iodine volatility at lower pH is true in the presence of high radiation fields. In the case of coolant flashing, the radiation level is much lower, some orders of magnitude. So there is no discrepancy between these results.

Evans (comment)

I believe there was no radiation in your tests. The comments regarding the importance of pH were made in the context of behaviour in the presence of a radiation field.
4.4 THE OXIDATION OF CESIUM IODIDE AEROSOLS DURING HYDROGEN COMBUSTION

W.C.H. Kupferschmidt, J.B. Buttazoni, G.J. Evans, D.R. Harris, D.R. Greig, G.W. Koroll and G.G. Sanipelli

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AECL Research
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CANADA ROE 1LO

ABSTRACT

The effects of hydrogen deflagrations on suspended CsI aerosols have been studied in a series of tests in the Containment Test Facility. In a 10 vol% steam environment, CsI oxidation was not observed, even in near-stoichiometric hydrogen-air-steam mixtures. In dry mixtures, significant yields of gas phase I₂ (15%) were observed at high hydrogen concentrations. High iodine:cesium ratios in collected aerosol samples and increased organic iodide yields provided additional evidence of CsI oxidation. These results are discussed in terms of the possible role that steam may have on the chemistry of CsI aerosols during hydrogen combustion.

1. INTRODUCTION

In the event of an accident in a water-cooled reactor, release of iodine to the containment building is expected to be primarily in the form of CsI-containing aerosols. Iodine transport within containment in the early stages of an accident, therefore, will be determined by aerosol agglomeration and settling. However, in the event of hydrogen combustion in the containment, conversion of involatile CsI to volatile forms of iodine, including I₂ and organic iodides, may result. Recently, bench-scale studies undertaken at Oak Ridge National Laboratory as part of the Advanced Containment Experiments (ACE) iodine project have shown that I₂ is produced in significant quantities in stationary hydrogen flames [1]. Large-scale tests conducted at Sandia National Laboratories have also demonstrated that up to 75% conversion of CsI to I₂ can occur during combustion of dry hydrogen-air mixtures [2]. These results thus suggest that hydrogen combustion can have a significant impact on the iodine source term.

Under accident conditions, however, the containment atmosphere will contain steam, which may influence the chemistry of CsI-containing aerosols in hydrogen deflagrations. Therefore, to verify independently the earlier studies [1,2] and to assess what effect, if any, steam would have on the oxidation of CsI aerosols, a series of intermediate-scale experiments were undertaken in the Containment Test Facility (CTF). This paper summarizes the results of that investigation.
2. EXPERIMENTAL FACILITIES AND PROCEDURES

2.1 Containment Test Facility

The combustion experiments were conducted in the 2.3-m-diameter (6.6 m³) CTF sphere, a 10 MPa instrumented vessel, insulated and trace-heated with steam for operation up to 135°C [3]. A schematic of this facility, as outfitted for these experiments, is shown in Figure 1. The combustion gases were added to the initially evacuated vessel by the method of partial pressure additions and were then mixed by two air-driven fans mounted on the horizontal mid-plane, diametrically opposite each other. Ignition was produced by a high-energy spark at the centre of the sphere. Pressure histories were recorded by four piezoelectric transducers and a capacitance pressure transmitter. A fast digital data acquisition system resolved pressure transients to ±1 μs. The interior of the carbon steel vessel was painted prior to the tests with a self-priming epoxy paint (Keeler and Long No. 4500, Watertown, CT). This is the same coating as was used in the ACE-sponsored tests conducted in the Containment Systems Test Facility [4] and Radioliodine Test Facility [5].

2.2 CsI Aerosol Dispersion

Anhydrous CsI powder (99.999% purity, APL Engineered Materials, Urbana, IL) was received in flame-sealed ampoules. Microscopic analysis by the supplier indicated that the CsI had a mean diameter of 7 μm, with the bulk of the powder in the 4- to 10-μm particle size range. All operations with this hygroscopic powder were performed in a dry box. Ampoules were opened and the CsI powder weighed and then transferred to a stainless steel moisture-proof device. This apparatus is shown in Figure 2. Once sealed with mylar membranes to protect the CsI from atmospheric moisture, the apparatus was removed from the dry box and connected to the CTF and a high-pressure (~150 psi) air supply. To inject the CsI, the apparatus was pressurized, rupturing the mylar membranes and dispersing the contents of the apparatus into the CTF vessel. The pressure and duration of the air charge required to break the membrane and completely empty the dispersion apparatus were determined in separate tests. Dispersion of the CsI aerosol was enhanced by a series of fins at the exit of the delivery pipe. These fins served to deflect the flow radially, thereby dispersing the jet. The delivery of the aerosol to the CTF sphere was timed to precede the spark ignition by 4 s. This interval was established during a commissioning test in which dispersion in the CTF vessel was videotaped with a high-speed video camera. The 4 s delay was sufficient to achieve optimum aerosol dispersion while allowing turbulence produced by the aerosol injection to dissipate prior to initiating combustion.

2.3 Analytical Methodology

2.3.1 On-line Sampling

Several aerosol and gas phase sampling loops were installed on the CTF, as shown in Figure 1. One loop (A) consisted of a teflon aerosol filter and four modified Maypacks filters, each containing, in order, a teflon filter, two silver membranes, a second teflon filter, charcoal filter paper, a third teflon filter and 10 g of granulated charcoal. The
teflon filters (0.2 and 2-5 μm porosity, Cole-Parmer, Chicago, IL) were used to remove aerosols and isolate other adsorbents, while the silver membranes (5-μm porosity, Osmonics Inc., Minnetonka, MN), charcoal filter paper (Schleicher and Schuell Inc., Keene, NH) and granulated charcoal (Charcoal Engineering Corp., Bellingham, MA) were used to separate elemental iodine, high-molecular-weight organic iodides (i.e., iodobutane) and low-molecular-weight organic iodides (i.e., iodomethane), respectively. The Maypack filters were placed in parallel and used individually to sample the gas phase at various times. The aerosol and Maypack filters were housed in an oven heated to 105°C to minimize condensation of water vapor; the 1/4-in. stainless steel sampling line also was heated to 100°C. A vacuum pump was used to withdraw samples from the CTF at a flow rate of about 2.5 dm³.min⁻¹.

The initial tests also utilized a second loop (B) in which gas samples were passed through bubbler. The nature of the scrubbing solutions in these bubbler varied from sample to sample: sodium thiosulfate solutions (0.1 mol.dm⁻³) were used to estimate the total gas phase iodine concentration and isooctane/water mixtures were used to trap gas phase elemental iodine. When desired, the in-line aerosol filter could be bypassed to provide an estimate of the total aerosol and gas phase iodine concentration. However, large line losses of aerosol occurred because of the small diameter of the sampling line (1/4-in. diameter). As a result, later tests used a different sampling loop (C) with wider diameter tubing (1-in. diameter). Higher flow rates were also possible (2.5 dm³.min⁻¹ vs 0.5 dm³.min⁻¹). Sampling times varied from sample to sample (2 min to 30 min), depending on the concentration of gas phase I₂.

2.3.2 Chemical Analysis

After each test, the Maypacks were disassembled and the various components analyzed. Teflon filters from the Maypacks and aerosol filter assembly were routinely rinsed with water and analyzed for total iodine by inductively coupled plasma spectroscopy (ICPS) and for cesium by atomic absorption spectrophotometry (AAS). The silver membranes were first rinsed with water to remove any CsI that may have bypassed the aerosol filters and were then equilibrated with 0.1 mol.dm⁻³ sodium thiosulfate in an ultrasonic bath. The resulting solutions were analyzed by ICPS and AAS for iodine and cesium, respectively. The charcoal filter papers and granulated charcoal were analyzed for iodine by neutron activation analysis. The detection limit for iodine on the charcoal filter paper was 1 μg per filter, whereas the sensitivity for iodine on the granulated charcoal was 5 μg per gram of charcoal. Gas phase samples were periodically analyzed for organic iodides using a gas chromatograph equipped with both electron capture and photoionization detectors.

2.4 ACE/CTF Test Conditions

The ACE/CTF experimental program is outlined in Table 2.1. In summary, four different test conditions were investigated in which hydrogen concentration (10 to 29 vol%) and steam concentration (0 to 10 vol%) were varied. Test 4 was undertaken to verify the results of Test 2.

In Tests 1 through 4, no effort was made to preheat the CsI aerosol prior to its injection into the CTF. For Test 5, the dispersion apparatus containing the CsI was heated to approximately 100°C prior to injection.
For each test, sampling was initiated within 2 min of the start of the test and, in general, was continued for approximately 4 h. After each test, the vessel was thoroughly washed to remove to remove residual iodine and minimize iodine and cesium carry-over between tests.

Table 2.1

ACE/CTF Test Conditions

<table>
<thead>
<tr>
<th>Test #</th>
<th>Gas Composition (vol%)</th>
<th>Dispersed CsI* Concentration (mol dm⁻³ x 10⁵)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 H₂, 80 Air, 10 Steam</td>
<td>4.1</td>
</tr>
<tr>
<td>2,4</td>
<td>29 H₂, 71 Air, 0 Steam</td>
<td>4.2</td>
</tr>
<tr>
<td>3</td>
<td>29 H₂, 61 Air, 10 Steam</td>
<td>4.3</td>
</tr>
<tr>
<td>5</td>
<td>25 H₂, 65 Air, 10 Steam</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Tests conducted at 101 kPa and 95 ± 2°C  
Assumes complete and homogeneous CsI dispersal

3. RESULTS

The combustion parameters for each of the ACE/CTF tests are listed in Table 3.1. The higher peak pressures and shorter time-to-peak pressures observed with 29% hydrogen, as compared with 10% hydrogen, are indicative of higher burnt gas temperatures and higher burning rates. The presence of 10% steam had minimal effect on the pressure histories.

Table 3.1

Summary of Combustion Parameters for ACE/CTF Tests

<table>
<thead>
<tr>
<th>Test #</th>
<th>Gas Composition (vol%)</th>
<th>Peak Pressure (kPa)</th>
<th>Time-to-Peak Pressure (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10 H₂, 80 Air, 10 Steam</td>
<td>290</td>
<td>1.37</td>
</tr>
<tr>
<td>2,4</td>
<td>29 H₂, 71 Air, 0 Steam</td>
<td>620</td>
<td>0.06</td>
</tr>
<tr>
<td>3</td>
<td>29 H₂, 61 Air, 10 Steam</td>
<td>590</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>25 H₂, 65 Air, 10 Steam</td>
<td>600</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Combustion parameters not determined for ACE/CTF Test 2

Chemical analysis results for each test are summarized separately below.

3.1 10% H₂-Air-10% Steam (Test 1)

Throughout the test, no iodine was detected by the gas scrubber system. Based on the volume of gas sampled, the quantity of CsI injected and the assumption that the sample was representative of the CTF gas phase,
this represents less than 0.4% conversion of CsI to I$_2$. Analysis of
Maypack silver filters revealed gas phase I$_2$ concentrations of less
than 2 x 10$^{-8}$ mol.dm$^{-3}$, which corresponds to less than 0.05% oxidation of the
CsI aerosol. The order of magnitude difference in sensitivity between the
two methods is due to the larger volumes of gas sampled by the Maypacks.
Elemental analysis of aerosol samples for iodine and cesium revealed that
the iodine:cesium mole ratio was 1.0 ± 0.1 throughout the test.

Iodine was not detected on any of the Maypack granulated charcoal
samples, which corresponds to less than 0.08% conversion of CsI to low-
molecular-weight organic iodides, based on the volume of gas sampled.
Similarly, analysis of the Maypack charcoal filter papers indicated less
than 0.0025% conversion to high-molecular-weight organic iodides. In
support of these results, only trace quantities of volatile organic iodides
(e.g., 4 x 10$^{-11}$ mol.dm$^{-3}$ CB$_3$I (10$^{-4}$%)) were detected by gas
chromatography.

3.2 29% H$_2$-Air-OZ Steam (Tests 2 and 4)

As noted in Table 3.1, pressure histories were not determined for
Test 2 because of a malfunction in the data acquisition system. Complete
combustion was confirmed, however, from the observed final pressure. The
energetic nature of this test was also established by examination of
collected aerosol samples, which contained resuspended iron corrosion
products from unpainted portions of the vessel, and from post-test
inspection of the interior of the CTF vessel. Large portions of the
painted interior had been scorched or burned, exposing at numerous
locations the carbon steel vessel. Undamaged portions of the painted
vessel surfaces changed colour from tan to orange.

The collected aerosols were analyzed for total iodine and cesium. For
the initial 1.2 h of the test, iodine-rich aerosols were obtained, with
iodine:cesium mole ratios in the range of 1.5 to 1.9. Later samples (2.5 h
and 3.6 h) were found to be cesium-rich.

Shown in Table 3.2 are the time-dependent concentrations of gas phase
I$_2$, as determined by both the gas scrubber and Maypack sampler systems.
The Maypack samplers indicated that the maximum airborne I$_2$ concentration
occurred immediately after combustion (8.6 x 10$^{-7}$ mol.dm$^{-3}$) and decreased
with time. Results from the first two scrubber samples are in reasonable
agreement with the first Maypack, but at longer times, there is poor
agreement. Indeed, while the Maypacks revealed decreasing gas phase I$_2$
concentrations, results from the gas scrubber sampling system in general
indicated increasing CsI oxidation to I$_2$.

Analysis of the Maypack charcoal filter papers revealed a continuously
increasing gas phase high-molecular-weight organic iodide concentration,
from 3.1 x 10$^{-8}$ mol.dm$^{-3}$ at 0.01 h to approximately 2 x 10$^{-7}$ mol.dm$^{-3}$ at
3.6 h. This represents conversion of approximately 0.07 to 0.5% of the
initially added CsI. On the other hand, based on the analysis of Maypack
granulated charcoal samples, the quantity of gas phase low-molecular-weight
organic iodides was relatively constant (3 x 10$^{-8}$ mol.dm$^{-3}$, or 0.06%
conversion) over the same time interval.

Test 4 was undertaken to corroborate the findings of Test 2 and to
obtain pressure histories not recorded in the earlier test. Test 4 was
conducted under conditions comparable to Test 2 except in addition to the
dispersed CsI (70.2 g), the CTF vessel contained unsuspended CsI aerosol
(53.4 g initially added) that had been exposed to two previous combustion
events. As shown in Table 3.3, I$_2$ was again detected in both the Maypack and gas scrubber systems. As for Test 2, the I$_2$ recoveries measured in the scrubber system were higher than in the Maypacks. Gas phase elemental iodine concentrations were again time-dependent.

Table 3.2
Gas Phase I$_2$ Concentrations in ACE/CTF Test 2 as a Function of Time

| Time (h) | Maypack | | Scrubber | |
|----------|---------| |---------|---------|
|          | $[I_2]_q$ (mol·dm$^{-3}$ x 10$^6$) | $\% I_2(g)$ Formation | $[I_2]_q$ (mol·dm$^{-3}$ x 10$^6$) | $\% I_2(g)$ Formation |
| 0.01     | 0.86    | 4.2 | 1.5 | 7.2 |
| 0.03     | 0.38    | 1.8 | 1.0 | 4.7 |
| 0.18     |         |     | 1.6 | 7.6 |
| 0.62     |         |     | 2.3 | 11. |
| 1.17     |         |     | 2.7 | 13. |
| 2.51     |         |     |     |     |
| 3.34     |         |     |     |     |
| 3.60     | 0.20    | 1.0 | 2.0 | 9.6 |
| 3.93     | 0.18    | 0.9 |     |     |
| 4.06     |         |     |     |     |

Table 3.3
Gas Phase I$_2$ Concentrations in ACE/CTF Test 4 as a Function of Time

| Time, h | Maypack | | Scrubber | |
|---------|---------| |---------|---------|
|          | $[I_2]_q$ (mol·dm$^{-3}$ x 10$^6$) | $\% I_2(g)^*$ Formation | $[I_2]_q$ (mol·dm$^{-3}$ x 10$^6$) | $\% I_2(g)^*$ Formation |
| 0.002   | 0.003   | 0.02 | 0.53 | 2.6 |
| 0.003   |         |     | 1.8  | 4.6 |
| 0.11    | 0.36    | 1.8  | 0.95 | 4.6 |
| 0.23    | 0.60    | 2.9  | 1.5  | 7.3 |
| 0.25    | 0.77    | 3.8  | 1.6  | 7.9 |
| 0.57    |         |     | 1.8  | 8.8 |
| 0.62    |         |     | 3.1  | 15. |
| 1.00    | 1.2     | 1.2  | 2.6  | 13. |
| 1.26    | 0.8     | 0.8  | 2.5  | 12. |

* Recoveries based on 70.2 g CsI.
Aerosol samples taken over the first 0.6 h revealed high iodine:cesium mole ratios (1.33 to 1.77). Maypack sampler results indicated that high-molecular-weight organic iodide concentrations were as great as $1.3 \times 10^{-7}$ mol dm$^{-3}$ (0.3%), whereas only $6.0 \times 10^{-9}$ mol dm$^{-3}$ low-molecular-weight organic iodides (0.014%) was observed. Alternatively, gas chromatography revealed increasing methyl iodide concentrations with time, reaching a concentration of $3 \times 10^{-8}$ mol dm$^{-3}$ (0.07%) by the end of the test.

3.3 29% $H_2$-Air-10% Steam (Test 3)

The collected aerosols were found to have iodine:cesium mole ratios of $1.0 \pm 0.1$ throughout the test. Iodine was not detected on either the silver membranes or in the gas scrubbers; based on the gas volumes sampled, this corresponds to a gas phase $I_2$ concentration of less than $6.5 \times 10^{-9}$ mol dm$^{-3}$, or less than 0.03% oxidation of CsI to $I_2$. The yields of high- and low-molecular-weight organic iodides were also low (<0.04% and <0.005%, respectively).

3.4 25% $H_2$-65% Air-10% Steam (Test 5)

In this test, 57.2 g of preheated CsI (100°C) was dispersed into the CTF. Gas phase $I_2$ was not detected over the 4.3-h sampling period following combustion. Based on the sampling conditions, this represents less than $4 \times 10^{-9}$ mol dm$^{-3}$ gas phase $I_2$ (<0.02%). However, when the collected aerosols were dissolved and analyzed spectrophotometrically, traces of $I_2$ (as $I_2$ and $I_3$) were detected (0.2%).

4. DISCUSSION

The principal findings of the ACE/CTF experimental program are listed in Table 4.1. In summary, Tests 1, 3 and 5, which were undertaken in a humid environment, exhibited negligible formation of $I_2$. Tests 2 and 4, which were conducted without added steam, resulted in significant oxidation of suspended CsI aerosols to $I_2$. Further evidence of CsI oxidation in the latter tests is demonstrated by the unusually high iodine:cesium ratios in collected aerosol samples. Increased organic iodide yields were also observed in Tests 2 and 4.

A comparison of Tables 3.1 and 4.1 reveals that the extent of CsI oxidation does not depend exclusively on the exothermic nature of the combustion process. For example, dramatically different $I_2$ recoveries were observed for Tests 2 and 3, yet pressure histories indicative of hot, fast-burning flames were measured in both tests [6]. Calculations also indicate that the flame temperatures for these two tests were comparable, 2700 and 2400 K, respectively [7]. As such, the differing behaviour of CsI in these tests cannot be rationalized on the basis of differences in combustion energetics.

One subtle difference between Test 3 and Tests 2 and 4 was the nature of the excess combustible gas. Tests 2 and 4 were conducted in the presence of a slight excess of oxygen (0.4 vol%). On the other hand, because of the replacement of 10 vol% air with steam, Test 3 was undertaken with a small excess of $H_2$ (3.4 vol%). As illustrated by the equilibrium reaction
CsI + H₂O = CsOH + 0.5H₂ + I.  \hspace{1cm} (1)

The presence of excess hydrogen may influence the extent of CsI decomposition and, therefore, may have been responsible for the negligible recovery of I₂ in Test 3. To test this hypothesis, Test 5 was undertaken under conditions similar to those of Test 3 but with a net excess of oxygen. Gas phase I₂ was still not detected. This suggests that other factors were responsible for limiting the oxidation of CsI in the presence of steam.

Table 4.1

Summary of ACE/CTF Results

<table>
<thead>
<tr>
<th>Test #</th>
<th>H₂ (vol%)</th>
<th>Air (vol%)</th>
<th>Steam (vol%)</th>
<th>[I₂]g (mol.dm⁻³ x 10⁶)</th>
<th>% I₂(g) Formation</th>
<th>Aerosol I:Cs Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>80</td>
<td>10</td>
<td>&lt;0.06 (ND)</td>
<td>&lt;0.4</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>2</td>
<td>29</td>
<td>71</td>
<td>0</td>
<td>2.7</td>
<td>13.</td>
<td>1.6 ± 0.3</td>
</tr>
<tr>
<td>3</td>
<td>29</td>
<td>61</td>
<td>10</td>
<td>&lt;0.07 (ND)</td>
<td>&lt;0.03</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>29</td>
<td>71</td>
<td>0</td>
<td>3.1</td>
<td>15.</td>
<td>1.5 ± 0.3</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>65</td>
<td>10</td>
<td>&lt;0.04 (ND)</td>
<td>&lt;0.02</td>
<td>NA</td>
</tr>
</tbody>
</table>

* Based on gas scrubber results
ND: Not Detected    NA: Not Analyzed

The observation that CsI undergoes oxidation in hydrogen deflagrations is in itself not a new finding. Nelson et al. [2] demonstrated in intermediate-scale experiments that I₂ yields increase with increasing H₂ concentrations (up to stoichiometric levels). Brown et al. [1] also showed that high recoveries of I₂ can be obtained when CsI is placed in standing hydrogen flames and proposed that oxidation occurred as a result of thermal decomposition of volatilized CsI, as represented by the equilibrium reaction:

CsI + H₂O = CsOH + HI \hspace{1cm} (2)

In support of their hypothesis, CsI oxidation in standing hydrogen flames was shown to be unaffected by combustion gas composition and free radical concentration in the flame but was inversely dependent on the quantity of CsI volatilized and decreased with the addition of CsOH. However, if reaction (2) adequately represents the process involved in the ACE/CTF experiments, enhanced oxidation, not suppressed I₂ formation, should have been observed for the CTF tests conducted in the presence of excess steam.

It is, in fact, difficult to account in chemical terms for the role of steam in these tests. Thermodynamically, CsI decomposition should increase with increasing steam concentration [8], as represented by reaction (2). Reaction (2) also shifts to the right with increasing temperature, yet, despite the comparable combustion temperatures of Tests 2 to 5, dramatically different yields of I₂ were observed. Similarly, steam should not significantly influence the concentration of oxidizing radicals such as OH, O and HO₂ in the reaction zone of the combustion front [7,9]. As a result, oxidative processes such as the reaction...
\[ \text{CsI} + \text{OH} \rightarrow \text{CsOH} + \text{I} \]

should be unaffected by the presence of steam. Indeed, steam is the principal combustion product and following combustion will be present in the gas phase whether or not it is deliberately added. Therefore, since CsI oxidation is observed only under initially dry conditions, the role of steam in mitigating oxidation likely is associated with its presence at or before the start of combustion.

One possible explanation for the steam effect is the adsorption of water by the dispersed CsI aerosol prior to combustion. Cesium iodide is hygroscopic and during the period between dispersal and combustion may absorb sufficient water to protect itself from the transient high temperatures associated with combustion; water itself has a large heat of vaporization (i.e., 40.67 kJ·mol\(^{-1}\)) [10]. Without volatilization, neither thermal decomposition nor reaction with flame front radicals would be effective pathways for CsI oxidation. For Tests 1 and 3, water adsorption may have been enhanced since room-temperature (approximately 25°C) CsI was injected into the 95°C 10% steam environment of the CTF. Given the difference in vapour pressure of water at these two temperatures, condensation of water onto the "cold" CsI aerosol could have occurred during the 4-s interval between CsI injection and combustion, thereby providing protection to the CsI aerosol. However, negligible oxidation of CsI also was observed in Test 5, for which the CsI was preheated to approximately 100°C. Under these conditions, condensation of water onto the dispersed aerosol would be unlikely. Indeed, recent measurements by Newbury and Bowsher of water vapour pressures above CsI-saturated solutions suggest that deliquescence will not occur in a 10% steam atmosphere at 95°C [11]. If these results can be extended to the ACE/CTF tests, then another mechanism, as yet unidentified, is responsible for the role of steam in these tests.

An unexpected finding in this study was the apparent time-dependent evolution of gas phase \(I_2\) in the dry combustion tests. As shown in Tables 3.2 and 3.3, data from the gas scrubber system suggest an increase in iodine volatility with time, followed at longer times by a modest decrease. Since \(I_2\) was not detected in tests conducted with steam, even after several hours, it is unlikely that this time-dependent increase in concentration is due to slow oxidation of CsI within the CTF. Rather, this behaviour is believed to arise primarily from vapour-aerosol interactions within the sampling systems. During early samplings of the CTF atmosphere, large quantities of aerosol were deposited on the in-line aerosol filters. If elemental iodine is formed during the combustion process, as we believe, then during sampling, significant interaction between the deposited aerosol and \(I_2\) would be expected. This could lead to \(I_2\) adsorption onto deposited CsI,

\[ \text{CsI} + \text{I}_2 \rightarrow \text{CsI}_2 \]

or reaction with CsOH, the most probable cesium species formed during combustion. As aerosol concentrations decrease with time because of agglomeration and settling, lower concentrations of aerosol would be retained by the filters and decreased adsorption of \(I_2\) would occur. As a result, higher apparent yields of \(I_2\) would be measured with time, consistent with our observations. This would also account for the
discrepancy in the \( I_2 \) yields between the Maypack and gas scrubber systems. The Maypack samplers used much smaller diameter sampling lines that would have quickly filled with aerosols, resulting in increased \( I_2 \)-aerosol interactions.

Further evidence of CsI oxidation and the importance of vapour-aerosol interactions is provided by the deposited aerosols themselves. As summarized in Table 5, aerosols from tests with steam exhibited the expected 1:1 mole ratio of iodine and cesium. Without steam, early aerosol samples revealed iodine:cesium ratios as large as 1.87. This is consistent with the hypothesis of CsI oxidation to \( I_2 \) and subsequent \( I_2 \) adsorption onto aerosols. Unfortunately, an accurate determination of the extent of CsI oxidation and vapour-aerosol interactions within the CTF cannot be readily extracted from the ACE/CTF data. Because of \( I_2 \) adsorption onto aerosols, both in the CTF and within the sampling systems, CsI oxidation is likely more extensive than suggested by the measured gas phase \( I_2 \) recoveries. Alternatively, because of enhanced vapour-aerosol interactions within the sampling systems, aerosol iodine:cesium ratios presumably overestimate the extent of CsI oxidation.

Gas chromatography and Maypack sampler results also revealed enhanced organic iodide formation in the dry combustion experiments. This is consistent with the formation of \( I_2 \) during combustion and its subsequent reaction with organic vapours or the organic-based surfaces of the CTF to produce organic iodides. As expected for such a process, organic iodide concentrations generally increased with time. Even at longer times, however, the yield of organic iodides was modest in comparison with \( I_2 \) formation.

5. SUMMARY

This paper describes the results of a series of tests conducted in the Containment Test Facility to assess the effect of steam on the oxidation of CsI aerosols during hydrogen combustion. This work has demonstrated that the presence of 10% steam can suppress oxidation of CsI to \( I_2 \). The mechanism for this effect has not been conclusively identified.

Tests conducted without added steam show significant oxidation of CsI to gaseous \( I_2 \) (15%), although time-dependent evolution of \( I_2 \) to the gas phase is observed. This apparent time dependence is believed to arise primarily from vapour-aerosol interactions within the sampling systems. In support of this suggestion, high iodine:cesium ratios were measured in early aerosol samples.

Increased organic iodide yields were also observed during the dry combustion tests. This likely arises from the reaction of organics in the CTF with \( I_2 \) formed during the combustion process.

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REFERENCES


Figure 1. Schematic diagram of Containment Test Facility as instrumented for ACE/CTF test program.

Figure 2. CsI dispersion apparatus.
The high volatility and radiobiological impact of radiiodine necessitate a sound understanding of iodine chemistry within the reactor coolant system and containment (5). Although progress has been made in developing a basic knowledge of aqueous iodine chemistry in both design-basis and severe reactor accidents, significant uncertainties remain when aerosols are generated and stabilised in the presence of radiiodine species (6). Furthermore, few studies have involved the generation of a realistic source of iodine to study the resulting aerosol/vapour exchange processes within appropriate containment conditions. Thus, the Falcon experimental facility has been developed at Winfrith Technology Centre to generate controlled concentrations of iodine by heating simulant or trace-irradiated fuel to 2000K in the presence of bulk materials such as boric acid and Ag-In-Cd control rod. The vapour/aerosol emission can be followed through a pathway representing aspects of a stainless steel primary circuit and containment. Various on-line and post-test analytical techniques are available to identify the chemical species and physical forms of the gas-borned debris.

Specific Falcon tests have been designed to focus on the behaviour of fission product iodine, and hence determine the chemical effects that can occur within the containment (i.e. exchange processes between vapour-aerosol, vapour-metal surface, vapour-painted surface and vapour-aerosol-water pool (sump). Gamma-ray detectors were used to follow the transport and deposition of radiiodine in the experiments with trace-irradiated fuel. Maypacks were also used in conjunction with these spectrometers to monitor changes in the concentration of specific iodine species (i.e. aerosols, molecular iodine and organic iodides). One intention has been to use the resulting experimental data to develop a theoretical understanding of iodine-aerosol interactions and incorporate such a model in a suitable code (e.g. INSPECT) so that the iodine transport and attenuation of this important fission product can be calculated with added confidence.

2. FALCON

Falcon has been developed to study the transport and deposition of fission products under severe reactor accident conditions. Simulant and trace-irradiated fuel pellets are clad in Zircaloy, and heated up to 2000K in the presence of bulk-core materials to generate representative aerosols. Fission product transport can be studied along a pathway designed to represent the upper plenum, hot-leg structures and containment (Figure 1). A range of analytical techniques are used to detect the chemical species and quantify the vapours and aerosols released from the UO₂ fuel and other sources.

Thermal-hydraulic calculations were carried out at the beginning of the Falcon programme to ensure that the experiments simulate, within practical limitations, the conditions in which the key phenomena will occur. This should ensure that valid data are generated to test and develop theoretical models. There have been extensive discussions between the UK experimentalists and theoreticians, and as a consequence Falcon has been modified to improve the data generated from the experiments.

The test matrix evolved during iterative consultations, and was designed to meet several technical criteria: determination of the chemical
species formed above the damaged fuel and within the containment, generation of experimental data sufficient to assess specific models in computer codes, and development of on-line and post-test analysis techniques (Table 1). Studies were also undertaken to determine the thermal-hydraulic conditions that could be satisfactorily achieved in the apparatus (eg. thermal-hydraulic tests (TH), smoke tests (ST) to visualise the flow patterns within the containment vessel, and humidity tests (HT) to monitor steam condensation at high relative humidities).

The main Falcon tests developed in five stages:

(i) simulant fuel (eg. FAL-1A),

(ii) simulant fuel and bulk-material aerosols (eg. FAL-3A),

(iii) simulant fuel, bulk-material aerosols and one painted containment wall (eg. FAL-5),

(iv) a simulant fuel bundle (six fuel rod samples), bulk-material aerosols, one painted containment wall and a water-based sump (FAL-7),

(v) trace-irradiated fuel, bulk-material aerosols, one painted containment wall and a water-based sump (eg. FAL-9).

The fuel bundle experiment (FAL-7) was performed to study aerosol agglomeration, while the tests with trace-irradiated fuel were identified with the development of on-line gamma-ray spectroscopy and quantification of iodine behaviour in the containment vessel. A comprehensive data report was produced after each test (apart from FAL-HT5), which contained details of the thermal-hydraulic conditions and the bulk and microscopic properties of the vapours and aerosols. These reports represent a major database to test and develop both primary circuit and containment codes. Details of the facility are given in reference 7, while some of the more important results have been assembled in references 8 and 9.

3. IODINE CHEMISTRY IN THE PRIMARY CIRCUIT

While the main aim of FAL-6 to 10 was to study exchange processes within the containment, these tests also provided insights into other aspects of iodine chemistry at higher temperatures. For example, data were obtained on the interaction of iodine-based species with aerosols generated from the Ag-In-Cd control rod sample and boric acid solution.

Aerosols were sampled from within the primary circuit of Falcon for analysis by scanning electron microscopy and x-ray energy-dispersive spectroscopy (SEM/EDS). Individual aerosol particles varied widely in their elemental and chemical composition in all of the Falcon tests, representing the formation and transport of heterogeneous aerosol ensembles. For example, the caesium-based aerosol consisted of several different types of particle in FAL-1A:

(a) high caesium concentration (0.6 to 1.3 μm mean volume equivalent diameter);
(b) approximately equal concentrations of caesium and iodine, i.e. CsI (1.0 to 3.0 \(\mu\)m mean volume equivalent diameter);

(c) significant concentrations of other elements such as tellurium and uranium as well as caesium (0.3 to 1.0 \(\mu\)m mean volume equivalent diameter).

Significant variations occurred in the caesium to iodine ratio of the aerosols that originated from the simulant fuel tests, implying the emission of species other than caesium iodide. There was evidence for the interaction of caesium iodide and caesium hydroxide vapours with boric acid to form caesium borate, which is a less volatile species than the reactant molecules (10):

\[
\text{CsI} + \text{H}_3\text{BO}_3 \rightarrow \text{CsBO}_2 + \text{HI} + \text{H}_2\text{O} \\
\text{CsOH} + \text{H}_3\text{BO}_3 \rightarrow \text{CsBO}_2 + 2\text{H}_2\text{O}
\]

X-ray photoelectron spectroscopy (XPS) and x-ray diffraction (XRD) analyses of the aerosol deposits indicated the generation and stabilisation of CsBO\(_2\) in the boric acid tests. This type of reaction would result in the rapid formation of numerous nucleation sites in the gas phase, and the instantaneous generation of caesium borate particles at relatively high temperatures.

Aerosol samples from the FAL-4 pipework were analysed by XPS, and shown to contain cadmium iodide (Cd\(_I_2\)). This could be formed via a two-stage reaction mechanism: the transient formation of hydrogen iodide from the reaction between caesium iodide and boric acid, followed by the interaction of hydrogen iodide with metallic cadmium aerosol generated from the control rod alloy. This process could result in the formation of aerosol particles with high iodine concentrations on their outer surface and cadmium-rich kernels (11).

4. IODINE CHEMISTRY IN THE CONTAINMENT

Some Falcon tests were designed to study the behaviour of iodine species within the containment vessel (9). These tests also involved the development of measurement techniques to follow the various exchange processes that can occur (i.e. vapour-aerosol, vapour-bulk surface, vapour-paint and vapour-aerosol-aqueous sump). In-situ analytical methods were used in conjunction with post-test measurements (e.g. SEM/EDS, XPS and XRD). Nine gamma-ray detectors were used to monitor the transport and deposition of radiiodine in the tests with trace-irradiated fuel, and were operated in conjunction with a series of Maypacks (iodine-species samplers) to determine the variation in concentration of specific forms of iodine-based species with time (particulate, molecular iodine (I\(_r\)) and organic iodides).

One wall of the containment vessel was painted with an appropriate phenolic paint in FAL-6 to 10. The quantities of iodine deposited on the various containment surfaces per unit surface area are listed in Table 2 for these tests. FAL-6 involved simulant fuel: the iodine partitioned between the painted wall and floor at a ratio of approximately 2:1. Similar results were obtained with irradiated fuel in FAL-10, and some
radioiodine was also detected on the unpainted walls (approximately 1/10 of the concentration on the painted surface). However, different behaviour was exhibited in FAL-7, 8 and 9: approximately 80% of the iodine deposited on the floor, while the remainder adhered to the phenolic paint.

An aqueous sump of 50 ml (pH 8, FAL-7 and FAL-10, or pH 5, FAL-9) was placed in one corner of the containment vessel. Iodine retention in the sump was at least an order of magnitude higher per unit surface area than deposition on the floor, as shown in Table 3.

Maypack filters were used to sample and analyse the containment atmosphere (12). A glass-fibre filter (traps aerosol particles), a charcoal-impregnated filter (retains molecular iodine) and a charcoal bed (absorbs organic iodide species) were contained in a stainless steel tube (length 120 mm, od 220 mm) and connected to the containment by a sampling tube (120 mm long). Gas samples from the containment atmosphere were passed through the Maypacks at different times after the fuel ruptured. FAL-6 data were obtained using inductively coupled plasma mass spectrometry (ICPMS), and are listed in Table 4; no organic iodides were detected, and the concentrations of the other forms of iodine were low. Equivalent studies with irradiated fuel, Maypacks and gamma-ray spectrometers were more sensitive, and included the detection of organic species on the charcoal bed (Table 5).

An additional Maypack with two charcoal-impregnated filters was used in FAL-8 and 9, in which the individual components were separated by relatively long distances and monitored by three independent scintillation detectors (NaI crystals interfaced to a standard counting system). I-131 (365 keV gamma-ray) and I-133 (526 keV gamma-ray) were readily quantified by this technique. The standard and elongated Maypacks were exposed simultaneously to the containment atmosphere, and both were subsequently analysed by gamma-ray spectroscopy at the end of each test. Up to four times more radiiodine was detected in the standard Maypack than the modified device; this was attributed to unavoidable deposition in the connecting lines which separated the various filters from the containment. Organic iodide species were detected as I-131 (980 Bq) and I-133 (260 Bq) on the compact sampler. The on-line measurements of I-131 were compared with the post-test analyses: 22,700 Bq collected on the glass-fibre filter paper compared with 27,000 Bq determined by post-test monitoring. However, a comparison of equivalent data for molecular iodine (I$_2$) was not as good: 370 Bq were detected by on-line gamma-ray spectroscopy compared with 26 Bq by post-test analysis. Iodine deposition profiles also differed in the standard and modified Maypacks used in FAL-9. Both sampling systems were similar in length, and these differences are difficult to explain. Twice as much organic iodide species was detected in FAL-9 than FAL-8, while still being two orders of magnitude lower than the concentration of aerosol particles.

Additional gamma-ray detectors were used in FAL-9. Two shielded detectors were positioned to monitor the gas volumes at the top and bottom of the vessel. As in FAL-8, a rapid increase in gas-borne iodine concentration was observed up to approximately 30 minutes after fuel rupture (Figure 2a). The radioactivity fell exponentially at the top of the chamber over a period of 8 hours, and then appeared to remain constant.
for at least 22 hours. Figures 2b and 2c show the rate of deposition of I-131 onto the wall and floor surfaces in the containment. The amount of radiiodine on the unpainted wall decreased significantly from a relatively high initial value (Figure 2b), implying the existence of a significant exchange process at this surface; the radiiodine concentration on the painted wall was retained and remained at a constant value during this period of time. These on-line measurements indicated that more iodine deposited initially on the surface of the unpainted than the painted wall, a transient effect that could not be detected by using post-test analysis techniques. Figure 2c shows the equivalent data for radiiodine uptake by the sump (50 ml Na_2PO_4 + HNO_3, pH 5) compared with a stainless steel section of the floor. These measurements were in agreement with the bulk chemical analysis data, and showed significant retention of the iodine species by the sump. As observed with the unpainted walls, a significant fraction of the radiiodine absorbed by the sump was apparently re-released to the containment atmosphere over a 4-hour period after fuel failure.

The iodine release and absorption data in FAL-6 to 10 indicated the formation of volatile, reactive species in the containment atmosphere. After an initial period of rapid gas-surface exchange, iodine deposited preferentially onto the surfaces covered with a phenolic paint (Table 2). The aqueous phosphate-buffered sump also acted as an iodine trap, with significantly higher radiiodine concentrations in the sump than on the floor (Table 3).

On-line monitoring of the gamma-rays emitted from each section of the Maypacks (Tables 4 and 5) indicated that different iodine species were produced from the simulant and trace-irradiated fuel. Organic iodides were formed in every test with trace-irradiated fuel, whereas no such volatile species were detected in the simulant fuel studies (eg. FAL-6). However, this observation may reflect the relatively low sensitivity of the ICPS analysis technique which was used in the experiments with simulant fuel. Fission product iodine was assumed to be present in the trace-irradiated fuel as isolated I atoms in the UO_2 matrix, and will be released in this form when the fuel ruptures. The iodine was added to the simulant fuel as caesium iodide, which will vaporise to react with boric acid and form hydrogen iodide and possibly cadmium iodide (see Section 3). High surface concentrations of iodide (I^-) on an aerosol particle will be amenable to oxidation when such gas-borne species are transported from the reducing environment of the primary circuit to the predominantly oxidising conditions of the containment. The relatively slow formation of molecular iodine via this process would account for the initial observation of high concentrations of iodide-based aerosols, and the re-release and subsequent reaction of I_2 on painted surfaces and dissolution in the sump.

5. CONCLUSIONS

Experiments have been conducted in the Falcon facility at Winfrith Technology Centre to investigate iodine chemistry in severe reactor accidents. A representative iodine source was generated by heating simulant or trace-irradiated fuel to 2000K in the presence of bulk materials such as boric acid and Ag-In-Cd control rod. The resulting vapour/aerosol was followed through a pathway designed to represent primary circuit pipework and the containment. A number of on-line and post-test
analytical techniques were used to generate information on the chemical species and the physical forms of the gas-borne debris. Specific tests focussed on the behaviour of fission product iodine by following the various exchange processes that can occur within the containment (ie. vapour-aerosol, vapour-metal surface, vapour-painted surface, vapour-aerosol-ump). Gamma-ray spectrometers were used to follow the transport and deposition of radiiodine in the experiments with trace-irradiated fuel. Maypacks were operated in conjunction with these detectors to monitor the time-dependent changes in concentration of specific iodine species (ie. iodine-based aerosol particles, molecular iodine and organic iodides). The resulting data will be used to develop suitable codes (eg. INSPECT for the containment) so that iodine behaviour during a severe reactor accident can be modelled with confidence.

The Falcon tests have provided evidence for the interaction of iodine-based vapours with aerosols generated from the bulkier materials within the reactor core. These reactions occurred in the high-temperature region of the facility simulating the primary circuit, while molecular iodine (I2) and organic iodides were formed in the containment vessel. Ten times more iodine became absorbed on a painted wall than on an equivalent unpainted surface, while significantly higher concentrations of iodine were found in the alkaline sump than on the stainless steel floor. The Maypack data supported these observations; while the initial release (1 to 2 hours after fuel failure) was dominated by the formation of iodine-based aerosol(s), volatile iodine species accounted for greater than 50% of the gas-borne material after a further 48 hours. These results can be interpreted in terms of enhanced oxidation of the iodine-based species that have stabilised on the surface of the multicomponent aerosols formed in the primary circuit pipework. When this debris enters the predominantly oxidising conditions in the containment vessel, volatile molecular iodine will be generated to modify the partitioning of species on the various collection media of the Maypacks.

ACKNOWLEDGEMENTS

The authors wish to thank B H Armitage, A M Deane, T W Packer and H E Sims for helpful discussions and technical support during the Falcon tests. This work was funded by the Commission of the European Communities, Joint Research Centre, Ispra and the UK Health and Safety Executive (FWR task SAA 3.2).

REFERENCES


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<th>Atmosphere</th>
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* All experiments except FAL-11 conducted in the containment configuration; FAL-11 undertaken in a thermal gradient configuration to test an on-line gamma-ray spectroscopy system to distinguish between radioactive suspensions and deposits.

* Simulant fuel bundle experiment.

$ Inlet pipe to containment was maintained at -20°C, resulting in steam condensation prior to the aerosol entering the vessel.

§ FAL-3A and 3B were conducted under identical conditions to assess experimental reproducibility.
### TABLE 2: IODINE DEPOSITION PER UNIT AREA ON WALLS AND FLOOR

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<thead>
<tr>
<th>Expt</th>
<th>Fuel</th>
<th>Painted Wall</th>
<th>Unpainted Wall</th>
<th>Floor</th>
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<td></td>
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<td>Mass (µg)</td>
<td>Activity (Bq)</td>
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<td>Simulant</td>
<td>220</td>
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ND, below limit of detection by ICP-OES (0.25 µg cm⁻²)

### TABLE 3: IODINE DEPOSITION IN THE SUMP AND ON THE FLOOR

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<td>FAL-9</td>
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<tr>
<td>Sump</td>
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### TABLE 4: IODINE SPECIES (FAL-6)

<table>
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<tr>
<th>Sampling Time (hours after fuel rupture)</th>
<th>Mass of Iodine (g)</th>
<th>Fraction of Inventory</th>
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<tr>
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<td>1-2</td>
<td>3.00 x 10⁻⁶</td>
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<tr>
<td>24-29</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>168-176</td>
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<td>8.00 x 10⁻⁶</td>
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</table>

ND, below limit of detection by ICP-MS (1 µg I per 20 g carbon granules or 0.5 g I per filter of area 14 cm²)
### TABLE 5: IODINE SPECIES (FAL-10)

<table>
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### TABLE 5: IODINE SPECIES (FAL-10) - Fraction of Inventory*

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<td>$1.30 \times 10^{-1}$</td>
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*Corrected to time of fuel rupture
Figure 2  On-line Gamma-ray Analyses During FAL-9
DISCUSSION

Evans

Have you noticed any isotopic effects in the iodine behavior.

Bowsher

No. Although data for specific FALCON tests appear to show isotope effects, there is no discernible trend over all the experiments.

Herranz

In low pressure sequences the failure of control rod could cause silver ejection as droplets providing an important surface reaction for Ag-I interaction. Why did not you consider this phenomenon in your studies?

Bowsher

We do not believe that silver aerosols represent as significant aerosol source in the early stages of an accident when volatile fission products are being released. We have conducted separate effects experiments to quantify the aerosol release from Ag-In-Cd samples during low pressure sequences. These experiments involved small samples and would maximum surface-to-volume effects. However, the aerosol was dominated by cadmium and indium oxide, with contributing about 1% of the airborne material. We do, however, believe that silver would be more important in the later stages of an accident, when the core slumps into the lower plenum as much of the silver may have relocated to this region. This could generate a late silver aerosol.

Vikis

Is there evidence for the gas-phase reaction of CsI with boric acid?

Bowsher

We have recently quantified the thermodynamic functions of gas-phase orthoboric acid. These new data are significantly different from those given in the JANAF compilations, and application of the new results shows that the reaction

$$\text{CsI}(g) + \text{H}_3\text{BO}_3(g) \rightarrow \text{CsBO}_2(c) + \text{HI}(g) + \text{H}_2\text{O}(g)$$

is forward over all temperatures of interest to reactor accidents. These calculations have been confirmed by experiments to follow the gas-phase reaction of CsI with H$_3$BO$_3$. These experiments gave extensive decomposition of CsI. Please see AEEW-R 2659 report.
4.6 DISCUSSION ON SESSION IV

Kupferschmidt

One of the conclusions coming out of this workshop is that if iodine volatility in containment is to be minimized, alkaline conditions must be maintained. With regard to the question "is maintaining alkaline pH sufficient?", the answer is probably yes. However, we should continue our efforts to find additional methods to mitigate iodine volatility.
5. Session V.A
MODELLING AND CODE DEVELOPMENT
5.1 VALIDATION OF IMPAIR 2 CODE USING ACE-TEST RESULTS
FROM THE RADIOIODINE TEST FACILITY (RTF)

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Paul Scherrer Institute
Program Light Water Reactor Safety
CH-5232 Villigen/PSI ; Switzerland

Abstract

The IMPAIR 2 (Iodine Matter Partitioning And Iodine Retention) code is based essentially on clean-condition data. Since the original version was published (1989), improvements are made with the aim to attempt a sufficiently realistic description of postulated iodine chemical conditions prevalent after a hypothetical severe accident in containment using a minimum of differential equations which define the important iodine reactions.

This code considers 6 iodine species in 21 differential equations. It also contains code to model relevant physico-chemical behaviour: transport from containment (time-dependent accidental leakage or intentional filtered venting simulation), droplet carry-over, liquid and gas phase deposition (on paint surfaces) and revolatilization (including surface-formed organic iodide), aerosol phase transfer and droplet precipitation.

The ACE/RTF\(^1\) tests are one of the most important sources for accident relevant conditions. An examination of the thermodynamic parameters of ACE/RTF Test 1 led to the addition of the Higher Molecular Weight organic Iodides (HMWT).

The radiolysis reactions, especially the pH-dependent iodide oxidation and iodate reduction reactions, are revised using data from the RTF Tests and other current literature.

\(^1\) Advanced Containment Experiments at (AECL) Whiteshell Nuclear Research Establishment, Pinawa, Manitoba, Canada
1 Introduction

The FORTRAN program IMPAIR 2 (Iodine Matter, Partition And Iodine Retention) describes the chemical behavior of different iodine compounds (species) in a volume with gaseous and aqueous phases as a function of time. The code serves principally the investigation of postulated conditions present in a containment sump and accompanying atmosphere after a beyond-design NPP accident.

IMPAIR 2 was first published in 1989 [1], being based mainly on the earlier KfK/PNS Code IMPAIR [2] and was largely influenced by preliminary work carried out at Oak Ridge [3]. The work at Oak Ridge excluded radiolysis effects and organoiodine chemistry.

The code and experimental development work during the last two years laid emphasis on the following points:

- Recognition of weaknesses recognised in the first published code version.
  - Thermal and radiolytic iodate reactions.
  - Thermal and radiolytic organoiodine reactions based on methyl iodide.
  - deposition and revolutilation reaction on and under surfaces (especially paint surfaces in water and gas phases, with emphasis on the gas phase).

- Consideration of new mechanisms with the aim to move the "clean condition" chemistry more in the direction of the very complex conditions prevalent during a real accident in a containment.
  - Interaction between vapour, aerosols and particularly elementary iodine.
  - Consideration of new iodine species, especially higher molecular weight organoiodine forms.

- Implementation of the "iodine chemistry" in a multi-compartment version, IMPAIR 2/M. The work of integrating IMPAIR 2 which permits a complete level 2 source term analysis is described in detail in [4].

- Code validation using new experimental data, especially the results from ACE/RTF Tests [5]. These tests form the focal point of this paper. In preparation is a comprehensive IMPAIR 2 update in user-manual form to provide details of this validation (available towards the end of 1991).

The most important changes mentioned below are therefore only summarized to provide an overview.

2 Code development

2.1 Broad Aims

IMPAIR 2 should remain comprehensible also for non-specialists. Using an absolute minimum of considered iodine species (I₂, I⁻, HOI, IO₃⁻, CH₃I, AgI) and recently the so-called HMWI (Higher Molecular Weight organic Iodides) and a minimum number of differential equations, the anticipated containment accident conditions should be sufficiently modelled.

"Sufficiently modelled" being defined here as: The concentrations of all significant iodine species in the gas and water phases and deposited are correctly calculated to less than an order of magnitude difference within postulated limits (pH: 4–10, Temp: 20–130 °C, Time: from minutes to 2–3 weeks).
2.2 Deposition reactions

Using the present formulation of the competitive "deposition reaction", a useful basis was found with the help of the I$_2$-deposition velocity and revolatilization rate. The formulation of a 10% conversion to methyl iodide under paint surfaces is, however, very tentative.

2.3 Particle–I$_2$ behavior in the gas phase

With reference to the ACE/Phase B large scale tests [6], the I$_2$-transfer from air/vapour to water phases (up to an assumed airborne limiting CsI concentration of $10^{-9}$ mol/l) is postulated to be based on the "aerosol settling rate" calculated by the NAUA aerosol code and only subsequently by the phase transfer reaction alone.

2.4 Iodate Reactions

The pH-dependent iodate formation rates from [7] are used. The missing radiolytic reduction of iodate, being one of the greatest weaknesses of IMPAIR 2, was recently formulated.

A model developed solely from our own measurements confirms the high stability of iodate at very low concentrations, with the help of a concentration-dependent reduction rate.

2.5 Consideration of higher molecular weight organoiiodine species

ACE/RTF Test 1 data [5], show clearly that higher molecular weight organoiiodine species (i.e. HMWI) are present in concentrations comparable to those of methyl iodide or lower alkyl iodides.

Based on [5], a provisional HMWI formation and reduction model was integrated in IMPAIR 2. However some important questions are still unanswered:

- A distinction between, and a definition of, high and low molecular weight organoiiodine and chemical form using two separate models or one model which considers all significant molecular weights?
- HMWI-stability: Hydrolysis and radiolysis?
- HMWI contribution by organic revolatilization from epoxy paint surfaces?
- Specific partition coefficients (function of molecular weight etc.)?

The calculated HMWI data to be compared with the ACE/RTF data are not presented here for these reasons.

3 Code assessment using ACE/RTF Tests 2 and 3

3.1 General Approach

A comparison with IMPAIR 2 [1] calculated data using the ACE/RTF Test 3 [5] set of start concentrations based on a CsI solution (Test 3B) partly showed some very significant discrepancies, which had to be initially studied.

Changes made on data material originating from "clean condition" experiments were avoided where possible. On the other hand, new and differing values were chosen whenever, by reason of tests under "real conditions", they became relevant, even when no detailed mechanistic description is yet available. The following two examples illustrate this point:
• The gas phase CH$_3$I equilibrium relation as shown in [8] and as used in [1] is clearly wrong if the initial CH$_3$I concentration is very high ($10^{-5}$ mol/l). The calculated gas phase decomposition compared with ACE/RTF Test 1B is several orders of magnitude too fast. Consequently the value of the corresponding equation in [1] was set to zero for all the following assessment work.

• Based again on RTF Test 1B, it can be shown that the CH$_3$I-hydrolysis originating from “clean condition” data is underestimated by about a factor of 2. “Real” containment sump conditions probably lie much closer to the RTF-conditions than to “clean conditions”. Hence RTF Test 1B derived hydrolysis rates were subsequently used.

3.2 Some important points

With regard to “real” accident scenarios, the emphasis is laid on an optimal representation of the conditions in ACE/RTF tests 2A and 3B using CsI as the main initial species.

To compare ACE/RTF Tests 2 and 3, it is clear that only the initial conditions (speciation, pH and temperature) were changed and all other parameters (rates, activation energies and geometrical constants) were left unaltered.

An evaluation of the ACE/RTF Test 3 high pH data was not performed. Since the deposition on the gas phase walls is the most dominant feature in this test, a pH change to 9 had a negligible effect during the remaining limited experimental time. The relevant ACE/RTF Test 4 data was not available during the evaluation.

The most important parameters of the ACE/RTF Tests are summarized in the following table.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Dose rate</th>
<th>pH</th>
<th>Surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>RTF 1</td>
<td>none</td>
<td>9 – 10</td>
<td>Epoxy paint</td>
</tr>
<tr>
<td>RTF 2</td>
<td>2.0 kGy/h</td>
<td>9</td>
<td>Epoxy paint</td>
</tr>
<tr>
<td>RTF 3</td>
<td>2.0 kGy/h</td>
<td>5.5 (73 h) then 9</td>
<td>Epoxy paint</td>
</tr>
<tr>
<td>RTF 4</td>
<td>2.0 kGy/h</td>
<td>5.5 – 9 recycled</td>
<td>Stainless steel</td>
</tr>
</tbody>
</table>

3.3 Presentation of results

In all diagrams below, the experimental results from RTF Test 2 and Test 3 are represented as solid lines and the IMPAIR 2 calculations are represented as dashed lines.
3.4 ACE/RTF Test 2

Neither radiolysis nor deposition are significant in this test due to the high pH (9.0). Consequently the total concentration in the water phase (Figure 1) phase will hardly change.

The shape of the total gas phase concentration (Figure 2) is exactly modelled and hence the total partition coefficient (H) curve is also correctly calculated (Figure 3).
The following diagrams (Figure 4 and Figure 5) show elementary iodine concentrations in the gas and water phases respectively. Although the experimental and calculated curves differ, in the worse case, by about an order of magnitude considering possible experimental errors, the deviations are significant. While the gas phase concentration is too low, the water phase concentration is overestimated. This discrepancy cannot be eliminated by a reduction of the specific (I₂) partition coefficient or a change of the phase transfer rate for I₂. There is, however, no reason to doubt the validity of the temperature-dependent partition coefficient function [9].
The correlation for methyl iodide in the gas and water phase between ACE/RTF Test 2A and calculated IMPAIR 2 concentrations is very good (Figure 6 and Figure 7), despite the restriction that the water phase CH₃I calculated concentrations are have to be plotted against the total organic experimental concentrations, since there is still no detailed speciation available.
The iodate concentration is surprisingly constant, while IMPAIR 2 postulates a slight increase (Figure 8). IMPAIR 2 presently uses a newly developed pH-independent model for the radiolytic reduction of iodate. Further work in this area is in progress.
Figure 9 shows that independent of the initial species (CsI, I₂, CH₃I) practically the same partition coefficients are reached after about one day.

In Figure 10 shows that this behavior is exactly calculated for the accident relevant initial species, CsI and I₂, while, in the case of CH₃I, a consistently high gas phase concentration is calculated, which leads to a low partition coefficient (about an order of magnitude lower). This is due to the CH₃I equilibrium reaction equation in the gas phase being set to zero. This equation produces an unrealistically high partition coefficient and would contradict the general aim, to remain on the conservative side.
3.5 ACE/RTF Test 3

The significant reduction of the total water phase concentration is, compared with ACE/RTF Test 2A, a very good fit (Figure 11). The shape and values of the total gas phase concentration curves also correlate well (Figure 12).

The missing iodine mass in the water phase has been practically all transferred to the gas phase walls. The IMPAIR 2 calculated component (66% after 70h) of the total iodine inventory as being deposited on the gas phase walls corresponds with the experimental data.
The shape of the distribution coefficient $H$ curve (Figure 13) apart from an initial, very short-lived deviation, also matches the experimental curve well as in ACE/RTF Test 2A.

![Fig. 13: RTF 3B Partition Coefficient](image)

The curves shown in Figures 14 and 15 for the $I_2$ concentrations in the gas and water phases display exactly the same discrepancy as was already mentioned for ACE/RTF Test 2. The discrepancies are, however, not important in accident scenarios for significant gas phase concentrations.

![Fig. 14: RTF 3B $I_2$ (a)](image)
The calculated CH₃I gas phase concentration is, again, a very good fit (Figure 16). The gas phase contribution of methyl iodide by organic revolatilization has been deliberately underestimated for want of experimental (speciation) data, although perhaps the iodine retention capacity of paint surfaces is thereby overestimated.
The discrepancy in the water phase is not very significant because the CH₃I concentrations have to be plotted against the total organic concentrations and hence the HMWI concentration component is missing (Figure 17).

Again in ACE/RTF Test 3, a time dependent iodate concentration is hardly noticeable and is also confirmed by IMPAIR 2 (Figure 18).
The direct comparison of the partition coefficients for assessment of ACE/RTF Test 2 with the ACE/RTF Tests 3E, 3B and 3D (Figure 19 and Figure 20) show that in the case of the CH$_3$I test, IMPAIR 2 will always underestimate the partition coefficient during the first two days, but calculates an exact correlation for both of the important initial species.
4 Conclusions

The ACE/RTF Tests are clearly today's best source data to assess the quality of a code required to model iodine behavior in a containment after a hypothetical severe accident.

The calculated results for RTF Tests 2 and 3 with their drastic pH difference show that for all iodine species in the gas and water phases and in deposition, there is a very good correlation between experimental data and calculation. Where discrepancies exist, they are less than an order of magnitude and, at the same time, lie on the conservative side, that is, they overestimate the iodine source term to the environment and/or the release to secondary rooms.

The data shown do not signify that IMPAIR 2 has reached the maturity of an assessed code, but has reached rather a confirmed step in its improvement.

Supported by the complete ACE/RTF data material, and, in particular, by ACE/RTF Test 4 results, by own experiments and in close collaboration with the international partners, further improvements on IMPAIR 2 will follow.
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DISCUSSION

Evans (Comment)
In relation to the difficulties with simulating the aqueous I2 concentrations, I believe the difficulty may be as much due to uncertainty in the experimental results as to any shortcoming in the code. We also have had little success in simulating HMWRI in the aqueous phase.

Bowsher
Do you plan to model the CSTF and CTF experiments conducted for ACE with the IMPAIR code?

Furrer
The particulate behavior of I2 down to a small fraction of the original total iodine concentration as shown in CSTF is modeled already. I2 is depleted into the sump with the settling rate of CsI-aerosol and the phase transfer rate at the phase boundary. At an arbitrary CsI-gas phase concentration (10^{-9} mol/l) the aerosol settling contribution to the I2-transport is switched off. This admittedly crude empirical model will possibly be refined in later version of IMPAIR-2. Other aspects of CSTF-experiments as well as the CTF-experiments will not be modelled in the near future.

Ritzman
Please comment on how the predictions of mass transfer rates in the RTF tests were done, because they seem to have been quite successful.

Furrer
Assuming that mass exchange resistance only occurs on the aqueous side of the boundary, a simple version of Fick's law was applied. The rate constant used was proposed by PSI specialists, based on an "educated guess" for the turbulence above a severe accident containment sump. Mass transfer rates, such as deposition velocities versus revolatilization rates, were initially proposed by Gesman Postners of Siemens/KWU and slightly adjusted in order to model deposition, especially of I2 in the RTF-3 test.

Evans (Comment)
In Canada, we have had some success in estimating the gas phase mass transfer in the RTF from correlations but have had less success with the aqueous phase mass transfer coefficient.
5.2 A COMPARISON OF THE PREDICTIONS OF THE INSPECT REACTION SET WITH EXPERIMENTAL DATA

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ABSTRACT

The computer program, INSPECT (Iodine SPECiation and Transport) is a mechanistic code for modelling the thermal and radiolytic chemistry of iodine in reactor faults. Because of the complexity of the program and especially the reaction scheme within it, it is necessary to validate or benchmark the code before it can be used with confidence for predictive purposes.

Validation of the reaction set has been attempted by comparison of data from laboratory experiments involving thermal and radiolytic reactions of iodine with the predictions of the program using the experimental conditions as input to the program.

This paper describes the results of this comparison exercise using a range of data from the UK and overseas. In general, prediction and data show good agreement and the INSPECT reaction scheme models the thermal and radiation chemistry of I₂, I⁻ and IO₃⁻ and the effects of temperature and pH well, but the exercise did show up some problems.

(1) Many papers do not give sufficient information such as pH, and the elapsed time between irradiation and measurement which is critical in iodine chemistry.
(2) The experimental yield of iodine from irradiated solution is particularly sensitive to pH and this is also the case with model predictions. This sensitivity is a result of the reaction of H₂O₂ with 'iodine' in near neutral and alkaline solution which is very important but the mechanisms and rate constants for the reactions are not accurately known.
(3) Uncertainties identified above lead to poor agreement when modelling irradiated neutral solution when post-irradiation reaction is taken into account.

It is concluded that it is possible to use a complex reaction scheme to model the chemistry of iodine with confidence, but there are some data required particularly concerning the reactions of H₂O₂ with I₂.

1.0 INTRODUCTION

Iodine and caesium are two of the most important fission products when considering potential radiological hazards arising from faults in water cooled nuclear reactors. This importance arises because iodine can exist in the volatile form I₂(g) and is biologically active being concentrated in the human thyroid gland. These factors make the ability to predict and understand the behaviour of iodine in reactor faults (such as LOCA faults) crucial for the formulation of safety cases and for the development of intervention strategies.

Unlike caesium, iodine has a complex inorganic solution phase chemistry with an ability to interconvert among oxidation states between -1 (I⁻) and +7 (IO₄⁻) as well as take part in a varied organic chemistry. In addition to its complicated aqueous thermal chemistry, it can also undergo a wide range of radiolytically induced reactions. This combination of properties makes it difficult to predict the chemistry of iodine in reactor fault conditions (apart from within a narrow range of conditions studied experimentally) without use of a computer model incorporating all the appropriate chemistry of iodine.
In addition to chemical aspects, allowance has to be made for mass transfer effects between vapour and aqueous forms which depend on the state of dispersion of the water, for example as aqueous aerosol, spray droplets or pools. Such a computer code called INSPECT (IodiNe SPECiation and Transport) has been developed at Harwell for the prediction of iodine behaviour in PWR LOCA faults.

However, use of such complicated models can have drawbacks, it is sometimes difficult to analyse the computed results in order to understand precisely why the result is as predicted, and in those circumstances agreement between model and experiment may occur by chance. Before being used with confidence a model has to be validated as far as is practical and be fully documented, both for those unfamiliar with it, and to allow incorporation of new aspects of phenomena.

The rest of this paper is concerned with the validation of the reaction scheme from the INSPECT code by comparison of model predictions with a range of laboratory data both from our own work and from the literature.

2. COMPUTER MODELLING

2.1 Background

There are essentially two different philosophies for the modelling of the complex chemical behaviour of a species, in this case iodine. First there is the empirical approach which uses correlations to model the system. There are two such models being developed, IMPAIR now being developed in Switzerland and IODE in France. Second there is the mechanistic approach which describes the chemistry in terms of the fundamental reactions which are involved. Such an approach is that adopted for the LIRIC (AECL Canada) and INSPECT (Harwell) codes.

There is of course a compromise whereby the model is basically mechanistic, but some of the mechanistic information derived are empirically formulated to fit the data and thus the model has reduced physical significance. An example of this is the TRENDS code which is being developed at ORNL.

The philosophy behind the development of INSPECT was to develop a model which was as far as possible mechanistic and to incorporate all the known inorganic reactions of iodine apart from those quite obviously outside the range of conditions in faults, for example strongly acid or alkaline solutions (although these can be simply incorporated at a cost of increased computing time if required). Obviously such a choice of reactions is to some degree done by best judgement, but in practice the range of equations included more than covers the range of conditions expected in a fault. This fact is important when employing empirical models which only cover the data base used to make the correlation and may subsequently need to be used by modellers with insufficient experience to know whether it is applicable in the particular circumstance under study.

A trivial example of this is that the rate of production of iodine from irradiated aqueous iodide solution is dependent on iodide concentration. In most experimental studies a concentration of $10^{-4}$ M I$^{-}$ was used, however there may be conditions when the iodide concentration is higher and in practice the production rate of iodine also increases. Such effects should be reasonably accurately modelled by mechanistic models but are unlikely to be adequately covered by empirical ones.

2.2 INSPECT

The INSPECT code is completely mechanistic, with a reaction scheme consisting of 140 reactions to cover the range of conditions of interest.

The model used for the comparison of prediction with experimental data contained only
part of the INSPECT code, as the whole program allows for a wide range of physical states of iodine eg. aerosol, pool, vapour etc. which are not applicable here. A smaller program consisting of the INSPECT reaction set and sections to calculate equilibrium constants and other run dependent parameters, was used and we refer to this model as INMECH.

Both INSPECT and INMECH are based on the high level FACSIMILE/CHEKMAT programming language which is essentially a facility which uses chemical equations as input in the form in which they are normally written and understood rather than as mathematical formulae. These equations are translated into their implied differential equations by the FACSIMILE/CHEKMAT code which are then solved by numerical integration methods. Thus the programs INSPECT and INMECH can be considered as data bases for subsequent numerical integration processes. The FACSIMILE/ CHEKMAT program is written in FORTRAN and the INMECH code will run on a range of computers including IBM compatible PCs. INSPECT is a rather more complex program and requires the facilities of computers such as VAX, SUN or mainframe systems.

It is not intended that this paper should be a user guide to the programs, but basically all the programs involving chemical equations for FACSIMILE/CHEKMAT are divided into five sections with the following tasks

1. The declaration of names of variables and parameters.
2. The calculation of initial values of parameters and variables; this section is only used once.
3. The calculation of time dependent parameters; this occurs several times during an integration step.
4. The advancement of integration indicated by chemical equations, by one time step.
5. Control of output.

3. INORGANIC IODINE CHEMISTRY

The detailed chemistry of iodine will not be discussed here, however the following description should be sufficient to allow a qualitative discussion of the comparison of model predictions with experiment. Although iodine can exist in a variety of oxidation states from −1 (I−) to +7 (IO7−) many of the intermediates are unstable and are only inferred by analogy with the chlorine and bromine systems. The following reactions should serve to give an indication of the most important processes.

In aqueous solution, I2 can be hydrolysed to HOI.

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$$  \hspace{1cm} (1)

HOI is thought to ionize to form the hypoiodite ion

$$HOI \rightleftharpoons H^+ + IO^-$$  \hspace{1cm} (2)

The hypoiodite ion can then disproportionate to the iodite ion

$$IO^- + IO^- \rightleftharpoons IO_2^- + I^-$$  \hspace{1cm} (3)

c this is then followed a rapid further reaction to form the iodate ion.

$$IO_2^- + IO^- \rightleftharpoons IO_3^- + I^-$$  \hspace{1cm} (4)

These reactions also occur with HOI replacing some or all of the IO− ions. The reverse of reactions (1) to (4), the reaction of the iodide ion with the iodate ion in acid solution to form I2 is often known as the Dushman reaction, however the mechanism for the reaction is still the subject of much debate and is certainly not the reverse of reactions (1) to (4) as written above.
Hydrogen peroxide is a radiolysis product which can both react as an oxidant with I\textsuperscript{−} and can itself be oxidised by reaction with IO\textsuperscript{−}. The oxidation of iodide occurs by a reaction which may be written as reaction (5) although the product may be HOI,

\[ \text{H}_2\text{O}_2 + \text{I}^− \rightarrow \text{IO}^− + \text{H}_2\text{O} \]  

(5)

and the reduction of IO\textsuperscript{−} by reaction (6) although the reaction is in doubt (see appendix)

\[ \text{H}_2\text{O}_2 + \text{IO}^− \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{I}^− \]  

(6)

Radiolytic reactions of iodine are very complex and all are needed to model all the features accurately, however the essence of the scheme is incorporated in the following reactions.

The iodide ion can be oxidised by the hydroxyl radical OH\textsuperscript{−}.

\[ \text{I}^− + \text{OH}^− \rightarrow \text{OH}^− + \text{I}^− \]  

(7)

This is followed by further reaction with iodide to form the radical anion

\[ \text{I}^− + \text{I}^− \rightarrow \text{I}_2^− \]  

(8)

which in turn disproportionates to give ultimately iodine and iodide.

\[ \text{I}_2^− + \text{I}_2 \rightarrow \text{I}_2 + 2\text{I}^− \]  

(9)

Two other radiolysis products, the hydrogen atom (H\textsuperscript{−}) and the hydrated electron (e\textsubscript{aq}\textsuperscript{−}) both react with oxygen in aerated solution to give the peroxy radical HO\textsubscript{2}\textsuperscript{−} or O\textsubscript{2}\textsuperscript{−} depending on pH.

\[ e\textsubscript{aq}^− + \text{O}_2 \rightarrow \text{O}_2^− \]  

(10)

\[ \text{H}^− + \text{O}_2 \rightarrow \text{HO}_2^− \]  

(11)

The two species are in acid/base equilibrium

\[ \text{HO}_2^− \rightleftharpoons \text{O}_2^− + \text{H}^+ \]  

(12)

Molecular iodine can then be reduced to I\textsubscript{2}\textsuperscript{−}, according to reaction (13)

\[ \text{I}_2 + \text{O}_2^− \rightarrow \text{I}_2^− + \text{O}_2 \]  

(13)

The radical yields, usually denoted by G-value eg. G\textsubscript{OH}\textsubscript{−} (G value = no. of species per 100eV of absorbed radiation energy) are G\textsubscript{OH} = 2.8, G\textsubscript{e\textsubscript{aq}^−} = 2.7, G\textsubscript{H\textsuperscript{−}} = 0.6 and the yield of the molecular product, hydrogen peroxide G\textsubscript{H\textsubscript{2}O\textsubscript{2}} = 0.7.

It should be noted that G\textsubscript{OH\textsuperscript{−}} < (G\textsubscript{e\textsubscript{aq}^−} + G\textsubscript{H\textsuperscript{−}}) and as a result, on the arguments presented above, the system should not be oxidising. However the system is oxidising at least at pH < 7 and this is because of one further reaction

\[ \text{H}_2\text{O}_2 + e\textsubscript{aq}^− \rightarrow \text{OH}^− + \text{OH}^− \]  

(14)

whereby a reductant is turned into an oxidant.

The above reaction scheme can explain qualitatively the trends observed in the experimental data used in the comparison in the next section, section 4.

The iodine yield from the radiolysis of iodide solution is seen to fall as temperature increases, which may be explained by assuming that although the reaction of H\textsubscript{2}O\textsubscript{2} to produce I\textsubscript{2} is more favorable at elevated temperature, the back reaction, reaction (6), is also more favorable at elevated temperature, the net effect is to reduce the amount of H\textsubscript{2}O\textsubscript{2} and
thus reduce the amount available for reaction (14). This in turn leads to less OH\(^-\) and less overall oxidation.

A second and even more marked effect is that of pH; if the pH is raised from pH 4.6 (0.2 M boric acid) to pH 7, the iodine yield falls by a factor of between 30 and 1000 depending on which experimental data are taken. Again this can be explained by reaction (6) which becomes more favorable as pH increases, mainly because of more hydrolysis of I\(_2\) to HOI through reaction (1) and subsequent ionization through reaction (2).

The formation and reaction of hydrogen peroxide is thus important because it holds the key to the balance between oxidising and reducing systems. And additionally, because it is stable enough to persist for considerable periods after irradiation, it can influence post-irradiation reactions and this can be a source of discrepancies between model predictions and experimental data.

4. COMPARISONS OF MODEL PREDICTIONS WITH EXPERIMENT

The choice of data for the comparison of the model with experiment was made on the following basis. First, the model will be applied to our own experimental data, where experimental conditions were chosen to span as closely as possible the range of conditions thought to apply in a LOCA fault.

Second, data from other laboratories were chosen where suitable, that is under conditions not too remote from those anticipated in faults and those not requiring too much extra programming which may then distort the overall reaction set. For example the majority of data from Lucas either requires extra mass transfer effects or the incorporation of carbon dioxide and caesium carbonate equilibria, which are beyond the scope of this exercise.

Because radiolytic reactions dominate in the oxidation processes, most of the comparisons consider radiolytic phenomena.

An important point to be noted at the outset is that it was not our intention to aim to obtain an exact coincidence of our predicted data and the experimental data by fine tuning those aspects whereby this could be achieved, for example by careful choice of elapsed time between end of irradiation and measurement. Our aim was to show an agreement to within reasonable limits and to show that the model predicted the main trends observed by varying pH and temperature.

A matrix showing the experimental conditions used for comparison with the model is given below.

<table>
<thead>
<tr>
<th>Source</th>
<th>Harwell</th>
<th>ORNL Radiolysis</th>
<th>Sawai</th>
<th>Lucas</th>
<th>Ishigure</th>
<th>ORNL Thermal</th>
<th>Harwell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>4.6</td>
<td>4/5</td>
<td>6.5</td>
<td>5.3</td>
<td>7</td>
<td>7/8</td>
<td>4.6</td>
</tr>
<tr>
<td>Temp. (Celsius)</td>
<td>25 50 70</td>
<td>90</td>
<td>20</td>
<td>43</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Initial iodide conc (micro mol.)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>1000</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial iodate conc (micro mol.)</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final dose (kGy)</td>
<td>25</td>
<td>30</td>
<td>1.9</td>
<td>20</td>
<td>35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.1 Comparison of model with Harwell radiolysis data

Data obtained from the radiolysis of CsI solutions have been reported.[1] Included here are comparisons of the model predictions for the temperature dependence of the production of I$_2$ from the irradiation of 10$^{-4}$ M CsI in 0.2M boric acid, pH 4.6 at a range of doses up to 25 kGy. The comparison of data with experiment is shown in fig. 1. In this case the model was constructed so that the simulated irradiation was turned off at the set dose and post-irradiation reaction allowed to occur for 20 minutes at the irradiation temperature. It can be seen that the agreement at 30°C is very good and at both 50°C and 70°C the model under-predicts the formation of I$_2$ by a factor of 40% at doses less than 10kGy.

Because there is some post-irradiation reaction, the effect of time and temperature at the end of irradiation was investigated using the model and the results are shown in figs. 2 and 3. Figure 2 shows the effect of maintaining the irradiation temperature after irradiation whereas figure 3 shows the effect of immediate cooling to 20°C. The similarity between the data in figures 2 and 3 shows that post-irradiation temperature is not an important factor in the simulation at this pH, but that the time interval before analysis is. These figures illustrate clearly why no attempt was made to optimise the fit. This would not be particularly helpful as it is far more instructive to note the span of iodine concentrations between the two extremes of no reaction and complete reaction. In this case the model predicts a span of iodine concentrations which increases as a proportion of the initial iodide concentration with increasing temperature.

Fig. 4 shows a comparison of model and experiment for the radiolysis of CsI0$_3$ solution. The model over-predicts the fall in concentration of iodate with increasing dose, although the initial trend is correct. It was noted that if a higher dose rate is used in the model (but the experimental doses) a much better fit is observed as shown in Fig. 5. The poor modelling of iodate radiolysis is not unexpected because this system is inherently more complicated than the iodide system because it involves the change in oxidation state from 0 or +1 to +5 (or the reverse), the intermediates are unstable and reactions are largely conjectural. The radiation chemistry of iodate is discussed in detail in ref 2. It is not surprising that the intermediates in the radiation chemistry of iodate are conjectural, as also the nature of the intermediate in the thermal reaction of iodide with iodate to form iodine is also uncertain. The reason for the apparent dose rate effect is not clear, it is possible that some thermal reaction is involved such as a reaction of H$_2$O$_2$ with one of the intermediates.

In conclusion, the data for CsI radiolysis are modelled to within a factor of 2 and the trend observed of decreasing iodine with increasing temperature is well modelled. The modelling of iodate radiolysis is not so good, but in general iodate is not an important species as it is not a stable radiolysis product apart from in very dilute solution.

4.2 Comparison of model with radiolysis data from Beahm et al.

The data from of Beahm et al. were in the form of a private communication. The data modelled are for 10$^{-4}$M I$^-$ at 92°C and pH 4 and 5. The comparison of data with experiment are shown in figs. 6 and 7. There is some scatter in the experimental data and in these cases shown in figures 6 and 7 post-irradiation reaction was not modelled, but even so it can be seen that the model prediction is accurate to within a factor of 2 of the amount of I$_2$ and additionally it adequately models the observed fall in I$_2$ concentration by a factor of 10 on increasing the pH from 4 to 5. The variation of iodine yield with time after irradiation for a dose of 1 MRad is shown in figs. 8 and 9, again the post-irradiation reaction would appear to be over emphasised particularly at pH 5. In these simulations the temperature was set to 25°C immediately after radiolysis; a period at 92°C would be more realistic and may give a less dramatic fall in I$_2$ concentration because oxidation of I$^-$ by H$_2$O$_2$, reaction (5), would be more favorable.
4.3 Comparison of model with data from Sawai et al.

Sawai et al. investigated the radiation chemistry of KI solutions over a range of conditions of pH and temperature, not only measuring I₂ but also H₂O₂, O₂ and H₂.[3] This study used buffered solutions and it is very difficult to model the radiation chemistry in such solutions because of pH changes resulting not only from the changing solution chemistry but also as a result of glass dissolution and the subsequent effects of silicic and boric acids. The data chosen for comparison were taken from Fig. 1 of their report and are for the irradiation of 10⁻⁴ M KI at pH 6.5. A comparison of model prediction and data and are shown in Figs. 10 and 11. It can be seen that the fit for all four radiolysis products is particularly good for this example, but this is probably fortuitous because of the problems in pH modelling mentioned above. Iodine radiation chemistry is particularly sensitive to pH because of the peroxide reactions, and in reality a worse fit would have been expected.

4.4 Comparison of model with data from Lucas

Although there is a considerable amount of published data by Lucas very little of it is suitable for modelling with this version of the code which has no mechanism for mass transfer considerations.[4] Most of his work was carried out in double tube experiments whereby volatilised iodine was trapped in a separate tube. This would require a considerable modelling exercise to simulate. Additionally many experiments were carried out using solutions containing saturated H₂ or CO₂ with Cs₂CO₃ present. Table 1. shows the comparison of one of his data points for 10⁻³ M CsI, pH 5.5 at 43° C. It does at least show that his datum compares well with our prediction for the higher I⁻ concentration.

4.5 Comparison of model with data from Ishigure et al.

As with the work of Sawai et al., Ishigure et al. used buffered solutions.[5] In their experiments 10⁻⁴ M CsI solution was irradiated in deaerated and aerated conditions. The data are shown in figures 12-14. In this case we predict significant post-irradiation reaction which apparently was not seen to occur to this extent. This over-emphasis of post-irradiation reaction suggests that the reaction of I₂ with H₂O₂ is not well modelled, this is discussed in the appendix, but one possible factor is that the reactions are catalysed by buffers and Ishigure, who used buffered solutions, found lower values for the relevant rate constants than Liebhafski who used phosphate buffer and whose rate constants are used in this model. Again these results may also be influenced by effects of dissolution of glass giving rise to small amounts of buffering silicic and boric acids, which would tend to lower the pH, increase the iodine yield and reduce the post-irradiation effect of H₂O₂. Even with the post-irradiation reaction the comparison of model and experiment shows they generally agree to within a factor of 4-5. These data should be compared with data described in section 4.1 where the same concentration of iodide was used but the pH was 4.6 rather than about 6.6 and the iodine yield was a factor of 30 greater. As the iodine yield under these conditions is much lower, in practice it would probably not present such a significant radiological hazard as at lower pH. The extra uncertainty in the model is probably not so significant although this does highlight an area where the data in the model are unsatisfactory and where further experiments are required.

The production of iodate from irradiated solution was not at all well modelled. The radiation chemistry of iodate is far more complicated than that of iodide and the mechanisms are not very well understood. In Ishigure’s paper it is not clear how iodate was measured and whether the presence of peroxide would affect the analytical results.
4.6 Comparison of model with thermal data from Beahm et al.

As with the radiolysis data of Beahm et al., these data from ORNL are in the form of a personal communication. The data are for the reactions involving the hydrolysis and disproportionation of iodine the so called 'reverse Dushman' reaction.

Figs. 15 and 16 show iodate formation from I\(_2\) hydrolysis and disproportionation at pH 7 and 8 (assuming that the solution was buffered and the pH did not change). The comparisons at pH 7 and pH 8 are good. There is some doubt as to whether the pH was constant throughout the experiment, which would affect the quality of the fit.

4.7 Comparison of the model prediction with Harwell thermal data

Fig. 17 shows a comparison of model with data from Harwell for the reaction of iodide with iodate to form iodine, the 'Dushman reaction'. The comparison shows good agreement between model and data. This reaction although known for many years has been the subject of much controversy; the overall reaction may be represented by

\[
5I^- + IO_3^- + 6H^+ \rightleftharpoons 3I_2 + 3H_2O
\]  

(15)

which gives no indication of the mechanism of the reaction. It is generally thought to be overall fifth order

\[
\text{Rate} = [I^-]^2[H^+]^2[IO_3^-]
\]

and in this model the rate measured by Palmer and an intermediate represented by H\(_2\)I\(_3\)O\(_3\) is used which then rapidly and irreversibly reacts with iodide and H\(^+\) to form I\(_2\) although the true mechanisms are unknown.[6]

5. DISCUSSION

Clearly section 4 in general showed good agreement between the model prediction and experimental data including effects of temperature and pH, and there is little to be said where agreement was good.

There are however some reservations:

1) The model predicts considerable post-irradiation reaction which is exaggerated by the model, for example in sections 4.2 and 4.5, which has not been studied experimentally in detail and will require investigation. Although there is a considerable amount of data on hydrogen peroxide/iodide reactions, the significant influence of its chemistry suggests that further careful experiments using boric acid solutions would be desirable; for a further discussion of these reactions see appendix.

2) There is evidence, not presented here, that the high temperature (>100°C) chemistry of iodine is not so well reproduced by our model and there are a number of effects such as surface reactions which could account for this but which are not in the model.

3) The radiation chemistry of iodate is also not well reproduced by the model, shown in section 4.1, which is not surprising because of the oxidation state change involved and although the iodate ion may not be a significant product in a fault, care should be taken if conditions prevail for which its formation could be of significance, or where the model predicts it to be significant.

Clearly these are three aspects of the chemistry of iodine which require further investigation and show where additional data for use in the model is required. It is possible that the potential problems referred to in items 1 and 3, both of which involve aspects of the chemistry of the hypoiodeite ion, are connected and the rate data involving IO\(^-\) are inferred from the equilibrium constants involving these species, and in some cases are suspect.

Although not included here, there is now a considerable amount of data from the large scale ACE radio-iodine test facility (RTF) tests which could be used in further
comparisons. Some of the results are difficult to interpret because of large amounts of organic material present, but an additional test has been carried out in the absence of organics at pH 8 and pH 5 which are potentially useful additional data. Another aspect of these data are the use of large gas volumes (300 L) over a solution volume of 30L both of which were monitored for changes in iodine concentration with time, which provides a test for the mass transfer aspects of the model.

6. CONCLUSIONS

This work has successfully demonstrated that the INSPECT chemical reaction set adequately models the radiation chemistry and most of the thermal chemistry of iodine over a wide range of conditions of pH and temperature to which the chemistry of iodine is particularly sensitive. These conditions of temperature (30°C – 90°C) and pH (4.6 – 8) are generally those expected for fault conditions.

The work gives confidence in the reaction scheme in two ways.

First the prediction of the trends of decreasing I₂ production both with increasing pH and and with increasing temperature shows that the reaction set incorporates sufficient reactions to span the conditions of interest and also that no major reaction has been omitted.

Second the good quantitative agreement between prediction and experimental data from our own laboratory and independent data from overseas gives confidence in the use of the model for the quantitative prediction of iodine chemistry not only in laboratory conditions but also in faults.

There are two aspects of uncertainty. In particular the reactions of hydrogen peroxide are suspect and it would need an experimental programme to resolve the kinetics and mechanisms. The radiation chemistry of iodate is also uncertain but is probably not so important as iodate is only important at low concentrations where the radiological hazard is reduced.

7. ACKNOWLEDGEMENTS

This work was funded by Nuclear Electric PLC. In particular we acknowledge the helpful comments and discussions with Dr. EW Thornton and Dr. WG. Burns.

8. REFERENCES
(11) K.J. Morgan, Quart. Rev. 8, 123, 1954.
APPENDIX The iodine/hydrogen peroxide reaction.

The reactions of $\text{H}_2\text{O}_2$ with iodine that are of interest here are generally thought to be:

$$
\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{IO}^- + \text{H}_2\text{O} \\
\text{H}_2\text{O}_2 + \text{IO}^- \rightarrow \text{I}^- + \text{O}_2 + \text{H}_2\text{O}
$$

(16)  

(17)

The kinetics of reaction (16) have been reasonably well studied although there must be some doubt as to the actual mechanism as it could also be written

$$
\text{H}_2\text{O}_2 + \text{I}^- \rightarrow \text{HIO} + \text{OH}^-
$$

(18)

Reaction (17) has not been so well studied. The only study in neutral or alkaline solution reported in detail was by Liebhafsky who derived a rate constant of ca. $1.5 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$. [7] Another measurement with no discussion of methods was by Ishigure who reported a value a factor of 100 lower. [8] In a conference discussion he also mentioned catalytic effects of buffers which may account for the different rate constants since Liebhafsky used 0.2M phosphate buffer. Phosphate has been shown to catalyse the disproportionation of iodine in alkaline solution and so catalytic effects in the peroxide system would not be surprising. [9]

Because $\text{IO}^-$ cannot be observed directly the rate constant was derived through use of its equilibrium reactions with $\text{I}_2$

$$
\text{I}_2 + \text{OH}^- \rightleftharpoons \text{HOI} + \text{I}^- \\
\text{HOI} \rightleftharpoons \text{H}^+ + \text{IO}^-
$$

(19)  

(20)

and so

$$
\frac{d[\text{I}_2]}{dt} = \frac{K' [\text{I}_2][\text{H}_2\text{O}_2]}{[\text{H}^+]^2[\text{I}^-]}
$$

where $K' = k_{17} K_{E10} K_{E20}$

Another factor for consideration arises from work by Cahill and Taube who found that all the $\text{O}_2$ liberated by this reaction arose solely from the $\text{H}_2\text{O}_2$ and they dismissed the reaction of hypoidite (reaction 17) as the mechanism for this reaction. [10] There is an alternative mechanism based on the reaction of ionized $\text{H}_2\text{O}_2$ with HOI which gives radical products but which is kinetically identical. [11]

Clearly since reactions of $\text{H}_2\text{O}_2$ are crucial to the radiation chemistry of iodine it is important to resolve some of the issues mentioned above.
Fig 1. Comparison of Model Prediction with Harwell Data for the Irradiation of CsI

Fig 2. Prediction of Post Irradiation Changes at Irrad. Temp. for Harwell Conditions.

Fig 3. Prediction of Post Irradiation Changes at 20C for Harwell Expt. Conditions.
Fig 4 Comparison of Model Prediction with Harwell Data for Irradiation of CsI03.

Fig 5 Comparison of Model Prediction with Harwell CsI03 Irrad at High Dose-Rate.
Fig 12. Comparison of Predicted I2 with Ishigure Irradiation of Oxygenated CsI

Fig 13. Comparison of Predicted I3- with Ishigure Irradiation of Oxygenated CsI.

Fig 14. Comparison of Predicted I2 with Ishigure Irradiation of De-oxygenated CsI.
DISCUSSION

Shiraishi (Comments)
I have two comments. First, our experimental data which you cite in Fig. 13 of your paper was found later to be spoiled by technical artifact. Remeasurement showed much lower yield of IO3− rather in agreement with your calculation. The second comment is about the reaction between H2O2 and O1−. I agree that the true reaction may possibly be reaction of HO2− with HOI. However, I reminded of a piece of evidence which is for the reaction between H2O2 and O1−. When we wanted to confirm the rate-determining step, we found that at low buffer concentration the overall rate of reaction tends to saturate, though slightly, at high H2O2 concentration. We thought that the rate determining step began to change from the reaction between H2O2 and O1− to dissociation of HOI into H+ and O1−. The evidence is not conclusive, however, because of the scatter in the data.

Vikis
1) You seemed very pessimistic about being able to deal with organic impurities. Could you elaborate on it?
2) Upto how high a temperature do we need to worry about for containment chemistry?

Sims
1) I was probably too pessimistic. I do not think we can test diagnostics mechanistically. There must be some rationalization and empiricism. There are several ways forward but we need benchscale data such as from AECL Whiteshell, Toronto or JAERI.
2) Probably about 150°C depending on accident scenarios.

Kupferschmidt
You have listed several areas where uncertainty in iodine chemistry remain. I agree with your assessment, however, one area you do not mention is the role of inorganic impurities. Could you comment on their importance to iodine chemistry, particularly under acidic pH conditions?

Sims
The effect of organic impurities is unclear. Inorganic impurities have been tested at Harwell. Molybdate and Mn2+ have been shown to reduce I2 production because of decomposition of H2O2. Concrete also reduces I2 because it is alkaline. In3+ and Fe2+ enhance I2 production at pH 4 to 6, it should be noted that they are multivalent and can alter the redox balance of the system. At alkaline pH these would be expected to be insoluble. There is alkaline systems I would expect impurities to have no detrimental effect and may well be beneficial.

Ishigure
I agree that we don't have enough data on temperature dependence of the relevant reaction rates. You are doing some calculations at higher temperature. How do you decide the rate constants? I would like to give one comment that all our experimental data come from unbuffered systems. In these systems, especially at neutral, we found funny pH changes of the systems. If I− is converted to I2 by radiation, pH should go to alkaline side. Actually we found pH shifted to acidic side. We think this is probably due to glass wears
in the experimental systems. This pH difference gives strong effect in the simulation. So we should be very careful when we make calculations on unbuffered and neutral systems.

Sims
Temperature dependence of rate constants is included in the model but is rather arbitrary. It is probably not important in radiolysis reactions but is important in thermal reactions such as that with H₂O₂, but in this case the room temperature rates and mechanisms are not known adequately and the temperature dependence is certainly not known. I agree that glass tends to wear and buffer the pH in irradiation fields,

Bowsher
Further to Andy Vikis's comments on high temperature processes, would you care to comment on the validity of some of the iodine models for evaporating solutions. In particular, I am thinking of concentrating solutions of boric acid which form complex polyborates, resulting in enhanced acidities.

Furrer
Swiss REFUND experiments showed a rapid decrease of the percentage of HI formed with increasing pH. Negligible volatilization occurs roughly above pH of 5. Effects of this reaction are therefore unimportant compared to the large I₂-production during evaporation of low pH.
5.3 VALIDATION OF THE IODE CODE ON ANALYTICAL EXPERIMENTS

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ABSTRACT

The ESCADRE system is a set of computer codes dedicated to realistic source term assessments in the case of water reactor severe accidents. In this system the IODE code is devoted to the containment iodine physico-chemistry. In the frame of iodine chemistry, a small scale experimental programme has been performed in CEA. Solutions of CsI or KIO₃ were submitted to γ irradiation at two temperatures 43°C, 95°C and various pH.

The paper is focused on the validation of IODE using the experimental results of this small scale programme. Three types of experiments are described and for each of them the following items are presented:

- modelling adopted,
- description of the calculated results for a typical case,
- comparisons of measurements and calculation for several experiments.

The interpretation of the experimental results by the code has led us to take into account: the interaction of I₂ with immersed paints, the IO₃⁻ radiolysis and to improve the modelling of pH effect on radiolysis reactions.

This work is still progress to extend the validity of the code for other conditions.
- a fixed mass transfer coefficient chosen by the code user, the Hewison data are recommended [4].

The temperature \(T\) in \(^\circ\text{K}\) dependence of the partition coefficient (equilibrium aqueous concentration / equilibrium gaseous concentration) is:

for I\(_2\) [5]: \[ H^* I_2 = 231 \exp(1.651017 \times 10^{-4} (T - 571.243) (T - 273.15)) \]

for CH\(_3\)I [6]: \[ H^* CH_3I = \exp(-6.97 + 2.641 T^{-1}) \]

b) Iodine dragging by steam condensation. The condensation rates on wall and water are issued from the JERICHO calculation, the volatile removed species are collected in the aqueous phase.

c) Leak rate.

d) I\(_2\) source to the gas phase: the mass flow rate is issued from a primary circuit calculation.

e) I\(^-\) source to the aqueous phase the mass flow rate is calculated by AEROSOL B2.

f) I\(_2\) deposition on surfaces.

(f\(_1\)) 3 types of surfaces for the gas phase

(f\(_2\)) 3 types of surfaces for the aqueous phase

The surfaces are defined by their area and I\(_2\) deposition velocity.

1.2 - Chemical reactions

* Iodine species

- aqueous phase \( I_{2w} \) \( CH_3I_w \) \( IO_3^-w \) \( HOI_w \) \( I^-w \) \( AgI_w \)
- gas phase \( I_{2g} \) \( CH_3I_g \) \( I_{4Og} \)
* Chemical reactions in the gas phase

(1) I₂ oxidation by O₃ radiotically formed
(2) CH₃I formation

* Chemical reaction in the aqueous phase

(3) I₂ hydrolysis classical inorganic aqueous iodine
(4) HOI dissociation chemistry : Bell modelling [7]
(5) HOI disproportionation

(6) I⁻ oxidation (by O₂ dissolved in water)
(7) I⁻ radiolytic oxidation
(8) CH₃I formation
(9) CH₃I radiolytic decomposition
(10) AgI radiolytic decomposition
(11) AgI formation
(12) CH₃I hydrolysis H₂O
(13) CH₃I hydrolysis (OH⁻)
(14) IO₃⁻ radiolytic reduction

The figure 3 gives a simplified scheme of the code IODE modelling.

1.3 - Code organization input and output data

The program solves a set of 22 differential equations using the solver STEP (Adam Pece method) [8]. The chart flow of the code is given in figure 2.
The object of the subroutines is the following:

**CLASN** : Arrangement of array values in increasing order

**DXDT** : Computation of the variables derivatives

**FCOND** : Computation of the thermal conductivity of gas mixture

**FCP** : Computation of the specific heat of gas mixture

**FDET** : Computation of equations coefficients f(i)

**FDIFG** : Computation of steam diffusion coefficient in a gas mixture

**FIL** : Linear interpolation in a table

**FVISC** : Computation of viscosity of a gas mixture or of each gas in the mixture

**INIT** : Initialisation of variables

**KC** : Computation of iodine transfer coefficients between water and gas

**LIRE** : Read of data

**LECTAB** : Read a table

**PAGE** : Print first page of the listing

**SAUVE** : Manage storage of results by blocks of 50 time steps

**SOLUT** : Manage computation

**SORTIE** : Manage results printing and storage

**STEP** : Resolution of differential equations system

\[ \frac{dx(i)}{dt} = f(i)(x_1, ..., x_n, t) \]

The time dependant data are: water temperature, gas temperature, total pressure, steam partial pressure, atmosphere composition, I\(_2\) source, I\(^-\) source, leak rate, condensation mass flow rate, pH, dose rate.
The other data are: geometry (volumes and surfaces), deposition velocities, initial concentration of chemical species. The output data at different times are divided in four groups:

- species concentrations in the gas phase,
- species concentration in the aqueous phase,
- iodine mass in the gas phase, in the aqueous phase, on the different surfaces,
- iodine fluxes and iodine partition coefficient.

2 - IODINE CHEMISTRY CEA ANALYTICAL PROGRAM

About 100 ml glass vessels filled with a solution of CsI or KIO₃ were exposed to two temperatures, 43°C and 95°C, with γ irradiation at a dose rate of 0.4 MRh⁻¹ and for different doses 2 MR, 6 MR, 24 MR.

The parameters for the aqueous solution were I concentration, boric acid concentration, Cs₂ CO₃ concentration. The gas above the solution was composed of air, air carbon dioxide or air carbon dioxide hydrogen mixtures. Measurements were made of I₂, IO₃⁻, I⁻ concentrations after irradiation and pH before and after irradiation.

The test conditions are summarized in the next section for more details see references [9] [10] and [11].

3 - IODE VALIDATION

3.1 - One compartment experiments

3.1.1 - Basic case

This type of experiment is schematized figure 4, the main characteristics of the test are:

- initial solution : I⁻ 10⁻³ M/l,
- dose rate D : 0.4 MR/h ; pH : 4.8 ; temperature : 43°C,
- test duration : 60 h (dose : 24 MR),
- liquid phase volume : 5 ml, gas phase volume : 100 ml.
The modelling adopted (fig. 5) leads to calculated concentrations evolution (fig. 6) characterized by the establishment of an equilibrium. This results is a consequence of the modelling choosen with no sink for any iodine species. The measurements of I$_2$ in the aqueous phase for different doses show the same tendency but the calculation overestimates the I$_2$ production (fig. 6).

3.1.2 - Other experiments : calculations and measurements comparisons

The measured and calculated (I$_2$) aqueous concentration after 60 h is the criteria adopted for the comparisons. The results are summarized in the figure 7, the different subject of this study are

- utilization of the code with its origin data,
- effect of a pH evolution during the test due to the reaction : 2 I$^-$ $\rightarrow$ I$_2$
  the loss of negative charges is compensated by an increase of OH$^-$,
- effect of the kinetic constant of I$^-$ and IO$_3^-$ radiolysis,
- effect of pH dependancy of I$^-$ and IO$_3^-$ radiolysis

3.2 - Two compartments experiments

3.2.1 - Basic case

In this type of experiment (fig. 8) one compartment is filled with a CsI solution, the second one is filled with an alkaline solution which acts as a trap for gaseous iodine I$_2$. Excepting the presence of the second compartment the characteristics of the test are identical to those described previously § 3.1.

In the modelling of these experiments (fig. 9) the trapping effect of gaseous I$_2$ by the second compartment is taken into account. The weight fraction of initial iodine in the CsI solution transferred to the trapping varies linearly with time at the beginning of the test as it has been observed experimentally figure 10. As in the case of the one compartment experiments the code overestimates the I$_2$ production.
3.2.2 - Other experiments: calculations and measurements comparisons

The experimental and calculated weight fraction of transferred iodine after 60 h are compared in figure 11. The utilization of the code with its origin data shows clearly that its overestimates the radiolysis effect and underestimates the pH effect. This suggest us to modify the equation of I₂ production by radiolysis.

- origin data

\[
\frac{d(l_2)_w}{dt} = k(l_w^*)D(H^*)^{0.25}
\]

D dose rate, same equation for IO₃⁻

- new data tested

\[
\frac{d(l_2)_w}{dt} = k'(l_w^*)D'(H^*)^{0.5}
\]

More satisfactory results are given by this new equation.

3.3 - Experiments with an immersed painted surface

3.3.1 - Basic case

The scheme of the experiment is given figure 12 and the main characteristics of the test are:

- initial solution I⁻ 10⁻³ M/l,
- dose rate D : 0.4 MR/h ; pH : 4.4 ; temperature 43°C,
- test duration : 60 h (dose 24 M.R),
- liquid phase volume : 25 ml ; gas phase volume : 100 ml,
- painted surface area : 7.6 cm².

The experimental results have shown that the main phenomena is the absorption of iodine by the painted surface, consequently we have adopted the modelling given in figure 13, the organic iodides formation has not been taken into account. The concentrations evolution are given in figure 14.

3.3.2 - Other experiments: calculation and measurement comparisons

The experimental and calculated iodine deposited fractions after 60 h are compared in figure 15. As in the previous experiments the modification of the radiolysis equation gives a better comparison.
4 - DISCUSSION

4.1 - A great number of parameters influence the iodine chemistry in the containment of a reactor in severe accident conditions:

- accident sequence,
- iodine source (amount, chemical forms),
- containment thermalhydraulic,
- radiation level,
- chemical parameters: pH, redox potential, impurities.

The ambition of IODE is to give to safety analyst people a realistic answer on the behaviour of iodine. The modelling approach is empirical specially concerning the effect of radiolysis on iodine species. The code is in a phase of development and this first step of validation on CEA analytical experiments has led us to different modifications of the initial version.

The experimental data show that the composition of the final solution is the same whatever the initial solution I\(^-\) or I\(^-\)\(_3\) is. It means that IO\(_3^-\) does not act as a sink and therefore its radiolysis has to be taken into account. In the modelling presented in Fig. 3 the radiolysis of IO\(_3^-\) leads directly to I\(_2\); in fact first kinetic results suggest an intermediate step (IO\(_3^-\) ---\(\rightarrow\) I\(^-\) ---\(\rightarrow\) I\(_2\)) but on this point we need more experimental data.

The tests with immersed painted surfaces show a strong sorption effect which has been added to the modelling.

4.2 - In the frame of the interpretation of the experiments described in section 2 and 3 we have performed sensitivity studies on:

- mass transfer,
- reaction kinetic constants,
- I\(_2\) hydrolysis and HOI disproportionation modelling,
- pH evolution during an experiment. An increasing of the pH has been experimentally observed, it can be interpreted as a consequence of the reaction I\(^-\) ---\(\rightarrow\) I\(_2\) (compensation of the electrical charges balance),
- evolution of the concentration of iodine species after a test and before the chemical analysis.
The modification of the radiolysis rate reported in the previous section has the more important effect in the improvement of the code, nevertheless the other parameters have to be taken into account.

4.3 - We have limited this validation to the main phenomena, for example the formation of organic iodides in the case of immersed painted surface experiments has been neglected. This phenomena may have an important safety impact even if the amounts of organic iodides generated are negligible compared to the iodine absorbed by the surface. The second important aspect concerning the limitation of this validation is that it has been done in a domain of concentration ($10^{-3}$ M Iodine) in which the role played by the impurities is negligible.

4.4 - The last remark concern the french position about the IODE validation strategy. The context is the following:

- Development of experimental programs
  - small scale experiments with the main objective: extension of the experimental domain (I concentration, impurities, pH, dose rate),
  - semi-scale experiments,
  - PHEBUS.FP: iodine chemistry with a realistic source

- Interpretation of this experimental programme
  - validation of IODE in an extended domain
  - organic iodides behaviour taken into account

- Participation to the ACE programme with a first priority given to the interpretation of the ACE/RTF experimental results.

- Comparison of IODE with other codes.
CONCLUSION

The study described in this paper has shown the ability of an empirical code handling with containment iodine physico-chemistry (IODE) to interpret small scale experiments.

The qualitative and quantitative representation of the experimental results has been obtained by taking into account:

- the interaction of I$_2$ with immersed paints,
- the IO$_3^-$ radiolysis,
- the adjustment of the radiolysis rate.

The validity of the code has to be extended mainly on the following items:

- behaviour of organic iodides,
- domain of concentration, pH, dose rate, level of impurities.

This work is still in progress by the interpretation of various experiments already performed or planed.

ACKNOWLEDGMENTS

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Fig 1 ESCADRE SYSTEM

Fig 2 Chart flow of the code

Fig 3 Code modelling
One compartment experiments

- Interface area: $A = 8.17 \times 10^{-4} \text{ m}^2$
- Aqueous phase volume: $V_W = 5.0 \times 10^{-3} \text{ m}^3$
- Gas phase volume: $V_g = 1.0 \times 10^{-4} \text{ m}^3$
- No surface deposition

Fig 4 Geometry

Fig 5 Modeling

Fig 6 Basic case

Fig 7 Experimental results calculations comparison
Two compartments experiments

**Fig 8 Geometry**

- Interface area: \( A = 8.836 \times 10^{-4} \text{ m}^2 \)
- Trapping surface: \( A_t = 7.854 \times 10^5 \text{ m}^2 \)
- Aqueous phase volume: \( V_w = 5.0 \times 10^{-4} \text{ m}^3 \)
- Gas phase volume: \( V_g = 1.0 \times 10^{-4} \text{ m}^3 \)

**Fig 10 Basic case**

**Fig 9 Modeling**

- Transferred fraction (measured)
- Water phase
  - Measured
  - Calculated
- Aqueous solution

**Fig 11 Experimental results calculations comparison**

- Graph showing transferred fraction (measured) vs. transferred fraction (calculated)
Experiments with immersed painted surface

\[ A = 4.9 \times 10^{-4} \text{ m}^2 \]
\[ A_p = 7.8 \times 10^{-4} \text{ m}^2 \]
aqueous phase volume: \[ V_w = 2.5 \times 10^{-5} \text{ m}^3 \]
gas phase volume: \[ V_g = 7.5 \times 10^{-5} \text{ m}^3 \]

**Fig 12 Geometry**

**Fig 13 Modelling**

**Fig 14 Basic case**

**Fig 15 Experimental results calculations comparison**
DISCUSSION

Evans

1) It appears that accounting for the pH shift helped improve the agreement between the experiments and IODE. Did you apply your sensitivity analysis to see whether varying the rate of mass transfer could do the same?
2) Are the pH values you report initial or final pH and how much did the pH shift?

Hueber

1) Yes we did. The analysis of this effect is in progress.
2) They are initial value. They shift of about 0.5.

Vikis

I noticed you use the reaction of I$_2$ with O$_2$ to form I$_3$O$_6$(s) as a means of suppressing gas-phase iodine. We proposed this reaction at the First Iodine Workshop. I also suggest that the reaction of oxygen atom with I$_2$, which is about a million times faster, should contribute to this mechanism.

Hueber

We shall examine this suggestion.
5.4 MODELLING OF IODINE CHEMISTRY: THE LIRIC DATABASE

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ABSTRACT

The LIRIC (Library of Iodine Reactions in Containment) database was developed to provide a better understanding of the behaviour of iodine under conditions relevant to reactor accidents through mechanistic modelling. It has undergone significant changes since it was first presented at the last CSNI workshop on iodine chemistry and now includes better reaction kinetic data for various thermal and radiolysis iodine reactions, a revised mass transfer model and a new reaction set, which addresses some of the recent Radioiodine Test Facility (RTF) test results. This paper describes tests of the validity of some of the LIRIC reaction schemes and highlights where sensitivities are. The reaction set for water radiolysis seems satisfactory. The paper then discusses several important reactions of iodine species with hydrogen peroxide and, by modelling results from RTF experiments, suggests a plausible reaction model and range of rate constants. However, these reactions are not really understood sufficiently for mechanistic modelling purposes. Finally, the paper describes a crude reaction scheme for organic radiolysis reactions that has been added to test the possible effect of organic oxidation reactions on the pH, dissolved oxygen and iodine volatility. This reaction scheme also requires much more work before it is sufficiently well established for mechanistic modelling.

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1. INTRODUCTION

Radiiodine is one of the most hazardous fission products to be released during a reactor accident. Because of its radiological significance, the ability to predict its behavior is important. In accidents, iodine would be released as CsI, which, being involatile and water soluble, would yield iodide ion upon contact with either blow-down aerosol or with the sump water. Oxidation of the iodide ion can lead to the formation of volatile molecular iodine (I₂) and thus increases the probability of iodine release to the environment.

One important mechanism for this oxidation is radiolysis [1-5]. The complex chemistry of iodine, with its extensive range of oxidation states, means that any mechanistic model must include most of the iodine reactions if it is to be used for predictive purposes over a wide range of conditions. An additional benefit of such a model is that it can act as an aid to highlight the important processes. It can be used to show where data are inadequate and where more experimental work is required. Thus, the LIRIC (Library of Iodine Reactions in Containment) model, which describes the thermal and radiation chemistry of water, iodine, other solutes and/or surfaces, has been and is continuously being developed and used for these purposes [6].

This paper describes work on the LIRIC model to test the validity of some of its reaction schemes and to highlight those areas where additional fundamental work is required before a mechanistic scheme can be used confidently for predictions.

2. BACKGROUND

Laboratory investigations of the radiolytic oxidation of CsI in aqueous solution have shown that this oxidation depends on I⁻ concentration, temperature and pH [1,2]. They have also shown that most of the dependence on these parameters is due to different reactions of hydrogen peroxide. Experiments in our integrated test facility, the Radiiodine Test Facility (RTF), have also confirmed that iodine volatility is strongly influenced by the effect of pH, including pH changes occurring during a test, and the influence of surfaces on the iodine volatility [7-11]. Each of these features and its implications for the LIRIC model is described in this paper.

3. RADIOLYSIS OF WATER

In dilute solution, the situation expected in a reactor accident, water radiolysis is the starting point for the model. The water radiolysis model in LIRIC was originally taken from that of Boyd et al. [12]. Subsequently, Buxton et al. [13] re-evaluated the rate constants and G-values for primary radiolysis products, and some of these values were incorporated into LIRIC. Because the water radiolysis model of Boyd et al. successfully reproduced various experimental results despite using less than optimum individual rate constants, there was concern that changing some of the rate constants and G-values, without examining the model as a whole, might yield incorrect results. When tested, both data sets predicted similar results for a system containing only water; most of the calculated results were comparable within a factor of two, indicating that the water radiolysis model is fairly robust. However, the effect of
different water radiolysis data, when combined with thermal reactions, has not been examined.

It was also found during this exercise that the changes in the pH and concentrations of other species, such as \( \text{HO}_2 \), could be very sensitive to the reactions of impurities or surface reactions. The latter are known to be the source of pH changes observed during the irradiation of unbuffered water. Nevertheless, most water radiolysis models do not attempt to properly describe the pH changes because, in general, water radiolysis experiments are carried out in buffered solutions and at relatively low dose rates. This is a potential limitation of the model when simulating laboratory experiments in unbuffered solutions at near neutral pH. Nevertheless, if the pH changes are caused by surface reactions, these would be much reduced in the large volumes that would be encountered in actual reactor accidents.

4. EFFECTS OF pH

The RTF experiments for the ACE (Advanced Containment Experiments) program showed that at pH 9 there was little volatility and also little surface uptake, whereas at pH 5.5, although the amount of iodine in the gas phase was still relatively small, as much as 40% of iodine was found on gas phase surface at the end of the runs [8]. This is a good example of the effect of pH.

There are two principal iodine reactions that are pH-dependent: the hydrolysis of \( \text{I}_2 \) to form HOI,

\[
\text{I}_2 + \text{H}_2\text{O} = \text{HOI} + \text{H}^+ + \text{I}^- \tag{1}
\]

and the reactions of iodine species with \( \text{H}_2\text{O}_2 \)

\[
\text{IO}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{I}^- + \text{O}_2 \tag{3}
\]

Nevertheless, the mechanisms and rate constants for these reactions are uncertain. When Liebhafsky originally derived a value for the rate constant of reaction (3) [14], he assumed that equilibria (1) and (2) were instantaneous. This may not be true and poses a problem in modelling because accurate rate constants for both the forward and reverse reactions, not just the equilibrium constants, are required to model the pH dependence of iodine volatility. The forward and reverse rate constants of equilibrium (2) can be estimated because acid-base reaction rates are, in general, nearly diffusion controlled. Therefore, the reverse reaction for equilibrium (2) is approximately \( 10^{10} \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \), and, since the equilibrium constant for (2) is about \( 10^{-11} \text{ mol} \cdot \text{dm}^{-3} \) [15], the forward rate constant is estimated to be 0.1 s\(^{-1}\). Nevertheless, the forward and reverse rate constants of equilibrium (1) are less certain. Eigen and Kustin reported the forward rate constant to be 3 s\(^{-1}\) [16], whereas results by Palmer and van Eldik [17] suggest a rate constant of about 10\(^3\) s\(^{-1}\).

The mechanism of equilibrium (1) is also uncertain. At high pH, it has been suggested that the equilibrium occurs through \( \text{I}_2\text{OH}^- \) [16,17],

\[
\text{I}_2 + \text{OH}^- = \text{I}_2\text{OH}^- \tag{4a}
\]

\[
\text{I}_2\text{OH}^- = \text{HOI} + \text{I}^- \tag{4b}
\]
However, it is equally possible that the equilibrium occurs through \( \text{IO}^- \):

\[
\text{I}_2 + \text{H}_2\text{O} = \text{IO}^- + 2\text{H}^+ + \text{I}^- \tag{5}
\]

and equilibrium (2). The equilibrium constant of reaction (5) would be \( K_5 = K_1 K_2 \).

Furthermore, if one assumes that equilibria (1) and (2) are instantaneous, as did Liebhafsky [14], reaction (3) cannot be distinguished kinetically from

\[
\begin{align*}
\text{HO}_2^- + \text{HOI} &= \text{I}^- + \text{H}_2\text{O} + \text{O}_2 \\
\text{H}_2\text{O}_2 &= \text{HO}_2^- + \text{H}^+ \tag{6}
\end{align*}
\]

The rate constant of reaction (6) would be \( k_6 = k_3 K_2 / K_7 \).

The effect on iodine volatility of the uncertainty in the reaction mechanisms and rate constants is shown in Figure 1. Four different sub-models for the iodine hydrolysis and hydrogen peroxide reactions, listed in Table 1, were tested. Shown in the figure are the calculated steady-state \( \text{I}_2(\text{aq}) \) concentrations from a larger set of models (LIRIC) that includes water radiolysis reactions, iodine thermal reactions and the reactions of iodine with water radiolysis products, in addition to the iodine hydrolysis and \( \text{H}_2\text{O}_2 \) reactions. Surface reactions and the reactions of organics were not included. Mass transport of \( \text{O}_2, \text{H}_2, \text{I}_2 \) and \( \text{HOI} \) between the gas and aqueous phases was included. Other conditions were those of typical RTF experiments.

In model 1, an increase in the iodine hydrolysis rate affects the \( \text{I}_2(\text{aq}) \) concentration near pH 9 only slightly, whereas this increase has a significant effect on the \( \text{I}_2(\text{aq}) \) concentration and its pH dependence in models 2 and 3. This difference suggests that, in model 1, the dissociation of \( \text{HOI} \) becomes rate determining at pH values greater than 7, thereby hindering reaction (3) and resulting in high concentrations of \( \text{I}_2(\text{aq}) \). All three models produce the same results at pH less than 6 or greater than 10. At lower pH, reaction (3) or (6) becomes rate determining and equilibria (1), (2) and (5) are in rapid equilibrium. As a result, changes in the value of the forward and reverse rate constants do not influence the results. At pH greater than 10, the reaction

\[
\text{OH} + \text{HO}_2^- \rightarrow \text{OH}^- + \text{HO}_2 \tag{8}
\]

becomes important and suppresses the initial oxidation of iodide ion

\[
\text{OH} + \text{I}^- \rightarrow \text{HOI}^- \tag{9}
\]

This results in very low \( \text{I}_2(\text{aq}) \) concentrations at any pH greater than 10.

The \( \text{I}_2(\text{aq}) \) concentrations calculated using models 2 and 3 show three pH-dependent regions: inverse linear dependence at low pH, nearly independent behaviour in the pH range 8 to 9, and a strong inverse dependence at a pH above 9.5. The lower pH region showing the linear dependence extends to higher pH as \( k_1 \) or \( k_5 \) increases. This linear dependence is due to the increase in the rate of reaction (3) or (6) as pH,
and thus OI⁻ and HO₂⁻ concentrations increase. The pH-independent region is due to the iodine hydrolysis reaction becoming rate determining.

Because of the importance of reaction (3) (or (6)) in a radiation field, the I₂(aq) concentration is also very sensitive to the rate constant used. Unfortunately, the uncertainty in this rate constant is two orders of magnitude [14,18]. When k₃ or k₆ is increased 100-fold (model 4), three pH-dependent regions were also obtained. However, because of the faster rate of reaction (3), the pH-independent region is reached at lower pH. At pH greater than 10, reaction (8) become important, yielding similar results.

An RTP experiment with a stainless-steel liner showed a significant increase in iodine volatility, from 5 x 10⁻¹² to 1.7 x 10⁻¹⁰ mol.dm⁻³, when the pH was decreased from 9 to 8 [11]. Assuming the partition coefficient of I₂ is 80, the gas phase iodine concentration at pH 9 corresponds to an aqueous phase iodine concentration of about 10⁻¹⁰ mol.dm⁻³. Thus, model 2 or 3 with k₃ or k₆ greater than 20 s⁻¹ appears to reproduce the RTP result most closely. However, until the rate constants and the mechanisms are confirmed experimentally, the accuracy of the model is uncertain.

5. pH CHANGES

It is particularly important to identify mechanisms that may lead to pH changes because of the increased rate of I₂ production as the pH is reduced. One cause of pH change from unbuffered alkaline solutions to neutral and acid is merely the absorption of CO₂ to form carbonate and bicarbonate, as would occur in a containment. However, the RTP tests have shown that during the tests the pH tends to drop even in CO₂ free air [7-11]. The pH drop is generally accompanied by a fall in dissolved oxygen concentration and a rise in iodine volatility.

Before the first ACE test it had been predicted that the pH would fall owing to nitric acid production resulting from radiolysis of moist air. The nitric acid formation may be predicted using an empirical formulation suggested by Burns et al. [19]

\[ N = 2C_o R [1 - \exp(-1.45 \times 10^{-5} GDt)] \]

where N is the concentration of nitric acid in mol.dm⁻³ at time t, C₀ is the concentration of nitrogen in the air, R is the air/liquid volume ratio, G is the yield of nitric acid per 100 eV absorbed (taken as 1.9) and D is the dose rate in MRad/h. For a typical RTP test this is about 2 x 10⁻⁶ mol.dm⁻³.h⁻¹. However, with surfaces that may react with intermediates the yield may be less than this. This predicted amount of nitric acid is too small to account for the pH changes observed or for the amount of alkali required to hold the pH constant in the RTP experiments.

Since the pH change was accompanied by the depletion of dissolved O₂ and occurred before the deliberate addition of organic material in some cases as well as after the addition of MEK (methyl ethyl ketone), it is probable that organic materials derived from painted surfaces are responsible for these phenomena.

6. RADIOLYSIS OF AQUEOUS ORGANIC SYSTEMS

Organic compounds, when irradiated, can undergo a wide variety of reactions but, for small organic molecules and at low radiation doses, the
nature of the processes are in general represented by the following reactions:

\[
\begin{align*}
\text{RH}_2 + \text{OH} & \rightarrow \text{RH}^+ + \text{H}_2\text{O} \\
\text{RH}_2 + \text{H} & \rightarrow \text{RH}^+ + \text{H}_2 \\
\text{RH}_2 + e^- & \rightarrow \text{products}
\end{align*}
\]

\[
\begin{align*}
\text{RH}^+ + \text{O}_2 & \rightarrow \text{RHO}_2^+ \\
2 \text{RHO}_2 & \rightarrow \text{RO}^- + \text{RHOH} + \text{O}_2 \\
& \rightarrow \text{RHO}_2\text{RH} + \text{O}_2 \\
& \rightarrow 2 \text{RHO}^- + \text{O}_2 \\
\text{RHO}_2^- + \text{HO}_2^- & \rightarrow \text{RHO}_2\text{H} + \text{O}_2
\end{align*}
\]

where R represents an organic functional group [20]. At larger doses and for large organic molecules, the mechanisms are unknown. However, when some of the above initial products have been formed, further reactions would take place and compounds containing multiple oxygen groups would be formed. Subsequently, after so much oxygen has been absorbed by the system, it is difficult to imagine that any large organic molecule could survive. Under these conditions CO$_2$ and its reaction products, formic acid, formaldehyde and oxalic acid, are the most likely products.

There are not enough data in the literature on such systems, and modelling can lead to significant problems. We have incorporated a crude reaction scheme for the organic radiolysis reactions into LIRIC:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{OH} & \rightarrow \text{CH}_3\text{CHCOCH}_3 + \text{H}_2\text{O} & 2 \times 10^7 & \text{(OR1)} \\
\text{CH}_3\text{CHCOCH}_3 + \text{O}_2 & \rightarrow \text{CH}_3\text{CHO}_2\text{COCH}_3 & 1 \times 10^8 & \text{(OR2)} \\
2 \text{CH}_3\text{CHO}_2\text{COCH}_3 & \rightarrow 2 \text{CH}_3\text{CHCOCH}_3 + \text{O}_2 & 1 \times 10^{-2} & \text{(OR3)} \\
\text{CH}_3\text{CHCOCH}_3 + \text{HO}_2 & \rightarrow 2 \text{CH}_3\text{COOH} & 1 \times 10^7 & \text{(OR4)} \\
\text{CH}_3\text{COOH} + \text{OH} & \rightarrow \text{CH}_2\text{COOH} + \text{H}_2\text{O} & 1 \times 10^9 & \text{(OR5)} \\
\text{CH}_2\text{COOH} + \text{O}_2 & \rightarrow \text{CH}_2\text{O}_2\text{COOH} & 1 \times 10^9 & \text{(OR6)} \\
2 \text{CH}_2\text{O}_2\text{COOH} & \rightarrow 2 \text{CH}_2\text{OCOOH} + \text{O}_2 & 1 \times 10^9 & \text{(OR7)} \\
\text{CH}_2\text{OCOOH} + \text{HO}_2 & \rightarrow \text{CO}_2\text{HCO}_2\text{H} + \text{H}_2\text{O} & 1 \times 10^9 & \text{(OR8)} \\
\text{CO}_2\text{HCO}_2\text{H} + \text{OH} & \rightarrow \text{COO}^- + \text{H}^+ + \text{CO}_2 + \text{H}_2\text{O} & 1 \times 10^9 & \text{(OR9)} \\
\text{COO}^- + \text{O}_2 & \rightarrow \text{CO}_2 + \text{O}_2^- & 1 \times 10^9 & \text{(OR10)} \\
\text{CH}_3\text{COOH} = \text{CH}_3\text{COO}^- + \text{H}^+ & K_{eq} = 1.75 \times 10^{-5} & \text{(OR11)}
\end{align*}
\]

The first reaction of the above set is the organic free radical formation from OH reaction. The rate of hydrogen abstraction from acetone by OH is known to be $1.1 \times 10^8$ dm$^3$·mol$^{-1}$·s$^{-1}$ [21]. Although another methyl group enhances the stability of the organic free radical, the steric hindrance may slow down the rate for the OH and MEK reaction. We chose $2 \times 10^7$ dm$^3$·mol$^{-1}$·s$^{-1}$ for the rate constant, because it yielded the RTP results more closely than a higher rate constant. It is also possible that
the reaction of MEK with e−, which is not included in the model, lowers the apparent rate of the OH reaction.

Reaction (OR2) is the formation of the peroxy radical. The rate of the oxygen uptake by small organic radicals is of the order of 108 dm−3·mol−1·s−1 (for example, HCO + O3 → -O2CHO, k = 7.7 × 108 dm−3·mol−1·s−1 [22]). Because the MEK free radical, CH3CHOCH3, is relatively stable and because of the steric hindrance, we chose 108 dm−3·mol−1·s−1 for the rate constant. However, the OH reaction is rate determining, and thus the effect of the rate constant for the oxygen uptake on the results was negligible.

Reaction (OR3) is the formation of oxy radicals from two peroxy radicals [23] and reaction (OR4) is an arbitrary reaction, which leads to formation of acetic acid. The rate constant for the type of reaction (OR3) is not well known; however, it is not likely that two large free radicals would react rapidly. Thus a rate constant of 1 × 10−2 dm−3·mol−1·s−1 was chosen. This low rate constant was also required to simulate the observed oxygen behaviour. Reactions (OR5) to (OR10) are the radiolysis reactions of acetic acid [24] and equilibrium (OR11) is that of acetic acid. The mass transport of CO2 and the equilibria of CO2 with water (CO2, H2CO3/HCO3−/CO32−) were also included because of its effect on pH.

The above reaction scheme was an attempt to test the idea of the organic radiolysis as a possible source of the pH change and to simulate the general RTF results when MEK was added. However, this scheme is obviously not a quantitative description of the actual processes occurring.

Examples of the predictions of the model are shown in Figure 2. Because in most RTF tests the aqueous iodine (mostly iodide) concentration was observed to decrease sharply with time [7,8,10], sometimes reaching as little as 4.4 × 10−7 mol·dm−3 from the initial concentration of 1 × 10−5 mol·dm−3, calculations were carried out with two iodide concentrations: 5 × 10−7 (Figure 2a) and 2 × 10−6 (Figure 2b) mol·dm−3. (The decrease in the iodide concentration results from the adsorption of iodine on the surfaces.) For these calculations, the initial pH and dissolved oxygen concentration were 6.2 and 5 ppm (1.6 × 10−4 mol·dm−3) respectively, and MEK was added to the solution at time 5 × 104 s. Other conditions, such as radiation field, gas and aqueous phase volumes, were close to those of the RTF tests. The effect of the initial oxygen concentration was also investigated.

The model predicted the general trends observed in the RTF tests (see Figure 3): the pH decrease, oxygen depletion and rise in the iodine volatility upon the MEK addition [7,10]. The iodide concentration strongly affects the O2(aq) and I2(aq) behaviour, because the initial oxidation of iodide by OH, reaction (9) competes with reaction (OR1) for OH. For the same reason, the O2(aq) and I2(aq) behaviour is sensitive to the rate constant of reaction (9). The rate constant is in the range 1.1 to 1.8 × 1016 dm−3·mol−1·s−1 [4,13,25], and 1.8 × 1010 was used for the calculations discussed here. Lowering the rate constant by half resulted in the same effect on the iodine concentration as lowering the initial iodide concentration by half.

The different O2(aq) behaviour observed in an RTF test with a vinyl surface [7] and one with a polyurethane surface [10] may be attributed to a different iodide concentration available at the time of the MEK addition. The iodide concentrations were about 1 × 10−6 and 5 × 10−7 mol·dm−3 respectively. The O2(aq) concentrations were also different in those tests 8 and 5.5 ppm respectively, although this is not so significant a factor.
The oxygen behaviour following a rapid initial decrease upon the MEK addition appears very sensitive to the rate constant of reaction (OR3). For the large free radicals formed from MEK, the reaction of the organic peroxy radical and HO₂

\[ \text{CH}_3\text{CHO}_2\text{COCH}_3 + \text{HO}_2 \rightarrow (\text{CH}_3\text{HO}_2\text{CHCOCH}_3 + \text{O}_2) \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{CHO} + \text{O}_2 \]  

(OR12)

may be a preferred path over reactions (OR3) and (OR4). In fact, the model with this reaction produced a better pH behaviour than the model with reactions (OR3) and (OR4). The proposed organic radiolysis model does not explain well the observed \( I_2 \) (aq) behaviour, assuming the observed gas phase iodine concentration reflects the change in the \( I_2 \) (aq) concentration. However, it should also be noted that the surface reactions and/or adsorption-desorption, which could significantly affect the iodine behaviour, were not included in these calculations.

It should be emphasized that the reaction set is a compromise to simulate the general results using the type of reactions observed, but is not quantitative or qualitative description of the actual processing occurring. Some further modelling is clearly required and the following questions require answers:

1) Is it possible to rationalise the number of organic molecules and their reactions?
2) Is it necessary to model anything other than \( O_2 \) and pH as a function of dose?
3) Is the pH change and \( O_2 \) concentration merely a function of carbon number, mass transfer properties of the system and dose?
4) To what extent is organic iodine formed in these solutions?

More experimental evidence in the form of products, rate constants and mechanisms for these processes are needed to evaluate the applicability of the model.

7. SURFACE EFFECTS

The effect of surfaces is not considered in detail here, apart from noting that surfaces act as sinks for molecular iodine and often as a source of organic iodine, which may re-dissolve and be destroyed. The effect of the sink is that iodine is removed from solution, but this does not necessarily show what the effect on the low partition coefficient will be. It should be kept in mind that the system is in dynamic equilibrium and will try to maintain this equilibrium if it is perturbed in any way, such as by removal of gaseous \( I_2 \).

8. SUMMARY

The reaction set for water radiolysis is satisfactory. The reactions of hydrogen peroxide, which are important in iodine chemistry, are not understood sufficiently well for mechanistic modelling purposes. A simplified reaction set for radiolysis of aqueous organic molecules is proposed but it is not truly mechanistic. Further experimental work on reaction rates and mechanisms of reactions of hydrogen peroxide with iodine is required. Experimental work on rates and products of decomposition of aqueous organic molecules is required.
Despite problems with some of the input data, mechanistic models are still useful, not only in a predictive way, which was their original use and is their ultimate role, but they are particularly useful at present as an aid to understanding the chemical and physical processes and as a guide to where experimental effort should be focussed. The act of constructing a model is often a very instructive process.

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**TABLE 1**

IODINE HYDROLYSIS AND HYDROGEN PEROXIDE REACTION MODELS

<table>
<thead>
<tr>
<th>Hydrolysis or $H_2O_2$ Reactions</th>
<th>Rate Constant(*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1</td>
<td></td>
</tr>
<tr>
<td>$I_2 + H_2O = HOI + H^+ + I^-$</td>
<td>$k_1 = 2 \times 2000$, $k_1/k_{-1} = 4.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>$HOI = H^+ + OI^-$</td>
<td>$k_2 = 0.1$, $k_2/k_{-2} = 10^{-11}$</td>
</tr>
<tr>
<td>$IO^- + H_2O_2 = H_2O + I^- + O_2$</td>
<td>$k_3 = 1.6 \times 10^7$</td>
</tr>
<tr>
<td>Model 2</td>
<td></td>
</tr>
<tr>
<td>$I_2 + H_2O = OI^- + 2H^+ + I^-$</td>
<td>$k_5 = 2 \times 2000$, $k_5/k_{-5} = 4.4 \times 10^{-24}$</td>
</tr>
<tr>
<td>$HOI = H^+ + OI^-$</td>
<td>$k_2 = 0.1$, $k_2/k_{-2} = 10^{-11}$</td>
</tr>
<tr>
<td>$IO^- + H_2O_2 = H_2O + I^- + O_2$</td>
<td>$k_3 = 1.6 \times 10^7$</td>
</tr>
<tr>
<td>Model 3</td>
<td></td>
</tr>
<tr>
<td>$I_2 + H_2O = HOI + H^+ + I^-$</td>
<td>$k_1 = 2 \times 2000$, $k_1/k_{-1} = 4.4 \times 10^{-13}$</td>
</tr>
<tr>
<td>$HOI = H^+ + OI^-$</td>
<td>$k_2 = 0.1$, $k_2/k_{-2} = 10^{-11}$</td>
</tr>
<tr>
<td>$HO_2^- + HOI = H_2O + I^- + O_2$</td>
<td>$k_6 = 9 \times 10^5$, $k_7 = 2 \times 10^{-2}$, $k_7/k_{-7} = 2 \times 10^{-12}$</td>
</tr>
<tr>
<td>$H_2O_2 = H^+ + HO_2^-$ (*)</td>
<td></td>
</tr>
<tr>
<td>Model 4</td>
<td></td>
</tr>
<tr>
<td>$I_2 + H_2O = OI^- + 2H^+ + I^-$</td>
<td>$k_5 = 2 \times 2000$, $k_5/k_{-5} = 4.4 \times 10^{-24}$</td>
</tr>
<tr>
<td>$HOI = H^+ + OI^-$</td>
<td>$k_2 = 0.1$, $k_2/k_{-2} = 10^{-11}$</td>
</tr>
<tr>
<td>$IO^- + H_2O_2 = H_2O + I^- + O_2$</td>
<td>$k_3 = 1.6 \times 10^9$</td>
</tr>
</tbody>
</table>

(a) In units of $s^{-1}$, $dm^3\cdot mol^{-1} \cdot s^{-1}$ and $dm^6\cdot mol^{-2} \cdot s^{-2}$ for first, second and third order rate constants respectively.

(b) This acid-base equilibrium was included also in the other model calculations.
REFERENCES:


FIGURE 3. Effect of MK on the $O_2$ (aq) and pH (a) Behaviours Observed in the KFP Tests: (a) Phase II - Test 1, [7] and (b) Phase II - Test 2 [10]. MK was added at 308 h and 165 h into the tests, respectively. The initial $O_2$ (aq) and $O_2$ concentrations were 6.3 x 10⁻⁷ and 4.4 x 10⁻⁷ mol dm⁻³, respectively. The oxygen concentrations measured prior to the MK addition were 8 and 6.5 ppm (or 2.5 x 10⁻⁴ and 2.0 x 10⁻⁴ mol dm⁻³), respectively.
FIGURE 2. Effect of MEK on the $O_2(aq)$ (----), $pH$ (-----) and $I_2(aq)$ (-----) Behaviour Calculated Using the LIRIC model. Surface reactions are not included. The initial $pH$ was 6.2 and MEK was added at $5 \times 10^4$ s. Other conditions were (a) $[I^-]_o = 5 \times 10^{-7} \text{ mol dm}^{-3}$ and $[O_2(aq)]_o = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$ (or 5 ppm); (b) $[I^-]_o = 2 \times 10^{-6} \text{ mol dm}^{-3}$ and $[O_2(aq)]_o = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$. 
FIGURE 1. Effect of Various Mechanisms and Rate Constants of the Iodate Hydrolysis and Hydrogen Peroxide Reactions on the Concentration of \( I_2 \) (aq) (mol·cm\(^{-3}\)). The models listed in Table 1 were used for these calculations. For each model, the rate constant of the iodine hydrolysis, \( k_1 \), or \( k_2 \), was changed from 2 s\(^{-1}\), ..., 2000 s\(^{-1}\), ..., and 20000 s\(^{-1}\).
DISCUSSION

Kupferschmidt (comment)
A point of clarification. In an RTF test conducted in a stainless steel vessel as part of the Canadian Iodine program, we observed an increase in the total gas phase iodine concentration from $5 \times 10^{-12}$ to $1.7 \times 10^{-10}$ mol.dm$^{-3}$ when the pH was decreased from 9 to 8. Such a large increase in iodine volatility was unexpected and suggests that further work on the pH-dependence of iodine volatility is required.

Sagert
Yes, looks like a typographical error here. At pH 9 (I$^+_2$)$_{aq}$ is $10^{-12}$ M?

Weber
Concerning your parametric study resulting in Fig.1, can you compare these calculations to real data, and thereby discern optimal parameter or model choices? While we have seen good evidence that Liebhabsky's work should be reconsidered, we should also recognize the genius of his work was in devising experiments that would reveal the differing effects of parallel competing reactions. It appears that this type of innovation is needed to reveal which of the many proposed reactions are truly important.

Sagert and Sims
It would certainly be desirable to compare the parametric study with experiments. We attempted to do this with the RTF data. However there are very few, if any, other data in this pH range. Experimental difficulties are substantial. We certainly recognize the genius of Liebhabsky's work over almost a 50 year span. He helped develop the basis of all our present iodine chemistry.
5.5 ADVANCED CONTAINMENT EXPERIMENTS (ACE): EVALUATION OF PRE-TEST CODE CALCULATIONS OF IODINE BEHAVIOUR IN THE RADIOIODINE TEST FACILITY

R.J. Fluke¹, J.B. Edward¹, K.R. Weaver², and G.J. Evans³

ABSTRACT

As part of the international Advanced Containment Experiments (ACE), pre-test code predictions were performed to simulate iodine behaviour in a set of experiments in the Radioiodine Test Facility (RTF). The experiments were conducted using an epoxy painted vessel, and variables included solution chemistry, initial iodine species and radiation. The codes predicted consistently low airborne iodine fractions (<0.25%) and significant radiation and pH effects, including adsorption onto the painted surfaces. The subsequent experiments qualitatively confirmed these effects. However, the codes differed in predicting the detailed iodine speciation, the magnitude of radiation effects, and whether surface adsorption was predominantly above or below the water level. The reasons for the differences were inconclusive because the code input was based on inconsistent assumptions about test operations and physical parameters. In a follow-up code exercise, these input assumptions were standardised so that differences in the chemistry models could be discerned better. It is concluded that the codes are well advanced, but have incomplete models to predict the effects of painted surfaces and organic materials on iodine behaviour in a radiation field.

1. INTRODUCTION

As part of the international programme on Advanced Containment Experiments (ACE), computer code calculations of iodine behaviour were performed by ACE participants to simulate a set of experiments in the Radioiodine Test Facility (RTF) at AECL Research, Whiteshell Laboratories. These intermediate scale experiments, conducted in an epoxy painted carbon steel vessel, have provided integral data on iodine behaviour as a function of initial iodine speciation, water chemistry and radiation [1]. In addition, bench scale tests were performed to help rationalise the results of the RTF tests [2], and several in-kind contributions from ACE participants have further enhanced the understanding of iodine behaviour.

The codes were developed in the various organisations and included specific chemical reactions, their kinetics and thermodynamics, and other factors such as mass transport phenomena.

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2 Shaftesbury Scientific Limited, 84 Shaftesbury Ave., Toronto, Ontario, CANADA M4T 1A5 (Under contract to Ontario Hydro)
3 University of Toronto, Dept. of Chemical Engineering, Toronto, Ontario, CANADA M5S 1A1
Depending on the expert judgement of the code developers, much of the available data was included. However, very little experimental data existed that combined "all effects" parameters. Thus, one objective of ACE is to provide integral iodine behaviour data as a benchmark for the validation of the iodine codes. Pre-test code predictions of the ACE-RTF tests were organised, and the results were examined. To help determine potential reasons for similarities and differences (e.g. common data sets, different assumptions), follow-up calculations based on standardised assumptions were organised and evaluated.

This evaluation focuses on three key issues: (a) the predicted airborne fraction of iodine species; (b) the main sinks for iodine species; and, (c) why the codes predicted such. Of interest are the conditions for stability of the dominant sinks and the rationalisation of key phenomena. The codes are evaluated using this criteria, by comparing the pre-test code predictions to key measurements, and by comparing the codes to one another in both the pre-test predictions and follow-up calculations. It must be acknowledged that the codes used in this exercise may have since undergone modification to account for new data or modelling strategies.

2. THE RTF EXPERIMENTS

The following relates to the procedures specified for the pre-test code predictions. Small deviations occurred in the actual experiments. A full description of the experiments as actually performed is given elsewhere [1].

A sketch of the Radioiodine Test Facility is shown to the right. A 35 L solution of specified iodine species and concentration, at a given pH, was injected into the epoxy painted vessel at "time zero", leaving a free air volume of 352 L. The radiation source was $^{60}$Co, from which the absorbed dose rate was about 2 kGy/h based on distributed TLD measurements.

A 3 test, 3 phase matrix was planned to assess the effects of radiation and solution chemistry. The three tests are given in the table to the right. For each test there were three phases (or nine test cases in total), each of six days duration, to assess the behaviour of different initial iodine species in solution injected into the RTF:

<table>
<thead>
<tr>
<th>Phase</th>
<th>Iodine Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1.0 \times 10^{-5}$ M CH$_3$I;</td>
</tr>
<tr>
<td>B</td>
<td>$0.5 \times 10^{-3}$ M I$_3$; and,</td>
</tr>
<tr>
<td>C</td>
<td>$1.0 \times 10^{-3}$ M CsI.</td>
</tr>
</tbody>
</table>

In each test phase, therefore, the total mass of iodine added to the vessel was 44 mg. An operating temperature of 80°C was also prescribed. These conditions, although providing important information for code benchmarking, are similar to expected accident conditions. Furthermore, in Test 3, the effect on iodine volatility of changing pH provides valuable information for developing accident management strategies.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Test 1</th>
<th>Test 2</th>
<th>Test 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>pH</td>
<td>9</td>
<td>9</td>
<td>0-4 days: 5.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4-6 days: 9.0</td>
</tr>
</tbody>
</table>
3. CODE CALCULATIONS

The pre-test code exercise was organised with the intent of predicting iodine behaviour in the specified RTF tests. However, inconsistent assumptions were made by the code users (discussed in detail in later sections). Although such assumptions were expressions of individual expert judgement (which led to some changes in the experimental phase), it made interpretation of the pre-test predictions difficult. Therefore, a follow-up exercise was organised to help discern differences among the iodine chemistry models, by parametric analysis using consistent input assumptions. All code calculations were performed by the ACE participants. The pre-test predictions and follow-up calculations are described below.

3.1. The Pre-test Predictions

The pre-test code predictions were coordinated by Oak Ridge National Laboratory. The codes used in this exercise, the responsible organisation and country were:

- TRENDS
- LIRIC/MITIMAKS
- INSPECT
- IMPAIR-2
- IODE

ORNL (U.S.)
AECL Research (Canada)
AEA Technology (U.K.)
PSI (Switzerland)
CEA (France)

Of the nine RTF test cases, five were selected for the pre-test predictions: 1C, 2C, 3A, 3B and 3C. Thus, radiation, pH and initial iodine species were the three main variables examined. The results were evaluated to help clarify inconsistencies between the code predictions, and to identify parameters having significant effects on both the simulations and the experimental results.

3.2. Follow-up Calculations

Of the five codes involved in the pre-test predictions, all but the TRENDS code are represented in the follow-up work. Since the emphasis was on using the codes for parametric studies to help isolate key issues, no attempt was made to model the experiments closely. The RTF Test 3C with CsI was chosen as the base case because it encompassed most of the important variables, including radiation, a period of low pH and the step change in pH. Some basic assumptions were standardised:

- pH would be controlled by adding sufficient acid or base;
- only I₂ would adsorb onto or desorb from paint;
- Organic materials would be in solution at 10⁻³ M; and,
- physical rate constants would be consistently applied.

Other vessel conditions were similar to the pre-test exercise for Test 3C as described in section 2 above.

Four parameters were varied. These were (a) "dry" painted surface adsorption and desorption, (b) "wet" painted surface adsorption and desorption, (c) mass transfer between the water and air, and (d) the presence of organic materials. "Dry" and "Wet" refer to the painted surface in contact with the air and water, respectively. The parametric matrix was as shown to the right.

Numerical values were specified for all physical input parameters, including adsorption and desorption rates, surface to volume ratios, and mass transfer coefficients. All codes used the same parameters except IODE, which did not have a desorption term in its paint model. For the cases
with organic materials present, the organics were entered as non-iodine species which subsequently reacted to form organic iodides, in three of the codes. For IODE, the organics were entered as CH$_3$I. The initial period of IODE outputs therefore differ from those of the other three codes. However, this was seen to be only a minor perturbation.

4. RESULTS

Results are presented in a format that facilitates evaluation according to the three primary issues cited in the Introduction. Thus, key results include the airborne iodine fraction, the iodine distribution among the main sinks, and various other parameters useful for interpretation.

4.1. Gas Phase Iodine

In reactor accident analysis, the airborne fraction of iodine is the most important prediction made by the iodine behaviour codes. The ability of the codes to calculate this is compared below.

Pre-test Predictions and Measurements

Table 1 summarises the predicted and measured steady state airborne iodine fractions for the pre-test code exercise. It is seen that the predictions were consistent with the measurements in that the absolute gaseous concentrations were low; less than 0.25% of the total iodine mass was present in gaseous forms. As a general observation, this agreement was encouraging, but it was tempered by the realisation that there was disagreement at a more detailed level, particularly in the predicted amount of organic iodide. Detailed observations from each of the five tests are discussed below.

Test 1C served as the reference non-radiation test at pH 9, and was the least complex. Therefore, it was unexpected to find that the code predictions varied by eight orders of magnitude, and in all cases, predicted less than the measured amount of airborne iodine. On the composition of the gas phase, three of the codes (IODE, LIRIC and INSPECT) predicted that organic iodides would dominate the gas phase (as was observed experimentally) while IMPAIR-2 predicted that I$_2$ would be the dominant gaseous form. For this latter code, the assumed I$_2$ residue on the paint from earlier tests may explain the different result compared to the other codes; because of this prediction, the test sequence was altered and so the "residue" effect is uncertain. There was no TRENDS prediction for this test because the code user assumed there would be no significant change from initial conditions.

Radiation was added for Test 2C, and the agreement among the codes on gas phase concentration was better; three of the codes were within an order of magnitude of the measurement. IODE, IMPAIR-2 and TRENDS predicted that I$_2$ would be the dominant gaseous form. LIRIC and INSPECT, however, predicted that organic iodides would dominate, as was observed experimentally. Code comparison was complicated by the fact that TRENDS and INSPECT allowed the radiolytic production of HNO$_3$ to depress the pH to relatively low values. For those codes that held the pH...
Table 1: Airborne Fraction (%) and Composition: Pre-test Predictions and Experiment

<table>
<thead>
<tr>
<th>CODE/TEST</th>
<th>1C</th>
<th>2C</th>
<th>3C Low pH</th>
<th>3C High pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TRENDS</td>
<td>Not Calculated</td>
<td>.047 14% ORG-I</td>
<td>.048 14% ORG-I</td>
<td>.046 14% ORG-I</td>
</tr>
<tr>
<td>LIRIC</td>
<td>.0000016 97% ORG-I</td>
<td>.004 67% ORG-I</td>
<td>.25 56% ORG-I</td>
<td>.052 6% ORG-I</td>
</tr>
<tr>
<td>INSPECT</td>
<td>.00057 99% ORG-I</td>
<td>.007 94% ORG-I</td>
<td>.021 90% ORG-I</td>
<td>No period of high pH</td>
</tr>
<tr>
<td>IMPAIR-2</td>
<td>.0000038 19% ORG-I</td>
<td>.0006 19% ORG-I</td>
<td>.009 18% ORG-I</td>
<td>.0032 10% ORG-I</td>
</tr>
<tr>
<td>IODE</td>
<td>1.8E-11 55% ORG-I</td>
<td>.000008 3% ORG-I</td>
<td>.0029 1% ORG-I</td>
<td>.00000038 7% ORG-I</td>
</tr>
<tr>
<td>DATA</td>
<td>.0011 86% ORG-I</td>
<td>.04 88% ORG-I</td>
<td>.16 80% ORG-I</td>
<td>.042 91% ORG-I</td>
</tr>
</tbody>
</table>

at 9, predictions under-estimated the gas phase iodine concentrations, for LIRIC by one order of magnitude, and for IODE by three orders.

Test 3C was like 2C except that the pH was 5.5 for the first four days, and then stepped up to pH 9 (the 2C condition). This was meant to show the effect on gas phase iodine of lower pH, an abrupt change in pH and to determine if pH "history" influences the longer term behaviour of iodine. LIRIC, IMPAIR-2 and IODE maintained pH at the specified level, but, as mentioned above, TRENDS and INSPECT allowed the pH to drop. For the step increase in pH (by addition of LiOH) INSPECT predicted that there would not be enough alkali added and so the pH remained low. TRENDS, however, did assume that pH would rise as planned.

Figure 1 shows the gas phase iodine predictions and measurements for Test 3C. Note that the pH was changed at 3 days in the experiment, instead of 4 in the code predictions. Since INSPECT did not predict any change in pH, its airborne iodine fraction did not change. In TRENDS also, the airborne iodine fraction did not change, but the pH did increase. The other three codes assumed the pH to be under control. LIRIC showed a slow drop in gas phase iodine following the pH change, whereas IMPAIR-2 and IODE showed a rapid drop. For IMPAIR-2 and LIRIC, a factor of three and five, respectively, was the predicted decrease in the gas phase iodine following the pH change. IODE predicted a large decrease, about four orders of magnitude. As seen in Figure 1, and Table 1, the measurement drop was a factor of four, which occurred slowly.

The predicted gaseous organic iodide fraction varied significantly across the codes, as seen in Table 1, not only in magnitude but also in the relative change (increase or decrease) following the increase in pH. RTF test results showed predominantly organic iodides in the gas phase before the change in pH, and even more so afterwards. This trend was not predicted by any of the codes.
Tests 3A, 3B and 3C compared the effects of different initial iodine species. Although the airborne fractions were initially different, they were ultimately independent of the initial species, consistent with the measurements [1].

Follow-up Calculations

Table 2 shows the calculated steady state airborne fraction of iodine for each of the follow-up cases. Unlike the pre-test predictions, the total gas phase fractions were in reasonable agreement, with some notable exceptions. For all effects included (case 3C-1), at low pH, LIRIC calculations showed an order of magnitude more airborne iodine than the other three codes, but at high pH, IMPAIR-2, INSPECT and LIRIC are in remarkable agreement. The IODE calculation can not be compared in this case because of it modelled the paint without a desorption term.

In case 3C-2, dry deposition is "switched off", and here, the code calculations show different trends. As seen in Table 2, INSPECT and LIRIC were in excellent agreement, both at low and high pH. This is because INSPECT showed an order of magnitude increase in airborne iodine when the dry surface was removed, compared to LIRIC which showed a very small change. IMPAIR-2 showed the largest airborne fraction (25%) at low pH, and an almost negligible airborne fraction at high pH. For the IODE code, switching off the dry surface caused the airborne fraction to increase, but the absolute amount was lower than the other codes because of the different paint model in IODE.

Because the wet surface was designed to be a very minor sink, by choice of deposition and desorption rates, no significant effects were expected by switching it off. This is shown to be the case
Table 2: Airborne Fraction (%) of Iodine Species: Follow-up Calculations at pH 5.5 and 9

<table>
<thead>
<tr>
<th>TEST / pH</th>
<th>IMPAIR-2</th>
<th>INSPECT</th>
<th>LIRIC</th>
<th>IODE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3C-1 5.5</td>
<td>0.54</td>
<td>0.22</td>
<td>3.1</td>
<td>0.0019</td>
</tr>
<tr>
<td>3C-1 9</td>
<td>0.26</td>
<td>0.22</td>
<td>0.26</td>
<td>7.4E-8</td>
</tr>
<tr>
<td>3C-2 5.5</td>
<td>25.</td>
<td>2.9</td>
<td>3.4</td>
<td>0.018</td>
</tr>
<tr>
<td>3C-2 9</td>
<td>0.0006</td>
<td>0.18</td>
<td>0.13</td>
<td>6.8E-7</td>
</tr>
<tr>
<td>3C-3 5.5</td>
<td>0.51</td>
<td>0.22</td>
<td>3.1</td>
<td>0.013</td>
</tr>
<tr>
<td>3C-3 9</td>
<td>0.26</td>
<td>0.26</td>
<td>0.26</td>
<td>4.7E-7</td>
</tr>
<tr>
<td>3C-4 5.5</td>
<td>26.</td>
<td>2.9</td>
<td>3.4</td>
<td>1.4</td>
</tr>
<tr>
<td>3C-4 9</td>
<td>0.0005</td>
<td>0.18</td>
<td>0.13</td>
<td>0.00007</td>
</tr>
<tr>
<td>3C-5 5.5</td>
<td>0.51</td>
<td>0.095</td>
<td>0.11</td>
<td>0.00049</td>
</tr>
<tr>
<td>3C-5 9</td>
<td>0.44</td>
<td>0.13</td>
<td>0.024</td>
<td>9.2E-8</td>
</tr>
<tr>
<td>3C-6 5.5</td>
<td>0.52</td>
<td>0.15</td>
<td>0.061</td>
<td>0.0022</td>
</tr>
<tr>
<td>3C-6 9</td>
<td>0.26</td>
<td>0.10</td>
<td>0.031</td>
<td>8.7E-8</td>
</tr>
<tr>
<td>3C-7 5.5</td>
<td>25.</td>
<td>2.8</td>
<td>0.22</td>
<td>0.022</td>
</tr>
<tr>
<td>3C-7 9</td>
<td>0.0006</td>
<td>0.062</td>
<td>0.0007</td>
<td>8.0E-7</td>
</tr>
<tr>
<td>3C-8 5.5</td>
<td>0.53</td>
<td>0.15</td>
<td>0.061</td>
<td>0.015</td>
</tr>
<tr>
<td>3C-8 9</td>
<td>0.26</td>
<td>0.10</td>
<td>0.035</td>
<td>5.3E-7</td>
</tr>
</tbody>
</table>

in Table 2, bearing in mind the difference in IODE. However, for case 3C-4, where both wet and dry deposition were turned off, IODE was in much better agreement with INSPECT and LIRIC.

When mass transfer was made slower (case 3C-5), all codes showed a reduction in airborne iodine, but to different extent. Removal of organics (3C-6, 7 and 8), had no significant effect except for LIRIC, which otherwise showed a predominance of organic iodides in the gas phase.

4.2. Main Sinks for Iodine

Since the airborne fraction is seen to be very small, it is important to be able to predict the main sinks that retain the iodine, and the conditions for stability of those sinks. The codes are compared below in their ability to predict where and how the bulk of the iodine would reside.

Pre-test Code Predictions and Measurements

In Test 1C, all codes predicted no significant transfer of iodine from solution, neither to the gas phase nor to the painted surfaces. This prediction was confirmed by the measurements. Furthermore, there was complete consensus that aqueous I- accounted for virtually all of the iodine, both predicted and measured, although there was no TRENDS calculation for this case. In Tests 2C
and 3C, however, the painted surfaces were predicted to become an important sink, but the amount predicted by the codes was inconsistent. A large part of the inconsistency was likely the result of inconsistent code input assumptions, notably pH behaviour. The common aspect was that deposition to paint only occurred under conditions of low pH, both as predicted and as measured. This is illustrated in Figure 2. Therefore, the code predictions are separated below according to their treatment of pH conditions.

LIRIC, IMPAIR-2 and IODE each assumed that pH would be controlled during the experiment, and therefore have identical solution boundary conditions. At pH 9 (Test 2C), these codes predicted almost complete retention of iodine in the water with no other sinks of any significance. This overall prediction was confirmed in the experiment, which showed less than 3% loss of iodine species from solution. In Test 3C, however, the LIRIC, IMPAIR-2 and IODE predictions showed substantial deposition onto the painted surfaces. The consistency among these codes, and the experiments, was good in five key areas:
(a) the rates of iodine evolution from water were slow;
(b) only the water and the dry paint were significant sinks;
(c) by four days, equilibrium had been reached;
(d) increasing pH halts or reverses iodine transfer from the water to the dry paint; and
(e) the dominant aqueous species was always I-
The inconsistencies among the above codes was in the details of minor species and absolute amount deposited, which is seen in Figure 2.

The two other codes, TRENDS and INSPECT, assumed that pH would drop because of nitric acid production, but details differed. In the TRENDS prediction for Test 2C, the pH was initially about 9, and dropped very slowly to around pH 8 at three days, after which it rapidly dropped as seen in Figure 2. Once it went below 8, the production rate of gaseous iodine increased substantially although it was quickly adsorbed by the dry painted surface. In test 3C, the pH was initially well below 8. The aqueous iodine was rapidly volatilised from the beginning. Gas phase iodine was again rapidly removed to the dry surface. The sudden pH ramp in test 3C had little effect because almost all of the iodine was by then bound to the paint. Although very little iodine remained in solution, according to the TRENDS prediction, the predominant species was aqueous I 2. This was at variance with all the other codes as well as the experimental data.

INSPECT had a different result. Like the TRENDS prediction, the pH dropped. Unlike TRENDS, however, there was not a sufficient time with the system at high pH to draw any conclusions about pH effects. In fact, the pH predicted by INSPECT for Test 2C was almost identical for Test 3C. INSPECT predictions of the major sinks were qualitatively very different from those of the other codes under low pH conditions. According to INSPECT, the wet paint became the dominant sink and the water and the dry paint soon became minor. The dominant aqueous species was I-, compared to I 2 in TRENDS. Thus, the different sinks predicted by INSPECT can not be rationalised based on the pre-test predictions, since either mass transfer rates or water chemistry could be factors.

Follow-up Calculations

In the design of this code experiment, physical rate constants for mass transfer and sorption were selected such that, for I 2: (a) the dry surface would be a strong sink; (b) the wet surface would be a weak sink; and, (c) the air and water would be sinks of equal strength. Therefore, the amount of dry deposition should be in proportion to the amount of I 2 calculated by the codes. Figure 3
shows the main sinks for Test 3C-1, for each code. INSPECT, IODE and LIRIC were in very good agreement on the amount of dry deposition, but IMPAIR-2 showed a much larger amount. Thus, IMPAIR-2 has significantly different chemistry than the other codes, producing more I₂. Removing the dry surface, as shown in Figure 4, results in re-distribution of the iodine, but to different sinks; that which was on the dry surface is now almost entirely taken up by the water, according to INSPECT and LIRIC, or to the wet paint according to IODE, but in the case of IMPAIR-2, only a portion of it is taken up by water, leaving 25% in the gas phase.

The dry surface also has a dramatic effect on the aqueous speciation in the IMPAIR-2 code, but no significant effect according to the other codes. This is seen by examining Figures 5 and 6, where the dry surface is present and absent, respectively. The dominant species is consistently I⁻ for all codes and in all cases except for IMPAIR-2 in the absence of the dry surface. When the dry surface is absent, I₂ and HOI account for over 80% of the aqueous species at low pH, but IMPAIR-2 becomes consistent with the other codes in calculating I⁻ to predominate at high pH. Under alkaline conditions, all codes (including IMPAIR-2) calculated less than 0.1% conversion of I⁻ to I₂. INSPECT shows no significant species other than I⁻. At low pH, both LIRIC and IODE calculate modest amounts of IO₃⁻ (about 20%), but the IO₃⁻ predicted by LIRIC disappeared when the pH was increased, compared to IODE where it remained stable.

The slower mass transfer rate (test 3C-5) reduced the amount of iodine transferred from solution to other sinks, as expected. Tests 3C-6, -7, and -8 had no organics; their presence or absence had no discernable effects on the main sinks, although it did affect the airborne fraction as previously noted, more so with LIRIC. Also, LIRIC showed somewhat less iodate and slightly more I₂ production with organic materials present, an observation not seen in any other code.

5. DISCUSSION

For reactor safety evaluations, the most important prediction is the total gas phase concentration. From Table 1, it is seen that in all cases the measured airborne fraction of iodine was small, confirming (at least qualitatively) the predictions of all the codes. From a more negative perspective, however, the codes often predicted less than the measured airborne concentration. This is most evident in the non-radiation test at high pH (Test 1C), conditions for which the knowledge of thermal iodine chemistry is perceived to be reasonable. This apparent shortcoming by the codes can be rationalised, however, because there were organic materials released from the epoxy paint in the RTF, which was not anticipated during the pre-test code exercise. The effect of the epoxy paint on iodine volatility was confirmed in bench-scale separate effects tests [2] and likely increased the iodine volatility in RTF Test 1C by a factor of at least five. Although lack of phenomenon in the codes can explain part of the shortcoming, the wide variance among the code predictions by several orders of magnitude is cause for some concern. There appears to be an inconsistent treatment of thermal oxidation of I⁻ to volatile species. This is most apparent in the IMPAIR-2 aqueous speciation calculations (see Figures 5 and 6). Both IODE and LIRIC assume that oxidation occurs in solution [3,4], but at radically different rates as deduced from the pre-test predictions. INSPECT assumes that volatile organic iodides are formed on painted surfaces from conversion of deposited iodine [5]. Furthermore, the different modelling approach in IODE for painted surfaces was seen to affect airborne iodine by soaking up nearly all (>95%) of the iodine in follow-up calculations. When paint is removed (test case 3C-4), the IODE calculation is much more consistent with INSPECT and LIRIC as seen in Table 2.
Figure 3: Main Sinks Calculated for Test 3C-1 (all effects)
Figure 5: Aqueous Species Calculated for Test 3C-1
Figure 6: Aqueous Species Calculated for Test 3C-2

- LIRIC
- IODE
- INSPECT
- IMPAIR-2

Each graph shows the percentage distribution of aqueous species over time (days) for different tests.
Radiation was seen to be a very important variable. In Test 2C, all the codes consistently predicted an increase in airborne iodine fraction with radiation, as observed experimentally. The inconsistencies were in the extent of the radiation effect, which varied from one to three orders of magnitude. A complicating factor in the pre-test predictions was the inconsistent assumption about pH control. This inconsistency was removed in the follow-up calculations, and the variance among the codes was likewise reduced. Also, the organic materials released from the paint likely increased iodine volatility by an order of magnitude in the presence of radiation [2]. The effect of adding an organic material (methyl ethyl ketone) was seen to increase volatility by two orders of magnitude in a separate Canadian experiment with radiation in the RTF [6]. All organic materials were removed in some follow-up calculations, which resulted in more consistent calculations of aqueous speciation, with the exception of IMPAIR-2 under low pH conditions. Under alkaline conditions, however, the approximate agreement on aqueous I\textsuperscript{3-} levels is reassuring as it indicates that the simulation of radiolytic I\textsuperscript{-} oxidation under basic conditions is reasonably well developed.

Low pH was seen experimentally to increase iodine volatility. Again, as examined in Test 3C, all codes predicted a similar trend, although this too was complicated by the inconsistent pH assumptions. The follow-up calculations showed that the codes were very consistent in predicting increased volatility at a lower pH. Given that high pH minimises volatility, it is desirable to maintain high pH conditions following an accident. This simple concept could prove more difficult in practice. A very significant observation is that INSPECT predicted that the amount of chemical specified in the pre-test code exercise to increase the pH from 5.5 to 9 would be insufficient; hence the pH would remain low. The pH histories for tests 2C and 3C are shown in Figure 2. It is evident from the large fluctuations around pH 9 that control was more difficult than at pH 5.5, and indeed, much more alkali was added than originally planned. The reason why high pH is difficult to maintain is not clear; production of HNO\textsubscript{3} may be a factor, but it may also involve radiolytic decomposition of organic materials forming organic acids that reduce pH [6]. The volatilisation seen at low pH may be difficult to recover from; in test 3C, measurements showed that an order of magnitude reduction in airborne iodine would take about a day to occur. Factors inhibiting recovery could be the slow removal of organic iodides formed at low pH, and desorption of iodine from paint, which was adsorbed at low pH. Therefore, it would seem appropriate to ensure that low pH conditions are prevented in the containment sump water at all times following a reactor accident.

Although the codes generally predicted the total airborne fraction of iodine with reasonable agreement to the experiments, they differed widely in the fraction of organic iodides, as seen in Table 1. LIRIC predicted the highest fraction of organic iodide, but none of the codes appeared to model this detail very well.

The main sink for iodine was predicted to be aqueous I\textsuperscript{-} with very good consistency under high pH conditions, with or without radiation. At low pH, the main sinks predicted by the codes were both the water and the paint. This was in good agreement with the experimental results. However, there was poor agreement among the codes on the conditions under which iodine would be retained in the water or adsorbed by paint, and whether the dry surface or the wet surface would predominate. This was probably because of differences in input assumptions, and perhaps differences in the models incorporated into the various codes. Of particular interest were the contradictory pre-test predictions of INSPECT and TRENDS as to the preferred sink under almost identical solution boundary conditions, particularly pH. The follow-up INSPECT calculation showed the dry surface to adsorb iodine which is in contrast with its original pre-test prediction, where most of the iodine was predicted to be adsorbed on the wet paint. Based on this, it is evident that the adsorption process is a physical, not a chemical process in the INSPECT model, and code user assumptions about mass
transfer can significantly alter the predicted iodine behaviour. The experiments provide little
ingformation on the role of dry versus wet surfaces. Limited coupon data indicates that the dry surface
plays a much more dominant role than the wet surface. The opposite behaviour was observed in a
similar experiment, but with the vessel surface painted with inorganic zinc primer instead of epoxy
[6]. This situation shows the need for better understanding of how iodine interacts with surfaces,
surface models, and more complete experimental data.

The TRENDS pre-test prediction showed the dry surface to adsorb more than 99% of the
total iodine, while also predicting a low partition coefficient due to a predominance of I\textsuperscript{2} in the small
amount of iodine that remained in solution. Thus the bulk of the iodine was rapidly transferred first
from the liquid to the gas phase, then quickly to the dry paint; these rapid transfer mechanisms
prevented any significant levels ever accumulating in the air. This would suggest that if the paint were
modelled in TRENDS as an inert surface, the airborne fraction would have been much larger.

Although the other codes predicted various fractions of dry surface adsorption, they differed
from TRENDS in the predicted solution species, showing mostly I\textsuperscript{1} rather than I\textsuperscript{2}. Thus, the codes
were inconsistent in the extent to which the waterborne fraction of iodine was determined by its
aerodynamic chemistry or by the influence of the paint. The very limited amount of experimental
information on painted surface behaviour has been incorporated into different models in different
ways. This raises another uncertainty because the differences in the predictions could be due to
differences in the underlying data base, different modelling strategies, or both.

To help unfold the effects of the chemistry models from physical assumptions, the follow-up
calculations were performed with consistent rate constants for mass transfer and surface adsorption
and desorption. All codes agreed on the low level of airborne iodine, with the presence of the painted
surface. All but one code agreed that this situation also existed in the absence of any active surfaces.
This would appear to indicate that solution chemistry is a major controlling factor, and that the
painted surface might "mask" the conditions of high iodine volatility.

The dry surface was modelled as a sink for any I\textsuperscript{2} that enters the gas phase, but the extent
to which this altered the aqueous iodine behaviour varied among the codes. For LIRIC, the dry
surface did not appear to have a strong influence on aqueous species distribution nor the level of
airborne iodine. This was not so with the other codes. In particular IMPAIR-2 predicted the largest
amount of airborne iodine and the largest change in the aqueous species distribution, in the absence
of dry deposition. Another effect of the paint observed in the follow-up calculations was that it
tended to reduce the impact of the change in pH, by acting like a "sponge" for iodine. At low pH,
there is more I\textsuperscript{2} produced which transfers from solution to the gas phase, and then to the paint; the
airborne fraction is therefore lower with the painted surface. However, when the pH is raised, I\textsuperscript{2}
production is curtailed. I\textsuperscript{2} adsorbed on the paint may then desorb into the gas phase; thus, the
airborne fraction would be higher due to the presence of the paint, until new equilibria is established.
Such behaviour remains unconfirmed, since there was no "inert" surface in the RTF experiment with
the appropriate chemistry to compare with.

Despite differences in the code results, the conclusion from all the comparison runs seems
to be that the approaches to modelling the combined effects of solution chemistry and surfaces are
appropriate. However, it is clear from the pre-test predictions and follow-up calculations that
simulation of paint as a sink for iodine is still in the formative stages. The fact that the assumed
physical parameters were so diverse in the initial pre-test predictions is also grounds for suggesting
that modelling of painted surfaces is contentious. Furthermore, the divergence among the predictions
of iodine adsorption by the paint suggests that efforts directed toward evaluating the role of this
potentially important sink in the RTF tests could prove profitable. Efforts should also focus on
reactions with organic materials and production of organic iodides, based on the observed predominance of organic iodide in the gas phase. Finally, since the codes differed in minor speciation (IO₃⁻, HOI, I₂) and effects of change in pH, there is scope for an organised review of the database including thermal oxidation rates as previously noted.

6. CONCLUSIONS

The results of the RTF experiments provide a valuable benchmark for comparison to the initial pre-test code predictions, and the follow-up calculations provide additional insight as to where the consistencies and inconsistencies lie, and reasons for such. From evaluation of the code comparison results, the following conclusions are drawn.

1. Agreement on the levels of airborne iodine and the trends in these levels under varying conditions is good. However, organic iodide production is seen to be dominant experimentally. Differences in the predicted organic iodide component of the gas phase indicate that further work is needed to develop more realistic models.

2. Painted surfaces were seen to play a very important role, both as a source of volatility by releasing organic materials, and as a major sink for iodine under the phases of this experiment with low pH. Because predictions of the existing models diverge on the magnitude of these effects, further work is needed to develop models for this very important component.

3. The major sinks for iodine identified by the codes are water (as predominantly I⁻) and painted surfaces (as deposited I₂). The codes were very consistent on this point, in agreement with the measured results.

4. The code follow-up calculations clarified the importance of modelling surface effects, and also showed that the basic solution chemistry models are consistent. Differences in minor species were noted, and details of specific effects of surfaces and organic materials varied.

5. With some notable exceptions, agreement on the specific effects of variables such as pH, radiation and initial iodine species is reasonable.

From the above, the general conclusion is made that the codes appear to be well advanced overall. Based on the follow-up calculations, there is good reason for optimism that the models can be refined to predict iodine behaviour to better than "order of magnitude" accuracy for postulated accident conditions.
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REFERENCES


5.6 IODINE CHEMICAL FORMS IN LWR SEVERE ACCIDENTS*

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IODINE CHEMICAL FORMS IN LWR SEVERE ACCIDENTS

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ABSTRACT

Calculated data from seven severe accident sequences in light-water-reactor plants were used to assess the chemical forms of iodine in containment. In most of the calculations for the seven sequences, iodine entering containment from the reactor coolant system was almost entirely in the form of CsI with very small contributions of I or HI. The largest fraction of iodine in forms other than CsI was a total of 3.2% as I plus HI. Within the containment, the CsI will deposit onto walls and other surfaces, as well as in water pools, largely in the form of iodide (I⁻). The radiation-induced conversion of I⁻ in water pools into I₂ is strongly dependent on pH. In systems where the pH was controlled above 7, little additional elemental iodine would be produced in the containment atmosphere. When the pH falls below 7, it may be assumed that it is not being controlled and large fractions of iodine as I₂ within the containment atmosphere may be produced.

1. INTRODUCTION

This study attempts to re-examine the chemical form of iodine in containment, focusing on two major effects: the form entering from the reactor coolant system (RCS) and actions that may produce volatilization within the containment. The results are based on quantitative (calculated) results of seven severe accident sequences for light-water-reactor (LWR) nuclear power plants, which are listed in Table 1. These sequences represent a wide range of conditions that are significant risks; each sequence was evaluated by the Source Term Code Package (STCP) and documented in previous U.S. Nuclear Regulatory Commission (NRC) reports [1,2]. Note that this analysis does not address the ultimate disposition of various species, only the likelihood of their formation or presence in the gas phase. Thus, the effects of deposition or various engineered safety features are not considered.

The primary motivation of this study is to re-evaluate the basis for Regulatory Guides 1.3 [3] and 1.4 [4] which state that:

1. 50% of the maximum iodine inventory of the reactor core is released to the primary reactor containment; 25% is available for leakage; and

Table 1. LWR accident sequences evaluated

<table>
<thead>
<tr>
<th>Plant</th>
<th>Reactor type</th>
<th>Accident</th>
<th>Accident type</th>
<th>Documentation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand Gulf</td>
<td>BWR — Mark III</td>
<td>TC (ATWS)</td>
<td>High pressure</td>
<td>BMI-2104, Vol. III</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TQUV (No makeup water)</td>
<td>Low pressure</td>
<td>BMI-2104, Vol. III</td>
</tr>
<tr>
<td>Peach Bottom</td>
<td>BWR — Mark I</td>
<td>TC2 (ATWS)</td>
<td>High pressure</td>
<td>NUREG-4624, Vol. I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AE (LOCA, no ECCS)</td>
<td>Low pressure</td>
<td>BMI-2104, Vol. II</td>
</tr>
<tr>
<td>Sequoyah</td>
<td>PWR — ice condenser</td>
<td>TBA</td>
<td>Low pressure</td>
<td>NUREG-4624, Vol. II</td>
</tr>
<tr>
<td>Surry</td>
<td>PWR — large containment</td>
<td>TMLB’ (Station blackout)</td>
<td>High pressure</td>
<td>BMI-2104, Vol V</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AB (LOCA, no ECCS)</td>
<td>Low pressure</td>
<td>BMI-2104, Vol. V</td>
</tr>
</tbody>
</table>

*See refs. 1 and 2 for complete reference description.
2. of this 25% available for leakage, 91% is in the form of elemental iodine, 5% is in 
the form of particulate iodine, and 4% is in the form of organic iodide.

Iodine is assumed to enter containment in the forms and amounts stated above with neither 
physical nor chemical changes occurring in containment. However, present knowledge may 
not support this distribution of iodine forms and the static state throughout the duration of 
an accident.

It is anticipated that a more realistic representation of the chemical speciation of 
fission product iodine would likely result in a large proportion of particulate iodine (CsI), 
with smaller amounts of gaseous iodine (HI or I). In addition, a continuous revolatilization 
of molecular iodine might occur within containment and would include some small 
complement of organic iodine.

2. CHEMICAL FORMS OF IODINE ENTERING CONTAINMENT 
FROM THE REACTOR COOLANT SYSTEM

The chemical forms of iodine in the RCS are closely tied to the chemical forms of 
cesium, as illustrated by the following reactions:

\[ \text{CsI} + \text{H}_2\text{O} \leftrightarrow \text{CsOH} + \text{HI} \] (1)

\[ \text{CsI} + \text{H}_2\text{O} \leftrightarrow \text{CsOH} + \text{I} + \frac{1}{2} \text{H}_2 \] (2)

Equation (1) is the reverse of an acid-base reaction and, thus, is unlikely to proceed unless 
one or both products are removed. Reactions of CsOH with other materials in the RCS will 
tend to lower the partial pressure of CsOH. Such reactions will shift the equilibrium to the 
right and enhance the formation of HI. At temperatures in excess of 1800 K and at low 
hydrogen pressures, atomic iodine is the favored product of the reaction between CsI and 
\( \text{H}_2\text{O} \), as shown in Eq. (2). Thus, in general, iodine chemical forms other than CsI are 
favored when steam pressures are much greater than cesium hydroxide pressures.

2.1 DATA MANIPULATION AND CALCULATIONAL TECHNIQUES

In order to evaluate the chemistry in the RCS, it is necessary to specify the 
thermodynamic conditions under which reactions would occur and a measure of the time 
span over which such conditions hold. Required quantities are temperature, pressure, 
volume, and molar inventories of constituent species \( \text{H}_2, \text{H}_2\text{O}, \text{I}, \text{and Cs} \) within each control 
volume. This evaluation has been undertaken for each of the accident sequences in Table 
1 using data from the STCP calculations \[1,2\]. See ref. 5 for a complete description of 
the data manipulations and calculational procedures.

Another necessary quantity is the mean residence time (s) for flow through a control 
volume. Figure 1 shows this quantity for each of the two control volumes above core in the 
Surry TMLB' sequence. A mean residence time greater than 1 s is usually sufficient to
Fig. 1. Mean residence time in volumes above core for Surry TMLB.

attain equilibrium for regions with a sufficiently high temperature. In Fig. 1, this condition holds for both volumes, although control volume 1 approaches this limit briefly at about 30 min.

Fission products released from the core will undergo changes in temperature and concentration as they pass through regions of the RCS. A chemical kinetic model used 20 reactions to determine the control volume where an equilibrium of the iodine, cesium, hydrogen, and steam species becomes "frozen." This means that the temperatures and concentrations of species in subsequent control volumes are not sufficient to reach an equilibrium in the mean residence time available. Separate equilibrium calculations were run, using the FACT system [6], to obtain the final distribution of iodine species.

2.2 OVERALL RESULTS OF CALCULATIONS

In six of seven calculations, the iodine was almost entirely in the form of CsI; the contribution of I or HI was less than 0.1% of the overall percentage of iodine. These
calculations considered only reactions involving cesium, iodine, hydrogen, and water. They covered a wide range of temperatures, hydrogen concentrations, steam concentrations, and fission product concentrations. Reactions with other RCS materials were not included in these calculations, but their effects were investigated with scoping or bounding calculations as described in Sects. 2.3 and 2.4.

During the second half of the Surry AB sequence, there is a period during which temperatures in the core region are in excess of 2000 K, and subsequent volumes of the upper grid plates and guide tubes are at temperatures of only 500 K. Because of this, equilibrium compositions in the core region would be "frozen" in by the rapid decrease in temperature. For this sequence, the overall iodine distribution was 2.8% as I and 0.4% as HI, with the remainder as CsI. Thus, a total of 3.2% as I plus HI was the largest fraction of iodine in a form other than CsI in this study.

2.3 REACTION OF CsOH WITH SURFACES

Of the possible reactions of CsOH in the RCS, the reaction with structural surfaces is the most amenable to evaluation. Johnson et al. [7] have studied the deposition of CsOH on oxidized stainless steel surfaces. They used the following simple expression to relate the thermodynamic activity of CsOH to the surface concentration:

\[ a = \exp \left( \frac{98.5 - 3.84 \times 10^4}{T} (x - 0.28) \right), \quad x < 0.28, \quad (3) \]

where \( a \) and \( x \) are the surface activity (atm) and concentration (mg/cm\(^2\)), respectively. The reaction of interest with stainless steel may be written as

\[ \text{CsOH}(\text{surface}) \rightarrow \text{CsOH} \ (\text{gas}). \quad (4) \]

Thermochemical data obtained from the FACT system [6] give the respective equilibrium constants for the reactions in Eqs. (1) and (4) as

\[ K_1 = \frac{P_{\text{CsOH}}}{P_{\text{H}_2\text{O}}} \frac{P_{\text{HI}}}{P_{\text{CsI}}} = \exp \left( -1.407 - \frac{1.626 \times 10^4}{T} \right), \quad (5) \]

\[ K_4 = \frac{P_{\text{CsOH}}}{a} = \exp \left( -1.189 \times 10^1 - \frac{1.500 \times 10^4}{T} \right), \quad 900 \leq T \leq 1263. \quad (6) \]

Calculations using Eqs. (3), (5), and (6), together with mass balances on cesium and iodine, indicate that the amount of HI formed due to the CsOH surface reaction is less than 0.6% for each of the accident sequences studied. This is because \( P_{\text{CsOH}} \) must be very small if the ratio \( P_{\text{HI}}/P_{\text{CsI}} \) is large enough to be significant. However, if \( P_{\text{CsOH}} \) is very small, then so is \( x \); hence, very little surface reaction could occur.
2.4 OTHER REACTIONS OF CsOH

Other reactions of CsOH may also remove it from the vapor phase, but there is generally a lack of information on the amounts and locations of other reactants. Several cesium borates may form in the reaction of CsOH with boric acid or boron oxide, which are introduced into the RCS as coolant additives. For example, the formation of cesium metaborate (CsBO₂) may occur by the following reaction:

\[ \text{CsOH} + \text{HBO}_2 \rightarrow \text{CsBO}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (7)

If sufficient metaboric acid (HBO₂) were available, it could result in a lowering of the vapor pressure of CsOH.

Several experiments using simulated fuel bundles have been done at Oak Ridge National Laboratory (ORNL) to evaluate such possibilities [8]. In general, boric acid and boron oxide were not available in the gas phase to react with cesium, because they reacted strongly with metal oxide surfaces, in particular ZrO₂. Thus, this mechanism is not expected to significantly alter the form of iodine in the RCS.

2.5 SUMMARY OF IODINE CHEMICAL FORMS IN THE RCS

Iodine entering containment from the RCS should be predominantly in the form of CsI. The examination of Cs-I-H₂O-H₂ interactions for seven accident sequences gave a maximum of 3.2% iodine as I plus HI, with the remainder as CsI. There are some uncertainties in the reactions of CsOH with oxides and in the revaporization of CsI that produce uncertainties to the extent in which iodine may exist in a form other than CsI. Cesium needs to be removed from reactions involving iodine if very much iodine is to be in a form other than CsI.

Based on this analysis, the chemical forms of iodine entering containment from the RCS may reasonably be described as a maximum of 5% as elemental iodine and HI, with not less than 1% as either elemental iodine or HI. The remaining 95% would be CsI.

3. PROCESSES THAT ALTER THE CHEMICAL FORMS OF IODINE IN CONTAINMENT

3.1 RADIOLYSIS

In the presence of radiation, the equilibrium formation of I₂ from I⁻ is strongly dependent on pH and less dependent on temperature and concentration. Ignoring the last two effects, this dependence can be written as

\[ F(\text{pH}) = \text{equilibrium fraction} = \frac{[\text{I}_2]}{[\text{I}_2] + [\text{I}^-]} \]  \hspace{1cm} (8)
where \([x]\) is concentration (g-atom/L). Data from Lin [9], as shown in Fig. 2, illustrate this effect for several initial concentrations and pH values using solutions that were at ambient temperature and had been irradiated for 1 h at 4.5 Mrad/h. The final pH values were not indicated but probably decreased slightly because no mention is made of buffering in the experiment. The values of pH >6 may not be quantitatively useful since the very small conversion fractions are probably incorrect due to measurement error. As seen in Fig. 2, \(F\) is near 0 for pH >7 and near 1 for pH <2 but experiences a drastic change in the range 3 < pH < 4. This can be effectively modeled by the functional form

\[
F = \left[1 + e^{\alpha \cdot \text{pH} + \beta}\right]^{-1},
\]

which was fit to Lin's data using nonlinear least squares, yielding \(\alpha = 1.72, \beta = -6.08\).

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**Fig. 2.** Radiolytic conversion of \(I^-\) to \(I_2\) [data from C. C. Lin, *J. Inorg. Nucl. Chem.* 42, 1101 (1980)].

If the pH is maintained sufficiently high through buffering or addition of sufficient basic material, very little conversion will occur. In this case, most iodine remains dissolved as \(I^-\). A quantitative treatment is more difficult. Lin's data generally indicate less than 1% conversion at pH = 7. This value declines as the total iodine concentration decreases.
ORNL data indicate that for a dose rate of 0.35 Mrad/h, an iodine concentration of $10^{-4}$ mol/L conversion was 0.003% after 4 h irradiation and 0.03% after 24 h. The last value, 0.03%, has been used in the present work.

If the pH level is not deliberately controlled, it may decrease sufficiently to allow considerable conversion of $I^-$ to $I_2$. The primary mechanism is radiolytic generation of nitric acid. If the pH is neutral initially, then this effect soon dominates, resulting in

$$[H^+] = 10^4 \frac{g(\text{HNO}_3)}{V_L N_a} ,$$

where

- $[H^+] =$ concentration of $H^+$ (mol/L),
- $g(\text{HNO}_3) =$ rate of $\text{HNO}_3$ production due to irradiation (molecules/100 eV),
- $E_{\text{dep}} =$ total energy deposition due to fission product decay (MeV),
- $V_L =$ volume of water (L),
- $N_a = 6.022 \times 10^{23}$ (molecules/mol).

ORNL measurements of pH change and nitrate ion formation at 30°C gave:

$$g(\text{HNO}_3) = 0.007 \text{ molecules/100 eV} .$$

This relationship is based on radiation absorption by the aqueous phase. The actual mechanism for the formation of nitric acid is not known. It may occur in the aqueous phase, in the gas phase, or at the gas-surface interface.

The energy deposition over a time $\Delta t$ is

$$E_{\text{dep}} = \dot{E}_{\text{dep}} \Delta t = \Delta t \sum m_j \dot{\epsilon}_j ,$$

where

- $\Delta t =$ time (h),
- $\dot{E}_{\text{dep}} =$ total energy deposition rate (MeV/h),
- $m_j =$ mass of nuclide group $j$ in pool (g),
- $\dot{\epsilon}_j =$ energy deposition rate per unit mass of nuclide group $j$ (MeV/s · g).

A grouping of fission products and actinides compatible with that used in STCP accident studies was selected and is shown in Table 2. The specific energy deposition rate $\dot{\epsilon}_j$ for each group was determined from a detailed analysis of Browns Ferry [a large boiling-water reactor (BWR) with Mark I containment] accident sequences using the ORIGEN2 code [10]. Complete details of this calculation can be found in ref. 11. These group energy deposition rates for the Browns Ferry BWR are assumed applicable to all plants and sequences considered in the present study.

The group masses $m_j$ are obtained by multiplying the total core inventory $\bar{m}_j$ by the estimated fractional release into containment:

$$m_j = f_j \bar{m}_j .$$

Total core inventories for the plants are those identified in previous reports [1,2]. Various estimates of the fractional releases $f_j$ can be obtained from a study by Nourbakhsh [12].
Table 2. Nuclide groupings and group-specific energy deposition rates

<table>
<thead>
<tr>
<th>Group index, $j$</th>
<th>Characteristic element</th>
<th>Included nuclides</th>
<th>Energy deposition rate, $\epsilon_i \times 10^{-13}$ (MeV/s $\cdot$ g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>I, Br</td>
<td>111.2</td>
</tr>
<tr>
<td>2</td>
<td>Cs</td>
<td>Cs, Rb</td>
<td>1.006</td>
</tr>
<tr>
<td>3</td>
<td>Te</td>
<td>Te, Se</td>
<td>3.497</td>
</tr>
<tr>
<td>4</td>
<td>Sr</td>
<td>Sr</td>
<td>7.879</td>
</tr>
<tr>
<td>5</td>
<td>Ba</td>
<td>Ba</td>
<td>2.348</td>
</tr>
<tr>
<td>6</td>
<td>Ru</td>
<td>Ru, Tc, Rh, Mo</td>
<td>1.706</td>
</tr>
<tr>
<td>7</td>
<td>Ce</td>
<td>Ce, Pu, Np</td>
<td>0.407</td>
</tr>
<tr>
<td>8</td>
<td>La</td>
<td>La, Am, Cm, Y, Pr, Nd, Pm, Sm, Eu, Zr, Nb</td>
<td>6.523</td>
</tr>
<tr>
<td>9</td>
<td>Xe</td>
<td>Xe, Kr</td>
<td>0.721</td>
</tr>
</tbody>
</table>

*Includes only fission products.

Finally, $\Delta t$ in Eq. (12) is the time needed to reach the approximate steady state. In general, the first phase of an accident can be considered to reach steady state in 10 to 15 h; the latter is the time value used for $\Delta t$ in this work. Combining Eqs. (9) through (12), the fractional conversion takes the form

$$F = \left[ 1 + e^{\frac{-a}{\ln 10}} \right]^{-1} = \left[ 1 + 5.55 \times 10^{13} \left( \frac{V_L}{E_{dep}} \right)^{0.747} \right]^{-1}.$$  \hspace{1cm} (14)

Thus, when pH is not controlled, fractional conversion is directly dependent on the liquid volume $V_L$ in which radiolysis occurs; the energy deposition $E_{dep}$, which itself depends on the amounts of radioactive species in water; and the time $\Delta t$ allowed for radiolysis processes to reach steady-state conditions.

### 3.2 GAS-LIQUID PARTITIONING

The equilibrium distribution of a single volatile species such as $I_2$ is represented by the partition coefficient:

$$P = \frac{[I_2 \text{ (aq)}]_{eq}}{[I_2 \text{ (g)}]_{eq}}.$$  \hspace{1cm} (15)
This quantity is inversely related to the Henry's Law constant $K$ (i.e., $P = 1/K$) and should not be confused with the overall iodine partition coefficients often used in reactor safety studies. In this study, partition coefficients for $I_2$ were calculated from the equation:

$$\log_{10} P = 6.29 - 0.0149 \, T.$$  \hspace{1cm} (16)

This relationship gives the experimental value reported by Eguchi et al. [13] and by Sanemasa et al. [14] at 298 K. Extrapolation of the experimental results of these investigators to 373 K yielded a partition coefficient of 3. Furrer et al. [15] reported a calculated partition coefficient at 373 K of 9. Some of the data used in his calculation were based on estimated parameters. Equation (16) gives a partition coefficient of 5.3 at 373 K, a reasonable average of these values.

Even though it may take considerable time to approach such equilibration in a large system such as a reactor containment, Eq. (15) can still be used to estimate $I_2$ volatility. In fact, instant equilibration is a conservative assumption since considerable holdup could be expected in real-life situations.

### 3.3 GAS-PHASE REACTIONS: FORMATION OF ORGANIC IODIDES

The process of converting $I_2$ into organic iodides (chiefly CH$_4$I) is still not fully understood. Postma and Zavodoski [16] reviewed production rates from about 70 containment tests and determined that the asymptotic steady-state conversion to CH$_4$I was

$$\text{percent } I_2 \text{ converted} = 0.19 \, C_{m_0}^{-0.26},$$  \hspace{1cm} (17)

where $C_{m_0}$ = initial $I_2$ concentration (mg/m$^3$). In a more recent review, Beahm et al. [17] described the steady-state organic iodide concentration (mg iodine/m$^3$) using the form

$$C^* = 0.0189 \, C_{m_0}^{0.82}$$  \hspace{1cm} (18)

in place of Eq. (17). This equation was based on containment experiments performed with irradiated fuel rather than simulated materials, resulting in a percent conversion somewhat greater than that obtained from simulant materials (cf. Fig. 4, ref. 17). By converting units to g-atom/L, Eq. (18) can be rewritten as

$$[\text{CH}_4I] = \beta \, [I_2]^{0.82},$$  \hspace{1cm} (19)

where $\beta = 0.0189 \times 10^5 \cdot \text{MW}^{-0.18}$, MW being the molecular weight of I. For MW = 130, then $\beta = 6.55 \times 10^{-4}$, which indicates that generally less than 1% of gaseous iodine will be organic.

### 3.4 OVERALL BEHAVIOR

As described in the previous sections, the distribution of species throughout the gas and liquid phases can be estimated from models for three basic processes: radiolytic
conversion of I\textsuperscript{−} to I\textsubscript{2} in water, evaporation of I\textsubscript{2}, and gas-phase formation of organic iodides. Defining the desired quantities as concentration variables (g-atom/L),

\[ C_1 = [I_2(aq)], \quad C_2 = [I_2(g)], \quad C_3 = [I^-(aq)], \quad C_4 = [\text{CH}_3\text{I}(g)] \]  

(20)

Eqs. (15), (8), and (19) can be rewritten as

\[ C_1 + PC_2, \quad C_3 = \frac{(1 - F)}{F} C_1, \quad C_4 = \beta C_2^{0.82}. \]  

(21a,b,c)

In addition, the total iodine inventory \( N_T \) (g-atom) is equal to the initial I\textsuperscript{−} entering the containment, and remains constant throughout the distribution process:

\[ N_T = V_L (C_1 + C_3) + V_g (C_2 + C_4). \]  

(21d)

These four equations, (21a) through (21d), can be solved in a straightforward manner to obtain the four unknown concentrations in Eq. (20).

Because organic iodide is such a small part of the total, it is helpful to examine the distribution behavior without considering organic iodide. By ignoring Eq. (21c), it is possible to combine and rearrange Eqs. (21a), (21b), and (21d) to get

\[ \frac{N_2}{N_T} = \left(1 + \frac{V_L P}{V_g F}\right)^{-1}. \]  

(22)

where \( N_2 = V_g C_2 = \) g-atom of I\textsubscript{2} in gas. Equation (22) is a convenient expression of the fraction of iodine that is volatilized. (Consideration of organic iodide will increase this fraction very slightly.) For the case of uncontrolled pH, substitution of Eq. (14) into Eq. (22) yields

\[ \frac{N_2}{N_T} = \left(1 + \frac{V_L P}{V_g} \left[1 + 5.55 \times 10^{13} \left(\frac{V_L}{E_{dep}}\right)^{0.747}\right]\right)^{-1}. \]  

(23)

Equations (22) and (23) are in particularly convenient form to quickly estimate iodine volatility.

3.5 CALCULATIONAL RESULTS AND DISCUSSION

The analysis described in this section has been applied to each of the seven accident sequences mentioned in Table 1. The gas volumes used for BWRs include all primary containment space, although it may sometimes be appropriate to use only wetwell airspace, depending on sequence considerations. The various data and the quantities calculated from them are described for each accident sequence in ref. 5.

The conversion data of Lin [9] were taken at a dose rate of 4.5 Mrad/h — in the range of PWR rates. The data taken at ORNL are generally in the range of BWR dose
rates (i.e., 0.35 to 0.6 Mrad/h). Both sets of data indicate that conversion is dominated by pH effects. In this study, two scenarios were evaluated: (1) control of pH above 7 and (2) uncontrolled pH with resulting drops below 7 due to nitric acid formation. For this calculation, it was not necessary to specify the material that was used to control the pH at 7 or above.

If the pH is controlled so that it stays above 7, the system of equations (21) is solved to yield the species distributions in Table 3. These results indicate a small production of volatiles for PWRs but virtually none for BWRs. Such results are strongly dependent on the aqueous conversion fraction of $F = 3 \times 10^{-4}$, which represents a best estimate of the maximum from ORNL data. Thus, if pH is maintained at 7 or above, only a small additional amount of I$_2$ is expected in the gas phase of PWR systems.

<table>
<thead>
<tr>
<th>Plant</th>
<th>Fraction of total iodine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grand Gulf</td>
<td></td>
</tr>
<tr>
<td>TC$_\gamma$</td>
<td>0.05</td>
</tr>
<tr>
<td>TQUV$_\gamma$</td>
<td>0.01</td>
</tr>
<tr>
<td>Peach Bottom</td>
<td></td>
</tr>
<tr>
<td>AE$_\gamma$</td>
<td>0.002</td>
</tr>
<tr>
<td>TC2$_\gamma$</td>
<td>0.002</td>
</tr>
<tr>
<td>Sequoyah</td>
<td></td>
</tr>
<tr>
<td>TMLB'$_\gamma$</td>
<td>1.9</td>
</tr>
<tr>
<td>Surry</td>
<td></td>
</tr>
<tr>
<td>AB$_\gamma$</td>
<td>2.4</td>
</tr>
<tr>
<td>CH$_3$I(g)</td>
<td></td>
</tr>
</tbody>
</table>

*Assuming an equilibration time of $\Delta t = 15$ h.

If the pH falls below 7, a system for controlling pH is not being used and the decreased pH results in a larger fraction of aqueous I$^-$ being converted to I$_2$. Evaporation of this volatile species to maintain equilibrium partitioning will result in greater atmospheric I$_2$. This, in turn, yields higher organic iodide concentrations. Results for this case are shown in Table 4 for the equilibrium species distributions. As expected, the levels of airborne volatiles are much higher than in the controlled case, indicating almost complete conversion for PWRs.

The gaseous I$_2$ fraction is considerably higher in PWRs than in BWRs because the large water volumes in the latter both lower the dose rate and retain greater quantities of dissolved I$_2$. This last effect also depends on the gas volume and the ratio of gas to liquid volumes. It is ironic that the relatively small gas space in the Peach Bottom reactor (generally a safety liability) permits noticeably less evaporation than other reactors, resulting in the lowest gaseous I$_2$ fractions.
Table 4. Distribution of iodine species for uncontrolled pH

<table>
<thead>
<tr>
<th>Plant</th>
<th>Accident</th>
<th>Fraction of total iodine (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$I_2(g)$</td>
<td>$I_2(L)$</td>
<td>$I^-(L)$</td>
<td>$CH_3I(g)$</td>
</tr>
<tr>
<td>Grand Gulf</td>
<td>TC$\gamma$</td>
<td>24.1</td>
<td>13.9</td>
<td>61.8</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>TQUV$\gamma$</td>
<td>6.0</td>
<td>16.6</td>
<td>77.7</td>
<td>0.05</td>
</tr>
<tr>
<td>Peach</td>
<td>AE$\gamma$</td>
<td>1.6</td>
<td>20.5</td>
<td>77.9</td>
<td>0.01</td>
</tr>
<tr>
<td>Bottom</td>
<td>TC2$\gamma$</td>
<td>10.1</td>
<td>16.7</td>
<td>73.2</td>
<td>0.06</td>
</tr>
<tr>
<td>Sequoyah</td>
<td>TBA</td>
<td>67.3</td>
<td>9.6</td>
<td>22.6</td>
<td>0.40</td>
</tr>
<tr>
<td>Surry</td>
<td>TMLB'γ</td>
<td>97.2</td>
<td>1.5</td>
<td>0.7</td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>AB$\gamma$</td>
<td>97.7</td>
<td>1.2</td>
<td>0.6</td>
<td>0.60</td>
</tr>
</tbody>
</table>

*Assuming an equilibration time of $\Delta t = 15$ h.

The other principal effect is due to temperature — the $I_2$ partition coefficient changes markedly over the range of temperatures used. This effect of temperature is most noticeable in the BWR sequences where different sequences at the same plant show large differences in the airborne $I_2$ fraction. Thus, an increase in containment temperature (at the gas-liquid interface) from 60 to 115°C produces nearly an order of magnitude increase in the airborne fraction.

The organic iodide is present in PWRs at about 0.5% of core inventory; in BWRs, this concentration is closer to 0.1%. The $I_2$ generated by the radiolytic conversion of $I^-$ dominates the amount released as $I_2$ from the RCS. Further, based on the equilibrium assumption, the presence of some $I_2$ already airborne will result in less evaporation of $I_2$ formed radiolytically. Hence, for the case of uncontrolled pH, the cumulative total is well represented by the equilibrium amount formed within containment.

4. TECHNICAL FINDINGS

This study assumed that iodine forms in containment can be delimited by an examination of the seven severe accident sequences in LWR plants, along with an evaluation of associated processes. The associated processes include the deposition of CsOH on RCS surfaces and the effects of radiolysis. The issue is the chemical form of iodine that may be produced in the RCS and in containment — not the ultimate disposition of the various chemical forms. For example, it is likely that much of the gaseous $I_2$ in containment would be removed by engineered safety features or would deposit on painted or metal surfaces.
4.1 ASSESSMENT OF IODINE CHEMICAL FORMS IN THE RCS

The maximum iodine as I plus HI calculated for the seven severe accident sequences is 3.2%. Iodine in all forms other than I, HI, and CsI is estimated to be less than 1%. Although this analysis only considered seven sequences at four plants, it is reasonable to consider that a maximum of 5% of the iodine would be present as elemental iodine and HI for all accident sequences. A minimum value would not be expected to be less than 1%. The remaining 95% of the iodine would be as CsI.

The gaseous forms of iodine that entered containment from the RCS were given in terms of both elemental iodine and HI, which are related by the reaction

\[ I + \frac{1}{2}H_2 \rightarrow HI. \]  

(24)

Lower temperatures and higher hydrogen pressures tend to favor HI over I, with the opposite conditions favoring I over HI. Five percent of iodine as I plus HI, with not less than 1% in either form, means that the ratio \( P_{HI}/P_I \) in Eq. (26) would range from 0.25 to 4. With a hydrogen pressure of 1 atm, this would occur in the temperature range of 1456 to 2404 K; with a hydrogen pressure of 10 atm, it would occur in the temperature range of 1251 to 1893 K. These conditions are reasonable for situations that lead to the formation of I or HI.

The major uncertainty is the extent to which CsOH will react with oxide materials and reduce its vapor pressure. If the reaction of CsOH is to have a major impact on the iodine chemical forms, most of it (certainly more than 90%) must be fixed at a very low vapor pressure.

4.2 ASSESSMENT OF IODINE CHEMICAL FORMS IN CONTAINMENT

The production of I\(_2\) in containment will be directly related to the pH levels of the water pools. Failure to control the pH at or above 7 could result in a dramatic increase in atmospheric I\(_2\). Essentially all of the I\(_2\) could become gaseous in the PWRs without pH control. For BWRs, as much as 25% of the core inventory could become gaseous. However, maintaining the pH above 7 results in negligible additional volatilization.

5. REFERENCES


6. FACT, a copyrighted product of THERMFACT Ltd., 447 Berwich Ave., Mount-Royal, Quebec, Canada, H3R 1Z8.


DISCUSSION

Evans
How are the organic iodides postulated to be formed?

Weber
Homogeneous gas phase reaction involving I₂.

Morell
Have you taken into account the influence of Ag on the behavior of Iodine?

Weber
It is possible that a variety of additional materials could react with iodine in both the RCS and the containment. This is a major source of uncertainty in reactor safety evaluations. In the present work, we did not consider such interactions that were non-conservative.

Bowsher (Comment)
I am concerned that some of the assumptions in this study make application of some of the results of limited value. In particular, I believe it is important to take account of chemical interactions and the role of aerosols. For example, cesium iodide will interact with boric acid to produce HI and CsBO₂. The HI will subsequently react with Cd aerosols to generate CdI₂. Whilst the studies at ORNL addressed some effects of boric acid, they did not, for example, address the initial blow-down and coolant volatilization phases which may coat the primary circuit surfaces with boric acid at a concentration of about 0.1 g cm⁻². Thus, application of the results from this study should take account of the approximations used, and limiting conditions set, in this work.

Soda
What is impact of uncertainties associated with STCP or MELCOR or the source term estimate?

Soffer
We may use the MELCOR code to get additional insights with regard to the chemical form of the iodine entering containment. We probably will also ask ORNL to investigate methods of pH control, as well. We are proceeding very cautiously with regard to removal of charcoal in filters, since a number of uncertainties have been expressed.

Dutton
1) Can you comment on how pH may be controlled?
2) In a high pressure sequence, such as TMLB', it is very difficult to see how the CsI could reach the sump without being accompanied by large quantities of corium. How would this effect your predictions?

Weber
1) The actual method of pH control is not considered in our work.
2) All CsI was assumed deposited in water pools, even though this may not happen in practice. This is a conservative assumption, since radiolytic conversion is the most likely way to generate additional volatile species.
5.7 IMPROVEMENT AND VALIDATION OF TELLURIUM TRANSPORT MODELS IN THE RAFT CODE

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ABSTRACT

The European Communities, within the Shared Cost Action on Reactor Safety 1988-1991 Programme, has been sponsoring a study on the Chemical Behaviour of Tellurium Species in the Reactor Pressure Vessel and the Reactor Cooling System under Severe Accident Conditions, which has been performed at the Chair of Nuclear Technology, Madrid Polytechnical University.

Apart from compiling a state-of-the-art report, including an assessment of the capabilities of transport codes, a validation/improvement effort on tellurium chemistry model in the RAFT code was undertaken.

The improvement consisted in the inclusion of new tellurium species, and of a simple model for the interaction of tellurium with silver aerosols. The validation consisted in the analysis of the MARVIKEN 4 and 7 experiments with the modified/improved versions of RAFT 1.0 and RAFT 1.1.

It was found that the presence of silver aerosols reduces the vapour pressure of Te\textsubscript{2} and modifies its deposition mechanisms.

1. THE RAFT CODE

RAFT (Reactor Aerosol Formation and Transport)[1] is the first reactor coolant system fission product transport code including homogeneous and heterogeneous nucleation mechanisms in competition with condensation of vapour on structures.

The chemistry package treats a flow system composed of steam, hydrogen, fourteen elements (Cs, I, Te, Xe, Ag, In, Cd, Sn, Sr, Mo, Ru, Ba, Zr and Mn), control rods and structural materials and a generalized inert gas. Depending on the local gas temperature and pressure along the flow, these elements and steam and hydrogen will chemically equilibrate to form various compounds. Those involving tellurium are: Te(gas=\textit{g}), TeO(g), Te\textsubscript{2}(g,condensed = \textit{c}), H\textsubscript{2}Te(g), TeO\textsubscript{2}(g,\textit{c}) and CdTe(g).

Chemical calculations are performed by either Gibbs free energy minimization or by algebraic elimination based on the ordering of the various chemical reactions as a function of their rates. Changes in elemental concentration result from vapour condensation in the gas phase, or on boundary surfaces.

A different approach is adopted for modelling chemisorption of chemically reactive species, such as CsOH and Te\textsubscript{2} on stainless steel. The overall rate is obtained by considering diffusion (from core to surface) and chemisorption processes to act in series, leading to equation

\[ Wv_j = (1/hm_j + 1/hc_j)^{-1} Pvj/R Tw, \]

where \( Wv_j \) is the vapour flux of \( j^{th} \) species; \( hm_j \), the mass transfer coefficient; \( hc_j \), the forward reaction rate due to chemisorption; \( Pvj \), the vapour pressure of \( j^{th} \) species; \( R \), the gas constant, and \( Tw \), the temperature.
of structural surface.

Recent experimental data suggest an Arrhenius type of expression for \( \dot{c} \) (kinetically controlled) for CsOH. For \( \text{Te}_2 \), RAFT 1.0 uses a value of \( \dot{c} \) equal to 0.00181 m/s, however, RAFT 1.1, version released on July 1990, uses \( \dot{c} = 0.1 \) m/s instead. The reason is that tellurium appears to be very reactive, so that the interaction is limited by diffusion rather than by chemisorption kinetics. This change has been included, along with some others, in the calculation of Sherwood number what confirms the trend of mass transfer controlled reaction. More detailed information on the chemistry model and the modifications introduced in the new version can be found elsewhere.[2-3]

The first approach of the authors took to the RAFT code was a detailed study of its chemistry model with special emphasis on tellurium aspects.[2] Given the characteristics and limitations of the model included in the code, an improvement effort was started which has been complemented with a validation exercise.

The modifications carried out are:
- The capabilities have been expanded to include new tellurium species.
- New variables and modifications have been incorporated to compute separately CsOH and \( \text{Te}_2 \) condensed on structures and chemisorbed on them.
- Some Fortran errors found in the as received version of the code have been detected and corrected.
- A new model has been included to calculate the interaction between vapours and aerosols focused towards the formation of Ag\(_2\)Te.

The validation effort includes the analysis of the MARVIKEN 4 and 7 experiments with the modified/improved versions of RAFT 1.0 and RAFT 1.1.

2. MODIFICATIONS INTRODUCED INTO THE RAFT CODE

Two modifications have been introduced into the RAFT code with the aim of improving its simulation capabilities. The first consists in the incorporation of new possible chemical species; the second is a new model to study the interaction of tellurium vapours with silver aerosols. The details for such modifications are given below, while the validation efforts are discussed in chapter 3.

2.1 Tellurium Chemistry Model

The RAFT code considers chemical equilibrium in the gaseous phase. Near the core, within the high temperature environment of a severe accident, the time constant of gaseous reactions is small, although there may be non-equilibrium with regard to condensed species. That is why the particles are not assumed to be in chemical equilibrium with the bulk gas. This enables nucleation and dynamic growth of particles due to condensation to be modelled more realistically.[6]

A priori, the species involving tellurium are: \( \text{Te}, \text{Te}_2, \text{TeO}, \text{TeO}_2, \text{CdTe}, \) and \( \text{H}_2\text{Te}_2 \) of which \( \text{Te}_2 \) and \( \text{TeO}_2 \) are able to condense.

The capabilities of RAFT have been expanded to incorporate new tellurium compounds, these are: \( \text{Te}_2\text{(g)}, (\text{TeO})_2\text{(g)}, \text{TeO(OH)}_2\text{(g)}, \text{TeOH(g)}, \text{Te(OH)}_2\text{(g)}, \text{InTe(g)}, \text{InTe}_2\text{(g)}, \text{SnTe(g)}, \text{AgTe(g)}, \text{MnTe(g)}, \text{Cs}_2\text{Te(g)}, \text{Sn}_2\text{Te}_2\text{(g)}, \text{BaTe(g)}, \text{BTe(g)}, \text{SbTe(g)}, \text{EuTe(g)}.\)

Thermochemical data necessary for the inclusion of these species in the equilibrium were obtained from different references [7-14].

When it was possible, the most recent studies were used. Probably there are many uncertainties in these data and there would be necessary the judgment of experts to clarify the values for certain species such as InTe and InTe\(_2\) and to assess the consistency of thermochemical data used. However,
and as consequence of the code structure, the change of values, as they become more accurate, does not represent any problem.

At the same time, new variables have been incorporated into the code to compute separately the vapour condensed on structures and chemisorbed in them. From now on, it is possible to distinguish both phenomena, what permits to analyse the contribution of each one to vapour deposition.

RAFT only considers the species in condensed phase if they are formed by means of nucleation processes. Following the same principles, and as consequence of experimental evidence[4,5] and some theoretical studies[17], Cs₃Te(c) and Sn₄Te(c) have been introduced into the code. It has been assumed that Cs₃Te(g) is the main vapour species prevailing over Cs₂Te(c)[7] and the corresponding saturation pressure has been obtained from the literature. [13] In the range of temperature where data were not available, they have been extrapolated.

In case of SnTe, it has been assumed that SnTe(g) and Sn₄Te₂(g) are the main vapour species prevailing over SnTe(c). The values for saturation pressure have been obtained from literature [16] and, as in the case of Cs₃Te, the values have been extrapolated in the range of temperature where they were not available.

2.2 Model for the Chemical Interaction of Tellurium Vapours with Silver Aerosols

A simple model to characterise this phenomenon has been included. It has been assumed that the rate of this process is limited by the mass transfer in the gaseous phase. It has also been assumed that the aerosol is nonporous and, as consequence, chemical reaction and mass transport are coupled in series. Considering that diffusion in the gaseous phase is the controlling process for chemical reaction, then the maximum attainable rate is being taken into account. That seems to be a good assumption if the conditions are low vapour pressure of tellurium, low flow rates and relatively high temperatures [19]. In the model, any structural change in the aerosol (assuming that is a solid) that were a result of chemical reactions have been neglected.

For the aerosol-tellurium interaction to take place, it is necessary that tellurium be in contact with the aerosol, and that tellurium vapour pressure were at or above the dissociation pressure, which is a characteristic for each compound at a given temperature.

Given that in the Marviken-ATT test 4 silver was included in the experiment, that there is data on Ag₂Te dissociation pressure, and considering that in a real accident 71.3% wt of aerosol are metallic, mainly from silver in control rods,[20] it has been decided to focus this simple model to the formation of Ag₂Te compounds through the interaction of Ag aerosol with Te₂ and Te vapours. That can be made because the RAFT code, where this model has been included, predicts the mass of the aerosol cloud and its composition.

For the chemical interaction of tellurium with aerosols, the approach used in the RAFT code to compute particulate growth rate has been used, assuming that the gas surrounding the particle is divided into two layers, the layer adjacent to the particle surface of one mean free path thickness, called Knudsen layer, and that outside. No collisions occur within the Knudsen boundary layer; while outside, gas is in kinetic equilibrium, and diffusion controls condensation.

For chemical interaction between tellurium and aerosols, the Fuch factor has been used to correct the diffusion model. This factor reflects the discontinuons medium formed by the aerosols. This factor will be specially
important at low pressures (higher mean path) and when particle size is small. It is given by the following expression

\[ \text{FUCH} = \left( \frac{(1 + \text{Kn})}{(1 + 1.71 \text{Kn} + 1.33 \text{Kn}^2)} \right) \]

Thus, the final expression for the rate of interaction of tellurium with silver aerosols will be

\[ \frac{\text{d}m}{\text{d}t} = 4 \pi r_p^2 \cdot \text{Km}(r_p) \cdot \bar{N}(r_p) \cdot G \cdot (\text{C}_{\text{eq}}) \cdot \text{FUCH}; \]

where \( m \) is the mass of species containing tellurium which have reacted in Kg; \( r_p \) is the particle radius in m; \( \text{Km} \), the mass transfer coefficient in m/s; \( \bar{N}(r_p) \), the number of particles of radius \( r_p \); \( G \), the fraction of silver aerosols in the total cloud of aerosols; \( \text{C}_{\text{eq}} \), the bulk concentration of species containing tellurium in gaseous phase (Kg/m\(^3\)), and \( \text{C}_{\text{eq}} \), the equilibrium concentrations of species containing tellurium over the mixture (Kg/m\(^3\)).

The interaction of tellurium with silver aerosol does not modify the size distribution. This mechanism reduces the presence of tellurium in gaseous phase. Heat transfer processes are not considered.

3. ANALYSIS OF MARVIKEN - ATT 4 AND 7 USING THE RAFT CODE

The purpose of the Marviken Aerosol Transport Tests (ATT) was "to create a data base on the behaviour of vapours and aerosols produced from overheated core materials in large-scale facilities representing typical water reactor primary systems and pressure vessels for risk dominant scenarios" [18]. The data obtained could be used in the validation of theoretical models assessing the transport of fission products and aerosols in degraded core accidents.

Five experiments, within the ATT series, have been performed at this facility. Four of them (1, 2a, 2b, 7) were designed to study the transport of Cs, I, and Te, while one of them (4) was intended to study the transport of Cs, I and Te along with Ag and Mn (called "corium aerosols").

From the experimental matrix it is deduced that tests 4 and 7 are the most exhaustive, because they use the complete facility; besides, in test 4, high density aerosols were included. Figure 1 shows a scheme of the facility [4].

![Figure 1](Marviken experimental facility)
Therefore, it was decided to analyse tests 4 and 7 because of their interest and availability of data; moreover they have been previously analysed by other users of RAFT, what permits a comparison of results.

3.1. Analysis of MARVIKEN-ATT 4

In the analysis of the fourth test, the "fissium chamber", where fission products were injected before entering the reactor vessel, has been modelled, as in this chamber, and due to the temperature conditions, it is where most of the nucleation of the Ag and Mn takes place. The inclusion of this volume in the nodalization will permit a more accurate analysis of the behaviour of products in the circuit. All thermohydraulic conditions, temperature, pressure and flow rates have been taken from literature.[5]

Test duration was 4740 s. During this time, 59.3 Kg of Cs, 10.9 Kg of Te, 210 Kg of Ag and 15.2 Kg of Mn were injected. The rates of steam, water, N₂, Ar and H₂ were respectively 36 g/s, 6.3 g/s, 81.0 g/s, 15.3 g/s and 0.3 g/s.

The nodalization of the facility used for the calculation is shown in Figure 2.[4] Seventeen volumes have been used. Dimensions are in mm.

![DIAGRAM](image)

**FIGURE 2** Nodalization of Marviken ATT facility for test 4.

3.1.1 Theoretical Results

The analysis of test 4 was performed with RAFT 1.0 and RAFT 1.1 with/without any modification. The results are compared in Figure 3, in terms of the ratio between the deposition of tellurium calculated and experimentally measured, where values obtained and those from other users of RAFT are given. In the graph, RV means the reactor vessel; PIPES PRES. the piping from reactor vessel to pressurizer; PRES. the pressurizer, and PIPES R.T. the pipes from pressurizer to relief tank.

In the vessel, tellurium deposition is mainly due to chemisorption on walls (see Figure 5). The decrease predicted by RAFT 1.1 modified (0.667 Kg) with regard to RAFT 1.1 (0.77509 Kg) is due to the presence of other species, different from Te₂, which will reduce the mole fraction of Te₂ and therefore its capability to be chemisorbed on walls.

In the pipes to pressurizer, again the deposition calculated by RAFT 1.1 modified is lower than that calculated by RAFT 1.1, and therefore fits experimental values better. The reason is the same explained before: a
reduction in the vapour pressure of Te₂ which impairs its condensation and
chemisorption. In Figure 4, it can be seen the contribution of both
phenomena, vapour and aerosol deposition, to tellurium retention. It is clear
that in all volumes until pressurizer (volume 12), vapour deposition
calculated by RAFT 1.1 modified is lower. In the figure, VAPOR 1.1 and PART.
1.1 means the deposition of tellurium both in vapour and condensed phase
(aerosols) as predicted by RAFT 1.1.

![Comparison of the ratio between calculated/experimental mass of tellurium deposited using the original and improved versions of RAFT. Marviken test 4.](image)

**FIGURE 3** Comparison of the ratio between calculated/experimental mass of tellurium deposited using the original and improved versions of RAFT. Marviken test 4.

![Contribution of vapour and particle deposition to tellurium retention using RAFT 1.1 & RAFT 1.1 modified. Marviken test 4.](image)

**FIGURE 4** Contribution of vapour and particle deposition to tellurium retention using RAFT 1.1 & RAFT 1.1 modified. Marviken test 4.

The modifications introduced in the code permit to distinguish the two
phenomena which contribute to vapour deposition onto walls: condensation and
chemisorption. Figure 5 shows the importance of each phenomenon on the
deposition of tellurium in each volume of circuit as predicted by RAFT 1.1
modified.

As it was envisioned before, in the reactor vessel, (volumes 2-5), and
the first part of the pipes to pressurizer, (volumes 6-7), it is where
chemisorption dominates deposition. However, in volumes 8-10, condensation
plays an important role, because of the high difference in temperature
between gas and surfaces.

In the pressurizer (volume 12), RAFT 1.1 modified predicts higher deposition (2.73 Kg) than that of RAFT 1.1 (1.97 Kg), and it is mainly due to aerosol deposition. The same happens in pipe L05 (volume 14).

![Mass Deposited vs Volume]  

**FIGURE 5** Contribution of condensation and chemisorption to tellurium deposition using RAFT 1.1 modified. Marviken test 4.

The lower vapour pressure of Te₂ calculated by RAFT 1.1 and the lower deposition produces more tellurium to remain in the gaseous phase by forming other species different from Te₂. Therefore, tellurium concentration in gaseous phase is higher for RAFT 1.1 modified, while the condensed phase remains quite similar, as the only species, among the new included, which can theoretically condense is C₂Te; however the vapour pressure of this species never reaches saturation pressure and therefore never condensates or nucleates. Figure 6 shows the evolution of the tellurium concentration in gaseous and condensed phase along the circuit. GAS 1.1 and CON.1.1 means respectively the concentration of tellurium in gaseous and condensed phase predicted by RAFT 1.1; similarly, GAS 1.1 MOD. and CON.1.1.MOD. are those from RAFT 1.1 modified.

![Concentration vs Distance]  

**FIGURE 6** Evolution of tellurium concentration in gaseous and condensed forms as predicted by RAFT 1.1 & RAFT 1.1 modified. Marviken test 4.
The higher concentration in gaseous phase predicted by RAFT 1.1 modified in the final part of circuit is mainly due to the presence of MnTe as predominant species. (See Figure 7).

The mole fraction of species containing tellurium predicted by RAFT 1.1 modified is given in Figure 7. The contribution of Cs₂Te is negligible, but the contribution of AgTe and MnTe is important. In the "Fissium chamber" and pressure vessel, AgTe and MnTe are predominant species, along with Te, Te₂, and TeO. Even MnTe becomes the dominant species in the final part of the circuit. AgTe disappears when most of Ag condenses. The same happens with Cs₂Te when all cesium condenses. The existence of MnTe and AgTe compounds was not noticed in the experiment. However it is mentioned the existence of cesium-telluride compounds.

There could be two reasons to explain the negligible importance found of Cs₂Te calculated by RAFT 1.1 modified. The first one is the uncertainty in the thermochemical data for the formation of Cs₂Te(g), and the extrapolation of the saturation pressure; and the second could be the fact that the nucleation mechanism of Cs₂Te(g), leading to the formation of Cs₂Te(c), would not be the most important. Probably the interaction of CsOH aerosols with tellurium compounds would produce Cs₂Te aerosols, being that the most important mechanism for the generation and transport of such compound. [15]

The contribution of TeO is also important in the reactor vessel and similar to TeOH (not represented in the graph). But the contribution of the other tellurium oxides and hydroxides is negligible.

![Graph showing mole fraction of various species vs distance (m)](image)

**FIGURE 7** Evolution of tellurium speciation as predicted by RAFT 1.1 modified. Marviken test 4.

Despite the fact that the modified versions do not represent a clear improvement in the ratio between calculated/experimental mass of tellurium deposited, the modifications introduced can be considered valid, although the effect can not be thoroughly evaluated because uncertainties remain in the thermochemical data base used. Moreover, the experiments do not provide data for the new species introduced into the codes.

3.1.2 Interaction with Silver Aerosols

Calculations have been performed with the new interaction model. The effect of this model can be appreciated in Figure 8 in terms of the ratio between the deposition of tellurium calculated and experimentally measured. In the figure, RAFT USA means the results obtained by other users of RAFT;
RAFT 1.1, the results form RAFT 1.1; RAFT 1.1 MOD., the results form RAFT 1.1 with the inclusion of new species, and RAFT 1.1 model, the results from RAFT 1.1 with the inclusion of the new species and new interaction model. RV, PIPES PRES, PRES and PIPES R.T. have the meaning explained for Figure 3.

![Graph](image)

**FIGURE 8** Effect of the inclusion of the new model on tellurium deposition in terms of the ratio between calculated/experimental results. Marviken test 4.

Tellurium deposited in the vessel (volumes 2-5) as predicted by RAFT 1.1 with model is higher than that predicted by RAFT 1.1 and by RAFT 1.1 modified due to the reaction of tellurium vapours with silver and the subsequent deposition of Ag$_2$Te. In pipes to pressurizer, the calculations performed with the new model reproduces quite accurately the experimental results (1.93), much better than RAFT USA (7.8) and RAFT 1.1 (8.37). The reason is that, as consequence of the reaction of tellurium with silver aerosols, there is not enough tellurium in gaseous phase to be chemisorbed and condensed on the surfaces of the pipes, what were the main phenomena taking place in this part of circuit.

![Graph](image)

**FIGURE 9** Effect of the inclusion of the new model on tellurium vapour and particle deposition. Marviken test 4.
In pressurizer, tellurium deposition depends on particle phenomena and therefore its retention will be controlled by the deposition of silver aerosols which have trapped tellurium. In pipes downstream the pressurizer, the results obtained (1.22) are again better than previous ones (no data from RAFT USA and 1.26 from RAFT 1.1).

The contribution of vapour and particle deposition on tellurium retention is given in Figure 9 for each volume of circuit. The results obtained with the new model, named VAPOR 1.1 with model and PART 1.1 with model in the figure, clearly show the decrease in the tellurium vapour retention in the circuit as consequence of their interaction with silver to give Ag₂Te.

3.2. Analysis of Marviken-ATT 7

In this test, the facility, including reactor pressure vessel with PWR internals, piping to pressurizer, pressurizer and piping connecting pressurizer and relief tank, have been modelled. Relief tank was not included because in this experiment the tank was full of water and the phenomena which would take place in this volume are not modelled by the RAFT code. All thermohydraulic conditions, temperatures, pressure, flow rates, and geometric parameters have been taken from available literature.[4]

Test duration was 89 min. During this time 55.2 Kg of Cs, 7.81 Kg of I, and 10.01 Kg of Te were injected. That gives a rate of 13.33 g/s, 1.89 g/s, and 2.44 g/s, for Cs, I and Te respectively. The rates of steam, water, N₂, Ar and H₂ were 31 g/s, 6.2 g/s, 86 g/s, 6.9 g/s and 0.35 g/s respectively.

The results obtained, related to deposition, have been compared with the mass balance made after the experiment was completed, and also with some results obtained by other users of RAFT.

The nodalization used for the facility is shown in Figure 10. Sixteen volumes have been used. Dimensions are in mm.

FIGURE 10  Nodalization of Marviken ATT facility for test 7.
3.2.1 Theoretical Results

The analysis of test 7 was initially performed with RAFT 1.0 and RAFT 1.1 (dated July 1990), without any modification, later on the modified versions were used.

Figure 11 reflects the results given by RAFT 1.1 and RAFT 1.1 with modifications in terms of the ratio between calculated/experimental results. In the vessel, tellurium deposition is mainly due to chemisorption on walls (see Figure 14). The slightly decrease of the tellurium deposition predicted by RAFT 1.1 modified in comparison with RAFT 1.1 is due to the existence of other species different from Te₂. However, the decrease is lower than that obtained in the analysis of test 4, where AgTe and MnTe were predominant; however, in test 7, none of the new species included, but TeOH, was important enough to produce a high decrease in the vapour pressure.

\[
\begin{array}{cccc}
\text{RAFT USA} & 0 & 14 & 0.5 & 0.7 \\
\text{RAFT 1.0} & 1.05 & 11.5 & 0.95 & 1.4 \\
\text{RAFT 1.0 MOD.} & 1.02 & 11.42 & 0.93 & 1.39 \\
\text{RAFT 1.1} & 2.42 & 15.43 & 0.02 & 0.3 \\
\text{RAFT 1.1 MOD.} & 2.4 & 15.43 & 0.02 & 0.12 \\
\end{array}
\]

FIGURE 11 Comparison of the ratio between calculated/experimental mass of tellurium deposited using the original and improved versions of RAFT. Marviken test 7.

\[
\begin{array}{cccc}
\text{RAFT 1.1 MOD.} & \text{EXPERIMENTAL} & \text{RAFT 1.1} \\
\end{array}
\]

FIGURE 12 Comparison of tellurium mass deposited in each volume as predicted by RAFT 1.1 & RAFT 1.1 modified. Marviken test 7.
In any case, both RAFT 1.1 and RAFT 1.1 modified clearly overpredict tellurium deposition in pipes to pressurizer (L01, B012 and L02) and underpredict deposition in pressurizer. This can be seen in Figure 12.

In pipes L01 and L02 vapour retention is the phenomenon which contributes mainly to tellurium deposition. However, in the pressurizer both phenomena (aerosol and vapour deposition) have similar influence as predicted by RAFT 1.1 and RAFT 1.1 modified. This can be seen in Figure 13, where the contribution of vapour and aerosol deposition to tellurium retention is given for each volume. In the picture, VAPOR 1.1 and PART. 1.1 means the deposition of tellurium in vapour and condensed phase (aerosols) respectively, as predicted by RAFT 1.1; VAPOR 1.1 MOD. and PART. 1.1 MOD. refer to those from RAFT 1.1 modified.

FIGURE 13 Contribution of vapour and particle deposition to tellurium retention using RAFT 1.1 & RAFT 1.1 modified. Marviken test 7.

As it was also explained in case of test 4, the modifications introduced in the code permit to distinguish the two phenomena which contribute to vapour deposition onto walls: condensation and chemisorption. This can be seen in Figure 14, where the mass of tellurium deposited for each phenomena is represented in the volumes of the circuit.

FIGURE 14 Contribution of condensation and chemisorption to tellurium deposition using RAFT 1.1 modified. Marviken test 7.
The mole fraction of species containing tellurium predicted by RAFT 1.1 modified is given in Figure 15. It is important to notice the negligible presence of \( \text{Cs}_2\text{Te} \) and the importance of \( \text{TeOH} \) in the inlet part of circuit.

![Figure 15](image)

**FIGURE 15** Evolution of tellurium speciation as predicted by RAFT 1.1 modified. Marviken test 7.

4. CONCLUSIONS

A validation/improvement effort on the RAFT code has been carried out. The validation includes the analysis of the Marviken ATT 4 and 7 with the two available versions RAFT 1.0 and RAFT 1.1, and with the improved versions. The improvement has consisted in the inclusion of new tellurium species in its chemistry model and in the incorporation of a simple model to simulate the interaction of \( \text{Te}_2 \) with silver aerosols. Some other minor changes have been performed to compute separately the chemisorption and condensation of \( \text{CsOH} \) and \( \text{Te}_2 \).

For Marviken 4, RAFT 1.0 and RAFT 1.1 give similar results and trends. However results from RAFT 1.1 predict more tellurium deposition than those of RAFT 1.0. The differences can be explained in terms of the changes introduced in RAFT 1.1, which alter the chemisorption rate for tellurium, the calculation of the Sherwood number in laminar flow regime and the deposition of aerosols in laminar and turbulent flow.

The introduced modifications reveal the importance of \( \text{AgTe}(g) \) and \( \text{MnTe}(g) \) at "fissium chamber" and pressure vessel. Even \( \text{MnTe} \) remains the most important tellurium species in the final part of the circuit. However, \( \text{Cs}_2\text{Te}(g) \) is not relevant for the Marviken 4 test conditions and its nucleation to form \( \text{Cs}_2\text{Te}(c) \) does not take place. Of the tellurium oxides and hydroxides included, only \( \text{TeOH} \) has a noticeable importance.

Both the presence of new species, and the inclusion of the new model for the interaction of tellurium with silver aerosols will reduce the vapour pressure of \( \text{Te}_2 \) and therefore its condensation and chemisorption on walls, what permits a better fit to experimental results in these parts of the circuit where the higher vapour pressure of \( \text{Te}_2 \) calculated by the code overpredicted tellurium deposition. The presence of silver telluride aerosols during the experiment is mentioned in some references.[21,22]

For Marviken 7, RAFT 1.0 fits better experimental results than RAFT 1.1. The discrepancies for the tellurium deposition values in the vessel and the piping to pressurizer can be explained in terms of the differences between both versions. However, there is not a clear explanation in terms of the
changes introduced in RAFT 1.1 for the greatest differences appeared in the
pressurizer and in piping downstream pressurizer.
Of the new species introduced, only TeOH has an important contribution.
Cs₂Te, as in test 4, never reaches saturation vapour pressure and its
nucleation does not take place.

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5.8 THE KINETIC BEHAVIOUR OF IODINE AND CESIUM UNDER SEVERE ACCIDENT CONDITIONS

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ABSTRACT

The European Communities, within the frame of a Shared Cost Action on Reactor Safety, 1988-91 Programme, have been sponsoring a study on the Modelling of the Chemical Behaviour of Cesium and Iodine Species in the Reactor Coolant System under Severe Accident Conditions, which has been performed at the Chair of Nuclear Technology, Polytechnical University of Madrid.

The usual procedure for assessing the chemical form of fission products released to the steam/hydrogen atmosphere is to assume that thermochemical equilibrium is immediately established. Nevertheless, for dilute mixtures of iodine and cesium, the reaction time may approach tens of seconds or larger\textsuperscript{1}, therefore kinetic aspects during transport need to be addressed.

A kinetic study has been performed with the aim of verifying the validity of the equilibrium assumption. The most important chemical reactions of iodine and cesium in a steam/hydrogen environment, including a surface reaction\textsuperscript{2}, have been chosen. The following step has been the estimation of the rate constants of the involved reactions through the Activated Complex Theory. The main problem encountered in this calculation has been the estimation of the activation energies, since these parameters are normally obtained by experimentation. In any case, experimental data were used when they exist.

After this, the concept of the ideal tubular chemical reactor was introduced to establish dynamic balance equations leading to systems of differential equations from which the distribution of iodine and cesium species in a flowing pipe that simulates the primary circuit can be obtained. This kinetic model has been applied to analyze several cases\textsuperscript{3} corresponding to PHEBUS-PP and severe fuel damage experiments. It can be pointed out that equilibrium values have not been achieved at the end of the pipe in most of cases and the surface reactions can play an important role in the phenomenology of severe accidents.

1 ELECTION OF REACTIONS: ASSUMPTIONS

Four elements will be present in the studied system: hydrogen, oxygen, cesium and iodine. The choice of the possible chemical species present in the system has been deduced from those stated in references \textsuperscript{1} and \textsuperscript{4}. These are: Cs, Cs\textsubscript{2}, CsO, CsH, CsO\textsubscript{2}, CsI, Cs\textsubscript{2}O, CsOH, CH\textsubscript{3}I, I\textsubscript{2}, HI, HOI, H\textsubscript{2}O, H\textsubscript{2}, O\textsubscript{2}, H, O and OH. Ten of them have been selected for the system: Cs, CsI, CsOH, I\textsubscript{2}, HI, H\textsubscript{2}O, H\textsubscript{2}, H and OH. The justification for this decision is given in reference \textsuperscript{3}.

After eliminating several reactions that seem to be improbable at the system conditions, a final set of 18 chemical reactions were obtained\textsuperscript{5}. Later, a new reaction between CsOH(g) and stainless steel surfaces was added. The chemical reactions included in this model are given in table I.
### TABLE 1 Chemical Reactions Included in this Kinetic Model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CsOH + H = Cs + H₂O</td>
</tr>
<tr>
<td>2.</td>
<td>Cs + H₂O = CsI + I</td>
</tr>
<tr>
<td>3.</td>
<td>Cs + I₂ = CsI + I</td>
</tr>
<tr>
<td>4.</td>
<td>CsOH + H₂O = CsI + H₂</td>
</tr>
<tr>
<td>5.</td>
<td>CsI + OH = CsOH + I</td>
</tr>
<tr>
<td>6.</td>
<td>H + I₂ = H₂ + I</td>
</tr>
<tr>
<td>7.</td>
<td>H₂ + OH = I + H₂O</td>
</tr>
<tr>
<td>8.</td>
<td>H₂O + OH = H₂O + H</td>
</tr>
<tr>
<td>9.</td>
<td>H₂ + H = I + H₂</td>
</tr>
<tr>
<td>10.</td>
<td>I₂ + H₂ = 2HI</td>
</tr>
<tr>
<td>11.</td>
<td>I₂ + 2I</td>
</tr>
<tr>
<td>12.</td>
<td>HI = H + I</td>
</tr>
<tr>
<td>13.</td>
<td>H + OH + R = H₂O + R</td>
</tr>
<tr>
<td>14.</td>
<td>H + I + R = HI + R</td>
</tr>
<tr>
<td>15.</td>
<td>I + I + R = I₂ + R</td>
</tr>
<tr>
<td>16.</td>
<td>Cs + I + R = CsI + R</td>
</tr>
<tr>
<td>17.</td>
<td>Cs + OH + R = CsOH + R</td>
</tr>
<tr>
<td>18.</td>
<td>H + H + R = H₂ + R</td>
</tr>
<tr>
<td>19.</td>
<td>CsOH(g) = CsOH(retained)</td>
</tr>
</tbody>
</table>

R is the third body needed to dissipate the heat of reaction.

## 2 THE KINETIC MODEL: IDEAL TUBULAR CHEMICAL REACTOR

To elaborate a model that could show the chemical behaviour of iodine and cesium within the primary system during a severe fuel damage accident in LWRs, the *ideal tubular chemical reactor model* has been chosen. This kind of chemical reactor is characterized by both continuous reactant feed and product exit. This reactor operates in stationary regime.

The *ideal tubular reactor* can be represented like a cylinder divided in elemental volumes. For each elemental volume the chemical and physical properties are uniform in any position (homogeneity), varying sequentially from one element to the next. Extrapolating to the limit, it can be concluded that the flow characteristics are uniform in any reactor transversal section at any time.

### 2.1 Assumptions

The mechanism of all the chosen reactions is assumed to be single or elemental. All the reactions take place in the same way they are written, that is, without any intermediate step. The term "reaction rate" is defined as the change in the molar number of any substance (reactant or product) per unit of time and unit of volume (homogeneous reactions) or unit of surface (heterogeneous reactions).

It has been assumed that all the gases can act as a third body. As H₂ and H₂O are the major components in the atmosphere considered, then (R) = (H₂O) + (H₂). The total flow has been assumed to remain constant, despite the fact that some cesium is retained by the walls. This assumption can be justified because the amount of cesium retained is very small compared to the total mass flow.

The condensation phenomenon has not been modelled, thus, this model is only useful at temperatures higher than condensation temperatures for iodine and cesium species at the system pressure. Generation and transport of aerosols have not been modelled, either, since these phenomena are out of the scope of this work.

On the other hand, the only possible gas-surface interaction seems to be the interaction between CsOH and stainless steel (see point 3.5).
At the beginning, it was assumed that the system was adiabatic because the primary system is usually isolated. However, the system was finally considered isothermal. The error committed with this assumption could be about 0.4%.^{3}

2.2 Mass Balance

The corresponding mass balance in any elemental volume has been performed. By solving the resulting differential system, the concentration profile for each species along the tube can be obtained as a function of the axial coordinate. The change of axial coordinates to temporal coordinates is easy since the inlet flow is known and it remains constant during all the calculation. Figure 1 displays the element of volume.

\[ F \frac{dx_i(z)}{dz} = F x_i(z+dz) + (-r_i) \frac{dV}{dz} + (-r_{i2}) \frac{dA}{dz} \]

where \( F \) is the total mass flow, \( x_i(z) \) the molar fraction of species \( i^{th} \) at \( z \) and \( (-r_i) \) the velocity of disappearance of species \( i^{th} \). The disappearance velocity when it is referred to reaction with surfaces is named \((-r_{i2})\).

Applying a mass balance for each species it has been obtained a system of coupled differential rate equations of the form

\[ \frac{dx_i}{dz} = \left( \frac{1}{F} \right) \left[ (\pm \frac{P}{RT}) \sum K^1_{jk} x_j \pm (\frac{P}{RT})^2 \sum K^2_{jk} x_j x_k \pm (\frac{P}{RT})^3 \sum K^3_{jk} x_j x_k x_l \right] - (\frac{P}{RT}) \sum K^w_{jk} x_j x_l \]

being \( K^1_{jk} \), \( K^2_{jk} \) and \( K^3_{jk} \) the first-, second- and third-order rate constants respectively and \( K^w_{jk} \) the first-order rate constant referred to interaction with surfaces. The value of the last term is equal to zero except when the species \( i^{th} \) is CsOH. The term \( (P/RT) \) is needed to get homogeneous dimensions.

It is given in moles of total mass/volume.

3 RATE CONSTANTS ESTIMATION

Rate constants have to be estimated for the bulk of the chemical reactions, because of the lack of available experimental data. The estimations have been performed through the Activated Complex Theory, which leads to rate constant expressions depending on the temperature. The greatest difficulty in the estimation of the rate constants has been the calculation of the activation energies. The activation energies have been calculated through empirical and theoretical models existing in the literature. The uncertainty associated to the estimation of the rate constants is mainly due to the calculation of the activation energies.

The rate constant expression according to the Activated Complex Theory
for a bimolecular reaction is

\[
K = \frac{kT}{h} \frac{(Q_a/N)}{(Q_a/N)(Q_b/N)} \exp \left( -\frac{E_a}{RT} \right),
\]

where \( k \) is the Boltzmann constant (erg \( K^{-1} \)), \( h \) the Planck constant (erg.s), \( T \) the absolute temperature (K), \( Q_a \) and \( Q_b \) the partition functions of the reactants, \( Q \), the partition function of the activated complex with the contribution of the reaction coordinate omitted, \( N \) Avogadro's number (molecules/mole), \( E_a \) the activation energy (cal mole\(^{-1} \)) and \( R \) the gas constant (cal mole\(^{-1} \) K\(^{-1} \)).

For unimolecular reactions \( A \rightarrow B + C \), the expression derived from the cited theory is

\[
K = \frac{kT}{h} \frac{(Q_a/N)}{(Q_a/N)} \exp \left( -\frac{E_a}{RT} \right).
\]

For atom recombination reactions \( A + B + R \rightarrow AB + R \), it has been used the expression

\[
K = \frac{kT}{h} \frac{(Q_a/N)}{(Q_a/N)(Q_b/N)(Q_c/N)} \exp \left( -\frac{E_a}{RT} \right),
\]

also derived from the Activated Complex Theory.

3.1 Estimation of Activation Energies

Experimental data on activation energies exist only for five of the nineteen chosen chemical reactions. These are:

6. \( H + I_2 = HI + I \) (refs.6 and 7) \( E_a \) forward = 0 cal mole\(^{-1} \) \( E_a \) reverse = 35900 cal mole\(^{-1} \)
8. \( H_2 + OH = H_2O + H \) (ref.8) \( E_a \) forward = 5000 cal mole\(^{-1} \) \( E_a \) reverse = 20000 cal mole\(^{-1} \)
9. \( HI + H = I + H_2 \) (refs.7 and 9) \( E_a \) forward = 0 cal mole\(^{-1} \) \( E_a \) reverse = 34100 cal mole\(^{-1} \)
10. \( I_2 + H_2 = 2 HI \) (ref.6 and 7) \( E_a \) forward = 40700 cal mole\(^{-1} \) \( E_a \) reverse = 43700 cal mole\(^{-1} \)
11. \( I_2 \rightarrow 2I \) (ref.10) \( E_a = 34000 \) cal mole\(^{-1} \)

In what follows, the estimation of the activation energies for the remainder reactions will be briefly described.

3.1.1 Maximum Attractive Force Method

This method, developed by Otozai\(^{11-12-13} \), is empirical although based on theoretical considerations. Otozai assumed that the bond distances in the activated complex are equal to the bond distances which correspond to the maximum attractive force between the pair of molecules in question. Otozai postulated that the sum of the energy of the activated bonds must be minimized, which means that the complex \( A-B-C \) must be linear\(^a \).

This method has been used to calculate the activation energies of the
It is important to point out that the retained CsOH, shown in each figure, is referred to the amount of CsOH that has reacted with the stainless steel of the pipe until that point, i.e. the amount of retained CsOH must be read as accumulated amount of retained CsOH until the lecture point.

TABLE III Values of the Rate Constants at 1000 and 1500 K.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>RATE CONSTANT VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000 K</td>
</tr>
<tr>
<td>1.</td>
<td>CsOH + H → Cs + H₂O</td>
</tr>
<tr>
<td>1.</td>
<td>Cs + H₂O → CsOH + H</td>
</tr>
<tr>
<td>2.</td>
<td>Cs + H₂ → CsI + H</td>
</tr>
<tr>
<td>3.</td>
<td>CsI + H → Cs + HI</td>
</tr>
<tr>
<td>4.</td>
<td>CsOH + HI → CsI + H₂O</td>
</tr>
<tr>
<td>4.</td>
<td>CsI + H₂O → CsOH + HI</td>
</tr>
<tr>
<td>5.</td>
<td>CsI + H → Cs + H</td>
</tr>
<tr>
<td>6.</td>
<td>CsI + H₂ → CsOH + H</td>
</tr>
<tr>
<td>7.</td>
<td>CsI + OH → CsOH + I</td>
</tr>
<tr>
<td>8.</td>
<td>CsI + I → CsI + OH</td>
</tr>
<tr>
<td>9.</td>
<td>H + I₂ → H + I</td>
</tr>
<tr>
<td>10.</td>
<td>H + I → H + I</td>
</tr>
<tr>
<td>11.</td>
<td>H + OH → H₂O + H</td>
</tr>
<tr>
<td>12.</td>
<td>H + H₂ → H + H₂</td>
</tr>
<tr>
<td>13.</td>
<td>H + H + R → H₂O + R</td>
</tr>
<tr>
<td>14.</td>
<td>H + I + R → I₂ + R</td>
</tr>
<tr>
<td>15.</td>
<td>H + I → H₂O → H + I₂ + H₂</td>
</tr>
<tr>
<td>16.</td>
<td>H + H + R → H₂O + H</td>
</tr>
<tr>
<td>17.</td>
<td>H + H₂ → H₂O + H</td>
</tr>
<tr>
<td>18.</td>
<td>H + H₂ → H₂O + H</td>
</tr>
<tr>
<td>19.</td>
<td>CsOH (g) → CsOH (r)</td>
</tr>
</tbody>
</table>

f = in the forward direction; **r = in the reverse direction.

5.1 PHEBUS-FP

As it was said in the Abstract, sequence AB for Phase B of the Phebus-FP Project has been chosen. For this sequence, the pressure at the circuit entrance will be 0.4 MPa. As the model assumes an ideal system, this pressure remains constant through the whole system. The temperature will be practically imposed by electrical heating at 1000 K. About the geometry, the internal diameter is the same for the upper plenum and hot leg, 5.2 cm. No pipe bends are considered. The total length, adding the upper plenum to the hot leg is 380 cm.

As the interest stays in the kinetics of reactions among atomic cesium, atomic iodine and the surrounding atmosphere (steam and hydrogen), the cesium and iodine have been introduced into the system as atomic cesium and atomic iodine, instead of CsOH and CsI.

Steam and hydrogen concentrations change linearly through the experiment. However, the proposed model is not able to consider a changing flow. As a result, it has been chosen a hypothetical case with reactant flows remaining constants during all the experiment. This case, named "Phebus-2", reflects the more diluted situation, when the steam and hydrogen flows are largest.
5.1.1 Case "Phebus-2"

The input data for this problem are given in table IV.

**TABLE IV** Case "Phebus-2": Input Data.

<table>
<thead>
<tr>
<th>T = 1000K</th>
<th>INITIAL MOLAR FRACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>P = 3.948 atm</td>
<td>Cs = 4.714763E-5</td>
</tr>
<tr>
<td>D = 5.2 cm</td>
<td>I = 4.428256E-6</td>
</tr>
<tr>
<td>L = 380 cm</td>
<td>H₂O = 0.598699</td>
</tr>
<tr>
<td>F = 1.854329 mole/s</td>
<td>H₂ = 0.401249</td>
</tr>
</tbody>
</table>

The flow velocity is 1813.5 cm/s. Therefore, the time needed to pass through the pipe is about 0.209 s.

In figure 2, the molar fractions of cesium and iodine species versus pipe length are plotted.

During the first centimeters, the atomic iodine concentration falls quite markedly (for example, from z=0 to z=6.3, it becomes half of the initial concentration). The major part of this iodine goes to form CsI. After this, the other species of iodine react to form CsI through several reactions. For this reason, all iodine species except CsI have a decreasing tendency. I₂ concentration is negligible with regard to total iodine. Cesium iodide practically reaches the equilibrium in ~ 50 cm (t = 2.7E-2 s). The molar fraction of atomic cesium decreases steadily.

The CsOH(g) concentration rises very fast at the beginning, increasing more slowly from z = 60 cm. The CsOH(g) does not reach equilibrium at the end of the pipe.

![FIGURE 2 Kinetics of Iodine and Cesium Species. Case "Phebus-2".](image)

Table V shows the molar fractions of cesium and iodine species at the end of the pipe and the equilibrium molar fractions obtained with SOLGAS MIX code and with FACSIMILE code. These equilibrium molar fractions have been obtained by two different methods: with the SOLGAS MIX-PV computer code and with the FACSIMILE computer code. The second method consists in running the
FACSIMILE code with the equation system until equilibrium concentrations are achieved. In both cases, reaction with surfaces has not been taken into account, because thermodynamical data on the formed compound are needed to run the SOLGASMIX code, and these data are unknown.

TABLE V  Molar Fraction Values at the End of the Pipe and Equilibrium Values (Case "Phebus-2").

<table>
<thead>
<tr>
<th>OUTPUT MOLAR FRACTIONS</th>
<th>EQUILIBRIUM MOLAR FRACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SOLGASMIX-PV</td>
</tr>
<tr>
<td>CsOH</td>
<td>2.4911E-5</td>
</tr>
<tr>
<td>Cs</td>
<td>1.7800E-5</td>
</tr>
<tr>
<td>HI</td>
<td>6.6257E-10</td>
</tr>
<tr>
<td>CsI</td>
<td>4.4219E-6</td>
</tr>
<tr>
<td>$I^-$</td>
<td>7.0451E-17</td>
</tr>
<tr>
<td>$I^+$</td>
<td>5.7127E-9</td>
</tr>
</tbody>
</table>

From table V one can observe that the final CsOH molar fraction is approximately 60% of the equilibrium value. The CsI molar fraction is 99.87% of the equilibrium value. The molar fraction of HI is higher than the equilibrium value, but is relatively near equilibrium. The other species are far from equilibrium.

The total amount of CsOH (retained) is insignificant compared to the cesium initial amount.

Percentages of molar fractions of iodine species at the end of the pipe and at equilibrium point with regard to the initial molar fraction of atomic iodine are displayed in table VI. Analogously, table VI shows the same percentages for cesium species.

TABLE VI  Percentages of Molar Fractions of Iodine and Cesium Species with Regard to the Initial Molar Fraction of Iodine and the Initial Molar Fraction of Cesium, respectively. "Phebus-2".

<table>
<thead>
<tr>
<th>X output iodine species .100</th>
<th>X output cesium species .100</th>
</tr>
</thead>
<tbody>
<tr>
<td>X initial atomic iodine</td>
<td>X initial atomic cesium</td>
</tr>
<tr>
<td>HI = 0.015%</td>
<td>CsOH = 52.8%</td>
</tr>
<tr>
<td>$I_2$ = Negligible</td>
<td>Cs = 37.75%</td>
</tr>
<tr>
<td>$I^-$ = 0.13%</td>
<td>CsI = 9.38%</td>
</tr>
<tr>
<td>CsI = 99.86%</td>
<td>CsOH (ret) = 0.07%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X equilibrium iodine species .100</th>
<th>X equilibrium cesium species .100</th>
</tr>
</thead>
<tbody>
<tr>
<td>X initial atomic iodine</td>
<td>X initial atomic cesium</td>
</tr>
<tr>
<td>HI = 0.01%</td>
<td>CsOH = 90.6%</td>
</tr>
<tr>
<td>$I_2$ = Negligible</td>
<td>Cs = 0.05%</td>
</tr>
<tr>
<td>$I^-$ = Negligible</td>
<td>CsI = 9.35%</td>
</tr>
<tr>
<td>CsI = 99.99%</td>
<td></td>
</tr>
</tbody>
</table>

5.2. Case "SFD-ST1"

These experiments were chosen because there is another kinetic study\(^1\)
which takes the conditions from them. In such study, authors concluded that cesium iodide takes ≈10 s to reach the equilibrium point in the SFD-ST (Severe Fuel Damage-Scoping Test) at 1500K. However, these authors did not take into account the interactions between CsOH and stainless steel surfaces. The geometrical data were taken from reference 30 and the pressure and temperature conditions and the initial flows from reference 31. The input data needed to run the program are given in table VII.

TABLE VII  Case "SFD-ST1": Input Data.

<table>
<thead>
<tr>
<th></th>
<th>INITIAL MOLAR FRACTIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>T = 1500K</td>
<td></td>
</tr>
<tr>
<td>P = 68.103 atm</td>
<td>Cs = 7.717949E-9</td>
</tr>
<tr>
<td>D = 0.66 cm</td>
<td>I = 1.909967E-9</td>
</tr>
<tr>
<td>L = 4420 cm</td>
<td>H₂O = 0.969999</td>
</tr>
<tr>
<td>F = 0.92 mole/s</td>
<td>H₂ = 0.030001</td>
</tr>
</tbody>
</table>

From the above data one can obtain the flow velocity, 4856.8 cm/s, and the time needed to pass through the pipe, 0.91 s.

An increase of the species HI during the first centimeter is noticed (figure 3). After this point, its molar fraction decreases very slowly until ≈150 cm (t= 3.0E-2 s.), then it starts to increase again. Focusing on CsI, a very marked initial increase, mainly produced by reaction 2 (forward), occurs. This increase is followed by a steady increase until ≈150 cm. From this point, the molar fraction of CsI tends to decrease.

CsOH is constantly disappearing through interactions with the walls.

FIGURE 3  Kinetics of Iodine Species: Case "SFD-ST1".

Figure 4 shows a high concentration of CsOH retained into the walls. When this amount of retained cesium is sufficiently large, the system characteristics change because retained cesium is not available to react with the other chemical species. In this way, taking into account that the total amount of cesium hydroxide is decreasing, reactions tend to shift to the hand side that produce this species.
In figure 3 an initial decrease of atomic iodine can be seen, due to several reactions giving mainly HI, followed by an increase until the end of the pipe. This increase could be caused by the iodine coming from CsI in order to produce CsOH. The I₂ amount is always negligible.

Molar fraction of atomic cesium decreases at the beginning, increases until \( \approx 77.5 \text{ cm} \) \((t = 1.6\times10^{-3} \text{ s.})\) and then decreases again (see figure 4). The first decrease is due to the formation of the cesium species, mainly CsOH. The further increase can be mainly produced by the reaction 1 (forward), and the last decrease is correlated with the decrease in the total amount of cesium available to react (a large amount of CsOH has reacted with the pipe surface resulting in retained CsOH).

![Graph of Molar Fraction vs. Pipe Length](image)

**FIGURE 4** Kinetics of Cesium Species. Case "SFD-ST1".

Table VIII displays the distribution of initial iodine and cesium into different species at the end of the pipe.

**TABLE VIII** Percentages of Molar Fractions of Iodine and Cesium Species with Regard to the Initial Molar Fraction of Iodine and the Initial Molar Fraction of Cesium, respectively. "SFD-ST1".

<table>
<thead>
<tr>
<th>X output iodine species .100</th>
<th>X output cesium species .100</th>
</tr>
</thead>
<tbody>
<tr>
<td>X initial atomic iodine</td>
<td>X initial atomic cesium</td>
</tr>
<tr>
<td>HI  = 94.01%</td>
<td>CsOH = 59.03%</td>
</tr>
<tr>
<td>I₂  = Negligible</td>
<td>Cs  = Negligible</td>
</tr>
<tr>
<td>I⁻  = 5.84%</td>
<td>CsI = 3.55E-2%</td>
</tr>
<tr>
<td>CsI = 0.14%</td>
<td>CsOH(ret.) = 40.93%</td>
</tr>
</tbody>
</table>

The most outstanding characteristics of this table is the high amount of cesium retained by the pipe walls. It reflects the great importance of pressure and temperature conditions on the surface reaction, besides the large available surface (the pipe has a length of 4420 cm in this case). This result must be observed with care because the model does not take into account transport phenomena such as turbulences and diffusion, which could be important.

The comparison between output and equilibrium ratios has no sense in this case, because of the great amount of cesium retained.
6 CONCLUSIONS

This kinetic model has been developed with the aim to elucidate the importance of kinetic aspects on the chemistry of a system containing iodine, cesium, water steam and hydrogen when the iodine and cesium are present in low concentrations.

- The estimation of the rate constants has been carefully performed through the Activation Complex Theory, using the available literature. Activation energy is the major source of uncertainty in the estimation of the rate constants.

- The study makes it evident the necessity to perform some tests with the aim of obtaining experimental data. These data are particularly scarce for reactions which involve cesium species. In particular, it would be very useful to have experimental activation energies for the cited reactions.

To study the kinetics of iodine and cesium in a steam hydrogen atmosphere under conditions of severe accident, the ideal tubular chemical reactor concept has been used. The results obtained for several cases leads to the following conclusions:

- In both cases, equilibrium values have not been achieved for all the species at the end of the pipe. Cesium iodide is farther from equilibrium at high temperatures and low concentrations (case "SFD-ST1")
- At high concentrations, molar fractions are nearer from equilibrium than at lower concentrations.
- The retention of CsOH into stainless-steel surfaces could be very important at high temperature. This retention can change the distribution of species into the system. This is a phenomenon poorly studied.
- Transport phenomena could play an important role in dilute systems at high temperatures, because superficial reaction depends on such phenomena.
- The distribution of initial cesium and iodine into different species qualitatively coincides with equilibrium predictions.
- Comparison of SOLGASMIX-PV calculations and FACSIMILE equilibrium predictions (without surface reaction) shows a good agreement.

As a final conclusion, the assumption of instantaneous equilibrium could be inaccurate when estimating the iodine and cesium species distribution under severe accident conditions.

8 REFERENCES

6. Session V.B
MODELLING AND CODE DEVELOPMENT
6.1 ANALYSIS OF IODINE SOURCE TERM FROM A SMALL BWR DURING A POSTULATED SEVERE ACCIDENT USING IMPAIR 2/M CODE

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Program Light Water Reactor Safety
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Abstract

The iodine source term expected to occur during a postulated severe accident is analyzed for a small (1000 MWt) Boiling Water Reactor. The accident was assumed to be initiated as a result of an anticipated transient with scram. The IMPAIR 2/M code which essentially employs the IMPAIR 2 code chemistry to the LWR containments modelled with multiple compartments is used for the analyses. The thermal-hydraulics, aerosol behavior, source term of various iodine species and the dose rates required for the IMPAIR 2/M analyses are calculated with other computer programs.

This paper introduces IMPAIR 2/M code and presents the capabilities of the code in predicting iodine behavior in postulated severe accident in a BWR, especially in the wetwell.

1. Introduction

The chemical reactions taking place in gas and water spaces in various compartments of a Light Water Reactor (LWR) will dynamically alter the chemical and physical form of the iodine initially formed in the reactor coolant system. Very high radiation fields expected to occur in a severe accident will strongly influence certain chemical reactions. Therefore, as the initially formed iodine species are transported from the primary coolant system to various compartments in the containment, new iodine species, some of which are airborne, will be created. A leak to the environment during a severe accident may eventually cause environmental release of certain amount of airborne iodine species. On account of the radiological properties of iodine $^{131}$ the behavior of fission product iodine in LWR compartments and its source term to the environment are of great importance under severe reactor accident conditions.
IMPAIR 2/M code [1] has been prepared at Paul Scherrer Institute/Program Light Water Reactor Safety (PSI/PLS) to apply the iodine chemistry as modelled in IMPAIR 2 [2] code to multiple compartment situations. The thermal-hydraulic and aerosol behavior are additional factors affecting the iodine behavior in addition to the chemistry.

Boundary conditions for an IMPAIR 2/M analyses necessitate multi-disciplinary input data. Main driving force for the iodine transport is the steam and non-condensible flows between compartments. They are to be determined with a containment thermal-hydraulic analysis. Gas and water temperatures are crucial thermal-hydraulic parameters for the IMPAIR 2/M code. The iodine source term (like iodine in gas or iodide form), generation in the reactor vessel during the degradation phase of the reactor and also during early phase of the core concrete interaction, and aerosol behavior (sedimentation rates and water pool retention efficiency) are to be calculated with fission product release and aerosol behavior calculations. The dose rates needed for the chemical reactions are the last pieces of the input information.

A set of codes, as shown in Figure 1, is used in a semi integral manner at PSI/PLS [3] to calculate the source term during a postulated severe accident in a Swiss nuclear power plant. IMPAIR 2/M provides the iodine source term to the environment as well as constitution of the iodine released to the environment and remained in the compartments as a function of time.

The work presented in this paper has the aim to demonstrate the capabilities of IMPAIR 2/M code in producing the chemical and physical behavior of various iodine species, especially in the wetwell where the water space there adds additional complexity to the problem.

2. Description of IMPAIR 2/M

IMPAIR 2/M is basically consisted of four parts. The first part reads the input data defining the system geometry, thermal-hydraulics, aerosol sedimentation rate, iodine species source terms and dose rates. The second part prepares current values of various parameters necessary for the chemical reactions and source terms from user input arrays. The third part is the part describing the rate equations, which are composed of chemical reactions, external source and depletion terms (due to generation or transport). The fourth part is the integrator. Current version of IMPAIR 2/M considers 18 rate equations for 18 different reaction species. Simultaneous solution of a stiff differential equation system containing a number of equations equal to 18 times the number of compartments (which is usually 5 or more) is usually beyond the capability of any differential equation solver with a good precision. The method adapted in the code is to handle each compartment separately.
for a given integration interval. The time proceeds into the next integration interval once all
the compartments are processed. The compartments are implicitly interlinked due to the
mass transfer between them. The only problem in this method is to provide a consistent and
logical order in which the set of differential equations associated with each compartment is
to be solved. The sequence of handling the compartments for every integration step is
dictated by user. The sequence should be defined in such a way that a compartment where
iodine is first released should be treated first. Rest of the compartments, where there is no
iodine release occurs, should be handled in a sequence dictated by the flow direction. A
compartment which receives flow should appear in the sequence after the compartment
where the flow is originated. As an example; the sequence for a high pressure sequence of a
BWR analysis could be: the reactor pressure vessel is to be handled first followed by the
wetwell, drywell and reactor building until the core concrete interaction starts, and then on,
it should be the drywell, wetwell, reactor pressure vessel and reactor building. In order to
avoid numerical problems, enough precautions are built in the program to limit the
integration step size.

3. Iodine Chemistry

Modelling of the iodine chemistry is taken from December 1989 version of the
IMPAIR 2 code. Description of the improved iodine chemistry in IMPAIR 2 (since 1989) is
a subject of another paper at this conference. Table 1 presents the chemical reactions
considered in the current version of the IMPAIR 2/M code. The water and gas space
chemistry is applied to the compartments containing water. The chemistry is limited only to
the gas side for the dry compartments.

4. Application of IMPAIR 2/M Code to a BWR-Mark 1 Source Term Analysis

A postulated severe accident in a BWR-Mark 1 reactor following an operational
transient is analyzed with the series of the computer programs shown in Figure 1.

Figure 2 shows the calculated average temperature behavior in the core as well as the
fraction of the initially available iodine released from the core. Various important events are
also indicated in the figure. The released iodine is assumed to be in atomic form but later
undergone various chemical reactions with H₂, CsOH. Constituents of the stable form of the
iodine are assumed to be CsI and I₂ once the gas temperature becomes low enough along
the flow path. Amount of molecular iodine in gas form is assumed to be 1 % of the released
iodine at this time. CsI is assumed to be in aerosol form. Approximately 99 % of the iodine
is calculated to be released within the pressure vessel during high temperature and melting
phases of the accident analysis. Once the pressure vessel breaches and the core concrete
interaction starts the remaining iodine in the core debris is also released but as a source in
the drywell atmosphere. Until the drywell breach occurs with the over-pressurization, the airborne iodine species are transported in the wetwell via the downcomer. After the breach, airborne iodine species are further transported from the drywell into the reactor building and from there to the environment. Figure 3 presents the calculated distribution of the iodine in the reactor pressure vessel, wetwell, drywell and reactor building. Main form of the iodine in the drywell and reactor building is predicted to be CsI. It is calculated that CsI mainly plated out on the surfaces. Due to the presence of water, other species are chemically formed in the wetwell water space.

Figure 4 presents the relative distribution of various iodine species with respect to the total iodine inventory in the wetwell gas space. Similar information is shown in Figure 5 in the water space. In addition to the I$_2$, iodide, iodate, HOI and methyl iodide in the water space, silver iodide is also generated as a result of I$_2$ and fission product silver reaction. The reactions creating different iodine species are governed by the reaction rate, the activation energy constants and the dose rate defined by the user. With the given rate constants, thermal-hydraulics and iodine species source terms, the code is consistently calculating build-up or decay of the considered species.

5. Conclusions

IMPAIR 2/M code is written to apply the IMPAIR 2 to multiple compartment applications with the boundary conditions taken from other thermal-hydraulic, aerosol and dose rate calculations. The code has the strength of calculating iodine species behavior in dry compartments and compartments containing water pool, as well as the transport of airborne iodine species into the environment.

References

Table 1: A Summary of Chemical Reactions Used in IMPAIR 2/M Code

<table>
<thead>
<tr>
<th>The gas phase reactions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$2I_2 + 4O_3 &lt;----&gt; I_4O_9 &lt;----&gt; 4IO_3^-$</td>
<td>oxidation of iodine</td>
<td>(1)</td>
</tr>
<tr>
<td>$I_2 + 2CH_3R &lt;----&gt; 2CH_3I + 2R$</td>
<td>organic iodine formation</td>
<td>(2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>The water phase reactions</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_2 + H_2O &lt;----&gt; HOI + I^- + H^+$</td>
<td>hydrolysis</td>
<td>(3)</td>
</tr>
<tr>
<td>$3HOI &lt;----&gt; IO_3^- + 2I^- + 3H^+$</td>
<td>oxidation to iodate</td>
<td>(4)</td>
</tr>
<tr>
<td>$2I^- + 0.5 O_2 + 2H^+ &lt;----&gt; I_2 + H_2O$</td>
<td>iodide oxidation by air</td>
<td>(5)</td>
</tr>
<tr>
<td>$2I^- + h &lt;----&gt; I_2$</td>
<td>iodide oxidation by aqueous radiolysis</td>
<td>(6)</td>
</tr>
<tr>
<td>$I_2 + 2CH_3R &lt;----&gt; 2CH_3I + 2R$</td>
<td>Methyl iodide formation</td>
<td>(7)</td>
</tr>
<tr>
<td>$2CH_3I + h &lt;----&gt; 2CH_3 + I_2$</td>
<td>Methyl iodide radiolytic decomposition</td>
<td>(8)</td>
</tr>
<tr>
<td>$IO_3^- + h &lt;----&gt; I^-$</td>
<td>Iodate radiolytic decomposition</td>
<td>(9)</td>
</tr>
<tr>
<td>$I_2 + 2Ag &lt;----&gt; 2AgI$</td>
<td>Silver iodide formation</td>
<td>(10)</td>
</tr>
<tr>
<td>$2AgI + h &lt;----&gt; I_2 + 2Ag$</td>
<td>Silver iodide radiolytic decomposition</td>
<td>(11)</td>
</tr>
<tr>
<td>$CH_3I + H_2O &lt;----&gt; I^- + CH_3OH + H^+$</td>
<td>Methyl iodide hydrolysis (H_2O)</td>
<td>(12)</td>
</tr>
<tr>
<td>$CH_3I + OH^- &lt;----&gt; I^- + CH_3OH$</td>
<td>Methyl iodide hydrolysis (OH^-)</td>
<td>(13)</td>
</tr>
</tbody>
</table>

where h denotes the radiation dose rate (Mrad/hr).
Figure 1: Computer Programs used for a Source Term Analysis of a LWR at PSI/PLS.
Figure 2: Calculated Average Core Temperature and Iodine Release as a Function of Time.
Figure 3: Distribution of Released Iodine in Compartments and Drywell Pressure.
Figure 4: Relative Distribution of Iodine Species with Respect to Total Iodine Mass in the Wetwell Gas Space.
Figure 5: Relative Distribution of Iodine Species with Respect to Total Iodine Mass in the Wetwell Water Space.

DISCUSSION

Evans
In IMPAIR/M, do you use the same reaction set in every compartment?
Furrer
IMPAIR-2/M has the same set of differential equations in all compartments.
6.2 THE MODELLING OF IODINE BEHAVIOR FOR ASSESSING
THE RADIOLGICAL CONSEQUENCES OF A DESIGN
BASIS ACCIDENT

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ABSTRACT

Recently, the Commission of the European Communities (CEC) has
initiated two studies with a view to developing a realistic model for
predicting the radiological consequences of a design basis Large Loss of
Coolant Accident (LOCA) at a Pressurised Water Reactor (PWR). This
paper describes the models that are considered to be the most
appropriate for predicting iodine behaviour and discusses their
importance in terms of the overall release to the environment.

1. INTRODUCTION

Recently, Working Group 1 on the Safety of Thermal Reactors of the
Commission of the European Communities initiated a series of studies
which had two objectives. The first was to identify any differences
there may be in the way the different countries in the Community
modelled the phenomena which effect the radiological consequences of a
key design basis fault. It was decided to consider first a successfully
terminated Large Loss of Coolant Accident (LOCA) at a Pressurised Water
Reactor (PWR), since PWRs account for most of the nuclear reactors in
Western Europe and the large LOCA is an important consideration when
assessing the safety of these reactors. The second objective was to
identify realistic calculational methods and data and to see how the
prediction of these compared with the results of the methods and data
that are used for licencing calculations which, in general, are
conservative.

These studies embraced the complete range of methodologies from
calculating the inventory of fission products in the reactor core to
determining the dose to a critical individual as a result of each of the
pathways to man. In this paper, the discussion is confined to those
aspects to which we related to the chemistry of iodine and how this
effects the release of radio-activity to the environment.

2. GENERAL DESCRIPTION OF THE FAULT SEQUENCE

The fault considered is a double ended guillotine break of one of
the main coolant pipes of the reactor coolant system when the reactor is
operating at full power. For most designs, the case which has the
highest probability of failing fuel is a break in the cold leg between
the steam generator and the reactor as shown in Fig 1. When the break occurs, there will be a massive flow of primary coolant into the primary containment. About half of this will flash to steam and the remainder will initially be airborne in the building atmosphere in the form of an aerosol of water droplets. This is the blowdown phase.

Most designs include fan coolers within the primary containment which control the air temperature during normal operation. In designs where they are qualified to operate in an emergency mode after a LOCA, the coolers will continue to remove heat and active species from the atmosphere of the primary containment. However, in many designs, the fan coolers are not qualified for post-LOCA conditions and credit cannot be claimed for them.

Most European designs include a primary containment spray system which will be initiated if the pressure within the containment exceeds a present value. This also removes heat and radio-active species from the atmosphere of the primary containment. The German Siemens-Kraftwerkunion (KWU) designs, however, do not have a spray system.

When the pressure of the reactor coolant circuit falls below a preset level, the accumulators will discharge water into the primary circuit and later the refill phase begins when the pumping of safety injection water starts. In most designs, this is only into the cold legs but, in KWU designs, injection is into both the hot and cold legs. This may affect the fraction of fuel cladding that fails and the fraction of activity released from the fuel pins that escapes from the break.

The two phase coolant is not adequate to remove all the fission product heat. The maximum temperature of the fuel cladding will occur before the core has filled to mid core height and, in most designs, the majority of fuel cladding failures that may occur are expected to happen in this period, that is 100 to 250 seconds after the LOCA occurs. Thus, the fission products will be released in two phases; a short term release into the steam and water above the reflood water, which is called the dry phase, and the subsequent wet phase, which is into the reflood water. The dry phase release will be carried along the coolant circuit by the steam and discharged from the break into the primary containment atmosphere. When injection is only into the cold legs, the route via the hot leg and the steam generator to the break will be empty.

In designs where injection is only into the cold legs, much of the injected water in the long term cooling phase will bypass the core. The water in the core will continue to boil until one of the operating high head safety injection pumps is realigned to inject water into the hot leg, which would be done within 24 hours. Until this time, the wet phase release will remain in the core region and volatile iodine produced by radiolysis will be released to the primary containment.

When a low level is reached in the refuelling water storage tank, the suction for the emergency core cooling pumps is realigned to the containment sump and the recirculation phase begins. In designs where the spray water is dosed with sodium hydroxide, the pH of the initial spray water is 10 and, when the spray water mixes with the coolant in the sump, the pH of the sump water increases from about 5 to 8. During the recirculation phase, the pH of the injection water increases in the same way.

In cases where the spray water is not dosed with sodium hydroxide, a pH of about 8 in the sump and recirculating spray water is achieved by providing a buffering agent in the sump. In KWU designs, no buffering
agent is provided.

3. THE INITIAL BENCHMARK STUDIES

In the initial phase of the work, six countries provided the results of calculations that were based on a reference design of plant and the licensing methods in the period leading up to 1988. Some of the results are summarised in Fig 2. It was found that there were wide variations in the assumed form of iodine released to the primary containment.

In some cases, 90% of the released iodine was taken to be molecular, while at the other extreme, all the inorganic iodine was taken to be associated with the aerosol of water droplets in the atmosphere. The proportion of organic iodine varied from 10% to 0.2%. No specific assumptions were made in Germany with respect to the chemical forms of iodine in the containment, but the instantaneous ratio of the concentration in the aqueous phase to that in the gaseous phase was taken to be $10^4$.

There were related differences in the rate at which iodine was assumed to be removed from the containment atmosphere. In some cases, the molecular and particulate forms were taken to be removed instantaneously in contrast to others where the aerosol form, was assumed to be removed with a coefficient of $0.45\text{h}^{-1}$. In only one case was the removal coefficient for organic iodine taken to be greater than zero.

These differences created a considerable interest in developing a realistic calculational route. The result is summarised in the following sections.

4. THE RELEASE OF IODINE TO THE PRIMARY CONTAINMENT

4.1 The Release from the Fuel Pins

The amount of iodine that is released to the primary containment depends on the amount of fuel cladding that fails, the amount of iodine that is released from the fuel and the fuel-cladding gap and the form of the released iodine.

Currently, different failure criteria are used in different countries and in most cases, conservative assumptions are made about thermal-hydraulic conditions in the core. Conservative calculations carried out in France and the UK for the case of cold leg injection only indicate that less than 33% of the fuel pins will fail. A probabilistic analysis covering all the pins in the core has been completed in Germany, which shows that only 3% of the fuel pins are expected to fail. The details of these calculations have not been compared and the values of 33% and 3% are adopted in this paper for the two injection scenarios although the relationship between the injection scenario and the failed fuel fraction has not been established.

The release from a failed fuel pin is based on measurements made on irradiated fuel and on the results of in-pile experiments carried out by CEA in France (Ref 1 and 2). On the basis of these measurements, 2% of the stable iodine inventory of the core, that is 2 moles in a four loop PWR would be released if 100% of the fuel pins failed. The corresponding release of I-131 is 0.7% of the core inventory.
4.2 The Form of the Release from the Fuel Pins

During normal operation, iodine in the gap between the fuel and the cladding is in the form of caesium iodide (Ref 3 and 4). When it is released to the coolant, it dissolves and becomes the iodide anion, \( I^- \), and the caesium cation \( Cs^+ \).

When the fuel fails following a LOCA, most of the iodine released from the fuel cladding gap and from any fragmented fuel will also be in the form of caesium iodide vapour. However, the disassociation of caesium iodide is significant at temperatures above 1000°C (Ref 5) and this is a potential source of molecular iodine. Typically, about 2% of the fuel pins experience temperatures above 1000°C and thus less than 2% of the fuel volume will experience this temperature. A smaller proportion of the caesium iodide in the fuel cladding gap will experience this temperature. As a result, an upper limit for the amount of \( I_2 \) that will be released from the fuel during the dry phase and transported to the containment atmosphere will be 2% of all the iodine released from the fuel.

All the \( I_2 \) is taken to be released in the dry phase. The FLASH series of experiments carried out by CEA indicated that 10% of the overall release would be in the dry phase (Ref 1 and 2). On this basis, 10% of the CsI released is taken to be in the dry phase and swept into the primary containment in the form of vapour for cases where injection is only into the cold leg. The case of simultaneous hot and cold injection has not been considered in detail but, in this case, some of the CsI vapour will be retained by the safety injection water and only 1% of the CsI released from the fuel is taken to reach the primary containment atmosphere with the \( I_2 \).

4.3 The Release from the Coolant

During the period while the water injected into the cold legs is largely bypassing the core, the wet phase release will be trapped in the boiling reflood water within the core region. Although the involatile \( I^- \) anion will not be released, radiolytic oxidation of \( I^- \) to \( I_2 \) will occur at an appreciable rate as a result of reactions between \( I^- \) and the radiolysis products of water (Ref 6 to 9).

The amount of \( I_2 \) that is produced is based on the experiments of Burns et al (Ref 9) and calculations carried out using the IODE code (Ref 10). The measurements reported in Ref 9 show that at high irradiation levels, such as occur in the shutdown core, the fraction of the total amount of iodine that is volatile reaches a steady-state value which is a function of temperature.

The volatile fraction can also be calculated using the IODE code and the corresponding results are compared with those of Ref 9 in Fig 3. It will be seen that there is good agreement between the two methods over the range of interest.

In order to calculate the rate of mass transfer of iodine to the steam in the boiling coolant, it would be necessary to measure or calculate the sizes of the steam bubbles and their concentration within the pressure vessel. Appropriate mass transfer coefficients for the water/steam interface could then be used to calculate the rate of release. However, the calculation of a time dependent size distribution for the steam bubbles would be complicated and thus evaluating the overall release of iodine from the coolant to the steam leaving the
vessel would be subject to considerable uncertainties. Instead, the bounding assumption is made that the iodine concentrations in the steam and water are in equilibrium. Using this method, 60% of the iodine released to the water is calculated to be released to the containment atmosphere before recirculation raises the pH of the water in the vessel and effectively ends the release.

In designs where hot leg injection is not delayed, this phenomenon does not occur and the wet phase release is quickly carried via the break to the reactor building sump.

4.4 The Modelling of Inorganic Iodine Behaviour

When the primary coolant escapes from the break during the blowdown phase, an aerosol of water droplets will be formed. The droplet size distribution is unknown, but the larger drops will rapidly settle to the sump as a result of gravity and at a faster rate in designs where a spray system is provided. By the time the release of fission products occurs, the airborne blowdown droplets are likely to be of the order of 10 micron radius or less.

When it reaches the atmosphere of the primary containment, the CsI vapour will condense in the bulk or on surfaces. Calculations using the AEROSOLS/B2 (Ref 11) and AEROSIM-M (Ref 12) codes show that the CsI is unlikely to agglomerate with the blowdown aerosol. However, it is hygroscopic and the condensed CsI vapour is likely to act as nuclei for steam condensation and produce droplets whose initial radius will typically be of the order of 0.5 microns. For a design where both one spray train and one fan cooler can be claimed to be operating after the LOCA, the contributions to the removal rate of 0.5 micron mass medium radius droplets is shown in Fig 4. The total rate approximates well to a removal rate constant of 1.3 h\(^{-1}\) for the first 0.6 h and 0.45 h\(^{-1}\) thereafter if sprays are present and 0.6 h\(^{-1}\) for the first 0.6 h and 0.3 h\(^{-1}\) thereafter if there is no spray system.

In practice, the size of the fission product aerosol will grow as a result of condensation and the droplets may be of the order of 10 microns. In which case, the removal rate will be much faster but, in the absence of a model for calculating the condensation rate on the fission product aerosols, the removal rates corresponding to 0.5 micron mass medium radius droplets have been used.

The behaviour of inorganic iodine has been modelled using the method described in Ref 9 in which the radiolysis reactions, hydrolysis and the oxidation and reduction of iodine are represented by a series of differential equations. These are solved to model a system containing the atmosphere of the primary containment, the condensation aerosol, the spray droplets and the sump as shown in Fig 5. Thus, the following processes are considered simultaneously:

- the radiolytic production of I\(_2\) and hydrolysis to HOI in the aerosol (Ref 8 and 9),
- the partitioning of volatile iodine between the condensation aerosol and the gaseous phase (Ref 13),
- the partitioning of volatile iodine between the gaseous phase and the spray water and the sump water and hydrolysis in the water (Ref 13).
the production of volatile iodine in the boiling coolant as
described in Section 4.3.

the movement of water from the condensation aerosol to the sump and

the changing pH of the spray water and the water in the vessel.

The rate at which I₂ is produced in the condensation aerosol is
proportional to the rate at which the aerosol absorbs energy which, for
a given dose rate, is proportional to the mass of water in the aerosol.

Most of the chemical data used in the modelling is well documented
and, apart from the mass transfer coefficients, the uncertainties are
relatively small (Ref 14). The other exception is the volume partition
coefficient of HOI for which measured values at 100°C range from 240
(Ref 15) to 10⁴ (Ref 16). The best supportable value is the
conservative value of 240, but no significant difference in the airborne
levels are predicted if the value of 10⁴ is used.

An alternative is to use the IODE code (Ref 10). Again, the basic
reactions are represented by a set of differential equations, but only
one water volume is represented as shown in Fig 6.

4.5 The Overall Behaviour of Inorganic Iodine

4.5.1 Cold Leg Break: Cold Leg Injection Only with Spray

With the assumptions of the previous chapter, the behaviour of
inorganic iodine is shown in Fig 7. Initially, 2% of the iodine
released from the fuel is airborne in the reactor building in the form
of I₂ and 9.8% is associated with an aerosol of small condensation
droplets. The remainder stays in the coolant in the reactor vessel.
The latter is converted into volatile forms of iodine as a result of
radiolysis and released until recirculation starts at about 1 hour.
Then, the pH of the vessel water rises and the release becomes very
slow. Radiolysis also results in a release of volatile iodine from the
aerosol.

It can be seen that after a short time, the release from the
vessel results in a much greater level of airborne iodine than is
initially present in the form of aerosol. The gaseous iodine is removed
by the spray and by mass transfer to the sump while the aerosol is
removed to the sump by the spray and phoretic effects.

The behaviour of the airborne iodine is shown in Fig 8. From
Section 4.2, 0.65 moles are released from the fuel if 33% of the pins
fail and 0.064 moles are initially airborne in the form of aerosol and
0.013 moles in the form of I₂. Initially, the gaseous phase is
molecular iodine, but this converts into HOI by hydrolysis and
eventually the airborne level of gaseous iodine is limited by
equilibrium between the HOI in the gaseous phase and in the sump water.

In Fig 8, it is assumed that 10⁻⁴ of the activity of the sump
water is persistently airborne in the form of fine droplets.

Sensitivity to Aerosol Size

The removal of iodine from the containment atmosphere will depend
on the size of the aerosol droplets. If, as a result of condensation,
the mass mean radius is 10 microns instead of 0.5 microns, the
airborne inorganic iodine as a function of time is as shown in Fig 9.
The iodine in the aerosol is removed rapidly, but the contribution of $I_2$ from the water in the vessel dominates the total airborne level so that after half an hour, the airborne level is only 10% less than in the 0.5 micron radius case.

Sensitivity to Spray Drop Size

It should be noted that the removal rate of gaseous iodine is design dependent because it is a function of the size of the spray droplets, which determines the surface area over which mass transfer occurs. This is illustrated in Fig. 10. A diameter of 526 microns is used in the present work but median values of 350 to 760 microns occur on commercial designs. The three removal rates illustrated in Fig. 10 correspond to removal rate constants of 0.2, 0.48 h$^{-1}$ and 2.2 h$^{-1}$ for droplet diameters of 760, 526 and 348 microns respectively.

Sensitivity to the pH of the Spray Water

The level of airborne iodine has been calculated for two values of the pH of the spray water. These were a pH of 10 corresponding to spray water dosed with sodium hydroxide and a pH of 5 corresponding to untreated spray water. It was found that the levels of airborne iodine differed by less than 1%. This is because the rapid rate at which $I_2$ hydrolyses into HOI in the spray droplets and the partitioning between the HOI in the spray droplets and the gaseous phase is very insensitive to the pH of the spray water. Because HOI is a very weak acid, it remains in its undissociated state even at high values of the pH.

This is consistent with the results of the CSE. In these experiments, test A6 used spray water which was dosed with sodium hydroxide and had a pH of 9.5 while test A7 used spray water with a pH of 5. The measured removal constants differed by only 5% or less (Ref. 17).

4.5.2 Hot Leg Break: Cold Leg Injection Only with Spray

In this case, there is no boiling pool and the wet phase release is quickly carried to the sump. Figure 11 shows that the airborne iodine is initially dominated by the aerosol, but after four hours the airborne level is mainly $I_2$ and after 16 hours HOI is dominant as before. The removal rate is 0.9 h$^{-1}$ for the first hour and 0.4 h$^{-1}$ until a reduction factor of $10^{-3}$ is achieved.

Because there is no contribution from the boiling pool, this case is much more sensitive to the aerosol removal rate and thus the aerosol size. If the latter increases to a mass median radius of 10 microns, the airborne iodine is as shown in Fig. 12 where the removal rates increase to 4.7 h$^{-1}$ for the first 15 minutes and 0.48 h$^{-1}$ until an attenuation of $10^{-4}$ is achieved.

4.5.3 Simultaneous Hot and Cold Leg Injection: No Spray

This case represents the major features of KWU designs. The pH of all the water phases is taken to be 6 corresponding to a pH (300°C) of 7.4. In this case, the dry phase release has to pass the incoming injection water before it escapes from the break and only 1% of the total release of CsI from the failed fuel pins is taken to be airborne together with the iodine that is released in the form of $I_2$. As in the case of the hot leg break, there is no boiling pool and the activity
that remains in the coolant is rapidly displaced and flows via the break to the sump.

The forms of airborne iodine are shown in Fig. 13. Initially, the airborne iodine consists of 2% of the release from the fuel in the form of I₂ (1.2 x 10⁻³ moles of I) and 1% in the form of I⁻ (6 x 10⁻⁴ moles of I) associated with the aerosol of condensation droplets. It can be seen that much of the airborne I₂ rapidly transfers to the aerosol and radiolysis results in the rapid formation of HOI. HOI becomes the dominant form of airborne iodine after an hour, by when phoretic effects have reduced the aerosol contribution to a third of the total.

Because the degree of hydrolysis of I₂ depends on the pH, the dominant form of the gaseous iodine is sensitive to the pH of the aerosol. If this is taken to be 5 instead of 6, the forms of the airborne iodine become as shown in Fig. 14. Much less of the initial I₂ enters the aerosol and I₂ remains the largest contribution to the total airborne iodine. However, a comparison of Fig. 13 and 14 shows that there is very little difference in the total amount of airborne iodine.

4.6 The Behaviour of Organic Iodine

The level of organic iodine in the primary containment is based on the measurements made by Cline et al (Ref 18) during venting of the containment after the TMI-2 accident. These are consistent with the laboratory measurements of Dean and Davies (Ref 19) who measured the production of organic iodine as a function of radiation level, pH and surface material. The TMI measurements indicate that organic iodine is produced at a rate of 0.01% of the containment iodine inventory per day until a level of 0.2% of the containment inventory is reached. The removal of methyl iodide by sprays will not be significant because of its low volume partition coefficient. In Fig. 15 and 16, the inorganic levels for the cold leg break of Section 4.5.1 are compared with the organic levels for the two cases in which the organic level is taken to be 0.2% of the containment inventory from the time the fission products are released from the fuel and the case where the production is 0.01% of the inventory per day. Even in the more conservative case, the inorganic iodine dominates the airborne level until 15 hours after the fault.

4.7 The Overall Release

An overall picture of the importance of modelling iodine behaviour is given in Fig. 17, which shows the I-131 activity at each stage between the core inventory and the integrated release. The release depends on the rate at which activity leaks from the primary containment to the environment which is design dependent. Cases 1 and 2 represent a cold leg break with cold leg injection only and sprays, and therefore correspond to Fig. 8, but with different primary containment leak rates. Case 1A is as for case 1 but is a hot leg break corresponding to Fig. 11. Case 3 corresponds to the case where there is simultaneous hot and cold leg injection, no spray system, no buffering of the sump water and no bypass of the secondary containment. Also shown is Case 2A which is the results of a calculation for cold leg injection only with an aerosol removal rate of 4 h⁻¹, typical of 10 micron mass median radius droplets, and a removal rate for molecular iodine of 20 h⁻¹, which would
be appropriate if hydrolysis of I₂ in the spray droplets and mass transfer from the spray to the gaseous phase were neglected. These results indicate the importance of correctly modelling the behaviour of both iodine and aerosols and the claims made for design features.

5 DISCUSSION AND CONCLUSIONS

The results of available experimental work and modelling have been used to develop an integrated calculational route to determine the radiological release following a design basis LOCA.

For most designs, where injection is only into the cold leg, the largest release of iodine into the primary containment is due to radiolysis of the iodide in the boiling coolant in the core. The proposed method is the bounding case which assumes equilibrium between the volatile iodine in the coolant and the steam leaving the vessel. A less conservative release could be claimed if an appropriate model were developed and validated.

The modelling of iodine in the containment atmosphere considers all the important liquid phases as well as the gaseous phase. It is based on well validated data and the kinetics of the relevant chemical reactions are straightforward. However, the model has not been validated by an integral experiment and there are differences between the mass transfer coefficients based on Ref 13 and those used by the IODE code. Thus, two areas of further work have been identified:
(a) the validation of the overall modelling of iodine behaviour in the primary containment atmosphere and particularly the degree of oxidation of iodine in simulated aerosols and
(b) the experimental validation of the mass transfer coefficients appropriate to the aerosol, spray, sump and steam bubbles in the vessel.

6 ACKNOWLEDGEMENTS

The contribution of our colleagues in GRS, Cologne and Vincotte, Brussels to the work summarised here is gratefully acknowledged.

7 REFERENCES

1 Bruet, M., 'Synthèse des relâchements de produits de fission des essais FLASH 01,02,03 et 04,' PMG 18/84, 15th October, 1984.


PWR - Reflood Phase Following a Guillotine Cold Leg Break

Fig 1

Instantaneous Relative Activity of I-131 in the Primary Containment Atmosphere Reported in the Benchmark Study

Fig 2
FIG 15
BEST SUPPORTIBLE AIRBORNE IODINE LEVELS IN THE PRIMARY CONTAINMENT ATMOSPHERE: COLD LEG BREAK; COLD LEG INJECTION ONLY WITH SPRAY

FIG 16
TIME DEPENDANT ORGANIC AND INORGANIC IODINE LEVELS IN THE PRIMARY CONTAINMENT ATMOSPHERE: COLD LEG BREAK; COLD LEG INJECTION ONLY WITH SPRAY

FIG 17
RESULTS FOR I-131
1: Core Inventory
2: Activity Released into the Primary Circuit
3: Activity in the Containment Atmosphere Shortly After the Accident
4: Activity in the Containment Atmosphere 2 Hours After the Accident
5: Integrated Released Activity After 2 Hours
6: Integrated Released Activity After 24 Hours
7: Integrated Released Activity After 720 Hours
DISCUSSION

Friederichs
I was wondering that in the case without spray and pH of 6 the main iodine species in the atmosphere is HOI. What partition coefficient did you take for HOI in this case?

Dutton
The partition coefficient we used was 240 at 100°C. The values in the literature range from 240 to $10^4$ and we took the conservative end of the range.

Evans
Could you please tell me the concentration of iodine in the sump.

Dutton
I'm afraid I can't remember but I will look it up for you.

Morell
Why do you end up with HOI as the dominant oxidation species in your study? Why do you ignore proceeding oxidation to IO$_3^-$?

Sims
HOI is important if it has a low pH because I$_2$ hydrolytic in the drop and is re-released at a fast rate. Rates of IO$_3^-$ formation are slow compared with the rate of volatilization particularly from a small drop at dilute solution.

Fluke
To what extent did the blowdown aerosol influence the release calculations?

Dutton
Initially, we in the UK assumed the CsI vapor would rapidly associate with the blowdown aerosol. However, the AEROSOLS B2 calculations carried out in France and our own showed that the CsI aerosol and the blowdown aerosol would not agglomerate and, as a result, the blowdown aerosol did not play a part in the final model.
6.3 A NEW CHEMICAL MODEL FOR THE REMOVAL OF IODINE VAPOUR FROM A REACTOR CONTAINMENT BY AQUEOUS SPRAYS

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ABSTRACT

This paper describes methods for the calculation of the removal rate of \( I_2 \) vapour by aqueous sprays from a large volume such as a reactor containment. The kinetic methods used involve the latest information on the reaction of dissolved iodine with water which causes the \( I_2 \) molecules to be quickly transformed into virtually involatile products. This hydrolysis increases the effective waterside mass transfer coefficient of \( I_2 \), and depends on the \( I_2 \) concentration, the acidity of the water and the temperature. Comparisons of calculated removal rates with a range of suitable experimental data show that for agreement with observation the hydrolysis product HIO, hypoiodous acid, must be considered effectively involatile. When the water is alkaline (pH 9) the overall mass transfer coefficient for \( I_2 \) can be put equal to that for the gas side. Acidic sprays can cause a major uptake of iodine by painted walls.

1. INTRODUCTION

Containment vessels for light water reactors, as part of their engineered safety arrangements, have aqueous spray systems which operate in the event of a reactor fault, such as loss of coolant accident. Spray nozzles, situated in the upper part of the containment far above the reactor vessel and its pipework, produce streams of aqueous drops in the containment atmosphere which help in reducing risks by lowering the temperature, washing out aerosol droplets, and absorbing vapour phase iodine. The consequent reduction in the airborne iodine mass is an important safety feature since any radioactive iodine leaked from the containment constitutes a potential radiological hazard to the general public, iodine being ingestible by human beings, whose metabolism causes the element to be concentrated in the human thyroid gland.

It is thus essential when considering engineering aspects of reactor safety, for example correct scaling from experimental tests to real plant, and possible intervention strategies, to have a proper conception of the physical and chemical processes involved in the interaction of iodine vapour with spray drops and the mechanisms whereby spray removal is effective. This subject has received a great deal of attention both in experiments and in modelling[1-19], but very few papers treat the interaction of the chemical reaction and mass transfer in a correct way, in spite of the existence of Danckwerts' paper[20] of 1951 and the excellent books and papers by Astarita[21,22] and Danckwerts[23] on this very topic. The present paper uses recent work on the mechanism of the aqueous hydrolysis of molecular iodine and its overall temperature dependence, and developments of the methods suggested by Danckwerts for combining mass transfer with chemistry[24]. These are applied in a numerical treatment rather than calculated analytically because the chemistry is rather more complex than the simple reactions treated by Danckwerts.
2. CALCULATIONS

2.1 Mass Transfer Without Reaction

We consider the aqueous absorption of gaseous molecular I₂ with gas and liquid volumes $V_g$ and $V_w$, $P_1$, the concentration ratio $C_w/C_g$ at equilibrium is known as the partition coefficient. It can be shown\[25\] that for starting concentrations $C_g = C_{go}$, $C_w = 0$, the occurrence of reaction (1)

$$I_2(g) \rightarrow I_2(aq)$$

causes $C_w$ and $C_g$ to change with time according to (2) and (2a)

$$C_w = \frac{C_{go}k_fp_1}{(k_f+k_fp_1/V_r)}\{1-\exp[-(k_f+k_fp_1/V_r)t]\}$$

(2)

$$C_g = C_{go} - C_w/V_r$$

(2a)

Here $V_r$ is $V_g/V_w$ and $k_f = K_oA/(V_wP_1)$, where $K_o$ is the overall mass transfer coefficient and $A$ the interfacial area. The rate constant $k_f$ is for partitioning from liquid to gas, the reverse of (1). $K_o$ in terms of the gas side mass transfer (mt) coefficient $K_g$ (1.1dm/s at 100°C) and $K_w$, the waterside mt coefficient (7x10⁻⁵dm/s at 100°C) is given by (2b).

$$1/K_o = 1/K_g + 1/(K_wP_1)$$

(2b)

At 100°C $P_1$ is 9, so for a typical spraydrop diameter of 0.6mm $k_f$ for $I_2$ is ca 0.8s⁻¹. For a large reactor containment or similar vessel $P_1/V_r$ is well below unity so (2) is well approximated by (3).

$$C_w = C_{go}P_1\{1-\exp(-k_ft_d)\}$$

where $t_d$ is the exposure time of the drop. For such large vessels $k_f t_d$ is above ca 5, so $C_w = C_{go}P_1$ and for well mixed phases the solute iodine entering the sump in a stream of drops is in equilibrium with gaseous iodine.

2.1.1 Effects of a continuous spray - no chemical reaction

We make the customary simplifications that both phases are well mixed, the drops have equal diameters and exposure times, there is no coalescence nor source of iodine, and the drops form a pool of negligible volume but from which iodine is involatile.

For this simple case the fractional rate of loss of gas concentration, $\lambda$ is given by (4)

$$\lambda = -\frac{1}{C_g}\frac{dC_g}{dt} = S\frac{P_1}{V_g}\{1-\exp(-k_f t_d)\}/V_g$$

(4)

where $S$ is the spray rate (volume of liquid per unit time).
For large vessels where $k_f t_d$ is 5 or above (4) is approximated by (5)

$$\lambda = -\frac{1}{C_g} \frac{dC_g}{dt} = SP_1/V_g$$  \hspace{1cm} (5)$$

This equation for $C_g$ is equivalent to the equation for the rate of change of the concentration $C_1$ of a fluid when a stream of fluid with solute concentration $C_s$ is being added at rate $S^1$. The equation is (6)

$$\frac{dC_1}{dt} = S^1(C_1 - C_s)/V_t$$  \hspace{1cm} (6)$$

where $V_t$ is the well-mixed volume. The effect of the spray is thus as if the gas were being diluted at a rate $SP_1$ by gas containing no iodine, and bleeding were occurring to keep pressure and volume constant. Similarly we can think of the spray as a body of water with area/volume equal to that of a single drop which at constant volume is being diluted at rate $S$ with iodine-free water, so that equation (7) has to be concatenated with any other equations for $C_w$

$$-\frac{dC_w}{dt} = S C_w/V_s$$  \hspace{1cm} (5)$$

where $V_s$ is the spray volume.

The vapour phase concentration changes as a result of the partitioning reactions. For a large vessel $S/V_s$ is $1/t_d$, and it is against the dilution 'reaction' with rate constant $S/V_s$ that partitioning competes.

The differential equations for partitioning (reaction (1)) may be written

$$\frac{dC_w}{dt} = -k_f C_w + k_f P_1 C_g$$  \hspace{1cm} (8)$$

$$\frac{dC_g}{dt} = -\frac{1}{V_r} \frac{dC_w}{dt}$$  \hspace{1cm} (9)$$

In Fig 1 are shown the results (concentrations in gas and water) of spray removal calculations using 'gas dilution', (equations (8), (9) and (5)) and 'liquid dilution' (equations (7), (8) and (9)). The solution of sets of differential equations, including those for chemical reactions, is effected by using the FACSIMILE[26] computer package. The liquid dilution method is seen to be a reasonably accurate method of dealing with the spray and will be useful in situations of complex chemistry. In Fig 1 the spray rate is $258 \text{dm}^3 \text{s}^{-1}$, $V_r$ is $8.8 \times 10^4 \text{dm}^3$, $t_d$ is $11s$, $P_1$ is 9, $K_g$ is $7 \times 10^{-5} \text{dm} \text{s}^{-1}$, $K_w$ is $1.1 \text{dm} \text{s}^{-1}$, the drop radius is $270 \mu m$.

2.2 Relevant Aqueous Iodine Chemistry

The first hydrolysis reaction[27] of $I_2$ to HOI, reaction (10)

$$I_2 + H_2O \rightarrow HOI + H^+ + I^-$$  \hspace{1cm} (10)$$
has been shown[28] to occur in stages, with the intermediate, $I_2OH^-$, also being formed by direct reaction between $I_2$ and $OH^-$. The relevant reactions are (11) to (15)

$$I_2 + H_2O \rightarrow I_2OH^- + H^+ \quad \text{(11)}$$
$$I_2OH^- \rightarrow HOI + I^- \quad \text{(12)}$$
$$I_2 + OH^- \rightarrow I_2OH^- \quad \text{(13)}$$
$$I_2 + I^- \rightarrow I_3 \quad \text{(14)}$$
$$H_2O \rightarrow H^+ + OH^- \quad \text{(15)}$$

Disproportionation occurs more slowly, with the stoichiometry of (16) but at a rate second-order in $[I_2]^2$ caused by the two stages (17) and (18)

$$HOI + HOI \rightarrow IO_3^- + 2I^- + 3H^+ \quad \text{(16)}$$
$$HOI + HOI \rightarrow IO_3^- + I^- + 2H^+ \quad \text{(17)}$$
$$IO_3^- + HOI \rightarrow IO_3^- + H^+ + I^- \quad \text{(18)}$$

At high pH HOI dissociates to form $IO^-$, which also takes part[36] in reactions like (17) and (18)

$$HOI \rightarrow H^+ + IO^- \quad \text{(19)}$$

Rate and equilibrium constants are in Table 1. The occurrence of reactions such as (13) and (19) and the laws of mass action ensure that iodine in solution is less volatile at high dilution and high pH. (For present we presume HOI involatile.)

2.2.1 Chemistry and partitioning into drops - equilibrium and kinetics

The faster chemical reactions of iodine, i.e., (11) to (15), come to equilibrium in a few seconds in an isolated body of water, but if we consider these equilibria occurring in a suspended drop in contact with $I_2$ vapour the process takes much longer, as seen in the example of Fig 2. This is because iodine removed by hydrolysis is continuously replenished from the vapour at a rate governed by mass transfer from the vapour to the drop. When hydrolysis is occurring it is thus important to consider the physico-chemical effects from a kinetic rather than an equilibrium standpoint, as was possible with no reaction. The mass transfer from gas to drop has been considered in two ways using (a) the overall mt coefficient for $I_2$ (equation 3) entering a well mixed drop, and (b) a detailed split of the mt processes for gas and liquid[22,23]. In method (b) a static boundary layer of thickness $D/K_w$ (where $D$ is the diffusion coefficient for aqueous $I_2$) at the spherical interface and divided into a number (40) of spherical shell sublayers. Mass transfer from the vapour to the outer surface sublayer entails no resistance to transfer by the liquid, and transfer across the whole boundary layer to the well mixed central circulating bulk is limited by diffusion, simulated by the TRANSPORT facility of FACSIMILE. In the first case considered hydrolytic reactions
of I\textsubscript{2} are allowed only in the central bulk region and the concentration profiles of aqueous species in the boundary layer quickly become straight lines joining the surface to the bulk concentrations. The equivalence of methods (a) and (b) is demonstrated in Fig 2 which shows bulk concentrations in the drop and the vapour for a drop suspended in I\textsubscript{2} vapour where V\textsubscript{T} (gas to liquid volume ratio) is the same as in Fig 1. The agreement depends on the boundary layer thickness being small compared with the drop diameter, which is appropriate for a falling drop of this size.

2.2.2 Effects of Recirculation

In some fault management situations for loss of coolant faults in reactors, the accumulated sump is made alkaline and after a time when the initial source of the spray water has become exhausted, the alkaline sump water is used to feed the spray. We have simulated these effects, using the two methods of Section 2.2.1 for partitioning into the spray and of equation (6) for the solute concentrations in the sump water. The liquid dilution method 2.1.1. was used to model spray effects. Results are shown in Fig 3 as iodine species concentrations in the spray water, the gas concentration and \lambda values. Sump concentrations are also part of the calculational output but are not shown here; we have included the disproportionation reactions since long times are involved. Note first that as in Fig 2 the two methods for modelling partitioning are in reasonable agreement. Because iodine is allowed to react to form involatiles in the bulk of the drops the spray removes it more efficiently from the vapour, with \lambda, the fractional removal rate ca 2x10^{-4} \text{s}^{-1} at pH 5 and 3x10^{-4} \text{s}^{-1} at pH 8. These values compare with 2.7x10^{-5} \text{s}^{-1} for Fig 1 with no hydrolysis. Note that at the recirculation time (1800s) an abrupt change in aqueous speciation occurs (less I\textsubscript{2}, more HOI and the removal rate is greater; for [I\textsubscript{2}(g)]\textsubscript{0} = 10^{-5} \text{the change is from 3x10^{-5} \text{s}^{-1} before recirculation to 2x10^{-4} \text{s}^{-1} after. This difference occurs because the dilute solution resulting from 10^{-5} M I\textsubscript{2} gas is already well hydrolysed by virtue of its high dilution and the more concentrated solution from 10^{-5} I\textsubscript{2} gas reacts at pH 5 as a liquid with virtually no hydrolysis.} The important point here is that with I\textsubscript{2} allowed to hydrolyse in the bulk liquid of the drops (but not also in the boundary layer) vapour removal rates can increase by a factor 10.\n
2.2.3 Mass transfer with reaction in both bulk and boundary layer

Calculations were also performed allowing hydrolytic reactions as well as diffusion in the aqueous boundary layer, the effect of this is that as I\textsubscript{2} diffuses inwards from the surface it is quickly transformed into hydrolytic products before reaching the bulk zone. Figure 4 shows concentration profiles for I\textsubscript{2}, HOI and I\textsubscript{2}OH\textsuperscript{-} in the boundary layer at 1s for a 270\mu m radius drop at pH 9 with V\textsubscript{T} as before at 8.8x10\textsuperscript{7}/2837. The surface concentration gradient for all forms of I\textsubscript{2} (especially I\textsubscript{2}OH\textsuperscript{-}), the driving force for iodine transport across the boundary, is greatly increased above its value without reaction in the boundary layer where [I\textsubscript{2}(aq)] would be 9x10^{-9} M at the interface side and virtually zero at the bulk side of the boundary layer. We believe that the situation described here, with reaction in the boundary layer as well as the bulk, is the one which obtains in reality. An example of a calculation of aqueous drop concentrations and [I\textsubscript{2}(g)] with the conditions used for other figures,
with \([I_1(g)]_o = 10^{-8} \text{M}\) and a pH of 5 in the aqueous phase is given in Fig 5. Note that on recirculation to give pH 8 the value of \(\lambda\) rises to ca. 2 \times 10^{-3}, an increase of another factor 10 above that where reaction in the boundary layer was not considered. In fact in some circumstances the resistance to transport offered by the water phase can be neglected. A similar calculation using homogeneous simulation (no boundary layer) was performed with the 'overall' mass transfer coefficient (normally \(K_0\) of equation (3)) set equal to \(K_g\). The results, in Fig 6, are very similar to those of Fig 5.

2.2.4 Summarised calculations for spray removal rates

A list of \(\lambda\) values (fractional rate of loss of gas concentration) is given in Table 2 at a number of times for a variety of calculational procedures and initial conditions. In all of these the spray rate is 258 dm\(^3\) s\(^{-1}\), \(V_s = 8.8 \times 10^{-3} \text{dm}^3\), \(V_y = 238 \text{dm}^3\), the temperature is 100°C, the spray drop radius is 270 \(\mu\text{m}\), \(P_i\) is 9, \(K_0\) is 7 \times 10^{-4} \text{dm s}^{-1}, \(K_y\) is 1.1 dm s\(^{-1}\) and \(t_d\) is 11s. The different initial conditions tested were (a) different values of \([I_1(g)]_o\), 10^{-8} M and 10^{-9} M, (b) different values of the initial aqueous pH, 5 or 9. The various calculational procedures tested were (a) 'liquid dilution' and 'gas dilution', see section 2.1.1, denoted L or G in column 4; (b) the use of a homogeneous drop together with the overall mt coefficient (equation 3), or the use of a 'layered' drop with the water-side mt coefficient modelled by diffusion through a boundary layer of thickness \(D/K_w\); these methods are denoted by H or L in column 5; (c) for the layered drop whether hydrolytic reactions are allowed only in the bulk zone of the drop or in all zones including the boundary layer; these methods are denoted B or A respectively in column 6 - unlayered drops are given a dash; (d) calculations which included recirculation at 1800s using the sump water with its burden of hydrolysis products (including those from disproportionation), with pH set to 9, as the spray feed; these are denoted R for recirculation included and N for not. Also included are two calculations where HOI was allowed to be volatile - entries 19 and 20, for which the partition coefficient of HOI used was 240. Entries 1 and 2 differ from the rest in that no hydrolysis was modelled.

Results vary over a wide range, from 2.7 \times 10^{-5} s^{-1} for rows 1 and 2 to 3.0 \times 10^{-2} s^{-1} for row 17. Chief effects to be noted are (i) that gas and liquid dilution methods are equivalent, (ii) that \(\lambda\) values are greater for lower \([I_1(g)]_o\) and higher pH\(_o\) values, (iii) that the homogeneous method using \(K_0\) from reaction (3) gives the same results as for the layered drops with reaction allowed only in the bulk, (iv) that the fastest removal rates are for the layered drop with reaction in all zones, which can give results equivalent to a homogeneous calculation with \(K_0\) set equal to \(K_g\), (v) that with HOI volatile removal rates are lower by factors up to ca. 40, (vi) that fresh water removes \(I_1\) vapour faster than the sump water at the same pH.

2.2.5 Comparison with measurements on large vessels

Measurements chosen for comparison were those made at temperatures closest to 100°C. When not at 100°C suitable adjustments were made in the partitioning and hydrolytic rate and equilibrium constants used. The method of calculation used was the layered drop and reaction in all zones and with only \(I_1\) volatile. Results are given in Table 3. The agreement,
considering the approximations of the calculations and the difficulties of the experiments is considered good for neutral and alkaline spray waters, where the greatest discrepancy is a factor 2. The measurements for acid water (pH 5) are considered to be probably misleading, as discussed in Section 3 below. Calculations were also performed with HOI volatile with partition coefficient 240. These gave worse agreement by a factor ca 2.

3. DISCUSSION

3.1 Effects in the Calculations caused by Chemistry

When only I₂ is volatile removal rates will be greater at higher pH and lower concentrations since the laws of mass action ensure that under these conditions the degree of hydrolysis is greater, and more iodine in all forms is removed per drop. This is because any molecular iodine changed into other species will be replaced from the gas phase. When HOI is considered volatile the spray stream plays two roles, the first to remove I₂ as molecular iodine and other iodine species in the outgoing spray, the second to change gaseous I₂ into gaseous HOI during the drop fall, and in general the second role acts to the detriment of the first even though the partition coefficient for I₂ is 9 and for HOI is 240.

3.2 Effects in the Experiments caused by Iodine Transfer to the Walls

In the test of ref 40 using boric acid solution of pH 5, the gas concentration over the first 17 minutes fell with a mean rate constant of 0.2 per minute but analysis of the accumulated spray liquid showed that only 13% of the iodine lost from the gas appeared in the water suggesting that 87% of the loss was to the painted wall (Phenoline 302). Correcting for this effect changes the t₁/₂ due to the spray from 3.6 to 27.3 minutes, agreeing with the calculation. If similar analysis were available for the acid spray test A7 of Ref 13 it might show an even greater percentage of the loss from the gas phase caused by wall absorption, because [I₂(g)]₀ was lower. The results in Ref 40 suggest that when acid sprays are used the main loss is due to increased velocity of the gas to the wall.

4. CONCLUSIONS

i) A new spray removal calculational method has been developed which agrees reasonably with experiment over a wide range of [I₂(g)]₀ values (7x10⁻¹⁰ to 1.2x10⁻⁸M), water pH values 5 to 14, flow rates (.007 to 10dm s⁻¹) and vessel sizes (5.3 to 595m³).

ii) Calculations and experiments show alkaline water to be greatly superior to acidic water in I₂ removal. Acid sprays may cause reasonably high removal rates by moving I₂ gas to painted walls.

iii) The calculations have taken no account of iodine sinks or sources. In some reactor faults a likely I₂ source is irradiated aerosol containing I⁻(aq). Our INSPECT code[39] is being upgraded to include the spray removal method described here as well as such sources.

5. ACKNOWLEDGEMENTS

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REFERENCES


Table 1. Equilibrium and Rate Constants for Iodine Chemistry

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* Rate constant derived from equilibrium constant and the other rate constant

Table 3. Comparison of Observed and Calculated removal half-lives

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* Revised value taking account of loss to the wall
↑ See discussion in section 3.2
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** $I_2(g)$ removed
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DISCUSSION

Ishigure  How do you estimate the thickness of boundary layer?
Sims     It is defined by D/KL where D is the diffusion coefficient and KL the water side mass transfer coefficient.
7. SUMMARY AND GENERAL DISCUSSION
SUMMARY AND GENERAL DISCUSSION

Dutton
I would like to make a comment on the importance of HOI. Even with the lowest partition coefficient it makes very little difference to the release because, by the time HOI becomes important, the containment has depressurized and the release rate is small. Thus, the use of a small partition coefficient makes a lot of difference to the long term iodine behavior, but it makes very little difference to the release.

Bowsher
It has been suggested to broaden the scope of the meeting to include other important fission products such as cesium and iodine. I believe consideration should also be given to barium, strontium and ruthenium chemistry which are perhaps the 'second division' of fission products. Even more importantly, we need to consider the behavior of the predominantly nonactive bulk materials that are released at the same time as the fission products. Such bulk-materials aerosols could dominate the air-borne material, and it is essential to understand the behavior of the control rod and absorber materials that could be released at the same time as the radiobiologically-important fission products and determine their transport behavior.

Bowsher
With respect to studying different painted surfaces, we should also remember that the containment is a 'dirty' system in real life. Scientists from the Nordic countries have shown that the containment inventory also includes materials such as copper pipes, zinc and miscellaneous organics. Fortunately, Dr. Sims' work indicates that such impurities generally lower the pH and reduce iodine volatility, but we need to talk such 'dirty systems into account in future experimental and analytical work.

Sims
I think these are a need to meet more closely with the accident consequences analysts. Effects of epoxy but at high pH may be different but is it important. Finally IO3- chemistry at low concentrations may not be well known but also may not be important.

Evans
Are there conditions implicit in your statement that homogeneous chemistry generally is well known?

Sims
10^-4 M to 10^-6 M. Below this the consequences of the fault are much reduced.

Soda
Mr. Morell's paper could be applicable to SGTR. Transient phenomena such as containment failure during a severe accident will be of importance.

Ritzman
If scope of next workshop is expanded to other fission besides iodine, what particular fission products would be best to address?

Soda
Cs, Te and some others which would become important in the late phase of melt-progression.
LIST OF PARTICIPANTS

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Tokai-mura, Japan, 11th-13th September 1991

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