A feasibility study on iodine behaviour during pyroprocessing of spent metallic fuel

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Abstract

This study examines the chemical behaviour of iodine arising from the pyroprocessing of used metallic fuel, U-TRU-Zr alloy, and proposed various potential chemical reactions for recovering the iodine from a thermodynamic point of view. As a result, it can be confirmed that iodine forms metal iodides through the reaction of metal alloy used as a fuel, and the metal iodides are then converted into potassium iodide and metal chlorides by reacting with KCl contained in a LiCl-KCl eutectic salt. It was predicted, however, that the iodine can be ultimately converted into CsI through a reaction with Cs in the salt. Finally, it was proposed that iodine can be recovered from the molten salt through a reaction with Cl_2 *gas generated from graphite anodes used during pyroprocessing. In addition, this study described a waste salt minimisation technology in treating spent metal fuel for recycling substantial amounts of salt at the electrorefiner after the regeneration of waste salt.*

Introduction

Korea has 21 nuclear power plants in operation, and as of 2011, about 11 000 tonnes of spent nuclear fuel is stored at four reactor sites. Currently, spent nuclear fuel is being continuously accumulated, generating at a rate of about 700 tonnes a year. However, it has been reported that the storage pools will begin to be saturated from 2016, and therefore the Korean Government is attempting to resolve the issues for the long-term management of spent nuclear fuel. As a promising option, KAERI (Korea Atomic Energy Research Institute) is developing pyroprocessing technology connected with a sodium-cooled fast reactor to transmute long-lived nuclides as well as minimise high-level nuclear waste for disposal [1].

Among long-lived fission products in spent nuclear fuel, ^{129}I has a very long half life of 15.7 x 10^6 years and a low cross-section for transmutation. In addition, it influences the biosphere for a long time even after disposal in a deep-geological repository [2] [3]. Therefore, ^{129}I is the most dominant nuclide of public exposure after disposal owing to its high solubility in underground water. For this reason, ^{129}I has to first be removed from the final waste form to strengthen the safety of the environment. Accordingly, iodine needs to be separately recovered from spent nuclear fuel and to be treated to limit its effect on the biosphere.

Information on the chemical behaviour of iodine in irradiated metallic fuel based on U-TRU-Zr alloy is little known, compared to that of oxide fuel [4-7]. In particular, iodine chemical behaviour in a molten chloride salt bath during pyroprocessing has not been reported and there is no known method for the isolation and recovery of iodine liberated from molten salt, either. In this respect, this study investigated various potential chemical behaviours of iodine, not only in irradiated metallic fuel itself but also in the course of pyroprocessing in terms of a thermodynamic feasibility assessment, and suggested a method to recover the iodine from molten salt.

In addition, this study proposed a new molten salt treatment technique for the recycling of waste salt into a processing unit to minimise high-level waste amounts for final disposal [8] [9].

Chemical behaviour of radiogenic iodine in metal fuel elements

Chemical behaviour of radiogenic iodine in metal fuel matrix

A nuclear fuel irradiated with neutrons generates various fission products. These fission products can chemically combine with nuclear materials to form a stable compound or can be released into the gap between the fuel matrix and the cladding, depending on the fuel burn-up. To date, for oxide fuel, many studies have been performed regarding the chemical reactivity between fission products and uranium oxide fuel, and they proposed and verified various potential products [4] [5], whereas we have little data and only limited information on the chemical behaviour between fission products and metal fuel components in relation to the irradiation of metal fuel. Of the fission products, in particular, information on the chemical behaviour of radiogenic ^{129}I in irradiated metal fuel and its release into the gap were not confirmed and were very limited. Radiogenic ^{129}I is one of the critical elements that affect the biosphere for a long time. Accordingly, the study thermodynamically predicted the chemical behaviours of iodine arising from the irradiation of metal fuel, and its behaviour related to releasing towards the gap.

Table 1 shows the anticipated chemical reactions of iodine with both oxide and metal fuels. All possible chemical reactions were predicted using the HSC code [10]. First, the average burn-up temperature of each fuel during irradiation was assumed to be 1 000°C when comparing the two fuels. This condition was created under the assumption that the fuels were not melted. As seen in the table, iodine occurring as fission products does not react with all the metal oxides including UO_2 except for cesium: that is, iodine does not produce metal iodides in the oxide fuel. In other words, it is likely that iodine exists in CsI or element form. In contrast, it is predicted from the HSC code that iodine will react with metal alloy, U-TRU-Zr. According to the results of the HSC code, all metallic components such as alkali, alkaline earth, rare earth, actinides, and some transition elements including Zr, except for a few transition elements like Ru, definitely show reaction with iodine to form metal iodides.

Table 1: Chemical behaviour of radiogenic iodine in oxide and metal fuels

in oxide fuel		in metal fuel	
Reaction	⊿G (kCal/mole)	Reaction	⊿G (kCal/Equivant-I)
$UO_2 + 2I_2(g) = UI_4 + O_2(g)$	128	$2Cs + I_2(g) = 2CsI$	-72.84
$2PuO_2 + 3I_2(g) = 2PuI_4 + 2O_2(g)$	95	$Sr + I_2(g) = SrI_2$	-60.60
$2CeO_2 + 3I_2(g) = 2CeI_3 + 2O_2(g)$	88	$2La + 3I_2(g) = 2LaI_3$	-39.32
$2La_2O_3 + 6I_2(g) = 4LaI3 + 3O2(g)$	48	$2Am + 3I_2(g) = 2AmI_3$	-38.21
$2Cs + I_2(g) = 2CsI$	-72	$2Ce + 3I_2(g) = 2CeI_3$	-37.07
$4Cs + O_2(g) = 2Cs_2O$	-58	$2Pu + 3I_2(g) = 2PuI_3$	-33.68
$2Cs_2O + 2I_2(g) = 4CsI + O_2(g)$	-43	$2U + 3I_2(g) = 2UI_3$	-24.33
		$Zr + I_2(g) = ZrI_2$	-20.11
		$Mo + I_2(g) = MoI_2$	-1.11
		$2Ru + 3I_2(g) = 2RuI_3$	17.30

Based on this assumption, while oxide fuels will have a fission gas release of the iodine source such as element iodine or CsI into the gap of the fuel element, it is expected that metal fuels will have a high possibility of including all iodine sources in their matrix in iodine form. However, as the surfaces of the metal fuel slug contacts with the bond sodium, which is provided into the gap to enhance the thermal conductivity between the fuel and cladding wall, iodine produced on the surface of the metal fuel slug will flow into the bond sodium and ultimately convert into sodium iodide. Its quantity will depend on the burn-up, but it is predicted that most of the iodine will still remain in the metal fuel slug. As shown in the table, iodine shows a stronger reaction with cesium

than with any other elements. In turn, the reactivity of iodine is in the order of alkali, alkaline earth, rare earth, and actinides as shown in Table 1. However, as uranium, plutonium, and zirconium are the major components in the fuel alloy, and it is clearly predicted that UI_3, PuI_3, ZrI_2, etc. will also appear in the matrix, including CsI. In a previous study, Casteman *et al.* [7] observed that iodine released from uranium heated to 1 250°C in helium gas atmosphere was not in a chemical combination with either cesium or any other fission product, but rather iodine combines with uranium. This indicates that iodine can be chemically combined with a major component group such as U, Pu, or Zr.

Behaviour of radiogenic iodine in sodium bond

When the iodine is migrated from the metal fuel matrix into the bond sodium, the iodine reacts with the bond sodium to produce NaI, which does not cause a corrosion of the cladding material. If iodine in the form of CsI is released into the bond sodium, CsI does not react with Na and remains in the bond sodium because CsI is more stable than NaI. However, if Cs is directly released into the bond sodium, Cs will certainly be converted into CsI by a reaction with NaI in the bond sodium. Thus, it is predicted that CsI will have a high potential to exist in the bond sodium.

Chemical behaviour of radiogenic iodine in a salt during pyroprocessing

Treatment of spent metallic fuel using pyroprocessing

Figure 1 shows a pyroprocessing concept diagramme for treating spent metal fuel. The original concept was previously developed by Argonne National Laboratory, US [11], but KAERI has modified the existing flow concept to minimise the waste stream. Figure 1 shows a modified flow diagramme for handling the spent metal fuel. The irradiated metal fuel pins are chopped into small segments of less than about 6 cm. In the course of this process, high volatile fission products such as Xe, Kr, and ^3H will be released into an off-gas steam. The bond sodium attached to the surface of the metal fuel is then removed using a distillation technique to minimise the contamination of the molten salt by the incorporation of sodium.

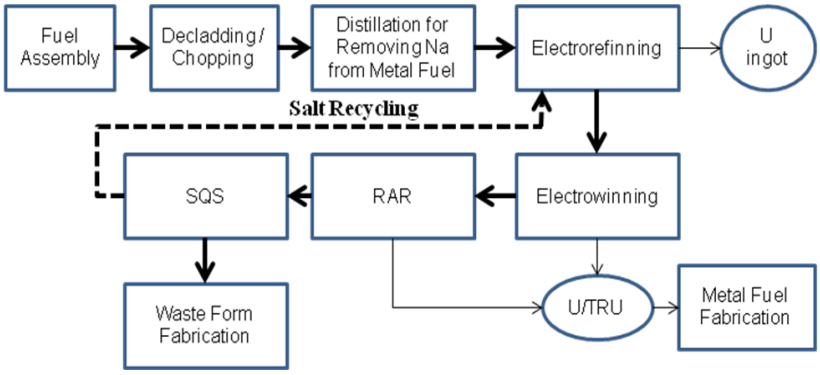
Following the removal of sodium residing on the surface of the metal fuel, the chopped pins are loaded into the anode basket of an elecrorefiner and submerged into the molten salt, where the metal fuel and some fission products are dissolved chemically or anodically. It has been reported that sodium is infused into the metal alloy during irradiation [12] because of the swelling of metal fuel. Thus, the infused sodium clearly enters into the molten salt during electrorefining.

In the electrorefiner, uranium is deposited on the solid cathode. All elements, except for noble metals are dissolved in the eutectic salt, LiCl-KCl. During this process, TRU are accumulated into the eutectic salt. When TRU contents reach to three of the ratio of Pu to U, TRU is recovered. Following this process, the salt is transferred to the electrowinner to recover enough TRU accumulated in the molten salt. The electrowinner consists of graphite as an anode and liquid Cd bath as a cathode [13]. While TRU is deposited on the cathode, Cl_2 gas is evolved on the anode. Electrowinning has a cell potential of 3 V, the potentials of the anode and cathode are +1.4V and -1.6 V, respectively. Normally, 70% TRU in the molten salt is deposited on the cathode and the remaining 30% TRU is recovered through a residual actinide recovery (RAR) system [14], which also consists of a system similar to an electrowinner, graphite as an anode and liquid Cd as a cathode .

Actually, the RAR process is composed of oxidative extraction and electrolysis systems, and these individual systems are all integrated. The role of this process is

similar to a draw-down technology used to recover residual actinides from the molten salt developed by the Idaho National Laboratory, US, but the two systems are completely different processes. On the other hand, iodine dissolved in the molten salt is removed by an elecrowinner and a RAR process. A detailed explanation is provided in the section below. After the RAR process, the salt has about 100 ppm TRU, most of the rare earths, alkali and alkaline earth elements. The salt is transferred during the purification process of waste salt to recycle the salt to the process unit, the electrorefiner. Further details on the purification process are described in the section below.

Figure 1: Flow diagramme of pyroprocessing for treating spent metal fuel



Chemical behaviour of iodides during electrorefining

Table 2 shows the chemical behaviour of radiogenic iodine compounds of the major components in the salt, LiCl-KCl, during electrorefining. In general, metals in the anode take part in the electrolysis reactions, but the metal iodides included in the irradiated metal fuel do not participate in electrolysis reactions since they are already oxidised. They are simply involved in a reaction with eutectic salt. Accordingly, it is expected that metal iodides will react with the eutectic salt.

The electrorefiner generally uses the salt composition of LiCl-KCl-(9-10 wt%)UCl_3 as the initial salt composition. As shown in Table 2, it was confirmed that UCl_3, a component of the salt, never reacts with metal iodides in a spent metal alloy. However, sodium infused in metal fuel can readily react with UCl_3 to produce U metal and NaCl at an anode. As shown in Table 2, the metal iodides react with both LiCl and KCl, and their reactions generate LiI and KI as byproducts, respectively.

However, the table shows that a reaction with KCl will be more dominant. Thus, it is predicted that the final product will be KI. Nevertheless, the thermodynamic results indicate that CsI will be most stable in eutectic salt, and ultimately even KI will be converted into CsI. Of the fission products it is known that Cs is 10-times higher than iodine in spent fuel. Thus, it is expected that CsI will occur in the salt, although the KCl content is huge.

$$CsCl + KI = CsI + KCl \ (\Delta G = -2.58 \text{ kCal/mole, at } 500^{\circ}C)$$

Recovery of iodine from the molten salt

A key to pyroprocessing is to recover or remove long-lived nuclides contained in a spent fuel and to significantly reduce hazards or radiotoxicity affecting the biosphere by transmuting them in a nuclear reactor such as a fast reactor or an accelerator-driven fast reactor.

For this, first, radiogenic iodine should be recovered from the molten salt. To date, the use of Cl_2 gas is predicted thermodynamically. According to the chemical reactions below, it can be seen that iodine compounds are easily converted into iodine elements by a reaction with chlorine gas, regardless of the chemical forms of iodine: KI or CsI. Therefore, the iodine gases released from the salt can be captured in a solid using a cold trap equipped at an off-gas line.

$$2KI + Cl_2(g) = 2KCl + I_2(g)$$

$$2CsI + Cl_2(g) = 2CsCl + I_2(g)$$

Table 2: Chemical reactions between metal iodides with the eutectic salt, LiCl-KCl

Reaction	⊿G (kCal/Equivant-I)
$UI_3 + 3LiCl = UCl_3 + 3LiI$	-0.532
$PuI_3 + 3LiCl = PuCl_3 + 3LiI$	0.919
$AmI_3 + 3LiCl = AmCl_3 + 3LiI$	3.298
$LaI_3 + 3LiCl = LaCl_3 + 3LiI$	-0.602
$NdI_3 + 3KCl = NdCl_3 + 3KI$	-0.411
$CeI_3 + 3LiCl = CeCl_3 + 3LiI$	-1.239
$ZrI_2 + 2LiCl = ZrCl_2 + 2LiI$	12.445
$LiI + KCl = LiCl + KI$	-5.608
$UI_3 + 3KCl = UCl_3 + 3KI$	-6.139
$PuI_3 + 3KCl = PuCl_3 + 3KI$	-4.679
$AmI_3 + 3KCl = AmCl_3 + 3KI$	-2.309
$LaI_3 + 3KCl = LaCl_3 + 3KI$	-6.019
$NdI_3 + 3KCl = NdCl_3 + 3KI$	-6.019
$CeI_3 + 3KCl = CeCl_3 + 3KI$	-6.846
$ZrI_2 + 2KCl = ZrCl_2 + 2KI$	6.837
$PdI_2 + 2KCl = PdCl_2 + 2KI$	15.153

Through this process, iodine in the molten salt can be completely recovered. On the other hand, chlorine gas which is used as a reactant of the reaction can be provided from the electrolysis results of anodes of both electrowinner and RAR processes. Both processes have graphite anodes to generate chlorine gases during the electrolysis as follows:

$$2PuCl_3 \text{ (in salt)} = 2Pu \text{ (on cathode)} + 3Cl_2 \text{ (on anode)}$$

Accordingly, we need to use chlorine gases as the reactant to remove iodine from the molten salt. This process, however, may produce a mixed halogen compound such as ICl [15] during the process. The occurring ICl can be preceded through two pathways. One is a result by a reaction of iodine with residual un-reacted chlorine in the cold trap chamber as follows:

$$I_2 (g) + Cl_2 (g) = 2ICl (g)$$

The iodine certainly makes iodine mono-chloride, which has a covalent bond, by reacting with chlorine gas. The iodine mono-chloride may be further converted into iodine tri-chloride, during the rich phase of chlorine gas.

The other method can be obtained through the electrolysis of an electrowinner or through RAR processes. These electrolysis processes have graphite anodes, as described previously. The following chemical reaction is thermodynamically anticipated at the anodes.

$$I^{-1}\text{(in salt)} + Cl^{-1}\text{(in salt)} = ICl (g) + 2e^-$$

In the case of the occurrence of mixed halogen compounds during pyroprocessing, such a compound needs to be dissociated to recover iodine only because iodine is a very long-lived nuclide and needs to be separately managed. In general, as ICl has a covalent bonding, the binding energy is relatively low. Thus, these chemicals are easily dissociated into each element even under UV radiation. Under a strong radiation field emitted from spent fuel, a mixed halogen compound is anticipated to be rapidly dissociated, but the dissociated elements may also be recombined in the forms of I_2 and Cl_2 to regenerate ICl. As an alternative, the physical properties of ICl and Cl_2 can be used such as the melting points. The melting point of ICl ranges from 10 to 30^{0}C, while chlorine has -101°C. Thus, using a cold trap, we can partition ICl solid from a chlorine gas stream.

The obtained ICl is converted into AgI and AgCl through the reaction with silver metal, which is a capturing substrate of iodine and chlorine. Both silver salts have a very low solubility in water, but AgI (*k*sp= 8.3×10^{-17} M^2) shows a far lower solubility than AgCl (*k*sp= 1.77×10^{-10} M^2) in water [16]. From the solubility data of both chemical compounds it is predicted that AgI can be separated from AgCl. Through the above processes or methods, it should be noted that iodine can be fully recovered from spent metallic fuel.

A change of chemical composition in the salt and salt treatment

As mentioned earlier, a part of the bond sodium is infused into the metal fuel matrix during irradiation due to the matrix swelling. The infused sodium is not removed from the metal fuel by a simple method such as distillation, which can simply evaporate residual Na attached to the metal fuel. Thus, the infused sodium is transferred to the anode of the electrorefiner together with the metal fuel.

During anodic dissolution, sodium is converted into NaCl and subsequently sodium salt is continuously accumulated in the salt. Ultimately, it was predicted that the binary salt phase, LiCl-KCl, will change into a ternary salt phase such as LiCl-KCl-NaCl. The change in the composition of the salt will result in changes in the physical properties of the salt such as the melting point, viscosity, and density. According to Lin's ternary phase diagramme of LiCl-KCl-NaCl [17], it should be noted that NaCl can be incorporated into

LiCl-KCl salt at up to higher than 20 wt% on the basis of a mass for keeping a liquid state at a temperature range between 500 and 600°C. This is the normal operating temperature range in electrorefining. Thus, it should be noted that sodium incorporation does not seriously affect the increase of temperature of the salt during pyroprocessing.

In addition to sodium accumulation in the salt, Cs, Sr and rare earth elements as fission products are accumulated in the salt as the pyroprocessing proceeds. To repeatedly reuse the salt, the contaminated salt should be refreshed or purified.

KAERI has developed a novel technology to significantly reduce the waste salt to be disposed of and to be recycled in a process unit, an electrorefiner. This technology is called the Sequential Separation (SQS) Process. The SQS process consists of oxide precipitation and zone freezing technologies [18]. The rare earth and residual actinides remaining in the salt are nearly precipitated at the bottom of reactor vessel through oxygen purging. After the oxide precipitation, heat emitting elements such as Cs and Sr still remain in the salt. To recycle the salt in an electrorefiner, heat emitting elements have to be removed from the salt.

For this reason, a zone freezing technology was adopted for the removal of Cs and Sr from the salt for recycling. The SQS process is an integrated technology in which oxide precipitation and zone freezing techniques occur consecutively.

Conclusions

This study presents the chemical behaviour of iodine during the entire process, including irradiated metal fuel. In conclusion, it was confirmed from the thermodynamic assessment that iodine exists in iodide form in irradiated metal fuel and can be separately recovered from the salt during pyroprocessing. In particular, chlorine gas was required for iodine recovery from the salt and a sufficient amount of chlorine gas can be supplied from the anodes of the electrowinner.

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