

## Review on behaviors of major fission product species for source term estimation

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### 1. Introduction

According to IRSN severe accident definition, it refers to an event causing a significant damage to reactor fuel and resulting in core meltdown. During severe accident, it is likely to release radioactive fission products to the environment. The type and amount of radioactive materials released is defined in source term. It is necessary to evaluate radiological consequences from severe accident. In this paper, review on literature regarding behaviors of major fission product species: iodine, cesium, and ruthenium was done.

In reference source term, which is based on reference accident scenarios and current knowledge of fission product behaviors, release fraction of fission product was suggested. Several reference source terms and their assumptions are shown below.

**TID-14844 source term:** In order to assess the feasibility of reactor site regarding offsite doses limit (10 CFR Part 100), US AEC published TID-14844 in 1962[1]. They assumed significant core melt and suggested the corresponding fission product release. The main assumptions are: Immediate release into containment of 100% of noble gas, 50% of halogen, and 1% of solid fission product regarding fuel inventory. Especially for iodine, half of the released fraction would be absorbed in the containment surface. AEC Regulatory Guide 1.4 in 1974 additionally specified the speciation of iodine: In containment air, there are 91% of elemental iodine, 5% of particulate form, and 4% of organic iodides.

**NUREG-1465 source term:** Based on enhancement of knowledge after TMI-2 accident and related research, US NRC in 1995 issued NUREG-1465[2] for replacing TID-14844. The report suggested fission product release into containment consists of 4 phases and 8 nuclide groups. Table I shows major fission product release fraction in PWR. For chemical form of iodine released, they applied NUREG/CR-5732 result, 95% of cesium iodide and 5% of I plus HI, with not less than 1% of each I and HI. For organic iodide, from WASH-1233 and NUREG/CR-4327, 3% of I is converted into organic iodide.

Table I: NUREG-1465, PWR major fission product release fraction

	Gap release	Early in-vessel	Ex-vessel	Late in-vessel
Duration (hours)	0.5	1.3	2.0	10.0
Halogens (I)	0.05	0.35	0.25	0.1
Alkali metals (Cs)	0.05	0.25	0.35	0.1
Noble metals (Ru)		0.0025	0.0025	

**French reference source term:** In 1979, IRSN suggested 3 types of environmental release based on WASH-1400 report. The three source terms S1, S2, and S3 are commonly based on loss of coolant plus blockage of power supply which lead to fuel melt. This result was used to evaluate the environmental impact of release. Table II shows fission product release to atmosphere. S1 corresponds to early (within a few hours) containment failure. S2 corresponds to direct release to the atmosphere within 24 hours after accident initiation. S3 corresponds to indirect, delayed release to the atmosphere after 24 hours.

Table II: French reference source term, percentage of radioactive material release to atmosphere

Elements	Represent. isotope	S1(%)	S2(%)	S3(%)
Mineral iodine	I-131	60	2.7	0.3
Organic iodine	I-131	0.7	0.55	0.55
Cesium	Cs-137	40	5.5	0.35
Ruthenium	Ru-106	2	0.5	0.03

### 2. Review on iodine behavior

Literature survey of iodine behavior regarding source term was conducted. Iodine production yield is relatively high compared with other fission products. In addition, due to its short half-life, iodine has a large contribution in activity within several hours after reactor shutdown. During early stage of the accident, accurate prediction of iodine behavior is necessary for emergency response and dose calculation.

#### 2.1 Iodine release and transport through primary circuit

Early experiments regarding iodine release from fuel(SASCHA, HI, HEVA) were conducted at the temperature not exceeding 1800°C, melting temperature of zirconium alloy. Around 1990s, experiments around fuel melting point (VI, VERCORS, VEGA) showed that most iodine was released from the fuel. About modeling of the iodine release, two models: correlation model of ASTEC/ELSA module and mechanistic model of MFPR well predict the release of iodine at high temperature [3].

During accident progression, control rod and burnable poison materials which affect iodine behavior would also release from the core, because control rod material has lower melting point than 2600°C, a melting point of UO<sub>2</sub>. In Phebus-FP test of FPT0 and FPT1, it was found that silver-indium-cadmium control rod material was

released into modelling containment, which shows the importance of the control rod degradation modeling.

In Phebus-FP test of FPT2, re-vaporization of iodine deposit in the primary circuit was observed in the oxidation condition after steam starvation phase. This could have significance during late release [4].

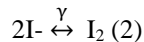
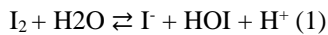
## 2.2 Iodine behavior in containment liquid

In containment, there is a pool such as sump and IRWST. In the pool, except silver iodide, most of the metal-iodides are soluble in water thus iodide ion would form. Other radioactive fission products in the pool contribute to dose rate which cause water radiolysis products  $\cdot\text{OH}$ ,  $\cdot\text{O}_2^-$ ,  $\text{H}_2\text{O}_2$ ,  $e^-(\text{aq})$  etc. Reaction between water radiolysis products and nonvolatile iodine such as  $\text{I}^-$  produce  $\text{I}_2$  which is volatile. The production is consisted of tens of reaction and depends on temperature, pH, and dose rate. The formation mechanisms except high temperature condition seem to be understood during 1980s. In order to simulate iodine chemistry in liquid phase, two complementary approaches were used. Mechanistic codes (LIRIC, INSPECT) describe large number of chemical reactions. On the other hand, semi-empirical codes (IODE, IMOD, IMPAIR) have major iodide species and limited number of reactions. Integral severe accident code (ASTEC) has taken latter approach. Existing model of iodide need to be continuously investigated and expanded with the help of new experiment such as EPICUR [3].

Effect of pH dominates volatile iodine production in liquid. In NUREG/CR-5950(1992), in-containment materials which change pool pH were shown: boron oxides, basic fission product compounds, Iodine as HI, pH additives, atmospheric species, core-concrete aerosols, and HCl from cable material [5]. Solution with more than pH 7 produces little  $\text{I}_2$ . The lower the pH, the more volatile  $\text{I}_2$  would be produced. Most iodine would convert to  $\text{I}_2$  if pH is less than 3.

In ISP-41, several iodine behavior codes and RTF experiments showed that there is a significant difference in codes about prediction of  $\text{I}_2$  production rate. The codes gives higher iodine release in low pH condition and lower iodine release in high pH condition [3].

After production,  $\text{I}_2$  removal exist and it determines the  $\text{I}_2$  production limit. Reactions are shown below.



Also, hydrogen peroxide from water radiolysis react with  $\text{I}_2$  to form  $\text{I}^-$ .

Silver has high affinity for iodine. Silver can react with iodine to form deposited silver iodide which results in less amount of volatile iodine formation during severe accident. The model has been developed to describe absorption of  $\text{I}^-$  and  $\text{I}_2$  at silver surface. It is shown that presence of silver is effective during low pH and high Ag/I ratio condition.

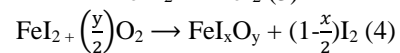
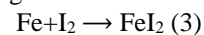
It is expected that impurities concentration is similar to iodine's. So impurity becomes significant during

volatile iodine formation in liquid. Impurities such as dissolved oxygen, air radiolysis products ( $\text{NO}_3^-/\text{NO}_2^-$ ), and small amount of steel ion ( $\text{Fe}_2^+/\text{Fe}_3^+$ ) from steel surface, and organic impurities (RH) can affect water radiolysis. Important reactions with impurities are: reaction with  $e^-(\text{aq})$  catalysis reaction of metal ion, pH reduction due to nitric acid, production of hydrochloric acid due to insulation cable, and production of organic iodide due to organic impurities. There are around 40 to 50 fundamental water radiolysis reactions with its data from 0 to 150°C are accumulated. However, modeling with integrated containment behavior is still insufficient. In addition, data regarding impact of impurities on concentration of water radiolysis product are also insufficient.

## 2.3 Iodine behavior in containment atmosphere

Form experiment during 1960s, it has known that containment surface is effect iodine sink and adsorption depends on various parameters. Adsorption of  $\text{I}_2$  would increase when there is a high humidity and a low temperature. Iodine interactions on surface: adsorption, resuspension and re-vaporization were investigated.

In 1990s, iodine adsorption/desorption behavior on stainless steel was established. The behavior is first-order behavior, but it is still complex process [6]. To understand the process, for example, two-step process was suggested from the result that adsorption/desorption rate is function of oxygen concentration as well as surface shape changes due to corrosion [7].



The problem with the adsorption study is, only overall first-order reaction rate was determined from observed results. This simplification is complex to interpret, and cause uncertainties when extrapolating the data. Recent version of the MELCOR (version 2.1.6840 2015) uses a chemisorption coefficient for given chemical species ( $\text{CsOH}$ ,  $\text{CsI}$ ,  $\text{HI}$ ,  $\text{I}_2$ ,  $\text{Te}$ ) on stainless or Inconel surface.

$\text{I}_2$  in humid air with high dose rate react with air radiolysis products to produce nonvolatile iodine oxide. From experiment, this reaction is rapid and iodine oxide concentration determines the reaction rate. However, the experiment was conducted with high  $\text{I}_2$  concentration so surface effect with air radiolysis product depletion was neglected. There exist an experiment considering surface/volume and computed the reaction rate of air radiolysis product. PARIS project expanded the database of air radiolysis product in severe accident condition and mechanistic code IODAIR-IRSN explains the results well [8].

## 2.4 Organic iodide

Properties of organic iodide are different with  $\text{I}_2$ . Some organic iodides do not readily adsorb on surface or dissolve in water thus it's not easy to remove it by

Engineering Safety Features. There are two formation mechanisms of organic iodide, homogeneous and inhomogeneous formation.

Homogeneous formation in water is from reaction between  $I_2$  and organic functional group ( $\cdot R$ ) formed by radiolysis of organic impurities from paints dissolved in water. The  $\cdot R$  either react with  $I_2$  to form organic iodide or react with dissolved oxygen to form  $CO_2$  which lower the pool pH.  $\cdot R-I_2$  as well as  $RI-e^-(aq)$  reaction rates are well established. Formation of final product ( $RI$ ,  $CO_2$ ) are determined by the ratio between  $\cdot R$  and reactants ( $O_2$ ,  $I_2$ ). This is because the rate of organic impurity leakage from paint is much lower than that of organic compound radiolysis.

Inhomogeneous formation is possible due to  $I_2$  evolution from acidic sump or the deposition of iodine-bearing aerosols onto surfaces. From recent analysis of Phebus test of FPT0 and FPT1, organic iodide can be dominant species among volatile iodine under condition where iodine uptake on surface is favored [9]. However, at higher pool pH, the rate of organic iodide would be higher at solution and surface reaction is likely to be low. Inhomogeneous formation depends on dose rate on surface rather than temperature change. From experiment results, "Funke model" the empirical expression was suggested, which describes the rate of radiation-induced organic iodide production [10].

For homogeneous formation, methyl iodide was considered main organic iodide species. However, comparison between aqueous and gaseous species shows that most of the organic iodides in water are low-volatile species. Organic compounds such as ketone, alcohol, and phenol can react with  $I_2$  and produce low-volatile and water soluble substances [11]. In order to determine the gaseous concentration of organic iodide, behavior of other organic iodides is also needed. Recent version of MELCOR models only methyl iodide formation regarding organic iodide.

### 3. Review on cesium behavior

Cesium is semi-volatile fission products with high fission yield and chemical reactivity. For given condition of oxidizing (steam, air) or reducing (hydrogen), cesium changes its chemical form. Cesium release in fuel during severe accident shows similar behavior as krypton and iodine [12]. It has known that cesium released from overheated fuel has element or ion form. This is because of two reasons. First, fuel grain, where diffusion of element of ion occur, release cesium. Second, molecules containing cesium such as  $CsI$  and  $CsOH$  are dissociated around 1800~2200°C. In colder condition, they can form  $CsI$  and  $CsOH$  [12].

#### 3.1 Cs-H-I-O system

NUREG-0772 showed the chemical form of cesium in the water. For Cs-H-O system in equilibrium, cesium mainly forms  $CsOH$  in oxidizing and inert condition

( $1.5 < H/O$  ratio  $< 2.0$ ). In reducing condition,  $CsOH$  is also main compound at low temperature. When the temperature is higher than 1000°C, Cs vapor fraction is increasing. If iodine is added to the system,  $CsI$  is rapidly produced because of the chemical reaction below.



Since cesium production yield is much higher than iodine yield,  $CsI$  can form without gaseous iodine. Formation of chemical compounds in Cs-H-I-O system in equilibrium was also suggested. But real system is much complicated than the model. The modeling of chemical reaction and calculation of reaction rate in Cs-H-I-O system is in progress [13].

#### 3.2 Cs-H-I-O-Mo-B system

If boron is added, formation of  $CsI$  is reduced in oxidizing condition. Instead,  $CsBO_2$  production was observed in WIND experiment in JAERI [14].

If molybdenum, which has high affinity for cesium, is added to the system, cesium product is being completely different. In oxidizing condition, almost all cesium form cesium polymolybdates and do not form  $CsI$ . In reducing condition,  $CsI$  is main chemical species [15]. In Cs-H-I-O-Mo-B system, most cesium released from the fuel rapidly convert into cesium borates and then into cesium molybdates if there is enough molybdenum [16].

The goal of considering Cs-H-I-O-Mo-B system is to get gaseous iodine production fraction. First model of gas phase chemistry concentrated on Cs-H-I-O system and it is included in ASTEC V2.0. Expansion of the model was based on *Gregoire, 2012* [17]. Molybdenum and boron are added in ASTEC V2.1. Additional modeling with control rod material is being developed by ongoing CHIP+ program [18].

#### 3.3 Re-vaporization of cesium

Re-vaporization and resuspension of deposited fission product in primary circuit is considered important source term during late phase of severe accident. In *Bottomley, 2014* [19], the phenomenon of cesium was investigated. From the analysis of the Phebus-FP test of FPT1 and FPT4, any changes regarding temperature, flow rate, and atmospheric pressure can contribute to vaporization or removal of deposited cesium during late phase. Furthermore, re-vaporization in Phebus-FP test of FPT3 [20] showed not only cesium but also every other fission product can undergo re-vaporization in various condition.

IRSN has conducted modeling of re-vaporization of cesium and iodine on surface by using 'ab initio' theoretical approaches. Reaction rate of deposited fission product on selected metal surface was modelled and it matches with re-vaporization of cesium and iodine on stainless steel 304L surface. Extension of the result on Inconel surface is suggested and the goal is to develop a model for ASTEC calculation [19].

### 4. Review on ruthenium behavior

Radioactive ruthenium has half-life of 369 days ( $^{106}\text{Ru}$ ) and 39.3 days ( $^{103}\text{Ru}$ ) as well as chemical toxicity. Ruthenium is a suspected carcinogen and its compounds can strongly stain the skin. Especially, ruthenium tetroxide ( $\text{RuO}_4$ ) is highly toxic and volatile.

#### 4.1 Formation of ruthenium oxides

In containment, ruthenium has form of  $\text{RuO}_2(\text{s})$ ,  $\text{RuO}_4(\text{g})$ ,  $\text{RuO}_4^-(\text{aq})$ , and  $\text{RuO}_4^{2-}(\text{aq})$ .  $\text{RuO}_2$  aerosol can deposit on primary circuit, containment pool and surface.  $\text{RuO}_4^-(\text{aq})$  and  $\text{RuO}_4^{2-}$  presents in containment pool. They are potential source of re-vaporization and production of gaseous  $\text{RuO}_4$ .

Oxidation of  $\text{RuO}_2$ , ruthenate or perruthenate can form gaseous  $\text{RuO}_4$  [21]. IRSN studied gaseous  $\text{RuO}_4$  formation from deposited  $\text{RuO}_2$  on pipe with varying temperature, oxygen concentration and humidity. In EPICUR gamma irradiation facility, gaseous  $\text{RuO}_4$  formation with radiation exposure on aqueous solution and ruthenium adsorbed painted surface was done [22].

### 5. Conclusions

This paper described major fission product behaviors: iodine release through primary circuit, iodine behavior in containment liquid and atmosphere, organic iodide formation, and re-vaporization of fission products. These behaviors can significantly contribute to environmental source term. From the review, important things that need more effort for accurate estimation of source term are:

- Role of control rod materials in Cs-H-I-O-Mo-B system
- Re-vaporization of iodine, cesium, and ruthenium species on various surface materials
- Detailed code for gaseous iodine production at given pH and impurities in pool
- Organic iodide production on surface and its behavior
- Integrated experiment of fission product behavior and comparison of results with existing severe accident code

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