

## Comparison of iodine behavior in a containment's sump water and in a FCVS's pool

Sojin Shim<sup>a\*</sup>, Sanggil Park<sup>b</sup>, Jaeyoung Lee<sup>a</sup>

<sup>a</sup>Handong Global Univ., Handong-ro 558, Buk-gu, 37554 Pohang, Korea

<sup>b</sup>ACT Co., Ltd., IT Venture Town 406, Techno-9-ro 35, Yuseong-gu, 34027 Daejeon, Korea

\*Corresponding author: sojin.shim@epfl.ch

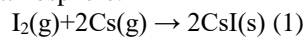
### 1. Introduction

Iodine is one of major source terms that would be released into the environment from containment under a very extreme accident conditions. This source term could severely affect the environment with a severe radioactive potentially, which has a high radioactivity and a high volatility in a high temperature. Difficultly caught and considered to give sustained damage on thyroid, the iodine source term is protected from releasing to the environment. Especially in the over-high temperature and pressure out of the limit of containment design during a severe accident, the research and experiments to improve the retention efficiency of iodine species in a containment and a FCVS (Filtered Containment Venting System) which vents containment atmosphere in order to stabilize the temperature and the pressure have been conducted.

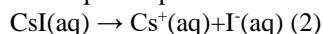
Iodine is produced in and released from fuel rod and converted to other species in a sump water bottom of the containment, which pass thorough a pool in a FCVS during venting. The sump water and the pool have dissimilar chemical and thermal conditions and cause different volatile and retentional mechanism of iodine. In this paper, studies of phase and species conversion of iodine have been reviewed in order to fine the efficient retention conditions in a containment and a FCVS.

### 2. Iodine retention in a containment's sump water

The majority of released iodine as the form of molecular iodine combines with cesium, produces cesium iodide aerosol and then is released to containment while a few proportion is emitted to containment atmosphere.



Cesium iodine is retained to a sump water via mechanical mechanisms such as gravitational sedimentation and inertial retention. This species is highly soluble so readily retained in the sump water with producing I<sup>-</sup> in the aqueous phase.



High pH with phosphoric acid that is from RCS leads to produce the species that comes from the fuel and structural materials, which promotes radiolysis and thermal oxidation of cesium iodide and increases solubility and retention of the aerosol.

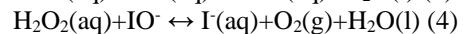
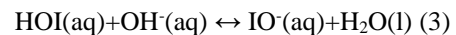
Most metal iodides are soluble and readily reduced into an I<sup>-</sup> in the sump water. However, because of the nuclides, this retained iodine is radiolytically and

thermally oxidated and emitted to containment's atmosphere with forming volatile molecular iodine. This molecular iodine emission rate from sump water can be represented as fractional rate, the proportion of oxidized I<sup>-</sup>, which consider both the oxidation of the ions and the reduction of iodine molecules. The fractional rate of oxidation varies on thermal-radiolytic environments and chemical conditions, dependent primarily on the pH and less on the I<sup>-</sup> concentration and the temperature of sump water.

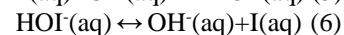
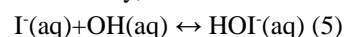
#### 2.1 Effect of pH on iodine's radiolytic oxidation

pH significantly affects the behavior of iodine in aqueous phase in a containment. [1, 7] Firstly, the rate of cesium iodine's radiolytic oxidation considerably decreases in a high pH, which emits molecular iodine. The volatile molecular iodine is converted from I<sup>-</sup> through radiolytic oxidation, the iodine oxidation reaction with the water radiolytic products, radicals (hydroxyl radical(OH), hydrogen radical(H) and electron(e<sub>aq</sub><sup>-</sup>)) and molecule (superoxide(H<sub>2</sub>O<sub>2</sub>) and molecular hydrogen(H<sub>2</sub>)) induced by the radiation from fission product in the sump water.

The oxidation's reaction rate and the reacting and produced species changes heavily depending on pH change. In a high pH, iodine reductant reaction is dominant and hydrogen peroxide and molecular iodine converts into I<sup>-</sup> through radiolytic oxidation. Cesium iodine's radiolytic oxidation is related to hydroxyl radical, hydroperoxy radical and oxide ion, and also the reaction is induced by hydrogen peroxide reacting as an oxidant. In the alkaline aqueous phase, molecular radiolysis productions, hydrogen peroxide and iodine, are considerably dependent on pH whose reaction is considered as the one between hydrogen peroxide and hypoiodite ion.



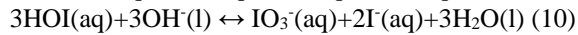
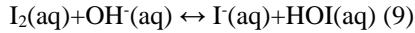
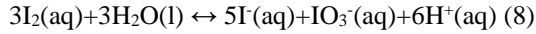
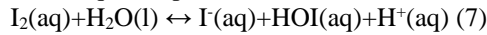
I<sup>-</sup> oxidation can produce iodine radical, which is expected to have a higher solubility than the atom having similar solubility, xenon.



In the range of pH 4 to 9, iodine volatility according to I<sup>-</sup> radiolytic oxidation decreases as pH rise. [7] There are still uncertainties for the optimal pH, but iodine volatility and emission decreases as pH increase. High pH decreases fraction of radiolytic oxidation and

promotes to produce iodate that is a thermally stable form, so radiolytic oxidation is dependent to pH.

Secondly, hydrolysis of molecular iodine is induced to produce hypoiodous acid that is the less volatile species. Iodine is soluble in water even though it still has less solubility than other halogen elements, and when it is dissolved in aqueous phase, it reacts.



The reaction occurs bilaterally according to the pH. In accordance with the equilibrium calculation, non-volatile iodine species such as  $\text{I}^-$  and iodate are dominant among the all oxidation-reductant potential with high pH, but molecular iodine and hypoiodous acid are dominant in an acidic and oxidizing conditions. That is, the fixed quantity of volatile iodine species formed in chemical reactions until reach the thermal equilibrium (Preliminary kinetic release model) is dependent on pH.

In severe accident, molecular iodine release rate is decreased by reducing the fraction of iodine transferred with high pH. In the meantime, not only starting with alkaline aqueous phase, but it is also critical to maintain the sump water's durational pH higher than the titrated pH. After the initial accident, the species that decreases sump water's pH inflows into the sump water continuously. Three species dominantly acidize the sump water with dissolved in aqueous phase: (1) carbon dioxide that makes up the containment atmosphere with the great proportion; (2) nitric acid formed by humid atmosphere's oxidation; (3) carboxylic acid formed by organic materials' radiolysis. The pH buffer solutions are available to compensate these continuously released acidic species.

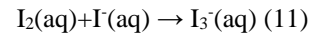
## 2.2 Effect of temperature on iodine's hydrolysis

When significant radiation released into water with amounts of the fission products in a severe accident, the release brings containment's inner temperature to rise. The iodine volatility shows the dependence on temperature especially at the initial accident, even though the pH dependence is dominant. In chemical reactions between iodine's ion species,  $\text{I}^-$  and  $\text{OI}^-$ , molecular species,  $\text{I}_2$ , and water, iodine volatility decreases as the temperature increases according to the transition of the thermal equilibrium. In a high temperature, activating the reaction of iodine hydrolysis that converts molecular iodine to non-volatile species, the iodine volatility significantly decreases. In an aqueous phase without chemical additives,  $\text{I}^-$ 's oxidation showed clear decrease in several experiments. Nevertheless, it is required to assess the dependence of hydrolysis equilibrium reaction constant in a high temperature refer to the numerous experimental data, and then the concern of thermal equilibrium constant change could be applied to the iodine behavior models.

## 2.3 Effect of concentration of iodine ion on iodine's radiolytic oxidation

The effect of  $\text{I}^-$  concentration on fractional oxidation is considered independent. In the concentration of  $\text{I}^-$ , some expects the oxidation rate will rise, but the increase of the reaction rate is compensated with the risen reaction rate between water radiolysis product.

Furthermore, molecular iodine converted from  $\text{I}^-$  species is more soluble into the  $\text{I}^-$  solution.



Even though the reaction violates the Octant rule, it follows Lewis theory of acid-base reaction, molecular iodine, a Lewis acid, and  $\text{I}^-$ , a Lewis base, react and produce triiodide ion, a Lewis adduct. This reaction has faster reaction rate than the reductive reaction of molecular iodine with water.

## 2.4. Organic material's radiolysis and organic iodide's conversion in a sump water

Organic materials affect iodine volatility with radiolysis into carboxylic acid and carbon dioxide that decrease the sump water's pH. The aqueous pH affects significantly steady-state concentration of molecular iodine in aqueous phase, the iodine volatility has a dependence on consequently radiolysis of organic materials.

The radiolysis of organic materials reacts with molecular iodine in an aqueous phase and induces the production of a volatile and non-volatile organic iodides. These organic iodides anticipate the decrease of pH and high volatile iodine concentration and that is, the organic iodides are given a secondary effect dependent on pH. [10]

## 3. Iodine retention in a pool in a FCVS

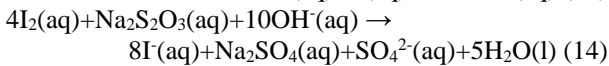
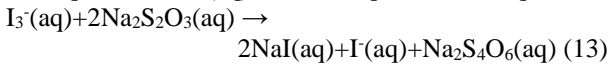
The component ratio of iodine in the atmosphere emitted from containment to FCVS is known as 95% of aerosol and 5% of molecular iodine and organic iodide in the documents of WASH-1233, NUREG/CR-4327, NUREG/CR-5950. Although only 5% of gaseous iodine compose the total emission of iodine, many researches have conducted about it because it is particular to retain the released iodine gas in FCVS. Especially for organic iodide, there are still uncertainties about attaining high decontamination factor(DF) in an accident condition, which is a big scale with radiation.

### 3.1 Effect of chemical additives on gaseous iodine retention

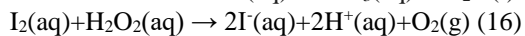
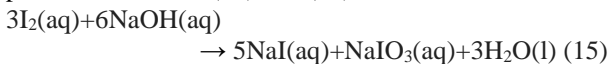
In order to increase the DF, chemical additives are inevitably added into FCVS's pool. Gaseous iodine from the containment is retained during passing the pool

through the inlet. During the contaminated species inflow in the initial stage of a severe accident, the chemical reactions occur in a dynamic state, not in a static, so DF depends on iodine reduction reactions' rate constants.

Molecular iodine's reduction into I<sup>-</sup> has comparably small rate constant, that is, reaction is slow, retention with hydrolysis is not sufficiently efficient to the retain contained species that remain in the pool only for a short resident time. It is possible to acquire the higher DF by inducing another chemical reaction with chemical additives that is faster and efficient for volatile iodine retention. Sodium thiosulfate, sodium hydroxide and hydrogen peroxide are used as the additives for the iodine retention. [4]

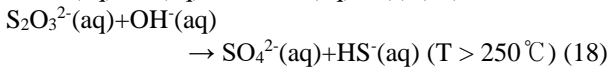
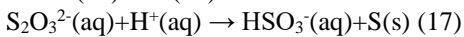


As seen in (14), thiosulfate's iodine retention is favorable in alkaline aqueous phase. Reaction of molecular iodine with sodium hydroxide and hydrogen peroxide occurs as (15) and (16).



### 3.2 Effect of pH on iodine retention with thiosulfate

In order to reliably remain retained iodine in the pool and simultaneously retain the iodine gas continuously inflowing into the pool, added thiosulfate is required to sustain without significant decomposition. Adequate pH is required to maintain the additive's efficient in retention which decomposes with hydron and hydroxide ion as (17) and (18).

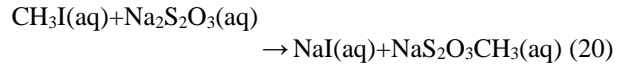
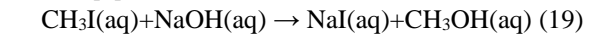


The thiosulfate decomposition is the endothermic reaction that occurs over 250 Celsius degrees. Considering the designed operation temperature of pool, much lower than the boundary temperature, even though decay heat from the containment is introduced into the pool, the heat absorption is not enough for thiosulfate to react with hydroxide. That is, the thiosulfate ion's maintenance depends on hydrogen ion's oxidation. It is consequently required to remain the pool alkaline in order to maintain the efficiency of retention of thiosulfate.

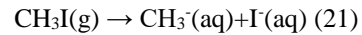
Contaminated species from containment and added chemicals into FCVS incur radiolytic or oxidative decomposition and oxidize the pool. Chemical pH buffers are able to compensate the drop in pH occurred by acidic materials continuously inflowing in the pool.

### 3.3 Chemical additives and a catalysis for organic iodine retention in a pool

Sodium hydroxide and sodium thiosulfate that are applied to retain molecular iodine do so for organic iodide. [3]



I<sup>-</sup> in organic iodide reacts with thiosulfate and is retained only when the organic iodide phase is transferred to aqueous from gaseous. The transformation, however, rarely occurs, so the retention is not efficient enough even with the additives. The phase transfer catalyst, Aliquat 336, promotes the transformation from gaseous to aqueous phase, helps the organic iodide be reduced into I<sup>-</sup>, which is retained by the chemical additives, and increase the organic iodide's DF. [12]



The pool solution's DF of organic iodide increases as the concentration of Aliquat 336 increases, and the DF becomes independent on other chemical additives and temperature after adding certain level of catalyst.

Nevertheless, some drawbacks and shortcomings exist in Aliquat 336. It has high retention efficiency in all variation of pH and I<sup>-</sup> concentration but not in a high temperature. [3, 5] It is known that Aliquat 336's contribution to iodine retention is valid under 110 Celsius degrees and the phase-transfer catalytic action does not work over 130 Celsius degrees. Aliquat, furthermore, consists of organic species, has a low ignition point, and radiolytically degrades in a radiation field, which reacts with I<sup>-</sup> to form organic iodide. The accurate research and calculation for the amounts of the decay heat and the steam from the containment and so the variation of the temperature of the pool in a FCVS in a severe accident are needed in order to verify the effectiveness and availability of Aliquant 336 applying to the pool scrubbing system.

## 4. Conclusions

In a sump water, high pH decreases the iodine's volatility and the nuclide's emission into the atmosphere. In a high temperature, the iodine volatility significantly decreases, but still it is required to assess the dependence of hydrolysis equilibrium reaction constant on the temperature. Molecular iodine that converted from an iodine ion species is reduced more easily when it is in the I<sup>-</sup> solution, so the reaction has the higher rate constant. Organic materials affect iodine volatility by the radiolysis into carboxylic acid and carbon dioxide that decrease the sump water's pH. It is considerable to use buffer solutions into the sump water to remain the pH high, but there is an uncertainty about the pH of the sump water which decide the utility of alkaline buffer.

In the retention in a FCVS's pool, chemical additives, such as sodium thiosulfate, sodium hydroxide and hydrogen peroxide, acquire the higher molecular iodide DF by inducing another chemical reaction with chemical additives that is faster and efficient. The additives' sustenance depends on the pool alkalinity. Aliquant 336 is available as phase transfer catalyst that helps organic iodide degrade and rise the DF. However, the reliable research for the variation of the temperature of the pool in a FCVS in a severe accident will help to verify the effectiveness and availability of Aliquant 336 applying to the pool scrubbing system.

### **Acknowledgement**

This work was supported by the Nuclear Safety Research Program through the Korea Foundation of Nuclear Safety (KOFONS), granted financial resource from the Nuclear Safety and Security Commission(NSSC), Republic of Korea (No. 1305008-0416-SB130)

### **REFERENCES**

- [1] B. Clement, L. Cantrel, G. Ducros, F. Funke, L. Herranz, A. Rydl, G. Weber and C. Wren, State of the art report on iodine chemistry, OECD/NEA/CSNI/R(2007)1, 23 Feb 2007
- [2] V. Peyres, R. Pampin, M.A. Montero and L.E. Herranz, Experimental study on pool scrubbing in contaminated pools, 2000
- [3] S. Buhlmann, C. Hutterer and N. Losch, High speed sliding pressure venting plus (AREVA's FCVS with enhanced organic iodine retention) design principles and qualification of severe accident equipment, September 2013
- [4] Status Report on Filtered Containment Venting, Committee on the Safety of Nuclear Installations, Nuclear Safety NEA/CSNI/R(2014), 7 July 2014
- [5] P. Zeh, A. Satahl, F. Funke and S. Buhlmann, Impact of Aliquant R336 Addition on Organic Iodide Retention in Containment Venting Scrubbing Solutions for Mitigation of Severe Accidents, Annual Meeting of Spanish Nuclear Society, p.2380, 28-30 September 2011
- [6] B. Pastina, J. Isabey, and B. Hickel, The Influence of Water Chemistry on the Radiolysis of the Primary Coolant Water in Pressurized Water Reactors, Journal of Nuclear Materials, Vol.264, 1999
- [7] C. B. Ashmore, J. R. Gwyther and H. E. Sims, Some Effects of pH on Inorganic Iodine Volatility in Containment, Nuclear Engineering and Design, Vol.166, p.347, 1996
- [8] S. Dickinson, F. Andreo, T. Karkela, J. Ball, L. Bosland, L. Cantrel, F. Funke, N. Girault, J. Holm, S. Guilbert, L. E. Herranz, C. Housiadas, G. Ducros, C. Mun, J.-C. Sabroux, and G. Weber, Recent Advances on Containment Iodine Chemistry, Progress in Nuclear Energy, Vol.52, p.128, 2010.
- [9] N. Girault, C. Fiche, A. Bujan and J. Dienstbier, Towards a Better Understanding of Iodine Chemistry in RCS of Nuclear Reactors, Nuclear Engineering and Design, Vol.239, p.1162, 2009.
- [10] J. C. Wren, J. M. Ball and G. A. Glowa, The Chemistry of Iodine in Containment, Nuclear Technology, Vol.129, p.297, March 2000.
- [11] J. McFarlane, J. C. Wren and R. J. Lemire, Chemical Speciation of Iodine Source Term to Containment, Nuclear Technology, Vol.138, p.162, May 2002.
- [12] S. Guentay, CCI-EWE Filter Qualification Programme Related to the PSEL- Project n.201- Experimental Investigations of Organic Iodide and Elemental Iodine Retention-Executive Summary, TM-42-10-28, Paul Scherrer Institut, Villigen, Switzerland, Confidential, 2010