

pH Effect on Generating Volatile Iodine Species in Solution

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1. Introduction

It has been recognized that radioiodine is potentially one of the most hazardous fission products that can be released from the fuel of nuclear reactors during a severe accident. According to the thermodynamic calculations and various experiments under the severe accident condition, the iodine released from the fuel would be primarily in its reduced state as cesium iodide (CsI) in the containment [1]. Iodide, which is one of the major iodine species if the CsI solution is dissolved in cooling water, is easily diffused into the gas phase after being oxidized into gaseous I₂ by gamma irradiation. Thus, for the gaseous iodine retention in a pool, the behavior of I₂ is important to evaluate and predict releases of the radioactive materials at an early stage of a severe accident.

In accidents involving steam and water, iodine may collect in the aqueous phase and undergo a variety of reactions depending on the oxidation potential and pH solution. The important chemical parameters which control iodine products in aqueous solution are pH, total iodine concentration, temperature and irradiation dose. Experiments have shown that the parameters such as pH and total iodine concentration have large impact on iodine volatility [2, 3]. The overall importance of pH for the irradiated system has been demonstrated in intermediate scaled experiments performed in the Radio iodine Test Facility (RTF) [4]. It is clear that the IPC (Iodine Partition Coefficient) at pH 9 is more than two orders of magnitude higher than that at pH 5. The predominant species at equilibrium also depends on pH at given temperature and a total iodine concentration as shown in the potential-pH diagrams (which calculated from Gibbs energies of formation). For a total iodine concentration higher than 10⁻⁶ mol.dm⁻³, nonvolatile iodide (I⁻) and iodate (IO₃⁻) are the predominant iodine species for most of redox potential and pH ranges. Volatile molecular iodine dominates at equilibrium only under acidic and oxidizing conditions. The concentration of HOI at equilibrium also becomes important under those conditions, and more at lower iodine concentration. Early studies of iodine volatile assumed that HOI was highly volatile [5] but this has been no longer considered to be valid [6, 7]. These thermodynamic equilibrium calculations led to the conclusion that iodine volatility can be minimized by keeping the high pH of aqueous solution.

However, under the radiation condition expected in a severe accident in a nuclear power, although some of

the conclusions reached from thermodynamic calculations still hold, many of the assumptions are no longer feasible. For example, in radiation field, water radiolysis significantly alters the redox characteristics of the aqueous phase. Iodine behavior is dominated by the reaction of iodine species with water radiolysis products that are produced continuously [8].

Many chemical modeling efforts have also been performed to predict the iodine behaviors under severe accident condition. There exist two basic approaches, that is, the empirical modeling and the mechanistic modeling, to estimate the generation of volatile iodine I₂ from nonvolatile iodide I⁻ in the aqueous phase by radiolytic oxidation. The empirical modeling with a limited set of reactions is practically used in severe accident codes, such as IODE [9], IMPAR-3 [10], and ASTEC [11]. The mechanistic modeling tried to represent the large number of elementary radiochemical reactions (typically including hundreds of important reactions in water) and solves the kinetics of these reactions using ordinary differential equation solvers. Typical codes adopted in the mechanistic approach include IodiNe SPECiation and Transport (INSPECT) developed by AEA Technology plc. (United Kingdom), which has been integrated with some changes into MELCOR 1.8.5 [12] and the Library of Iodine Reactions In Containment (LIRIC) model developed by Atomic Energy of Canada Limited (AECL). In general, the existing iodine models can provide reasonable predictions of iodine volatility under some conditions.

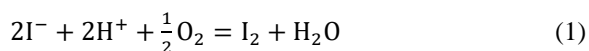
In this study, the pH effects on various reactions of iodine in solution were evaluated to find volatility of iodine in solution. The individual effect of several parameters on the formation of volatile iodine can be examined by ignoring radiolysis. This effect of pH on generating of volatile iodine was considered by the thermodynamics in non-radiolytic conditions. These calculations are presented in terms of the partition coefficient which is a ratio of gaseous phase to total iodine in aqueous solution with 3.0 to 10.0 of pH and 10⁻³ to 10⁻⁶ of the total iodine concentration. The model has been also used for predicting the release of iodine from aqueous solution including the presence of a radiation field. In the presence of a strong irradiation field, the rate of production of the volatile iodine species is controlled by the radiolysis in the aqueous phase and mass transfer to the gaseous phase [13].

2. Methods and Results

Thermodynamic and chemical kinetic calculations of iodine have been established under the severe accident condition. The iodine released from fuel into containment would be primarily in its reduced stated cesium iodide (CsI). The cesium iodide can dissolve in water during the severe accident progression and mitigation process as nonvolatile I^- and would be oxidized to form volatile molecular iodine that could be re-vaporized in the aqueous phase by thermal or radiolytic processes.

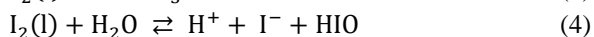
2.1. Iodine reactions under non-radioactive condition in the aqueous phase

If the iodine in solution is originally present only as iodide, then this may be converted to I_2 under oxidizing iodide conditions by present of oxygen.



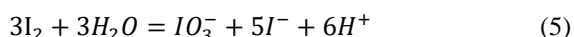
In acidic solutions, this uncatalyzed oxidation is slow. When the solution is irradiated, reaction (1) is catalyzed and this effect may accelerate formation of I_2 from iodide in the containment building.

I_2 can be converted to the various forms in aqueous solution and especially in dilute iodine solution.



The concentrations of various iodine forms are governed by the various equilibrium constants from Eq. (2) to (5). In order to calculate the equilibrium concentrations of its various species, it is assumed that the total iodine in the pool is constant and the electric charge balance between the reactants and products in the solution. The distribution of each various iodine species then is determined as a functions of I_2 and I^- .

It is known that the disproportionation of HIO tends to IO_3^- formation when the pH increases as following reaction:



This reaction is important under non-radiation conditions because there is a discrepancy of the partition coefficients between the disproportionation reactions and the fast initial reactions.

2.2. Iodine reactions under radioactive condition in the aqueous phase

In radiation field, the oxidized reaction of iodine species with water radiolysis products becomes important, the iodine species eventually combine to form I_2 :



Under gamma irradiation, the formation of gaseous iodine species is a function of radiation dose, pH solution, and total iodine concentration. However, determinations of the rates of all chemical processes are rather complicated because iodine could exist in various kinds of oxidation states with ranging from -1 to +7 such as I^- , I_2 , HIO, IO_2^- , IO_3^- , etc. To determinate the concentration of iodine volatility in containment, iodine species as a function of time must be considered. Generally, the overall rate of formation of I_2 can be modelled as following differential equation:

$$\frac{d[I_2]}{dt} = k_1[I^-]D[H^+]^{0.5} - k_2[I_2] \quad (12)$$

2.3. Results

Fig.1 showed molecular iodine concentrations in different pH solutions with 10^{-3} mol.dm⁻³ to 10^{-6} mol.dm⁻³ of the total iodine concentrations. As shown in Fig.1, the I_2 concentration in solution decreases when pH is higher than 6 under the equilibrium condition.

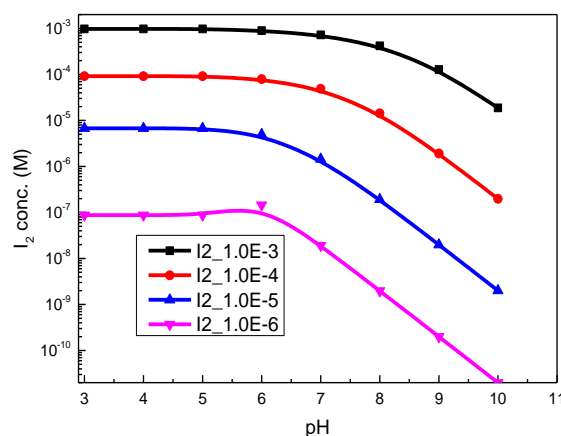


Fig.1. I_2 concentrations in various pH solutions under no radiation

Fig.2 shows that the partition coefficient of iodine in various pH solutions. As shown in Fig.2, the gas/water phase partition coefficients that means gaseous iodine concentration to the total iodine concentration at the equilibrium increases more rapidly as the pH increases.

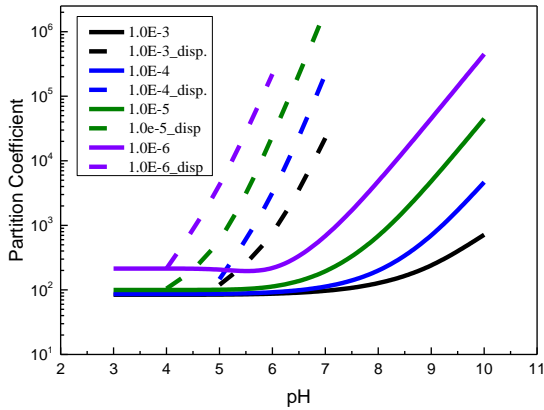


Fig.2. Partition coefficient of iodine in various pH solutions at 25°C under no radiation

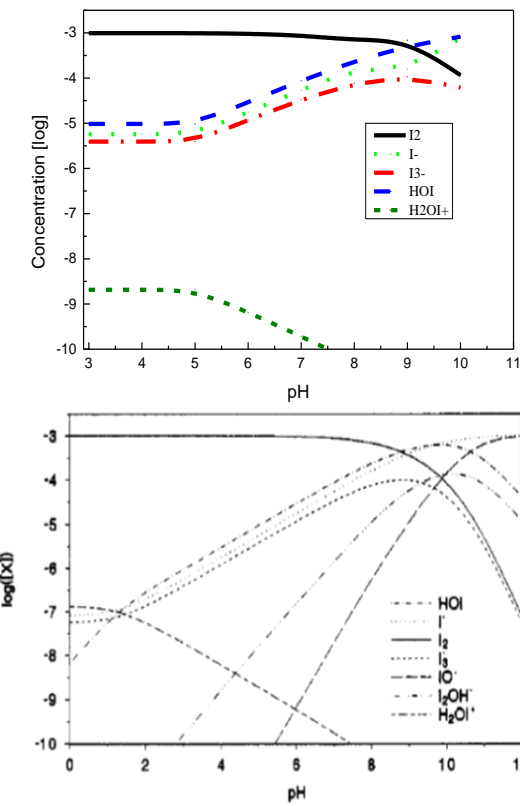


Fig.3. Concentrations of iodine species in hydrolysis calculation [14]; $[I]_0 = 1.0 \times 10^{-3} \text{M}$

Iodine dissolved into aqueous phase undergoes many complex reactions and the final chemical species in the solution at equilibrium are I_2 , I^- , I_3^- and HIO . The concentrations of iodine species by the hydrolysis in pH solution have been expected by calculation from the equilibrium constants as shown in Fig.3. By comparing with reference [14], the species concentrations are quite similar.

When the pH is high and total iodine concentration is low, IO_3^- species becomes important due to the disproportionation of HIO as shown in Fig. 4

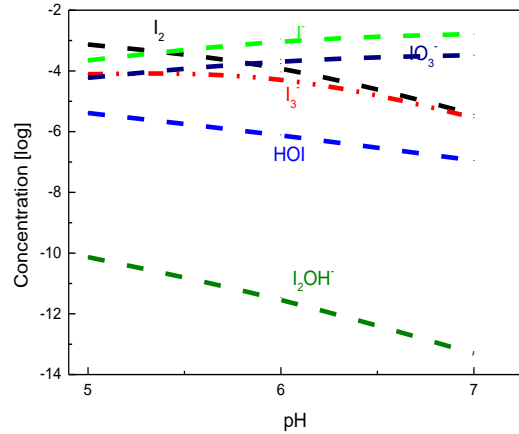


Fig. 4. Concentrations of iodine species by hydrolysis with IO_3^- species considered; $[I]_0 = 2.0 \times 10^{-3} \text{M}$

Using Eq (12), I_2 concentration changes and partition coefficients in various pH solutions during 1.0 irradiation hour were calculated as shown in Figs.5 and 6. It is note that I_2 concentrations under the radiation decrease fast at high pH value and that the partition coefficient has higher than 10^4 in strong radiation field if pH in solution is higher than 5 as shown in Fig.6.

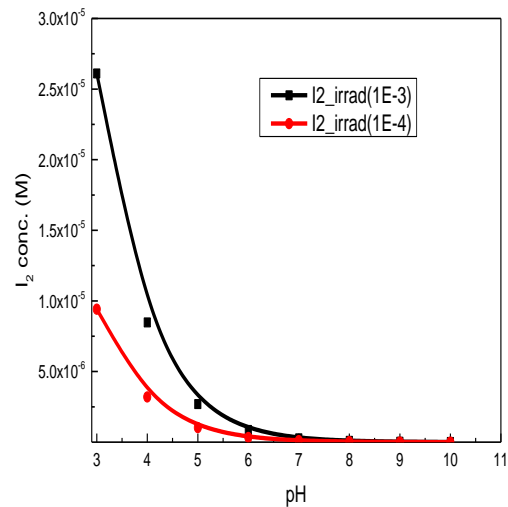


Fig.5. I_2 concentrations in various pH solutions under radiation of 2.0kGy/hr

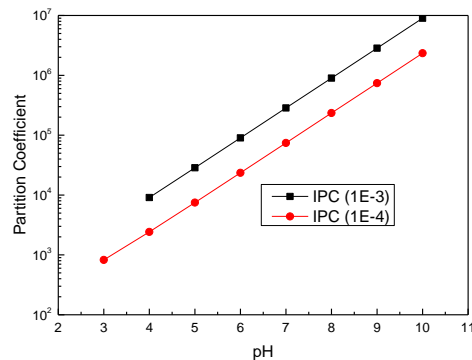


Fig.6. Partition coefficient of iodine in various pH solutions under radiation; $[I] = 10^{-3}$ and 10^{-4}mol/l

3. Conclusions

Molecular iodine concentrations and partition coefficients of the gaseous iodine in various pH solutions were evaluated to find volatility of iodine in solution with / without radiation. The gas/water phase partition coefficients that means gaseous iodine concentration to the total iodine concentration at the equilibrium increases more rapidly as the pH increases without radiation. I₂ concentrations under the radiation decrease fast at high pH value and that the partition coefficient has higher than 10⁴ in strong radiation field if pH in solution is higher than 5.

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