Validation of the KICHE Iodine Chemistry Models for Radiolysis of Aqueous Iodine

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1. Introduction

The amount of radionuclides released into the containment and to the environment is always the focus of public safety for a nuclear power plant. In particular, since a large amount of radioactive materials might be released under the condition of a a severe accident, it is very important to estimate the behaviors of radioactive materials under severe accident conditions. The steam generator tube rupture (SGTR) associated with a core melt under severe accident conditions might possibly releases large amount of radionuclides into the environment bypassing the containment building [1]. However, the radionuclides release mechanism for this case is very complex and the mechanistic analysis methodology has not been fully developed yet.

Iodine and Cesium are the major radionuclides released from the primary heat transfer system for operating light water reactors (LWRs), considering their core inventories and release fractions. The radionuclides that are released from the core and circulate inside the reactor coolant system (RCS) during a postulated severe accident are injected into the building (or containment) atmosphere in the forms of aerosol and gas. 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 I_2 by gamma irradiation. Thus, for the gaseous iodine retention in a pool, the behavior of I_2 is important to evaluate and predict releases of the radioactive materials at an early stage of a severe accident. The important chemical parameters which control iodine products in aqueous solution are pH, total iodine concentration, temperature and irradiation dose [2].

The objectives of this study are to characterize the KICHE chemical reaction models for analyzing the aqueous iodine radiolysis including the effect of pH, so as to estimate the simulation capability of the KICHE code for radiolysis of aqueous iodine. Studies on the containment iodine chemistry including the effects of irradiation dose, temperature, and pressure etc. are in the future research plan.

2. KICHE Code

2.1. Code Overviews

The KICHE(Kinetics of Iodine CHEmistry) code is an iodine chemistry simulation tool, developed by JAEA for analyses of chemical kinetics relevant to iodine volatilization in the containment vessel of light water reactors (LWRs) during a severe accident. It consists of a FORTRAN code to solve chemical kinetics models, reaction databases written in plain text format, and peripheral tools to convert the reaction databases into FORTRAN codes to solve corresponding ordinary differential equation sets.[3] The KICHE code, used in this study, is a KICHE 1.3 (NEA-1865) computer program provided by the OECD/NEA Data Bank system [4].

The processes included in the kinetics model are in two categories which are chemical reactions and non-reaction processes which are not expressed by chemical reaction equation such as adsorption, and desorption, etc. For both categories of the chemical reaction and the non-reaction processes, change of every concentration can be expressed by a polynomial of arbitrary order including potentially all the concentrations in the system,

$$\frac{dY_k}{dt} = f_k\left(Y_1, Y_2, \cdots, Y_M\right) \tag{1}$$

where Y_k is the concentration of species k; subscript M is the number of species included in the system; and f_k is a polynomial of concentrations.

KICHE solves the simultaneous ordinary differential equations for the system, Eq. (1), by a simple first order finite difference method with implicit temporal discretization. The finite difference equations have nonlinear terms of concentrations, and are solved by Newtonian iteration. The latest chemical reaction set as of 2011, named “11a”, and another set following the method of LIRIC 3.2 model developed at AECL/Canada [5] are explained in the next section, which contain the information on every term in Eq. (1).

2.2. Iodine Chemistry Databases

KICHE 1.3 computer program provides following iodine chemistry databases, one of which can be adopted for the calculation by a user. Modification of the given databases or creation of a new database is possible by utilizing the KICHE tool set.

2.2.1. Default Iodine Chemistry Models (11a)

The iodine behavior modeling in KICHE involves aqueous reactions, gas-aqueous mass transfer of volatile species and wall adsorption of I_2. Chemical reactions of KICHE code are assumed only in the aqueous phase, because it is the primary reaction field to produce volatile iodine due to the high concentration of materials and water radiolysis effect. As volatile iodine species, I_2 and organic iodides are considered. The organic iodides are divided into two groups, high volatility organic iodides (HVRI) and low volatility organic iodides (LVRI), following the method of LIRIC 3.2 model [5]. Alkyl iodides, typically CH_3I, are assumed for HVRI; other more hydrophilic larger molecules are assumed for LVRI.

The latest reaction set of the year of 2011, named “11a”, consists of 52 water radiolysis reactions, 31 inorganic-iodine reactions, 26 organic-iodine reactions, 23 miscellaneous reactions, and 86 non-chemical reactions.

2.2.2. LIRIC Models

LIRIC(Library of Iodine Reactions In Containment) 3.2 is a comprehensive mechanistic model for the chemical and mass transport behavior of iodine in containment under postulated nuclear reactor accident conditions, developed at AECL/Canada.[5]

This model consists of 46 water-radiolysis reactions, about 80 inorganic iodine reactions including thermal aqueous iodine reactions and the reactions of iodine with water-radiolysis products in the aqueous phase, dissolution of organic solvents from painted surfaces in contact with the aqueous phase, radiolytic decomposition reactions of organic compounds in the aqueous phase, organic iodide formation and decomposition in the aqueous phase, 6 reactions of inorganic impurities such as buffers and metal ions with water-radiolysis products, mass transfer of O_2, H_2, CO_2, I_2 and organic iodides between the aqueous and gas phases, and surface interactions, including adsorption and desorption of iodine species on surfaces in contact with the aqueous or gas phase, and absorption on condensing water film.

3. Validation against Experimental Data

3.1. Radiolysis of Aqueous Sodium Iodide

Jung et al. [6] used a high gamma radiation dose source with a source activity of ~ 280 kCi. The gamma dose rate was controlled to be 2.0 $kGy \cdot h^{-1}$. The I^- solutions with the various concentrations from 0.2 mM to 5.0 mM were exposed to high intensity gamma radiation during the experiment. Separate irradiation experiments were performed to investigate the effect of the gamma dose rate on the oxidation rate of I^-. The changing of pH during irradiation time in Jung’s experiment was described in Table 1. The initial pH of three different NaI solutions were 3.04, and the average measured temperature at irradiation laboratory was 15 ^oC.

Figure 1 shows the KICHE prediction results by using 11a and LIRIC chemical models, compared with the experimental data. The 11a chemical reaction model gives better matched pH values with the measured.

As described by Jung et al. [6], I^- ions are oxidized with the following steps. In the first step, I^- is oxidized into I_2 by $HO\cdot$. In the second step, most of I_2 molecules are stabilized into I_3^- by I^-, as long as the concentration of I^- is high enough. Because the oxidation reaction of I^- proceeds during irradiation, the concentration of I^- available for stabilizing I_2 certainly decreases, and as the irradiation exposure time progresses, the concentration of I^- becomes insufficient to stabilize I_2. In the final step, I_3^- eventually ceases to exist in the irradiated solution because of the equilibrium reaction ($I_2 + I^- \leftrightarrow I_3^-$). Figure 2 presents the concentration changes of I^-, I_2, and I_3^- in the NaI solutions as a function of gamma irradiation time, which were simulated by the KICHE with 11a model. It was clearly shown that all the I^- concentrations decrease as irradiation time increases.

Figure 3 shows concentration change of I_3^- in 5.0-mM NaI solution under 2 kGy/h gamma irradiation, which is the same case as Figs. 1(c) and 2(c). The discrepancy between the measured and simulated I_3^- concentrations might be caused by the fact that KICHE was made for solving chemical kinetics models and could not provide solutions of chemical equilibrium. Therefore, the equilibrium reaction of ($I_2 + I^- \leftrightarrow I_3^-$) might not properly predicted in the KICHE simulations.

3.2. Radiolysis of Aqueous Cesium Iodide

In T. I. Gorbovitskaya experiment [7], the radiolysis of 10^{-5} to 10^{-3} M solution of cesium iodide was studied theoretically and experimentally at 323 K, a dose range 1~30 kGy, and pH 3~9. The main radiolysis products are molecular iodine (at 323 K and the given starting concentration of iodide ion it exists in the form I_2) and iodate ion. The ratio of I_2-IO_3^- concentration depends on pH and the initial concentration of iodide ion. The stationary concentration of both the main products in the liquid phase is attained about 0.5 h after start of radiolysis.

The changing of the measured pH values on CsI radiolysis was described in Table 2, in which experiments the gamma dose was 4.5 kGy/h and the laboratory temperature was 50 ^oC. Figure 4 compares the simulation results by the KICHE with 11a and LIRIC models with the experimental data as well as the predictions by Gorbovitskaya et al. [7]. It was shown that the KICHE with 11a model gives as similar accuracy level as the Gorbovitskaya’s simulations [7]. However, more detailed investigation on modeling radiation-chemical transformations in iodine-containing aqueous systems is still needed for better agreement between the measured and the predicted.

4. Conclusions

In this study, KICHE code was applied for simulating radiolysis of aqueous iodine. As a result of the simulation, it was revealed that the KICHE calculations with default(original) 11a chemistry model provide reasonable results, compared with the experimental data. However, the discrepancies between the measured and the calculated were quite noticeable in some parts, so that more detailed investigation on modeling radiation-chemical transformations in iodine-containing aqueous systems is still needed for better agreement. The limitation of a chemical kinetic equation solver should be also studied, especially concerning the prediction of chemical equilibrium reactions.

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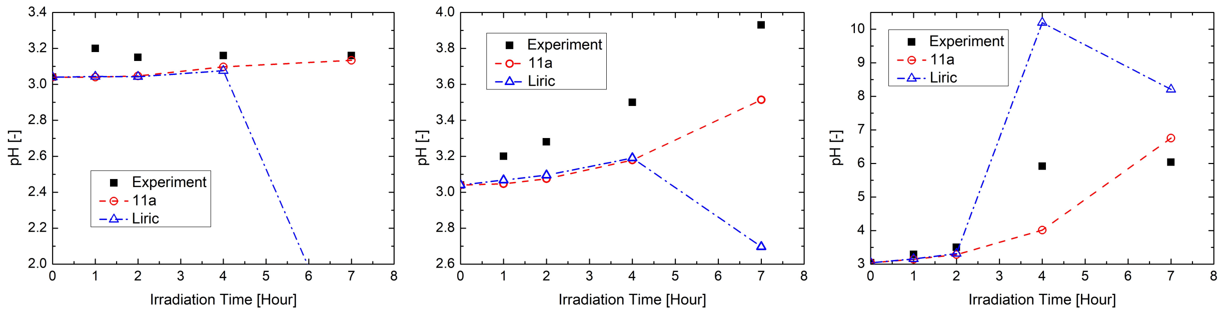
Table I: The pH values of NaI solution after gamma irradiation experiments with 2 kGy/h [6]

Irrad. Time (h)	pH Values of NaI Solutions After Irradiation		
	0.2 mM NaI	1.0 mM NaI	5.0 mM NaI
0	3.04	3.04	3.04
1	3.20	3.20	3.29
2	3.15	3.28	3.50
4	3.16	3.50	5.92
7	3.16	3.93	6.04

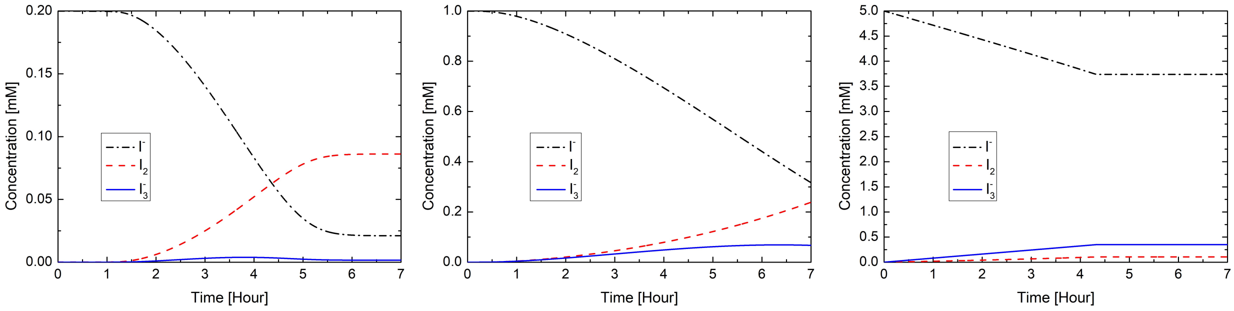
Table 2: Change of the measured pH values on CsI radiolysis [7]

Time [h]	Initial pH 3.0	Initial pH 4.0	Initial pH 5.0	Initial pH 7.0	Initial pH 9.0
0	3.00	4.00	5.00	7.00	9.00
0.25	3.02	4.15	6.01	-	8.60
0.50	3.03	4.19	5.85	7.05	8.60
1.00	3.14	4.89	5.63	7.03	8.40
2.00	3.42	6.20	6.10	6.93	8.20
3.00	3.37	6.27	6.54	-	7.90
4.00	3.25	6.30	6.58	-	8.10
5.00	3.27	6.10	6.60	-	7.86
5.50	3.35	6.14	6.68	-	7.80
6.00	-	6.12	6.70	-	7.78



(a) 0.2 mM NaI (b) 1.0 mM NaI (c) 5.0 mM NaI

Fig. 1. pH Values of NaI solution after gamma irradiation experiments with 2.0 kGy/h.



(a) 0.2 mM NaI (b) 1.0 mM NaI (c) 5.0 mM NaI

Fig. 2. Concentration changes of I^-, I_2, and I_3^- in the NaI solutions during gamma irradiation experiments with 2.0 kGy/h, simulated by the KICHE with 11a model.

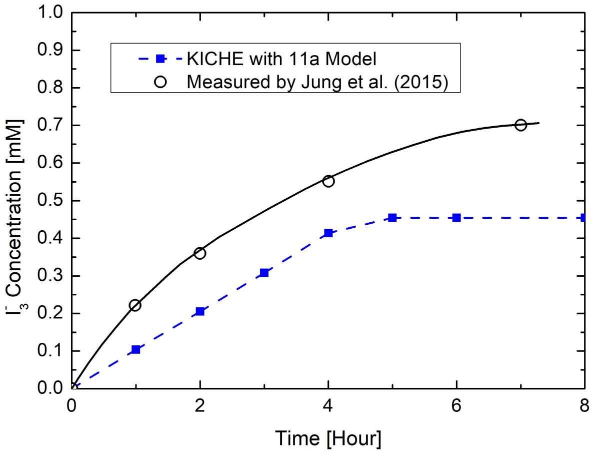
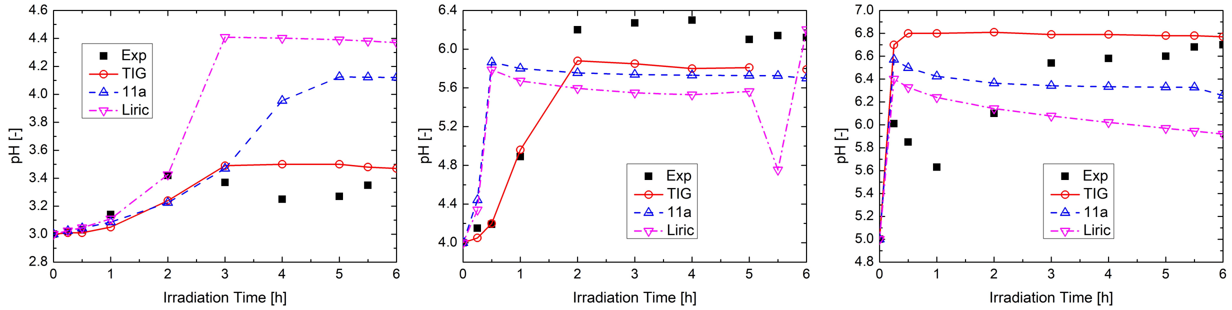
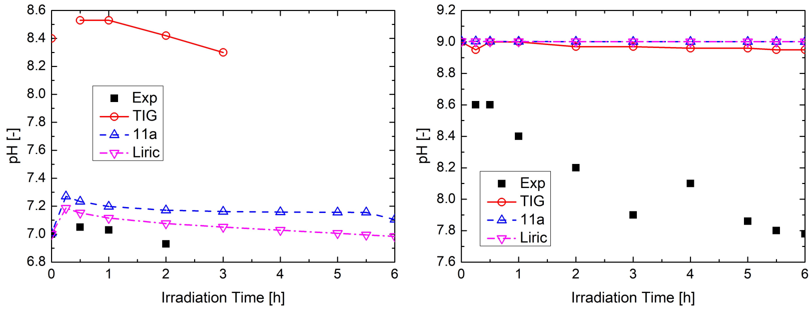


Fig. 3. Concentration change of I_3^- in 5.0-mM NaI solution under 2 kGy/h gamma irradiation.



(a) Initial pH 3.0 (b) Initial pH 4.0 (c) Initial pH 5.0



(d) Initial pH 7.0 (e) Initial pH 9.0

Fig. 4. Change of pH on CsI radiolysis.