

## Studies on Iodine Chemistry in NPP Containments by Using the KICHE Code

Churl Yoon\*, Sung Il Kim, Kwang Soon Ha

Korea Atomic Energy Research Institute, 111 Daedeok-daero 989 Beon-gil, Yuseong-gu, Daejeon 34057, Korea

\*Corresponding author: cyoon@kaeri.re.kr

### 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 core melt accident (that is, 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 ( $I^-$ ), 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 Korea Atomic Energy Research Institute (KAERI) has developed a severe accident integrated analysis code system, CINEMA (Code for Integrated severe accident Management Analysis), since 2011. The CINEMA consists of three parts; 1) analysis module of in-vessel phenomenon (CSPACE), 2) analysis module of ex-vessel phenomenon (SACAP), and 3) analysis module of fission product (FP) behavior (SIRIUS) [3]. The SIRIUS (Simulation of Radioactive nuclides Interaction Under Severe accidents) code has been developed to predict the behaviors of the radioactive materials in the reactor coolant system and in the containment under severe accident conditions [4].

The objectives of this study are to analyze the containment iodine chemistry including the effect of pH without irradiation dose by using the KICHE code as

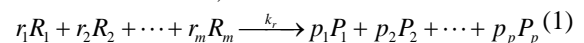
the first step of this series of studies, and to estimate the simulation capability of the KICHE code for nuclear safety analysis. Studies on the containment iodine chemistry including the effects of irradiation dose, temperature, and pressure etc. are in the future research plan.

### 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.[5] The KICHE code, used in this study, is a KICHE 1.3 (NEA-1865) computer program provided by the OECD/NEA Data Bank system. 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.[6]

In the chemical reaction processes, a general reaction  $r$  is written as follows,



where  $k_r$  is the rate constant of the reaction  $r$ ;  $R$  and  $P$  are the reactant and product species, respectively;  $r_x$  and  $p_x$  are corresponding stoichiometric coefficients, respectively. Based on this reaction, the concentration change rate of a reactant component  $R_i$  and a product component  $P_j$  include a consuming and a producing contribution terms, respectively, as follows,

$$\frac{d[R_i]}{dt} = \dots - r_i k_r [R_1]^{r_1} [R_2]^{r_2} \dots [R_m]^{r_m} - \dots \quad (2)$$

$$\frac{d[P_j]}{dt} = \dots + p_j k_r [R_1]^{r_1} [R_2]^{r_2} \dots [R_m]^{r_m} + \dots \quad (3)$$

On the other hand, the concentration changes of species  $X_i$  due to a non-reaction process are expressed as follows,

$$\frac{d[X_i]}{dt} = \dots + k_n [X_{n,1}] [X_{n,2}] + \dots [X_{n,l}] \quad (4)$$

where  $k_n$  is the rate constant of the process  $n$ . This expression indicates the product of the concentrations of

species  $X_{n,1}$  through  $X_{n,i}$  drives the evolution of the concentration change of a species  $X_i$ .

Combining above two categories of the chemical reaction and the non-reaction processes, change of every concentration is expressed by a polynomial of arbitrary order including potentially all the concentrations in the system,

$$\frac{dY_k}{dt} = f_k(Y_1, Y_2, \dots, Y_M) \quad (5)$$

where  $Y_k$  is the concentration of species  $k$ ;  $M$  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. (5), 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.

## 2.2. Iodine Chemistry Databases

KICHE 1.3 computer program provides following two iodine chemistry databases, one of which can be adopted for the calculation by a user.

### 2.2.1. Default Iodine Chemistry Models

The concept of the iodine behavior modeling by KICHE is illustrated in Fig. 1. Aqueous reactions, the gas-aqueous mass transfer of volatile species and wall adsorption of  $I_2$  are involved.

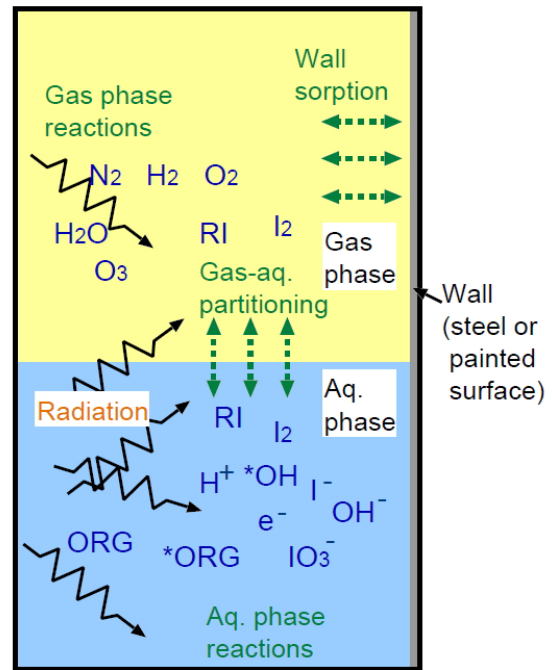
Chemical reactions of KICHE code are assumed only in the aqueous phase, because it is the primary reaction field to produce volatile iodine due to the high concentration of materials and water radiolysis effect. As volatile iodine species,  $I_2$  and organic iodides are considered. The organic iodides are divided into two groups, high volatility organic iodides (HVRI) and low volatility organic iodides (LVRI), following the method of LIRIC 3.2 model [7]. 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.[7]

This model consists of 46 water-radiolysis reactions, about 80 inorganic iodine reactions including thermal



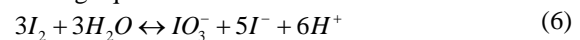
RI : Organic Iodine compounds

Fig. 1. Concept of the iodine behavior model

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. Simulation of Disproportionation of Iodine

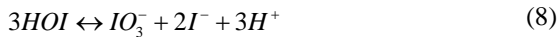
A dictionary definition of 'disproportionation' is a redox reaction in which a compound of intermediate oxidation state converts to two different compounds, one of higher and one of lower oxidation states. Especially the disproportionation of iodine is considered as the reaction in which molecular iodine added to alkali is converted into iodate ( $I^{+5}$ ) and iodide ( $I^{-1}$ ) as in the following equation.



Hydrolysis of iodine is known to take place in two stages.[8] The first fast stage is the equilibrium as follows,

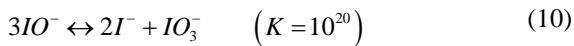
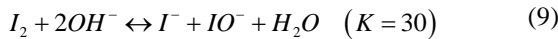


The second stage is a slow disproportionation of HOI, which is a complex reaction, leading to the production of iodate.



Note that combination of Eqs. (7) and (8) gives Eq. (6). Through these chemical processes,  $I_3^-$  (and  $I_2$ ) is simultaneously disproportionated to form two different species in the alkaline solution above pH 9. However, current understanding of all the above chemical mechanisms which occur at high pH is insufficient.

Among various chemical reaction procedures in the iodine disproportionation taking place above pH 9, the rate determining steps are simply shown in reactions (9) and (10) as follows,[9]



As a part of the experimental studies on the oxidation behavior of iodide ion under gamma irradiation conditions, S. H. Jung et al.[9] measured  $I_3^-$  concentration according to the solution pH changes showing the disproportionation phenomena. Figure 2 shows measurement of the concentration changes of the initially 0.5-mM  $I_3^-$  solution as a function of pH without gamma irradiation. Above pH 9.0, the concentration of  $I_3^-$  decreased rapidly due to the disproportionation reaction. Within a pH range of 2.0 to 9.0, the concentration of the  $I_3^-$  was maintained at about the 0.5-mM level. And, little  $I_3^-$  was observed above pH 10.0.

KICHE provides users an option to printout the runtime equation sets which are being used to the concentration calculation for each product species. Table I and II summarize the runtime equation sets used for  $I_3^-$  concentration calculation in KICHE with the 11a and the LIRIC model, respectively, under the condition of  $pH > 9.0$ . Since the working equations for the  $I_3^-$  concentration calculation with both the 11a model (KICHE default) and LIRIC model do not have Eqs. (9) nor (10), they could not properly predict the abrupt  $I_3^-$  concentration decrease above pH 9.0.

The 11a model was modified by adding Eqs. (9) and (10) with a control parameter to activate the above equations only when pH goes over 9.0. Three simulation results using different iodine chemistry models are displayed in Fig. 2, along with the experimental data. The 'modified 11a' model predicts the iodine disproportionation in the best agreement. Note that the reaction rate  $K$  of Eq. (10) was reduced from  $10^{20}$  to  $10^{11}$  to avoid numerical instability.

To investigate the effects of Eqs. (9) and (10) on the content changes in low pH conditions, these added equations were activated over all pH range by removing the IF statement for conditional activation over pH 9.0. Figure 3 shows the concentration changes of some selected species during the disproportionation reaction in 0.5-mM  $I_3^-$  solution with Eqs. (9) & (10) activated over all pH range. As a result, it was found that volatile

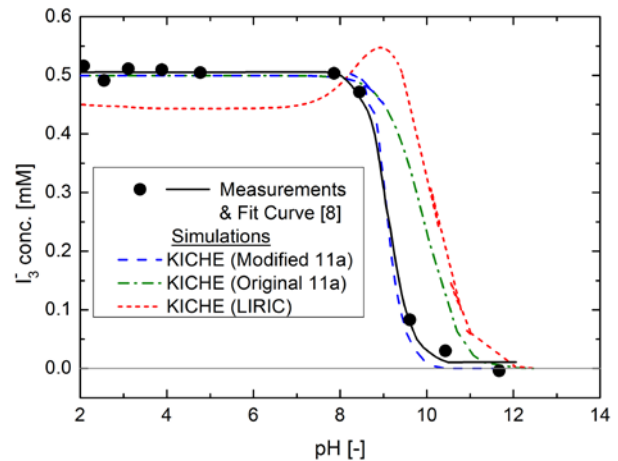


Fig. 2. Effect of the solution pH on the disproportionation reaction of  $I_3^-$  in 0.5-mM  $I_3^-$  solution

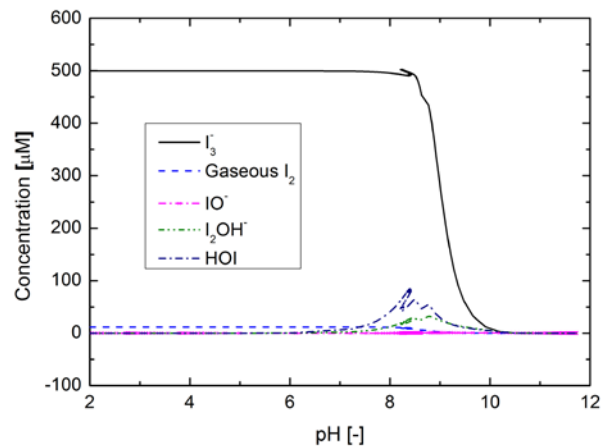


Fig. 3. Concentration changes of some selected species during the disproportionation reaction of  $I_3^-$  in 0.5-mM  $I_3^-$  solution: Eqs. (9) & (10) are activated over all pH range.

iodine such as gaseous  $I_2$  or HOI were not produced significantly in low pH conditions below 5 and that the concentration of HOI was increased above pH 8.0 leading the disproportionation.

#### 4. Conclusions

In this study, the governing equations, solving mechanism, iodine chemistry model, and code structure of KICHE code were investigated. The disproportionation of iodine was simulated by using KICHE code. As a result of the simulation of disproportionation, it was revealed that the given default(original) 11a chemistry model and the LIRIC model could not adequately predict the abrupt  $I_3^-$  concentration decreases when  $pH > 9.0$ . Therefore, a 'modified 11a' chemistry model was newly constructed by adding two essential equations (Eqs. (9) & (10)) for disproportionation and adopted for the simulation. The

modified 11a model predicted the disproportionation of iodine in the best agreement. The knowledge, obtained in this study, could be used to develop an iodine chemistry module in a severe accident analysis code.

### ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science and ICT) (No. NRF-2017M2A8A4015280)

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Table II: Runtime equation set solved for  $I_3^-$  concentration calculation in KICHE with LIRIC model under pH > 9.0

Species	Related Reactions to the Given Species' Concentration Calculation
$I_2$	$I_2 + I^- \leftrightarrow I_3^-$ $I_2 + OH^- \leftrightarrow I_2OH^-$
$I_3^-$	$I_2 + I^- \leftrightarrow I_3^-$
$I^-$	$I_2OH^- \leftrightarrow HOI + I^-$ $2HOI \leftrightarrow HIO_2 + H^+ + I^-$ $HOI + IO^- \rightarrow IO_2^- + H^+ + I^-$ $2OI^- \rightarrow IO_2^- + I^-$ $I_2OH^- + IO^- \rightarrow IO_2^- + H^+ + 2I^-$ $HIO_2 + HOI \leftrightarrow IO_3^- + 2H^+ + I^-$ $IO_2^- + OI^- \rightarrow IO_3^- + I^-$ $IO_2^- + I_2OH^- \rightarrow IO_3^- + H^+ + 2I^-$ $HOI + HIO_2 + I^- \rightarrow 2HOI + IO^-$ $I_2 + I^- \leftrightarrow I_3^-$ $I^- + H_2O_2 \rightarrow IO^- + H_2O$ $I_2OH^- + H_2O_2 \leftrightarrow HIO_2 + I^- + H_2O$ $HIO_2 + OH^- \rightarrow I^- + O_2 + H_2O$
$IO^-$	$HOI + IO^- \rightarrow IO_2^- + H^+ + I^-$ $2IO^- \rightarrow IO_2^- + I^-$ $I_2OH^- + IO^- \rightarrow IO_2^- + H^+ + 2I^-$ $IO_2^- + IO^- \rightarrow IO_3^- + I^-$ $HOI + HIO_2 + I^- \rightarrow 2HOI + IO^-$ $HOI \leftrightarrow IO^- + H^+$ $I^- + H_2O_2 \rightarrow IO^- + H_2O$
$IO_3^-$	$HIO_2 + HOI \leftrightarrow IO_3^- + 2H^+ + I^-$ $IO_2^- + OI^- \rightarrow IO_3^- + I^-$ $IO_2^- + I_2OH^- \rightarrow IO_3^- + H^+ + 2I^-$ $2X^*HIO_3^- \leftrightarrow IO_3^- + IO_2^-$

\* Assigned variables in KICHE

Table I: Runtime equation set solved for  $I_3^-$  concentration calculation in KICHE with 11a model under pH > 9.0

Species	Related Reactions to the Given Species' Concentration Calculation
$I_2$	$I_2 + I^- \leftrightarrow I_3^-$ $I_2 + OH^- \leftrightarrow I_2OH^-$
$I_3^-$	$I_2 + I^- \leftrightarrow I_3^-$
$I^-$	$I_2 + I^- \leftrightarrow I_3^-$ $I_2OH^- \leftrightarrow HOI + I^-$
$IO^-$	$HOI \leftrightarrow IO^- + H^+$