

Establishment of Advanced Technique for the Prediction of pH in the Sump Solution

Hee Cheol Kim, Sang-Nyung Kim*

Kyunghee Univ. Global Campus, Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do

Corresponding author: snkim@khu.ac.kr

1. Introduction

During LOCA Iodine is leaked from RCS along with the coolant in the form of CsI and finally collected in the sump. When the iodine in the sump is regasified, the material of the containment vessel is likely to be damaged, and the iodine is highly likely to be leaked to the outside due to the cracks in the containment vessel or through the vent. So it can threaten the safety of the NPP to a considerable degree. Accordingly, to prevent the regasification of the iodine inside the sump solution, it is stipulated that the pH of the sump solution should be 7.0 or greater and 8.5 or less.[1]

The pH of the sump solution is determined by the boric acid-neutralizing additive (referred to as TSP hereinafter) reaction, organic reaction, and the chemical equilibrium of fission products. Accordingly, correct pH estimation in consideration of them is necessary

As the pH calculation method considering only the boric acid-TSP reaction is presently used in Korea, the results are not accurate and calculation was complicated. Accordingly, this study intends to take other compounds affecting the pH of the sump solution into consideration, and to use the free minimization, a theory of chemical equilibrium, and the Lagrange Multiplier Technique to establish a simple and accurate method of calculating the pH.

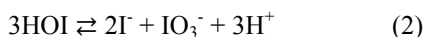
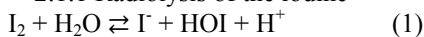
The first-year study investigated the correlation of the pH-Iodine behavior and the substances affecting pH. In this year's study the program for calculating the pH of the sump solution will be established by improving the SOLGASMIX-PV code, the chemical equilibrium calculation program.

2. Methods and Results

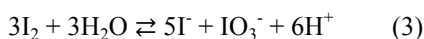
2.1 Understanding of the iodine behavior in the containment vessel during LOCA

It has been disclosed that the conversion of iodine into a molecular form ($I^- \rightarrow I_2$) is possible only in acidic liquids. This mechanism is briefly described in the following subsection.

2.1.1 Radiolysis of the iodine



These two reactions can be summarized as follows:



As the pH of the solution increases, the equilibrium between reactions (1) and (2) shifts to the right, and the concentration of I_2 consistently decreases. I_2 of reaction (1) is the dominant component until pH 5, and HOI becomes dominant from pH 5 to pH 10, whereas OI is the dominant component in excess of pH 10. As for reactions (2) and (3), I_2 strongly decreases from pH 4 and up, and I and IO_3^- become the main components that exist at a mol ratio of 5:11 at a higher pH.

2.2 Substances affecting the sump pH

Actually, during LOCA, various substances, which affect pH, are generated inside the containment building by radiolysis and core-concrete reaction. As they are strongly acidic or alkaline, a small amount can influence pH. Accordingly, they must be taken into consideration for accurate prediction.

2.2.1 Acidic compounds generated by the organic reaction

If the electric cable insulating substances are exposed to radiation during LOCA, HCl is generated, and a small amount of H_2SO_4 is also generated in small amounts.

$$R = R_\gamma + R_\beta \quad (4)$$

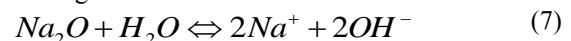
$$R_\gamma = 1.65 \times 10^{-14} \frac{\dot{E}_\gamma N}{V} (1 - e^{-3.74 \times 10^{-k_\gamma r}}) \quad (5)$$

$$R_\beta = 8.70 \times 10^{-16} \frac{\dot{E}_\beta N}{V} \quad (6)$$

- R_γ, R_β = HCl production rate due to the γ ray and β ray (gmol/sec)
- E_γ, E_β = Energy absorption rate of γ ray and β ray due to the fission products (Mev/sec)
- N = Total weight of the cable hypalon (lb)
- V = Volume of the free space in the containment building (cm^3)
- r = Average range of the radiation in air (cm)
(r is 1/2 of the radius or height of the containment building)

2.2.2 Fission products

If the core-concrete reaction takes place, alkaline substances including CaO and Na_2O, K_2O will be emitted and flow into the sump. When they come in contact with water, they will form hydrates due to the following reaction.



If these substances are analyzed by water, pH may greatly increase.

2.3 pH calculation model

Input was generated in accordance with the standard status of the substances added to the sump solution during LOCA with reference to NRC JCN J2452.[1]

Table 1. Free energy coefficients

Species	Free energy coefficients		
Na ⁺	649599.24	7.083	-7.34
H ⁺	0	0	0
Cl ⁻	263231.2	3.059	-2.976
OH ⁻	549675.54	6.285	-6.21
B(OH) ₃	3399284.3	35.026	-38.394
B(OH) ₄ ⁻	4063742.3	42.559	-45.901
B ₂ (OH) ₇ ⁻	7451295.1	77.436	-84.162
B ₃ (OH) ₁₀ ⁻	10891770	112.987	-123.022
B ₄ (OH) ₁₄ ⁻²	15139080	157.176	-170.994
PO ₄ ⁻³	3209627.4	35.999	-36.265
HPO ₄ ⁻²	3678417.1	39.408	-41.553
H ₂ PO ₄ ⁻	3704863.6	39.574	-41.852
H ₃ PO ₄	3684191.5	39.3	-41.619
H ₂ O	67802.026	7.889	-0.798
Ar(g)	0	0	0

2.4 Improvement of the pH calculation code

The conventional SOLGASMIX-PV program was used to calculate the activity of each substance in the balanced solution by means of free-energy minimization. Therefore, to calculate the pH of the solution, the activity of the hydrogen ion in the produced output had to be converted to a natural log, which is quite cumbersome. Accordingly, this study modified the SOLGASMIX-PV program so that the sources can be improved and pH can be calculated directly from the output.

1 Pure Water test				
OT = 298.15 K				
P = 1.000E+00 ATM				
	X*/MOLE	Y/MOLE	P/ATM	ACTIVITY
Ar(g)	0.10000E+00	0.10000E+00	0.96831E+00	0.96831E+00
H2O(g)	0.00000E+00	0.32722E-02	0.31685E-01	0.31685E-01
MOLE FRACTION				
H2O(l)	0.00000E+00	0.55508E+02	0.10000E+01	0.10000E+01
H+(ao)	0.55511E+02	0.55798E-05	0.10052E-06	0.10052E-06
OH-(ao)	0.55511E+02	0.55798E-05	0.10052E-06	0.10052E-06
PEHA OF THE SUMP SOLUTION = 7.00				

Fig 1. Purewater pH test output

3. Conclusions

The input was applied to the modified code, and the result showed that the calculated pH value was very high, about 2 times the existing resulting value. The presumed reason is that the water (H₂O), used as input in previous studies, was perceived to be in the ion state

(H⁺+OH⁻) by the improved SOLGASMIX-PV program, and consequently a higher hydrogen ion concentration than previously was calculated. Accordingly, the code sources will be improved, and the input of the program will be improved so that not only the ion state, but also the molecular form of the input can be perceived.

Species	moles	molality	activity	act. coeff.
Ar	0.0000E+00			
H2O	5.5411E+01			
Na+	6.9700E-02	6.9823E-02	4.8691E-02	6.9735E-01
H+	1.4592E-07	1.4618E-07	1.1675E-07	7.9874E-01
Cl-	0.0000E+00	0.0000E+00	0.0000E+00	6.9735E-01
OH-	1.3637E-07	1.3661E-07	9.5264E-08	6.9735E-01
B1.0 (aq)	4.2692E-02	4.2767E-02	7.6830E-04	1.0000E+00
B1.1	3.0807E-04	3.0861E-04	2.2242E-04	7.2073E-01
B2.1	4.1900E-09	4.1974E-09	2.9271E-09	6.9735E-01
B3.1	4.1081E-10	4.1154E-10	2.8698E-10	6.9735E-01
B4.2	0.0000E+00	0.0000E+00	0.0000E+00	2.3649E-01
PO4---	5.3784E-07	5.3879E-07	2.8272E-08	5.2474E-02
HPO4--	2.6401E-02	2.6447E-02	7.1316E-03	2.6983E-01
H2PO4-	1.6589E-02	1.6618E-02	1.1977E-02	7.2073E-01
H3PO4 (aq)	9.9059E-06	9.9234E-06	1.7827E-07	1.0000E+00
pH = 6.93				
Temp (C) = 298.15				
ionic strength = 0.096				

Fig 2. NRC pH calculation

1 NRC pH Calculation				
OT = 298.15 K				
P = 1.000E+00 ATM				
	X*/MOLE	Y/MOLE	P/ATM	ACTIVITY
AR(g)	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
MOLE FRACTION				
H2O(l)	0.00000E+00	0.32968E-03	0.13621E-02	0.13621E-02
Na+	0.00000E+00	0.00000E+00	0.00000E+00	0.00000E+00
H+	0.00000E+00	0.55343E-13	0.22865E-12	0.22865E-12
Cl-	0.00000E+00	0.43000E-01	0.17765E+00	0.17765E+00
OH-	0.00000E+00	0.16083E-04	0.66447E-04	0.66447E-04
B1.0aq	0.00000E+00	0.34343E-03	0.14189E-02	0.14189E-02
B1.1	0.00000E+00	0.69352E-01	0.28653E+00	0.28653E+00
B2.1	0.00000E+00	0.16853E-05	0.69629E-05	0.69629E-05
B3.1	0.00000E+00	0.30524E-06	0.12611E-05	0.12611E-05
B4.2	0.00000E+00	0.18195E-07	0.75172E-07	0.75172E-07
PO4---	0.00000E+00	0.86330E-01	0.35667E+00	0.35667E+00
HPO4--	0.00000E+00	0.42670E-01	0.17629E+00	0.17629E+00
H2PO4-	0.00000E+00	0.14025E-06	0.57943E-06	0.57943E-06
H3PO4aq	0.00000E+00	0.40884E-17	0.16891E-16	0.16891E-16
PEHA OF THE SUMP SOLUTION = 12.64				

Fig 3. NRC pH calculation by modified SOLGASMIX-PV

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- [1] C. F. Weber and E. C. Beahm, Calculation of pH and Iodine Volatility Under Reactor Accident Conditions, ORNL/NRC/LTR-99/3, Oak Ridge National Laboratory (March 1, 1999).