Analysis of pH on Water Temperature in the Recirculation Sump

Sang Nyung Kim [a*], Hyoung Ju Yoon [a]
[a]*The Kyunghee Univ., Nuclear Engeering Dept., Seocheon-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-701*
[*]*Corresponding author: snkim@khu.ac.kr*

1. Introduction

During a loss-of-coolant accident (LOCA) in a pressurized water reactor (PWR), remedial actions initiated automatically include actuation of the containment spray system (CSS) in most plants and actuation of the emergency core cooling system (ECCS) to provide an emergency supply of borated water from the in-containment refueling water storage tank (IRWST). The reactor coolant, containment spray, and borated water injected by the ECCS drain to the floor of the containment building and are collected by the recirculation sump [1].

After the initiation of these actions, the recirculation sump would contain boric acid and tri-sodium phosphate (TSP) that is held dry in the sump to neutralize the boric acid [2]. These materials have influence on pH and the sump pH is dependent on the amount of TSP under the variable conditions such as sump water level, boron concentration for each water source and sump water temperature.

The equilibrium sump solution pH should be above 7.0 according to the Standard Review Plan. The purpose of controlling the sump pH is to provide assurance that significant long-term iodine revolution does not occur, and to be within material compatibility constraints [3].

It has been the domestic practice that the pH value of sump water following a LOCA was computed by a chemical equilibrium calculation involving equilibrium constants or ionization constants [4]. However, in this paper, the sump pH analysis has been performed by the modified SOLGASMIX-PV program which computes thermodynamic equilibrium compositions involving the Gibbs free energy and pH for each sump condition.

2. Methods and Results

In this section it explains what has been modified on the FORTRAN source in the SOLGASMIX-PV code, which materials and conditions have been contained in some input files, and which results have been drawn from the output file for each input file.

2.1 Modification of SOLGASMIX-PV program

With knowledge of any additives and all species likely to be present, the sump solution pH at equilibrium can be determined by finding the minimum free energy. Free energy minimization, in the sump, is performed using the principal subroutine of the SOLGASMIX-PV code, which has been modified for use in accident sequence calculations [5]. To analyze the sump solution pH, new subroutine for pH calculation has been added on the FORTRAN source in the modified SOLGASMIX-PV code, from which the pH is derived from its definition given by eq. (1)

$$\mathrm{pH} = -\log_{10}(a_{H^+}) = \log_{10}\left(\frac{1}{a_{H^+}}\right) \quad (1),$$

where a_{H^+} is the dimensionless activity of hydrogen ions.

2.2 Verification and Validation

The modified SOLGASMIX-PV code was applied to several chemical systems in which the pH is well known and verified. A comparison of calculated and measured pH values in these systems, given in Table I, shows that this technique is quite effective in yielding good calculated values of pH since each error is within about 0.3 pH unit [2].

Table I: Comparison of measured and calculated pH values

Materials (mol/m^3)	Measured pH	Calculated pH
50.76 NaOH 44.9 H_3BO_3 44.9 H_3PO_4	6.0	6.3
69.7 NaOH 43.0 H_3BO_3 43.0 H_3PO_4	7.0	7.2
83.7 NaOH 41.6 H_3BO_3 41.6 H_3PO_4	8.0	7.7

2.3 Assumptions and Input data for LOCA condition

The sump pH results in this paper are calculated by the conditions based on the following assumptions: A loss-of-coolant accident is postulated as a design basis accident. During a LOCA in a PWR, ECCS provides core cooling to prevent fuel damage and then fission products do not enter containment. The maximum expected re-circulated containment spray solution is composed of the sources of water such as IRWST, reactor coolant system with pressurizer, four Safety Injection Tanks (SITs), Safety Injection System (SIS) piping, and Containment Spray System (CSS) piping. The minimum pH value for the sump solution is calculated with consideration of maximum water source volume and maximum initial boron concentration whose values are 3,367,213 liter and 4,400 ppm respectively at minimum containment temperature of 120℉ (48.89℃). On the other hand, the maximum pH value is calculated with consideration of minimum water source volume and minimum initial boron concentration whose values are 2,452,467 liter and 3,400 ppm respectively at maximum containment temperature of 300℉ (148.89℃). The dissolution rate of TSP is high enough to dissolve all TSP as soon as it is submerged into water.

Under such conditions, input data is written by materials that are introduced into containment as a result of LOCA itself. These materials included in the calculation of pH are listed in Table II.

Table II: Thermodynamic Parameters for Input Species

Species	Coefficient in the expression ΔG^0			
	b ($\times 10^5$)	c ($\times 10^2$)	d ($\times 10^{-1}$)	e ($\times 10^{-4}$)
Ar(g)	0.000	0.000	0.000	0.000
$H_2O(l)$	-2.900	1.920	-0.526	0.0870
Na^+	-2.420	-0.560	-0.434	0.300
H^+	0.000	0.000	0.000	0.000
Cl^-	-1.680	1.540	-2.090	3.660
OH^-	-2.350	3.060	-2.830	4.360
$B(OH)_3$	-10.60	2.780	1.750	-1.020
$B(OH)_4^-$	-13.10	3.910	4.720	-1.170
PO_4^{-3}	-12.80	10.00	-7.970	13.90
HPO_4^{-2}	-12.90	7.430	-4.400	8.150
$H_2PO_4^-$	-12.90	5.580	-1.250	3.030
H_3PO_4	-12.90	9.330	-0.490	-1.220

For all the species, the four coefficients in the expression ΔG^0 for each species are determined by plotting its Gibbs free energy versus temperature and then using cubic regression to find equation for each line. Gibbs free energy information of each species is obtained from the HSC Chemistry 5.1 program and the expression ΔG^0 is of the cubic form given by eq. (2)

$$\Delta G^0\ (J/mole) = b + cT + dT^2 + eT^3 \quad (2),$$

where T is the reaction temperature in K [6].

2.4 Result for Calculated pH values

The pH analysis of the sump solution is performed on following two cases. First, at 322.04K (48.89℃) and 1atm, the minimum pH value is calculated by the constant boron molarity of 0.407 mole/l (4,400ppm) and the time-dependent dissolved TSP molarity up to 0.021075 mole/l. Second, at 422.04K (148.89℃) and 1atm, the maximum pH value is computed by the constant boron molarity of 0.3145 mole/l (3,400ppm) and the time-dependent dissolved TSP molarity up to 0.028937 mole/l. The results of the calculations for such input data are illustrated in Fig. 1, as a graph of the pH value in the sump solution versus the dissolved TSP molarity or the time elapsed after a LOCA.

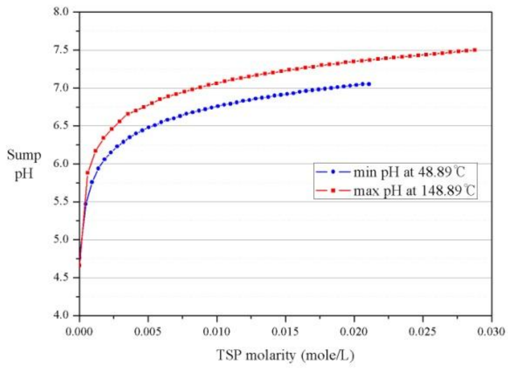

Fig. 1. pH in the recirculation sump solution as a function of the dissolved TSP molarity.

3. Conclusions

As shown in Fig. 1, when all TSP dissolves, the recirculation sump solution pH calculated by the modified SOLGASMIX-PV program is 7.05 for the minimum pH value and 7.51 for the maximum pH value. When the sump water temperature increases, the basicity of the sump solution is stronger. These pH values are satisfied for pH requirements of the Standard Review Plan. In other words, it could say that long-term iodine retention and material compatibility are achieved by these pH values. In addition, for the spray water re-circulated from the containment sump, the higher the pH in the 7.0 to 9.5 range, the greater the assurance that no stress corrosion cracking will occur according to the Standard Review Plan [7].

To assure the more accurate prediction, it is necessary to investigate fission product release rate dependent on the extent of the fuel damage during a LOCA in a PWR and then calculate by the modified SOLGASMIX-PV code applied to the input condition that fission products do enter containment.

REFERENCES

[1] Sang Seob Lee, Sung Hwan Kim, and Kune Yull Suh, The Design Features of the Advanced Power Reactor 1400, Nuclear Engineering and Technology, Vol.41, No.8, p. 995~1004, 2009
[2] E.C. Beahm, R.A. Lorenz, and C.F. Weber, Iodine Evolution and pH Control, NUREG/CR-5950, and ORNL/TM-12242, p. 9, A.3~A.4, 1992
[3] NRC staff, 6.5.2 Containment Spray as a Fission Product Cleanup System-Rev. 4, NUREG-0800, p. 5, 2007
[4] Hyung Won Lee, Yung Hee Kang, and Jae Hee Kim, Analysis of Post-LOCA pH for Korea Nuclear Units, Journal of the Korea Nuclear Society, Vol.15, No.3, p. 179~187, 1983
[5] C.F. Weber and E.C. Beahm, Calculation of pH and Iodine Volatility under Reactor Accident Conditions, ORNL/NRC/LTR-99/3, p. 6~11, 1999
[6] T.M. Besmann, SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical System, ORNL/TM-5775, 1977
[7] NRC staff, Branch Technical Position 6-1 pH For Emergency Coolant Water for Pressurized Water Reactors, NUREG-0800, p. 2, 2007