Theoretical Approach to Calculating the pH When Using Sodium Hydroxide to Prevent the Vaporization of Iodine in Post LOCA

Seung-Ho Lee *, Hyuk-Chul Kwon, Cho-Rong Kim, Da-Seul Ham, Yong-Sang Cho, Kyu-Min Song
Korea Hydro & Nuclear Power Co, Ltd. Central Research Institute
**Corresponding author: Davidlee@khnp.co.kr*

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1. Introduction

In case of an emergency at nuclear power plants, we plan to implement strategies that involve supplying boric acid water to prevent re-criticality caused by external cooling water supplied during accidents. The OPR and APR reactors use tri-sodium phosphate (TSP) for maintaining a neutral-alkaline environment in their coolant chemistry during emergencies; however, there is difficulty in dissolving large amounts of solid TSP before injecting them when using externally supplied cooling water. We have calculated the injection amount and pH values needed for sodium hydroxide, which must be injected as a base chemical to prevent iodine volatilization.

2. Calculation Equation

2.1 Derivation of equation for calculating amount of sodium hydroxide

2.1.1 Ionization constant

(Boric Acid)

$$H_3BO_3 + 2H_2O \overset{K_1}{\rightleftarrows} H_3O+ + B(OH)_4^- \quad (1)$$

$$H_3BO_3 \overset{K_2}{\rightleftarrows} H_3O^+ + B_3O_3(OH)_4^- + H_2O \quad (2)$$

(Sodium Hydroxide)

$$NaOH \overset{K_3}{\rightarrow} Na^+ + OH^- \quad (3)$$

[Water]

$$2H_2O \overset{K_W}{\rightleftarrows} H_3O^+ + OH- \quad (4)$$

(Ionization constant)

$$K_1 = [B(OH)_4^-][H_3O^+] / [H_3BO_3] \quad (5)$$

$$K_2 = [B_3O_3(OH)_4^-][H_3O^+] / [H_3BO_3]^3 \quad (6)$$

$$K_3 = [Na^+][OH^-] / [NaOH] \quad (7)$$

$$K_w = [H3O^+][OH^-] \quad (8)$$

2.1.2 Material Balance

$$[H_3BO_3]_0 = [H_3BO_3] + [B(OH)_4^-] + 3[B_3O_3(OH)_4^-] \quad (9)$$

$$[NaOH]_0 = [Na^+] \quad (10)$$

2.1.3 Charge Balance

$$[Na^+] + [H_3O^+] = [OH^-] + [B(OH)_4^-] + [B_3O_3(OH)_4^-] \quad (11)$$

2.1.4 Solution of Equation

$$[B(OH)_4^-] = K_1 \times [H_3BO_3] / [H_3O^+] \quad (12)$$

$$[B_3O_3(OH)_4^-] = K_2 \times [H_3BO_3]^3 / [H_3O^+] \quad (13)$$

$$[NaOH] = [Na^+][OH^-] / K_3 \quad (14)$$

2.1.5 Determination of $[NaOH]_0$

By substitution of Equation (5), (6) into Eq. (9)

$$[H_3BO_3] = [H_3BO_3]_0/(1+K_1/[H_3O^+]) - 3K_2[H_3BO_3]^3/(K_1+[H_3O^+]) \quad (15)$$

From Eq.(11) and by substitution of Eq. (12), (13), (8)
At pH7, $[H_3O^+] = [OH^-]$

$$[Na^+] = K_1 \times [H_3BO_3]/[H_3O^+] + K_2 \times [H_3BO_3]^3/[H_3O^+] \quad (16)$$

From Equation (10) by (16)

$$[NaOH]_0 = K_1 \times [H_3BO_3]/[H_3O^+] + K_2 \times [H_3BO_3]^3/[H_3O^+] \quad (17)$$

2.1.6 Determination of pH and $[H_3BO_3]$

By substitution of Equation (12), (13) into Eq. (9)

$$[H_3BO_3]_0 = [H_3BO_3] + K_1 \times [H_3BO_3]_0 / [H_3O^+] + 3K_2 \times [H_3BO_3]_0^3 / [H_3O^+] \quad (18)$$

$$[H_3O^+] = (K_1 \cdot [H_3BO_3] + 3K_2 \cdot [H_3BO_3]^3) / ([H_3BO_3]_0 - [H_3BO_3]) \quad (19)$$

From Equation (19)

$$K_2 \cdot [H_3BO_3]^3/[H_3O^+] = (1/3)\{([H_3BO_3]_0 - [H_3BO_3]) K_1 \cdot [H_3BO_3]/[H_3O^+]\} \quad (20)$$

From Equation (21) into (17)

$$[H_3BO_3] = (3([NaOH]_0 - [H_3BO_3]_0)/(2K_1/[H_3O^+] - 1) \qquad (21)$$

2.2 Calculating ionization constants

2.2.1 Water ionization constant(K_w) Calculation

$$Log_{10}K_W = A + BT_{℃} + CT_{℃}^2 + DT_{℃}^3 + ET_{℃}^4$$

Temperature coefficient[1] : A=-14.9378, B=.0424044
C=-2.10252E-4, D=6.22026E-7, E=-8.73826E-10

2.2.2 Boric acid ionization constant(K_1, K_2) Calculation

$$K_1 = [B(OH)_4^-][H_3O^+] / [H_3BO_3]$$

$$Log_{10}K_1 = A/T + B + CT + Dlog_{10}T$$

T : Kelvin temperature

Temperature coefficient[1] : A=1573.21, B=28.6059, C=.012078, D=-13.2258

$$K_2 = [B_3(OH)_4^-]/[OH^-] \times [B(OH)_3]^3$$

$$Log_{10}K_1 = A/T + B + CT + Dlog_{10}T$$

Temperature coefficient[1] : A=3339.5, B=-8.084, D=1.497

2.2.3 NaOH ionization constant(K_3) Calculation

$$K_3 = [Na^+][OH^-] / [NaOH]$$

$$Log_{10}K_3 = A/T - B - CT + Dlog_{10}T – E/T^2 – log_{10}K_w$$

Temperature coefficient[1] : A=132570, B=221175, C=.288747, D=-784227, E=9033430

3. Calculation and Test Result

3.1 Calculation condition and Result

- External Raw Water : 5,700 m^3 /503 ppm
- Target pH : 7.0
- Start Value : $[NaOH]_0$ = 0.0001 mole/l
- Adding 100% NaOH
- Calculate repeatedly Eq.17, Eq19, Eq21
- Calculation result : 100.07 Kg
  (45% NaOH 222.37 Kg)

3.2 Lab Test Condition and Result

- pH Titration Test Result : 0.1N NaOH 16.8g
  Boric Acid 4 L(C_B 500 ppm)
  Adding 0.1N NaOH and pH Measurement
- 0.1N NaOH 16.8 g(4L Boric Acid) is converting 45% NaOH 255.36 Kg(Boric acid water 5,700 m^3)

Table1. NaOH Calculation Result

$NaOH_0$	*H_3BO_3*	*NaOH*	*H_3O^+*	*pH*
(Mole/l)	*(Mole/l)*	*(Kg)*	*(Mole/l)*	*-*
0.0001	*4.700E-02*	*103.05*	*9.34E-08*	*7.03*
0.000452	*4.592E-02*	*99.95*	*1.00E-07*	*6.99*
0.0004384	*4.596E-02*	*100.07*	*1.00E-07*	*7.00*
0.0004389	*4.596E-02*	*100.07*	*1.00E-07*	*7.00*
0.0004389	*4.596E-02*	*100.07*	*1.00E-07*	*7.00*
0.0004389	*4.596E-02*	*100.07*	*1.00E-07*	*7.00*

Table2. NaOH Lab Test Result

Add(g)	*Accum(g)*	*pH*	*Temp(℃)*
0	*0*	*5.24*	*47.3*
10	*10*	*6.77*	*46.9*
1	*11*	*6.82*	*46.8*
1	*12*	*6.86*	*46.9*
2	*14*	*6.92*	*46.8*
2	*16*	*6.98*	*46.6*
0.1	*16.1*	*6.98*	*46.6*
0.2	*16.3*	*6.98*	*46.4*
0.5	*16.8*	*7.00*	*46.4*
1.6	*18.4*	*7.04*	*46.3*

4. Conclusion & Future works

The pH and injection amounts for the use of sodium hydroxide in the Post-LOCA were calculated and the difference between the calculated value and the lab test value was confirmed.

The main cause of difference is expected to be due to the difference from the lab test temperature and calculation temperature condition, using the ionization constant as a constant value at 25℃ for repeated calculation.

Comparing the results of calculating the acid-reduce neutralization of various methods, the accuracy of the repeatedly calculation equation is evaluated to be relatively high, but it is necessary to establish the equation corresponding to the temperature change.

REFERENCES

[1] EPRI, MULTEQ Version 9.0 (Equilibrium of an Electrolytic Solution with Vapor-Liquid Partitioning and Precipitation – The Database), TR-3002013656, p. 2, 122~126, 2018.