MCB Issues List APR1400, FSAR SECTION 6.5.2

Issue #1(6-18.1)

In APR1400 FSAR Section 6.5.2.3.2, the applicant describes the Containment Spray pH control. The applicant states that the calculations show that the pH in the in-containment refueling storage tank (IRWST) will reach a pH of 7.0 by 157 minutes after a DBA. However, there is no information on the initial pH of the IRWST.

Provide additional information that identifies the initial pH of the IRWST and explains the initial scenario before the DBA.

Response

The calculation assumes that all the water from the IRWST, RCS (including the pressurizer), 4 SITs, and SI and CS pipes accumulate in the IRWST with a maximum initial boron concentration of 4400 ppm immediately after the LOCA, as described in section 1 of the appendix to this response. At this initial condition, the pH in the IRWST is approximately 4.15.

Impact on DCD

There is no impact on the DCD.

Impact on PRA

There is no impact on the PRA model.

Impact on Technical Specifications

There is no impact on the Technical Specifications.

Impact on Technical/Topical/Environmental Reports

There is no impact on any Technical, Topical, or Environmental Report.

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Issue #2(6-18.2)

Although the timing of the pH rising above 7 appears reasonable and in agreement with Standard Review Plan (SRP) Section 6.5.2 recommendations, the staff will need to corroborate this timing with the applicant's calculation. To do so, the staff requires additional information regarding the applicant's calculations and modeling assumptions which support the determination of how pH changes with time.

Explain in more detail how the evolution of pH was modeled and supply specific details of the pH calculation (e.g., actual calculations, assumptions, pH/time graphs). Please include technical justification for all of the assumptions and details of the specific methodology being used. If a technical report which contains this information already exists, the applicant may choose to provide it to the staff in response to this issue.

Response

The general procedure to determine the time-dependent minimum pH is summarized as follows:

- Determine the maximum volume of water, including inventory of the IRWST, RCS, SITs, CCS, and related piping, and adjust the water volume to account for the peak containment design temperature.

- Determine the maximum boron concentration in the water sources.

- Calculate the time-dependent molarity (mole/liter of water) of TSP dissolved in the water sources. It is assumed that TSP dissolves in water as soon as it is submerged in the HVT. The dissolution of the TSP is uniform and constant during the time required to recirculate the total volume of the water source (1 turn recirculation).

- Calculate the time-dependent pH of the water sources in the IRWST.

- Check that the pH in the water sources reach and remain over 7.0 during long-term cooling operation.

Details of the methodology for the pH calculations in the IRWST are indicated in the appendix to this response.

Impact on DCD
There is no impact on the DCD.

Impact on PRA
There is no impact on the PRA model.

Impact on Technical Specifications
There is no impact on the Technical Specifications.

Impact on Technical/Topical/Environmental Reports
There is no impact on any Technical, Topical, or Environmental Report.

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Appendix

For the responses to issue #1 and #2, the methodology of the pH calculation is summarized as follows;

1. Assumptions

The assumptions for the time-dependent pH analysis are as follows;

- A Large Break LOCA is postulated as a design basis accident, and the CS pumps operate just after accident initiation, without any time delay.

- After the LOCA, the following sources of water combine to form the maximum expected volume of containment spray solution.

    · In-containment Refueling Water Storage Tank (IRWST)

    · Reactor Coolant System, including the pressurizer

    · 4 Safety Injection Tanks (SIT)

    · Safety Injection System (SI) Piping

    · Containment Spray System (CS) Piping

- The minimum pH value is calculated with consideration of the maximum water source volume and the maximum initial boron concentration (4400 ppm).

- The dissolution rate of TSP is high enough to dissolve all TSP as soon as it is submerged into water. For the time-dependent pH calculation, it is assumed that the TSP dissolution rate is constant and independent of the pH value, and that TSP dissolves into the IRWST water uniformly over the time required to pump the maximum recirculated spray solution through one CS pump.

- It is assumed that the water from the RCS and the containment spray enter the IRWST through the HVT 10 minutes after the LOCS (filling time with one CS pump running).
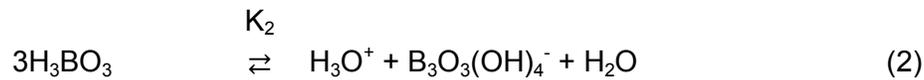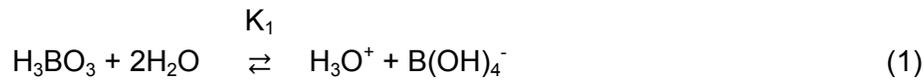
2. Main Equations

The equations used to solve the acid and base equilibrium problem are as follows:
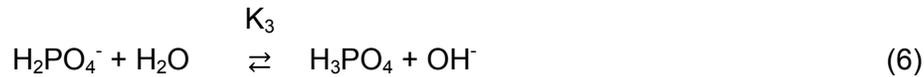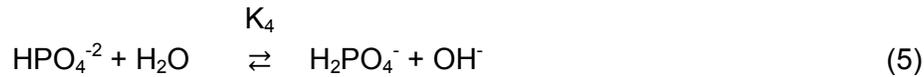
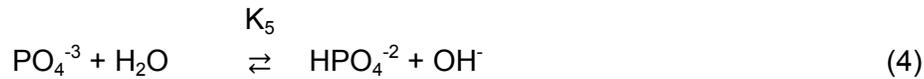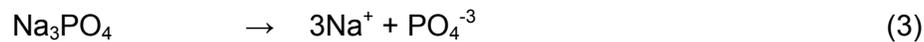### 1) Chemical Reaction Form

Basic equations to calculate pH between TSP and Boric Acid are arranged as follows;

<u>Boric Acid</u>

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

$$3H_3BO_3 \quad \overset{K_2}{\rightleftarrows} \quad H_3O^+ + B_3O_3(OH)_4^- + H_2O \tag{2}$$

<u>Trisodium Phosphate</u>

$$Na_3PO_4 \quad \rightarrow \quad 3Na^+ + PO_4^{-3} \tag{3}$$

$$PO_4^{-3} + H_2O \quad \overset{K_5}{\rightleftarrows} \quad HPO_4^{-2} + OH^- \tag{4}$$

$$HPO_4^{-2} + H_2O \quad \overset{K_4}{\rightleftarrows} \quad H_2PO_4^- + OH^- \tag{5}$$

$$H_2PO_4^- + H_2O \quad \overset{K_3}{\rightleftarrows} \quad H_3PO_4 + OH^- \tag{6}$$

<u>Water</u>

$$2H_2O \quad \overset{K_W}{\rightleftarrows} \quad H_3O^+ + OH^- \tag{7}$$

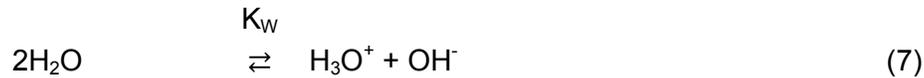### 2) Equilibrium Equation

By using the basic equations, 3 kinds of equilibrium equations are given as follows:

· **By Ionization Constant**

$$\frac{[H_3O^+][B(OH)_4^-]}{[H_3BO_3]} \quad = \quad K_1 \qquad\qquad (8)$$

$$\frac{[H_3O^+][B_3O_3(OH)_4^-]}{[H_3BO_3]^3} \quad = \quad K_2 \qquad\qquad (9)$$

$$\frac{[HPO_4^{-2}][OH^-]}{[PO_4^{-3}]} \quad = \quad \frac{K_w}{K_5} \qquad\qquad (10)$$

$$\frac{[H_2PO_4^-][OH^-]}{[HPO_4^{-2}]} \quad = \quad \frac{K_w}{K_4} \qquad\qquad (11)$$

$$\frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]} \quad = \quad \frac{K_w}{K_3} \qquad\qquad (12)$$

$$[H_3O^+][OH^-] \quad = \quad K_w \qquad\qquad (13)$$

· **By Material Balance**

Using Equations (1) and (2),

$$[H_3BO_3]_0 \quad = \quad [H_3BO_3]+[B(OH)_4^-]+3[B_3O_3(OH)_4^-] \qquad (14)$$

From Equation (3) to (6),

$$[Na_3PO_4]_0 \quad = \quad [PO_4^{-3}] + [HPO_4^{-2}]+[H_2PO_4^-]+ [H_3PO_4] \qquad (15)$$

$$[Na_3PO_4]_0 \quad = \quad \frac{1}{3}[Na^+] \qquad\qquad (16)$$

· **By Charge Balance**

From Equation (1) to (7),

$$[H_3O^+]+[Na^+] \quad = \quad [OH^-]+ [B(OH)_4^-]+[B_3O_3(OH)_4^-]+ \qquad (17)$$

$$3[PO_4^{-3}]+2[HPO_4^{-2}]+[H_2PO_4^-]$$

where,

K_1	:	First Ionization(or Dissociation) Constant of Boric Acid
K_2	:	Second Ionization Constant of Boric Acid
K_3	:	First Ionization Constant of Phospheric Acid
K_4	:	Second Ionization Constant of Phospheric Acid
K_5	:	Third Ionization Constant of Phospheric Acid
K_w	:	Ionization Constant of Water
$[A]$	:	Molar Concentration of a Particular Ion A in Equilibrium
$[A]_o$	:	Initial Molar Concentration of A

3) Governing Equations

Equations (18) and (19), shown below, are derived by equations (1) through (17) as follows:

$$[H_3O^+]=\frac{K_1[H_3BO_3]+3K_2[H_3BO_3]^3}{[H_3BO_3]_0-[H_3BO_3]} \qquad (18)$$

$$[H_3BO_3]=\frac{3}{\left(1-\dfrac{2K_1}{[H_3O^+]}\right)}\left(\frac{[H_3BO_3]_0}{3}+\frac{K_w}{[H_3O^+]}-[H_3O^+]-\mathbf{A}\right) \qquad (19)$$

Where,

$$\mathbf{A}=(\frac{K_3K_4[H_3O^+]+2K_3[H_3O^+]^2+3[H_3O^+]^3}{K_3K_4K_5+K_3K_4[H_3O^+]+K_3[H_3O^+]^2+[H_3O^+]^3})\,[Na_3PO_4]_0$$

Equation (18) is the correlation equation between molarity of the boric acid and TSP based on fixed pH values in step i, and equation (19) is the equation to evaluate the new pH in step i+1 by using molarity of boric acid given from equation (18).

3. Molarity of TSP in the IRWST

The amount of TSP which dissolves in recirculated spray solution per minute can be expressed as follows:

$$M(t) = 0 \qquad\qquad (t < \Delta T_2) \qquad\qquad (20)$$

$$M(t) = M_{TSP} \times (t - \Delta T_2)/\Delta T_1 \qquad (\Delta T_2 \leq t < \Delta T_2 + \Delta T_1) \qquad (21)$$

$$M(t) = M_{TSP} \qquad\qquad (t \geq \Delta T_2 + \Delta T_1) \qquad\qquad (22)$$

where,

$M(t)$ = mass of TSP dissolved in IRWST water at time t (grams)

M_{TSP} = total mass of TSP stored in the HVT (grams)

t = time after LOCA (minute)

ΔT_1 = time required to pump the total water volume through a CS pump (180 minute)

ΔT_2 = delay time for RCS water to enter into the IRWST after LOCA

(HVT is filled with RCS water for 10 minute after LOCA)

The concentration of dissolved TSP in recirculated spray water can be expressed as follows.

$$Mol(t) = 0 \qquad\qquad (t < \Delta T_2) \qquad\qquad (23)$$

$$Mol(t) = \frac{M_{TSP}}{MW_{TSP} V_{WATER}} \frac{(t - \Delta T_2)}{\Delta T_1} \qquad (\Delta T_2 \leq t < \Delta T_2 + \Delta T_1) \qquad (24)$$

$$Mol(t) = \frac{M_{TSP}}{MW_{TSP} V_{WATER}} \qquad\qquad (t \geq \Delta T_2 + \Delta T_1) \qquad\qquad (25)$$

where,

$Mol(t)$ = molarity of TSP in water source at time t (mole/liter)

MW_{TSP} = molecular weight of TSP (= 380.12 grams/mole)

V_{WATER} = water volume (liter)

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The TSP concentration in the IRWST based on the equations (23) through (25) is increased linearly as shown in Figure 1, and the pH is determined according to Section 4.
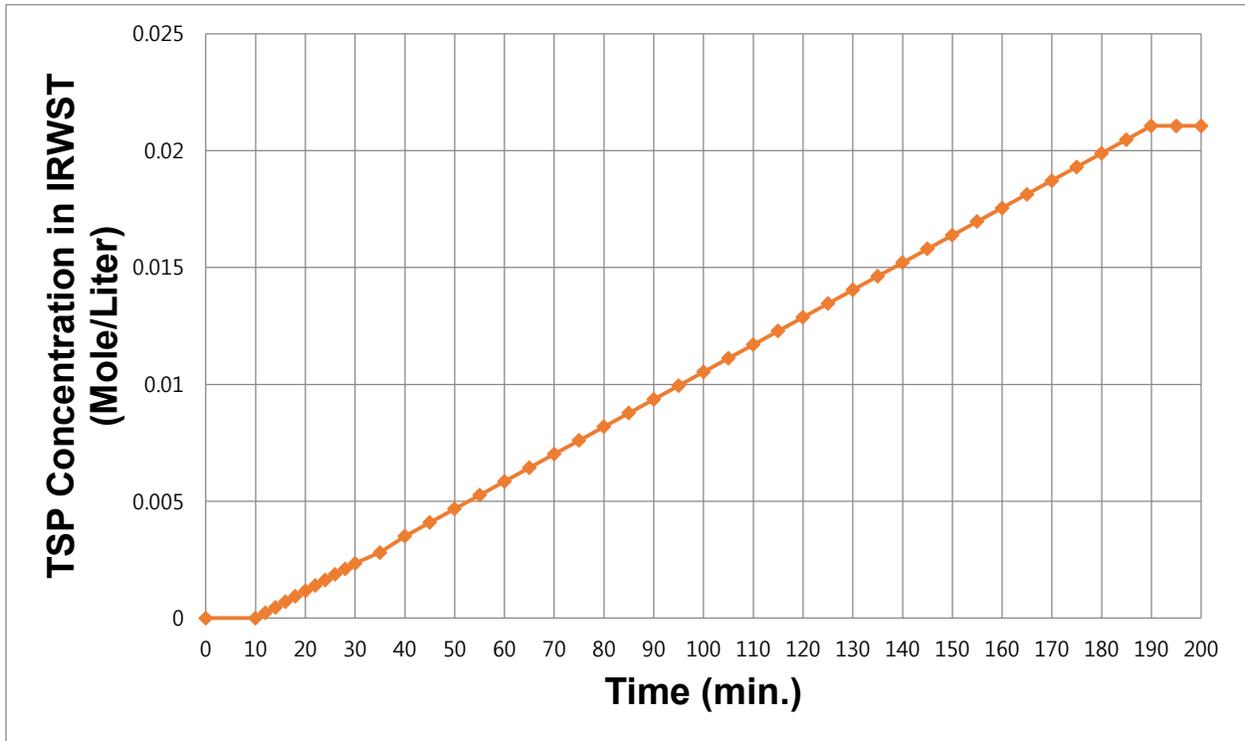

Figure 1 Variation of the TSP concentration in the IRWST after LOCA

4. pH calculation

The calculation procedure to determine the pH in the IRWST based on the concentration of TSP and Boric acid at each time step is as follow;

    Ⓐ Calculate the TSP molarity $[Na_3PO_4]_o$,t at time t

    Ⓑ Assume a trial value for $[H_3BO_3]_i$ (approximately $[H_3BO_3]_o$)

    Ⓒ Calculate $[H_3O^+]_i$ by equation (18)

    Ⓓ Calculate $[H_3BO_3]_{i+1}$ by equation (19)

    Ⓔ Calculate $[H_3O^+]_{i+1}$ by equation (18)

    Ⓕ Calculate the relative uncertainty = { $[H_3BO_3]_i$ - $[H_3BO_3]_{i+1}$ } / $[H_3BO_3]_i$

    Ⓖ Determine the new $[H_3BO_3]_i$ = { $[H_3BO_3]_i$ + $[H_3BO_3]_{i+1}$} / 2

Repeat steps Ⓑ through Ⓖ until the relative uncertainty falls below 1.0×10^{-5}. Equations (18) and (19) are solved to get the unknown values of H_3BO_3 and H_3O^+ by the iteration method described above.

Using the calculated molarity of $H3O^+$, pH can be calculated with the following equation. Results are shown in Section 5.

$$pH = - \log_{10} [H_3O^+].$$

5. Results

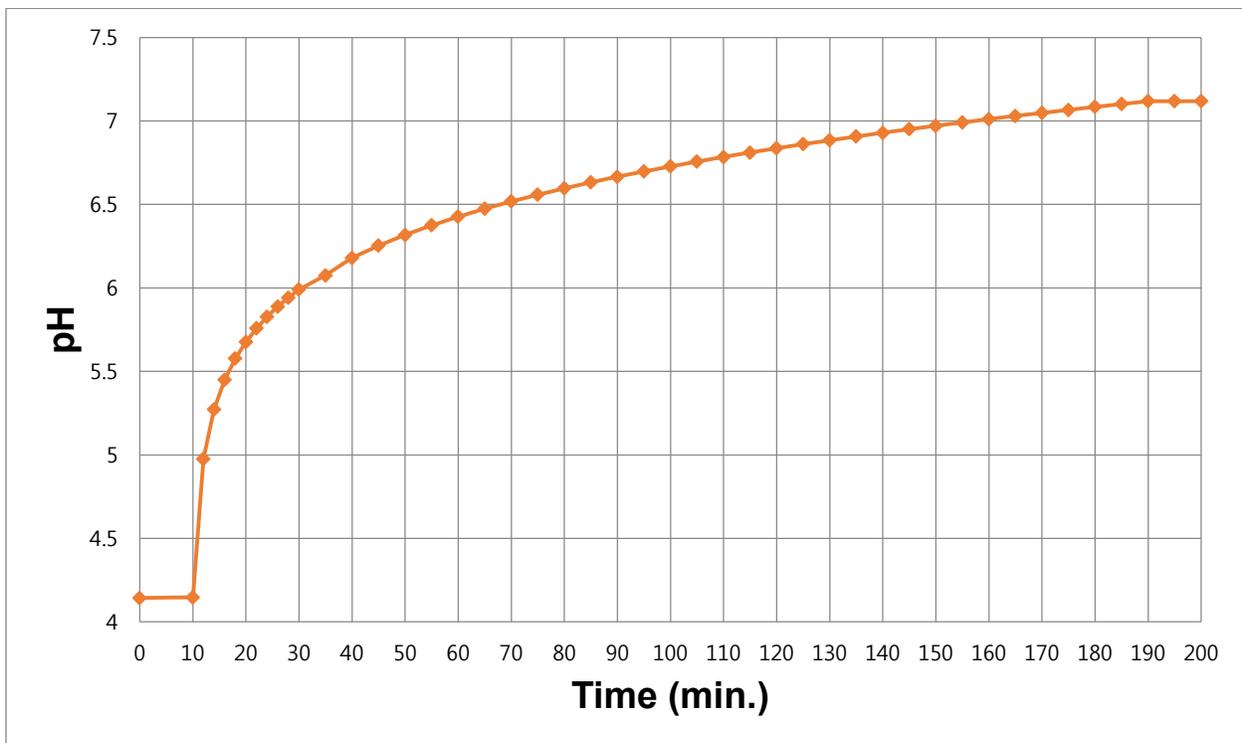The calculation results of the minimum pH value as a function of time are shown in Figure 2. The pH reaches 7 at 157 minutes after the LOCA.

Figure 2 Time Dependent pH Calculation