

SHEARON HARRIS NUCLEAR POWER PLANT, UNIT NO. 1
DOCKET NO. 50-400/RENEWED LICENSE NO. NPF-63
APPLICATION FOR REVISION TO TECHNICAL SPECIFICATION
CONTAINMENT SPRAY EDUCTOR FLOW RATES

“HNP CSAT VOLUME, FLOW AND NaOH CONCENTRATION RANGE REVISIONS”

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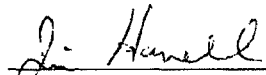
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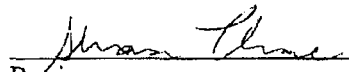
The purpose of this report is to summarize the inputs, analyses and results associated with the proposed Harris Nuclear Plant Containment Spray Additive Tank (CSAT) maximum volume, eductor test flow range and sodium hydroxide concentration range revisions. The proposed maximum contained NaOH solution volume is 3768 gallons. The proposed eductor test flow range is 17.2 gpm to 22.2 gpm. The proposed NaOH concentration range in the CSAT is 27 weight % to 29 weight %.



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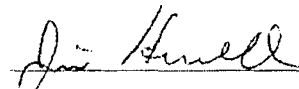
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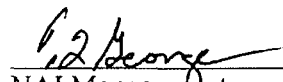
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Project Documentation Checklist:

- Project QA Requirements Form.
- Project QA Plan.
- Project Organization.
- Project Work Scope and Design Plan.
- Project Calculation and Document Index including a listing for this report.
- Project Engineer Training and Qualification Forms for engineers involved with this report.
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- Supporting documents reviewed and signed.
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1. Purpose

The purpose of this report is to summarize the inputs, analyses and results associated with the proposed Harris Nuclear Plant Containment Spray Additive Tank (CSAT) maximum volume, eductor test flow range and sodium hydroxide concentration range revisions. The proposed maximum contained NaOH solution volume is 3768 gallons. The proposed eductor test flow range is 17.2 gpm to 22.2 gpm. The proposed NaOH concentration range in the CSAT is 27 weight % to 29 weight %.

2. Background and Introduction

Currently the Shearon Harris Unit 1 Technical Specification Surveillance Requirements (Reference [10.22], Section 4.6.2.2.d) for the Containment Spray Additive System require that the eductor flow rate using the RWST as a test source be between 19.5 gpm and 20.5 gpm. This test range is very restrictive when uncertainties are considered. This test range is based in part on an historical requirement that the containment spray and sump pH both be greater than or equal 8.5 at the end of NaOH addition. Based on more recent data and regulatory documents (References [10.9], [10.13] and [10.20]), the historical pH requirement of 8.5 for the containment spray and sump is no longer applicable.

Additionally, the original pH analyses for Harris Nuclear Plant were performed utilizing boric acid equilibria data from a paper presented by R.E. Mesmer in 1971 (Reference [10.21]), which included minor errors. In order to correct the minor errors and to properly consider ionic strength dependence, the boric acid equilibria data of D.A. Palmer et. al. (Reference [10.2]) are utilized for the analyses supporting the proposed changes.

The currently applicable pH requirements for the Harris Nuclear Plant are based on prevention of iodine re-evolution, corrosion considerations and precipitate formation. These requirements dictate that the equilibrium containment sump pH be greater than 7 at the onset of the spray recirculation mode (Reference [10.20]) and that the maximum containment spray and sump pH profiles do not cause an increase in the mass of precipitates previously evaluated for Harris Nuclear Plant. The proposed eductor flow rate range (with the RWST as a test source), along with the other proposed changes, will assure these requirements are met.

3. Results

The key pH results are documented in Table 1, Figure 1, Figure 2 and Figure 3. The results indicate that a CSAT concentration range of 27 wt.% to 29 wt.% NaOH with a CSAT volume range of 3268 gallons to 3768 gallons produces acceptable pH results. Acceptable pH results are defined as the containment sump minimum pH exceeding 7 by the time of recirculation to prevent iodine re-evolution and the containment sump and spray maximum pH profiles resulting in acceptable levels of precipitates as determined in Reference [10.19].

Table 2 presents a comparison of the current licensing basis/tested precipitate amounts with those resulting from the proposed changes. The precipitate amounts resulting from the proposed changes are less than the currently analyzed/tested precipitate amounts. Table 3 presents the new test values for eductor flow rates. These values are based on the proposed changes and result in acceptable pH values.

4. Proposed Technical Specification Revisions

The analyses discussed in this report consider and support the following Technical Specification revisions to Reference [10.22] (revisions are in **bold and underlined**):

CONTAINMENT SYSTEMS

SPRAY ADDITIVE SYSTEM

LIMITING CONDITION FOR OPERATION

3.6.2.2 The Spray Additive System shall be OPERABLE with:

- a. A Spray Additive Tank containing between **27** and **29** weight % NaOH and a contained volume of between 3268 and **3768** gallons ~~which will be ensured by maintaining an indicated level between 90.7% and 93.9%~~, and
- b. Two spray additive eductors each capable of adding NaOH solution from the chemical additive tank to a Containment Spray System pump flow.

APPLICABILITY: MODES 1, 2, 3, and 4.

ACTION:

With the Spray Additive System inoperable, restore the system to OPERABLE status within 72 hours or be in at least HOT STANDBY within the next 6 hours; restore the Spray Additive System to OPERABLE status within the next 48 hours or be in COLD SHUTDOWN within the following 30 hours.

SURVEILLANCE REQUIREMENTS

4.6.2.2 The Spray Additive System shall be demonstrated OPERABLE:

- a. At least once per 31 days by verifying that each valve (manual, power-operated, or automatic) in the flow path that is not locked, sealed, or otherwise secured in position, is in its correct position;
- b. At least once per 6 months by:
 1. Verifying the contained solution volume in the tank, and
 2. Verifying the concentration of the NaOH solution by chemical analysis.
- c. At least once per 18 months by verifying that each automatic valve in the flow path actuates to its correct position on a containment spray or containment isolation phase A test signal as applicable; and
- d. At least once per 5 years by verifying each eductor flow rate is between **17.2** and **22.2** gpm, using the RWST as test source containing at least 436,000 gallons of water.



Table 1: Maximum and Minimum pH Results for HNP Cases

Case	Time of Recirc (sec)	pH at Recirc	Time of Maximum pH (sec)	Maximum pH
Minimum Sump pH w/A train running	1973	7.146	17538	8.505
Spray A Minimum pH	1973	8.276	17538	9.107
Minimum Sump pH w/B train running	1973	7.196	17742	8.505
Spray B Minimum pH	1973	8.365	17742	9.077
Maximum Sump pH – 77F	1557	7.898	8237	9.420
Spray A Maximum pH – 77F	1557	9.014	8237	10.578
Spray B Maximum pH – 77F	1557	8.936	8237	10.433

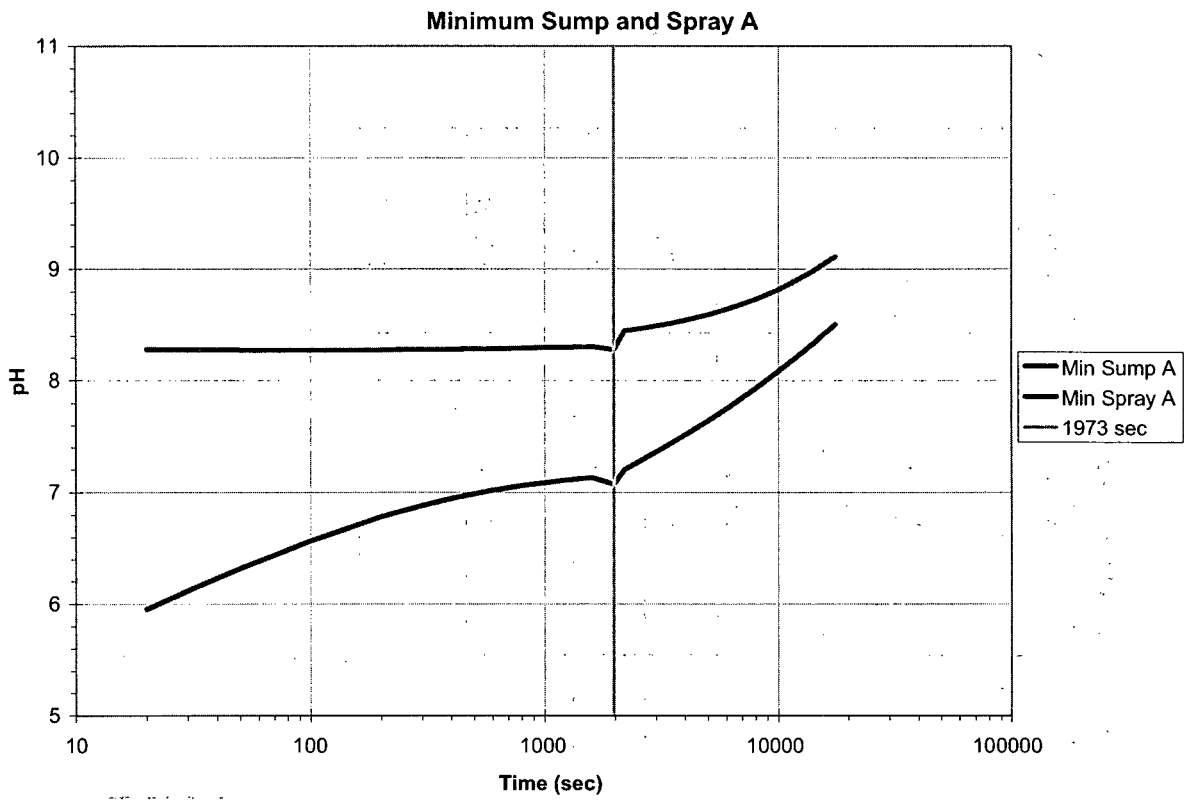


Figure 1: Minimum Sump and Spray A pH profile

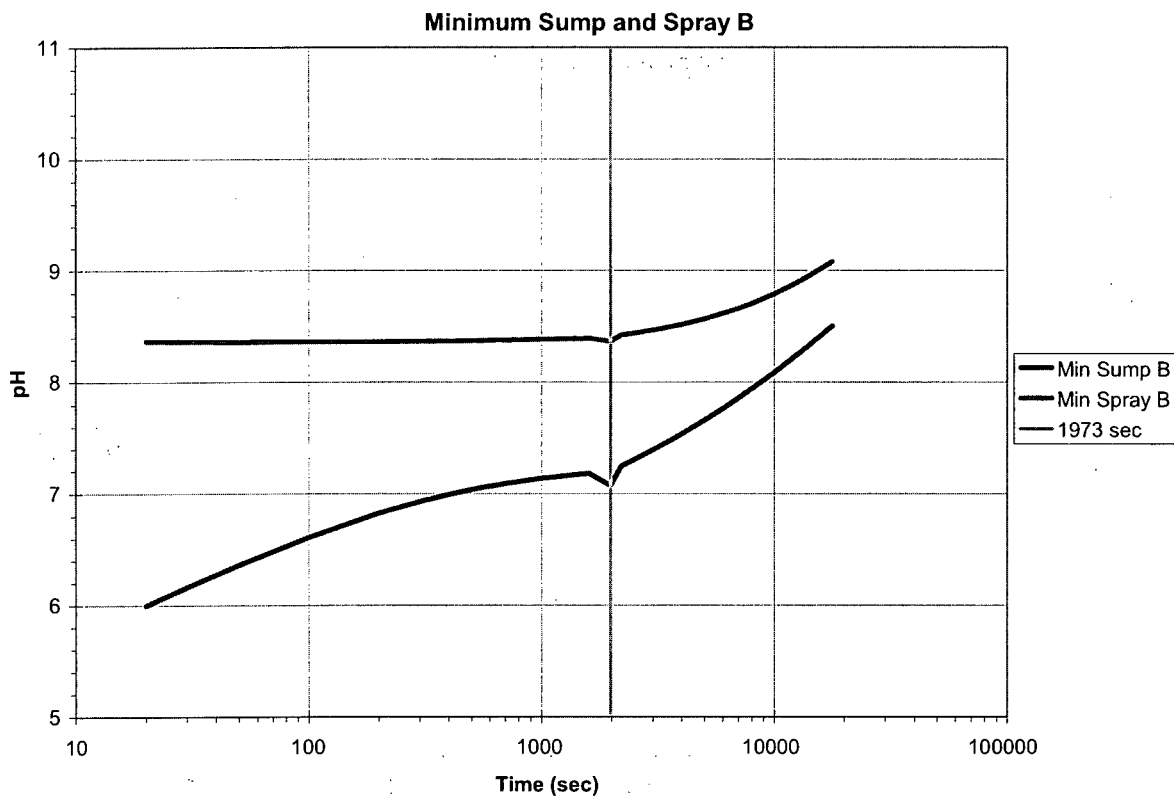


Figure 2: Minimum Sump and Spray B pH profile

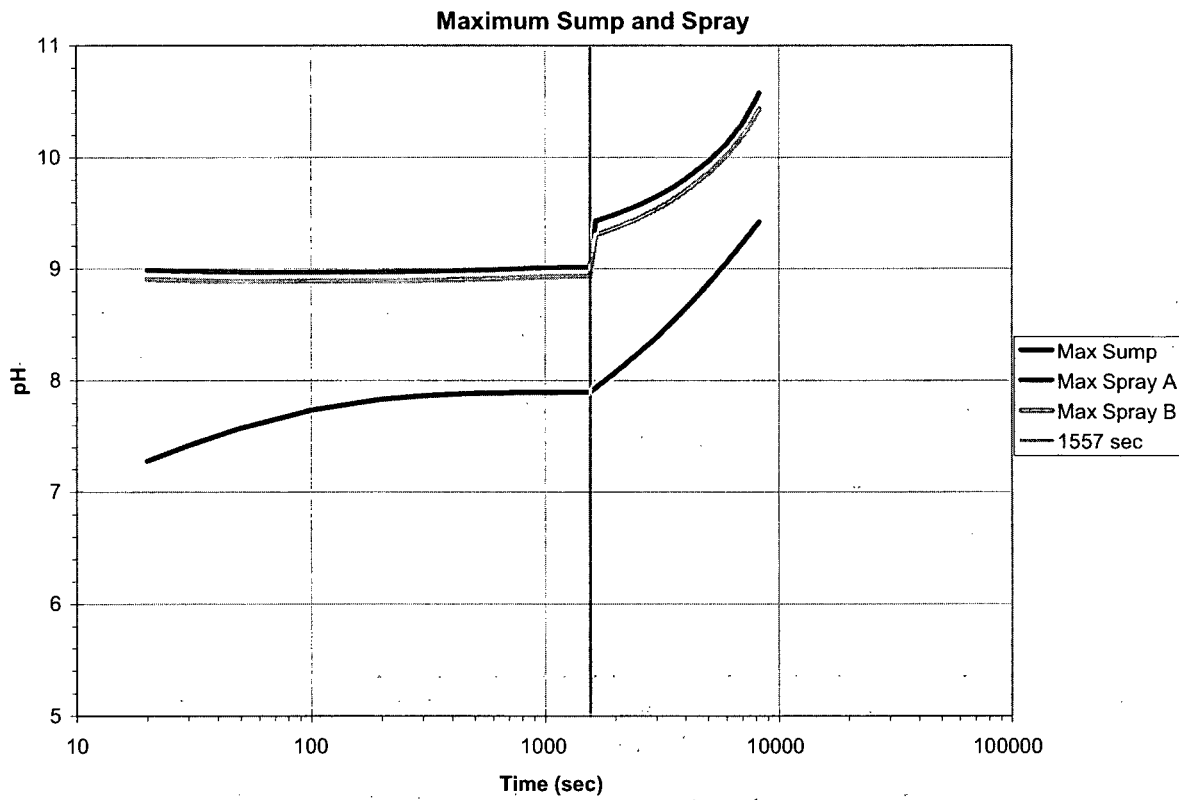


Figure 3: Maximum Sump and Spray pH profile



Table 2: Chemical Precipitates with Proposed Revisions

Break Location	NaS (kg)	AlOOH (kg)
RCS Loop (fiberglass the dominant debris species)	107.40 (108.72)	0.00 (0.00)
RV nozzle (Microtherm the dominant debris species)	35.52 (35.53)	10.97 (11.33)
PZR Safety Line (Min-K the dominant debris species)	33.80 (33.81)	11.16 (11.52)

Note: Current licensing/design basis and tested values in parentheses.

Table 3: Eductor Flow Rate Proposed Technical Specification Test Values

	Train A	Train B
Minimum test flow	17.2 gpm	17.2 gpm*
Maximum test flow	22.2 gpm	22.2 gpm

* The Train B analysis actually supports a slightly lower value based on system configuration, but the more limiting Train A value is utilized.

5. pH Methodology

5.1 pH Calculations

The hydrogen ion concentration ($[H^+]$) in a solution is measured using the pH scale where:

$$pH = -\log([H^+]) \quad (1)$$

The concentration of hydrogen ions is based on the relative concentrations of acids and bases and other ions in the solution. For evaluating the post-LOCA sump pH the following chemical compounds are considered:

- Boron/Boric acid (B and $B(OH)_3$)
- Sodium Hydroxide (NaOH)
- Hydrochloric acid (HCl)
- Nitric acid (HNO_3)
- Hydriodic Acid (HI)
- Cesium Hydroxide (CsOH)

The minor contributions from any other acidic and basic species are assumed to offset and are negligible compared to the chemicals above. The boron/boric acid is introduced to the sump due to the borated water from the RCS, RWST, and accumulators which travels to the sump following a LOCA. In order to offset the effect of the boric acid, sodium hydroxide is added to the containment spray and then the sump to act as a buffer and raise the pH to 7.0. Hydrochloric acid is generated as a result of the irradiation of the cable insulation in containment and tends to reduce the sump pH. Nitric acid is formed due to the irradiation of water in the sump and also decreases the pH. Hydriodic acid is an iodine chemical form that may be released in containment after a LOCA. Cesium hydroxide is a cesium chemical form that may be released in containment after a LOCA. The relative concentration of these chemical species impacts the resulting sump pH.

The following sections provide the method for determining the pH of a solution with the chemical species identified above.

5.1.1 Conservation laws

In order to determine the equilibrium conditions for a solution two general relationships are utilized. The law of conservation of charge and law(s) of conservation of mass can be combined into a single proton balance equation. This equation can be solved to determine $[H^+]$ and the resulting pH of the solution.

In general, a solution is macroscopically electro-neutral (law of conservation of charge). Thus, the sum of all cations and anions in the solution is zero. This relationship can be described mathematically for species A^- , B^{2-} , C^+ , and D^{2+} as:



$$(-1)[A^-] + (-2)[B^{2-}] + (+1)[C^+] + (+2)[D^{2+}] = 0 \quad (2)$$

In a given solution, the mass of a single atomic species must also be conserved. For example, given an acid, HA , with a known stoichiometric concentration, C , the mass conservative law is written as:

$$[HA] + [A^-] = C \quad (3)$$

This equation conserves the quantity of $[A^-]$ ions in the solution.

5.1.2 Equilibrium constants

Many chemical species reach an equilibrium which takes the following form:



For such chemical species, the mass action law specifies that a fixed relationship exists between the concentrations of the chemicals and their stoichiometric coefficients. This law can be written in equation form as:

$$K = \frac{[A]^a [B]^b [C]^c}{[X]^x [Y]^y [Z]^z} \quad (5)$$

where K is defined as the equilibrium constant. For the example acid, HA , the equilibrium equation and mass action law can be written as:



$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (7)$$

5.1.3 Activity coefficients

Direct use of the mass action law omits the impact of the interaction of solute particles on the equilibrium of the solution. To account for this interaction, an activity coefficient, γ , is introduced which accounts for these effects on the equilibrium constant. The individual activity coefficients are based on the ionic strength of the solution, I , which is defined as:

$$I = \frac{1}{2} \sum_i z_i^2 C_i \quad (8)$$

where z_i is the ionic charge and C_i is the concentration of the ion.

The Debye-Hückel equation (p. 1.300 of Reference [10.5]) provides the activity for an ion of a specific valency (charge), z_i , ionic radius, a_i , and solution ionic strength, I , as:

$$\log(\gamma) = \frac{-Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} \quad (9)$$

These activity coefficients are included in the equilibrium equations which define the dissociation constants. For the example acid, HA , the dissociation constant from equation (7) is rewritten in the following manner:

$$K_a = \frac{\gamma_{H^+} [H^+] \gamma_{A^-} [A^-]}{\gamma_{HA} [HA]} \quad (10)$$

5.1.4 Water speciation

The equilibrium constant for water, K_w , is typically defined assuming the concentration of water is constant. Thus, the equilibrium equation and equilibrium constant can be defined as:



$$K_w = [H^+] [OH^-] \quad (12)$$

As with other equilibrium constants, the value is dependent on temperature and ionic strength based on the activity coefficient. Thus, the equilibrium constant is rewritten as:

$$K_w = \gamma_{H^+} [H^+] \gamma_{OH^-} [OH^-] \quad (13)$$

5.1.5 Boron/boric acid speciation

Using simple dissociation constants for boric acid from literature does not account for polyborate species that typically form in borated water buffers. In order to determine the equilibrium concentrations of the boron species, equilibrium quotients from experimental data are utilized for this analysis. Reference [10.2] considers the formation of the following polymeric boric acid species: $B(OH)_3$, $B(OH)_4^-$, $B_2(OH)_7^-$, $B_3(OH)_{10}^-$, $B_4(OH)_{14}^{2-}$. The general form of the equilibrium equation for the polymeric species formed by the boric acid is given below:



The molal equilibrium constant, $Q_{x,y}$, is defined for the above equation as:

$$Q_{x,y} = \frac{[B_x(OH)_{3x+y}^{y-}]}{[B(OH)_3]^x [OH^-]^y} \quad (15)$$

The equilibrium equation and molal equilibrium quotients from Reference [10.2] are given below for each of the species considered. Additionally, the temperature and ionic strength dependent correlations for each of the equilibrium quotients are provided from Reference [10.2].

Species (1,1)



$$Q_{1,1} = \frac{[B(OH)_4^-]}{[B(OH)_3][OH^-]} \quad (17)$$

$$\log(Q_{1,1}) = p_1 + \frac{p_2}{T} + p_3 \log(T) + (p_4 + p_5 T) \log(\rho_w) - p_6 I - \frac{p_7 I(f_i)}{T} + p_8 I^2 \log(\rho_w)$$

$$f_i = \frac{1 - (1 + 2\sqrt{I} \exp(-2\sqrt{I}))}{2I} \quad (18)$$

where T is temperature in Kelvin, ρ_w is the density of water, I is the ionic strength, and p_1 - p_8 are the parameters listed in Table 4.

Table 4: Parameters for $\log(Q_{x,y})$ equations.

Parameters	Values
p_1	-36.2605
p_2	3645.18
p_3	11.6402
p_4	16.4914
p_5	-0.023917
p_6	0.11902
p_7	36.3613
p_8	0.72132

Species (2,1)



$$Q_{2,1} = \frac{[B_2(OH)_7^-]}{[B(OH)_3]^2 [OH^-]} \quad (20)$$

$$\log(Q_{2,1}) = -3.935 + \frac{1780.5}{T} + 0.95183 \log(T) + p_6 I + \frac{p_7 I(f_i)}{T} + p_8 I^2 \log(\rho_w) \quad (21)$$

Species (3,1)



$$Q_{3,1} = \frac{[B_3(OH)_{10}^-]}{[B(OH)_3]^3 [OH^-]} \quad (23)$$

$$\log(Q_{3,1}) = -6.495 + \frac{3219.1}{T} + 0.95186 \log(T) + p_6 I + \frac{p_7 I(f_i)}{T} + p_8 I^2 \log(\rho_w) \quad (24)$$

Species (4,2)



$$Q_{4,2} = \frac{[B_4(OH)_{14}^{2-}]}{[B(OH)_3]^4 [OH^-]^2} \quad (26)$$

$$\log(Q_{4,2}) = -5.031 + \frac{6001.3}{T} - 1.3572 \log(T) + u_1 I + u_2 IT + u_3 \sqrt{I} + u_4 T \sqrt{I} \quad (27)$$

where u1-u4 are the parameters described in Table 5.

Table 5: Parameter values for log (Q_{4,2}).

Parameter	Value
u1	0.11830
u2	-0.0013078
u3	0.23298
u4	0.0021211

The mass balance for the boron is defined by the following equation:

$$C_B = [B(OH)_3] + \sum x Q_{x,y} [B(OH)_3]^x [OH^-]^y \quad (28)$$

where C_B is the stoichiometric boron concentration in the solution. This equation can be rewritten for the boron species considered here as follows:

$$C_B = [B(OH)_3] + Q_{1,1} [B(OH)_3] [OH^-] + 2Q_{2,1} [B(OH)_3]^2 [OH^-] + 3Q_{3,1} [B(OH)_3]^3 [OH^-] + 4Q_{4,2} [B(OH)_3]^4 [OH^-]^2 \quad (29)$$



5.1.6 Sodium hydroxide and cesium hydroxide speciation

Sodium Hydroxide ($NaOH$) is used to control the containment spray and sump pH. Sodium hydroxide is a strong base. The equation for the dissociation of sodium hydroxide in water may be written as follows: $NaOH + H_2O \Rightarrow Na^+ + OH^- + H_2O$

Cesium hydroxide is created from fission product releases. Cesium hydroxide is a strong base. The equation for the dissociation of cesium hydroxide in water may be written as follows: $CsOH + H_2O \Rightarrow Cs^+ + OH^- + H_2O$

5.1.7 Hydrochloric, hydriodic and nitric acid speciation

The impact of hydrochloric, hydriodic and nitric acid is also considered in this evaluation. For conservatism, these species are assumed to dissociate completely in the sump. This is equivalent to having a very small dissociation constant. Thus, the hydrochloric, hydriodic and nitric acid dissociate as follows:



Thus, the mass balance equations for these acids are:

$$[Cl^-] = C_{HCl} \quad (33)$$

$$[I^-] = C_{HI} \quad (34)$$

$$[NO_3^-] = C_{HNO_3} \quad (35)$$

where C_{HCl} , C_{HI} and C_{HNO_3} are the stoichiometric concentrations of hydrochloric, hydriodic and nitric acid, respectively.

5.1.8 Equilibrium pH determination

Post-LOCA the containment sump contains a solution of the boric acid, sodium hydroxide, hydrochloric acid, hydriodic acid, nitric acid and cesium hydroxide. The pH of the sump is determined by balancing the charges of the individual species in the solution. By utilizing the equations developed above, $[H^+]$ (and pH) can be determined. Generalizing equation (2) to consider the six chemical compounds in the sump, in addition to the hydrolization of water, gives the following equation:

$$[H^+] - [OH^-] - [B(OH)_4^-] - [B_2(OH)_7^-] - [B_3(OH)_{10}^-] - 2[B_4(OH)_{14}^{2-}] - [Cl^-] - [I^-] - [NO_3^-] + [Cs^+] + [Na^+] = 0 \quad (36)$$

The mass balance equations and equilibrium constants (with activity coefficients) calculated above can be substituted into equation (36) to solve for $[H^+]$. Due to the non-linearity of the boric acid speciation scheme and solution ionic strength, this equation must be solved iteratively. This process is completed using Microsoft Excel.

5.2 Sump pH

As described in Section 5.1, the sump pH is calculated based on the relative concentrations of sodium hydroxide, boric acid, and other species contained in the sump. Note that the methods for determining minimum and maximum sump pH are identical; the inputs are simply biased in the appropriate direction to obtain the bounding results. The inputs for the minimum and maximum sump pH cases are given in Section 9. The following describes the methodology for determining the pH for the Harris Nuclear Plant configuration.

5.2.1 Boron & water inventory

In general, the methodology utilized allows for the use of time-dependent RCS, RWST, and Accumulator (or SIT) inventories in the sump. These inventories are time dependent based on assumptions regarding the vessel blowdown, number of ECCS pumps operating, etc. Boron concentrations for these sources are generally given in concentrations of parts-per-million (ppm). The quantity of boron added to the sump from these sources is calculated based on the definition of concentration:

$$C_{Boron} = \frac{m_{Boron}}{m_{Boron} + m_{Water}} \quad (37)$$

Rearranging equation (37) gives:

$$m_{Boron} = \frac{C_{Boron}}{(1 - C_{Boron})} \times m_{Water} \quad (38)$$

The total boron and water inventory in the sump is determined and is used to determine boron concentrations for the pH and dissolution analyses.

5.2.2 Sump properties

Sump properties including the boron concentration, temperature, volume, etc. impact the pH calculations. The sump boron concentration is calculated using equation (38) from above. A time-dependent sump temperature may be utilized and converted from °F to K for use in evaluating other chemical properties. This temperature conversion is given by:

$$T[K] = \frac{T[°F] - 32}{1.8} + 273.15 \quad (39)$$

The sump density is determined based on the sump temperature in Reference [10.26]. The volume is calculated based on this density:

$$V = \frac{m}{\rho} \quad (40)$$

5.2.3 Acid generation

There are three additional sources beyond boric acid that can decrease the pH of the sump. The irradiation of cable insulation can generate hydrochloric acid which will affect the sump pH. In addition, irradiation of the sump water itself generates nitric acid which also decreases the pH. Also, hydriodic acid is formed from reactions of the iodine released from post-LOCA fuel damage. To properly evaluate the pH of the sump, these sources must be considered in the pH analysis.

The amount of hydrochloric acid (HCl) produced by irradiation of electrical cable insulation is given in Section 2.2.5.2 of Reference [10.9] as $4.6E-4$ g-mol HCl / $\text{lbm}_{\text{insulation}}\text{-Mrad}$. The quantity of HCl produced at any given time is given by the following equation:

$$M_{\text{HCl}} = 4.6E-4 \frac{\text{g-mol HCl}}{\text{lbm}_{\text{insulation}}\text{-Mrad}} \times M_{\text{insulation}} \times \gamma_{\text{containment}} \quad (41)$$

Similarly, the nitric acid produced by irradiation of the sump water is given in Section 2.2.4 of Reference [10.9] as $7.3E-6$ g-mol HNO_3 / L-Mrad . The quantity of nitric acid produced is given by the following equation:

$$M_{\text{HNO}_3} = 7.3E-6 \frac{\text{g-mol HNO}_3}{\text{L-Mrad}} \times V_{\text{sump}} \times \gamma_{\text{sump}} \quad (42)$$

The maximum potential amount of hydriodic acid is assessed based on the releases described in Reference [10.13].

5.2.4 Basic Fission Product Compounds

Cesium hydroxide formed from reactions of the Cesium released from post-LOCA fuel damage can increase the pH of the sump. The maximum potential amount of cesium hydroxide is assessed based on the releases described in Reference [10.13].

5.2.5 Basket/buffer dissolution

Harris Nuclear Plant does not utilize trisodium phosphate, sodium tetraborate or any other dissolving solid for pH control, so dissolution is not applicable.

5.2.6 Species concentrations

Using the water inventory calculated in Section 5.2.1, the concentrations of each of the chemical species in the sump is calculated according to the following equation:

$$[A] = \frac{m_A}{\frac{MW_A}{V_{sump}}} \quad (43)$$

where:

m_A is the mass of species A

MW_A is the molecular mass of species A

V_{sump} is the volume of the sump water

These concentrations are used to calculate the pH of the sump.

5.2.7 Activity coefficients

Individual activity coefficients for the hydrogen ion and hydroxide ion are calculated using equation (9) from Section 5.1.3. Since this equation includes a term for ionic strength, an assumed value is used for this parameter which is verified at the end of the pH calculation. Activity coefficients for the remaining species are either included in their respective solution methods (e.g., boric acid) or conservatively are assumed to be unity (e.g., sodium ion and nitric acid ion).

5.2.8 Equilibrium pH determination

The post-LOCA containment sump contains a solution of the boric acid, sodium hydroxide, hydrochloric acid, hydriodic acid, nitric acid and cesium hydroxide. The pH of the sump is calculated by balancing the charges on the individual ions as described in Section 5.1.8. This process is completed using Microsoft Excel.

6. Chemical Precipitate Methodology

Westinghouse developed a methodology for predicting the species and quantities of chemical precipitates that could form in the post-accident containment environment by the reactions of the buffer agent (sodium hydroxide for HNP) with aluminum, insulation materials, and concrete. This methodology is based on bench testing and is documented in Reference [10.23]. Along with this WCAP, Westinghouse developed an Excel spreadsheet for plants to predict the plant-specific chemical precipitates to use as an input into head-loss testing for the replacement recirculation sump screens.

After appropriate benchmarking against Reference [10.24], HNP used this spreadsheet to predict the species and quantities of chemical precipitates that were used in the prototypical head-loss testing of the current sump screens. This testing is documented in Reference [10.25].

Based on the proposed HNP CSAT and eductor flow range changes, new pH profiles resulted for the containment sprays and sump. Any potential impact of the new pH profiles with respect to



chemical precipitates was assessed in Reference [10.19] using the methodology of Reference [10.23].

The new pH profiles resulting from the proposed HNP CSAT and eductor flow range changes were demonstrated to produce less than or equal to the chemical precipitate masses utilized in the testing documented in Reference [10.25].

7. Eductor Flow and Test Flow

Reference [10.26] and Reference [10.27] determine the NaOH flow from the CSAT for pH determination and the RWST test flow through the eductor. NaOH flow from the CSAT is determined using eductor performance curves and system resistance. Conservative values are utilized for fluid properties, tank level/head and containment spray flow depending on whether minimum or maximum pH are being calculated. Once the minimum and maximum acceptable (with respect to pH criteria) NaOH flow rates are determined, those values are converted to RWST test flow values based on the RWST conditions, eductor performance curves and system resistance.

The minimum and maximum delivered concentration of NaOH are then input into the minimum and maximum pH calculations.

8. Assumptions

The following section documents assumptions for the analysis.

- 8.1 All ionic species in the solution are assumed to be in equilibrium. Thus, the pH results at any given time are based on a steady-state analysis.
- 8.2 The individual activity coefficients are based on the Debye- Hückel theory which utilizes the effective ionic radius. The ionic radii utilized are provided at 25°C and the impact of temperature on the approximate ionic radii is assumed to be negligible.
- 8.3 The hydrochloric acid, hydriodic acid and nitric acid are assumed to fully dissociate in the sump.
- 8.4 The CSAT concentration range is 27 wt. % - 29 wt. %.
- 8.5 The CSAT maximum volume is 3768 gallons.
- 8.6 Although lithium hydroxide is used in the RCS for pH control, it was not credited in the minimum pH analyses nor modeled in the maximum pH analyses. A maximum sump sensitivity case with 5 ppm LiOH in the RCS indicated that the impact of LiOH on the maximum sump pH was small.

9. Inputs

The following sections provide the development of inputs for determining the minimum and maximum sump pH.

9.1 Common Inputs

The following section provides inputs that are common to both the minimum and maximum sump pH cases.

9.1.1 Water Density

The temperature-dependent specific volume of water is taken from Appendix 24.A of Reference [10.4] and is converted to density using the following relation:

$$\rho = \frac{1}{v}$$

The table of specific volume is given as follows.

Table 6: Water specific volume

Temp. (deg-F)	Specific Volume (ft ³ /lbm)
40	0.01602
50	0.01602
60	0.01604
70	0.01605
80	0.01607
90	0.0161
100	0.01613
110	0.01617
120	0.01621
130	0.01625
140	0.01629
150	0.01634
160	0.01639
170	0.01645
180	0.01651
190	0.01657
200	0.01663
210	0.0167
212	0.01672
220	0.01677
230	0.01685
240	0.01692
250	0.017
260	0.01708
270	0.01717
280	0.01726
290	0.01735
300	0.01745

9.1.2 Water Ion Product

The temperature-dependent ion product of water is from the equation given in Table 3.2 of Reference [10.10] which is as follows:

$$-\log(K_w) = \frac{4470.99}{T} - 6.0875 + 0.01706T$$

Note that the temperature, T , specified in the equation above is in units of Kelvin. This parameter is calculated for temperatures between 0°C and 150°C in 5°C increments. An additional data point for 148.88°F (300°F) is also included. The table generated using this equation is given as follows.

Table 7: Water ion products

Temp. (deg-C)	-log(K _w)
0	14.941
5	14.732
10	14.533
15	14.345
20	14.165
25	13.995
30	13.833
35	13.679
40	13.532
45	13.393
50	13.261
55	13.136
60	13.016
65	12.903
70	12.796
75	12.694
80	12.598
85	12.506
90	12.420
95	12.338
100	12.260
105	12.187
110	12.118
115	12.053
120	11.992
125	11.934
130	11.880
135	11.830
140	11.783

Temp. (deg-C)	-log(K _w)
145	11.738
148.88	11.706
150	11.697

9.1.3 Debye-Hückel Constants

The Debye-Hückel constants that are used to calculate the activity coefficients are taken from Table 1.59 of Reference [10.5]. These parameters are given in the table below. Note that an additional point is added for 148.88°C (300°F) and the value of the constants are assumed to be the same as those at 100°C. This extra point is not utilized in the final, reported Harris Nuclear Plant pH analyses, but was utilized in sensitivity cases.

Table 8: Debye-Hückel constants

Temp. (deg-C)	A	B
0	0.4918	0.3248
5	0.4952	0.3256
10	0.4989	0.3264
15	0.5028	0.3273
20	0.507	0.3282
25	0.5115	0.3291
30	0.5161	0.3301
35	0.5211	0.3312
40	0.5262	0.3323
45	0.5317	0.3334
50	0.5373	0.3346
55	0.5432	0.3358
60	0.5494	0.3371
65	0.5558	0.3384
70	0.5625	0.3397
75	0.5695	0.3411
80	0.5767	0.3426
85	0.5842	0.3440
90	0.5920	0.3456
95	0.6001	0.3471
100	0.6086	0.3488
148.88	0.6086	0.3488

9.1.4 Water Density in gm/cm³

The water density is required in gm/cm³ for solution of the Palmer boric acid species equations. This data is taken from Reference [10.1] as follows.

Table 9: Water Density for Palmer Equations

Density of Water		
Temp (deg.C)	Temp (deg K)	Density (g/cm3)
0	273	0.9999
4	277	1.0000
20	293	0.9982
40	313	0.9922
60	333	0.9832
80	353	0.9718
100	373	0.9584
101	374	0.957662
103.00	376.15	0.956207
105.00	378.15	0.954733
107.00	380.15	0.95324

9.2 Minimum Sump pH

For the minimum sump pH case, the current minimum volume and the new minimum sodium hydroxide concentration for the CSAT are considered (3268 gallons and 27 wt.% NaOH). This reduces the amount of base and decreases the pH. The maximum boric acid concentration is considered for the RCS, pressurizer, accumulators and RWST. This increases the amount of acid and decreases the pH. The maximum volume/mass of the RCS/pressurizer and RWST are also utilized to increase the amount of acid in the sump and decrease the pH. To minimize the pH, the generation of hydrochloric acid, nitric acid and hydriodic acid is considered in the minimum sump pH case. The generation of cesium hydroxide is conservatively not considered in the minimum sump pH case.

Only a single train of containment spray is credited to reduce NaOH addition, so the minimum sump pH calculation is completed twice, once for the A train of containment spray and once for the B train of containment

9.2.1 Containment Air and Sump Water Dose

In order to calculate the production of HCl and HNO₃ in containment, the integrated doses must be calculated. Typical radiation release signatures for both gamma and beta radiation are given in Figures 1 and 2 of Reference [10.12], respectively. By integrating the area under each of these curves from the beginning of the event to 30 days post-LOCA, a time-dependent integrated dose fraction can be calculated for each time point. Table 10 gives the time, energy release rate, and integrated energy release for gamma radiation using the trapezoidal rule. For example, at time of 19 seconds, the integrated energy release is calculated as follows:

$$E_{release} = \frac{(\text{Current Rate} + \text{Previous Rate})}{2} \times (\text{Current Time} - \text{Previous Time}) + \text{Previous Energy}$$

$$E_{release} = \frac{\left(9.87E + 6 \frac{MeV}{s - W} + 1.89E + 7 \frac{MeV}{s - W}\right)}{2} \times (1.90E + 1s - 1.80E + 1s) + 8.90E + 7 \frac{MeV}{W}$$

$$E_{release} = 1.03E + 8 \frac{MeV}{W}$$

Table 10: Gamma radiation signature and integrated energy releases

Time (sec)	Energy Release Rate (MeV/sec/W)	Energy Release (MeV/W)
1.80E+01	9.87E+06	8.90E+07
1.90E+01	1.89E+07	1.03E+08
4.61E+01	2.71E+08	4.04E+09
5.16E+01	3.36E+08	5.71E+09
5.59E+01	3.85E+08	7.23E+09
6.07E+01	4.30E+08	9.18E+09
9.53E+01	7.53E+08	2.97E+10
9.71E+01	7.60E+08	3.11E+10
1.88E+02	1.11E+09	1.16E+11
2.08E+02	1.09E+09	1.38E+11
4.65E+02	8.91E+08	3.93E+11
5.54E+02	8.59E+08	4.71E+11
9.30E+02	7.25E+08	7.69E+11
1.06E+03	7.02E+08	8.63E+11
1.86E+03	5.66E+08	1.37E+12

Time (sec)	Energy Release Rate (MeV/sec/W)	Energy Release (MeV/W)
2.16E+03	5.41E+08	1.54E+12
3.39E+03	4.37E+08	2.14E+12
3.90E+03	4.06E+08	2.35E+12
4.71E+03	3.56E+08	2.66E+12
5.23E+03	3.43E+08	2.84E+12
9.37E+03	2.37E+08	4.04E+12
1.09E+04	2.25E+08	4.40E+12
1.92E+04	1.64E+08	6.02E+12
2.08E+04	1.61E+08	6.28E+12
4.20E+04	1.15E+08	9.19E+12
4.48E+04	1.13E+08	9.51E+12
5.34E+04	1.07E+08	1.05E+13
8.14E+04	8.87E+07	1.32E+13
8.56E+04	8.81E+07	1.36E+13
1.02E+05	8.58E+07	1.50E+13
1.95E+05	7.31E+07	2.24E+13
2.02E+05	7.29E+07	2.29E+13
3.45E+05	6.91E+07	3.31E+13
3.48E+05	6.90E+07	3.32E+13
5.00E+05	6.62E+07	4.35E+13
5.08E+05	6.61E+07	4.41E+13
8.37E+05	6.25E+07	6.52E+13
8.44E+05	6.25E+07	6.57E+13
1.96E+06	6.14E+07	1.35E+14
2.01E+06	6.14E+07	1.38E+14
2.59E+06	6.10E+07	1.73E+14

Table 11: Beta radiation signature and integrated energy releases

Time (sec)	Energy Release Rate (MeV/sec/W)	Energy Release (MeV/W)
1.80E+01	9.36E+06	8.45E+07
1.90E+01	9.86E+06	9.38E+07
4.61E+01	1.75E+08	2.60E+09

Time (sec)	Energy Release Rate (MeV/sec/W)	Energy Release (MeV/W)
5.16E+01	2.09E+08	3.66E+09
5.59E+01	2.48E+08	4.63E+09
6.07E+01	2.92E+08	5.92E+09
9.53E+01	5.41E+08	2.04E+10
9.71E+01	5.54E+08	2.13E+10
1.88E+02	7.57E+08	8.09E+10
2.08E+02	8.02E+08	9.66E+10
4.65E+02	6.53E+08	2.83E+11
5.54E+02	6.00E+08	3.39E+11
9.30E+02	4.90E+08	5.44E+11
1.06E+03	4.51E+08	6.07E+11
1.86E+03	3.63E+08	9.30E+11
2.16E+03	3.29E+08	1.03E+12
3.39E+03	2.69E+08	1.40E+12
3.90E+03	2.44E+08	1.53E+12
4.71E+03	2.16E+08	1.72E+12
5.23E+03	1.99E+08	1.83E+12
9.37E+03	1.49E+08	2.55E+12
1.09E+04	1.30E+08	2.76E+12
1.92E+04	9.47E+07	3.70E+12
2.08E+04	8.79E+07	3.85E+12
4.20E+04	5.91E+07	5.40E+12
4.48E+04	5.54E+07	5.56E+12
5.34E+04	5.10E+07	6.02E+12
8.14E+04	4.04E+07	7.30E+12
8.56E+04	3.89E+07	7.46E+12
1.02E+05	3.63E+07	8.09E+12
1.95E+05	2.85E+07	1.11E+13
2.02E+05	2.80E+07	1.13E+13
3.45E+05	2.47E+07	1.51E+13
3.48E+05	2.46E+07	1.51E+13
5.00E+05	2.28E+07	1.87E+13
5.08E+05	2.27E+07	1.89E+13



Time (sec)	Energy Release Rate (MeV/sec/W)	Energy Release (MeV/W)
8.37E+05	2.09E+07	2.61E+13
8.44E+05	2.09E+07	2.62E+13
1.96E+06	1.85E+07	4.82E+13
2.01E+06	1.84E+07	4.90E+13
2.59E+06	1.81E+07	5.97E+13

The tables above can be used to generate the general shape of the integrated dose for the containment air and sump. The total integrated dose at each time is divided by the 30 day integrated dose to obtain an integrated dose fraction. These fractions are multiplied by the Harris Nuclear Plant 30 day integrated doses for the containment air and sump from References [10.8] and [10.18]. Conservatively, the containment sump integrated dose is assumed to be 9.03E06 rads gamma and 1.34E08 rads beta, which are the one month integrated accident dose in EQ zone C1 from Reference [10.8]. EQ zone C1 results in the highest one month accident integrated dose in the containment sump. Note that Attachment B of Reference [10.18] indicates that only 75.7% of the gamma dose in EQ zone C1 is to the sump. This reduction factor is not credited. Conservatively, the containment air integrated dose is assumed to be 7.75E06 rads gamma and 1.34E08 rads beta, which are the one month integrated accident dose in EQ zone C2 from Reference [10.8]. EQ zone C2 results in the highest one month accident integrated dose outside of the sump in containment. Note that Attachment B of Reference [10.18] indicates that 55.9% of the gamma dose in EQ zone C2 is to the sump and not the air. This reduction factor is not credited. An example of this calculation is completed below to obtain the integrated beta dose fraction to the containment air at 1.8E+1 seconds.

$$F_{beta} = \frac{8.45E+07}{5.97E+13} \times 1.34E+08 \text{ rad} = 1.90E+02 \text{ rad}$$

This process is repeated for the sump and atmosphere beta and gamma doses. The total doses for the containment sump and containment atmosphere are added together and provided in the tables below.

Table 12: Integrated containment air dose

Time (sec)	Integrated Dose (Rads)
1.80E+01	1.94E+02
1.90E+01	2.15E+02
4.61E+01	6.02E+03
5.16E+01	8.47E+03
5.59E+01	1.07E+04



Time (sec)	Integrated Dose (Rads)
6.07E+01	1.37E+04
9.53E+01	4.71E+04
9.71E+01	4.92E+04
1.88E+02	1.87E+05
2.08E+02	2.23E+05
4.65E+02	6.53E+05
5.54E+02	7.82E+05
9.30E+02	1.26E+06
1.06E+03	1.40E+06
1.86E+03	2.15E+06
2.16E+03	2.38E+06
3.39E+03	3.24E+06
3.90E+03	3.54E+06
4.71E+03	3.98E+06
5.23E+03	4.23E+06
9.37E+03	5.90E+06
1.09E+04	6.39E+06
1.92E+04	8.57E+06
2.08E+04	8.92E+06
4.20E+04	1.25E+07
4.48E+04	1.29E+07
5.34E+04	1.40E+07
8.14E+04	1.70E+07
8.56E+04	1.74E+07
1.02E+05	1.88E+07
1.95E+05	2.59E+07
2.02E+05	2.64E+07
3.45E+05	3.54E+07
3.48E+05	3.54E+07
5.00E+05	4.39E+07
5.08E+05	4.44E+07
8.37E+05	6.15E+07
8.44E+05	6.18E+07

Time (sec)	Integrated Dose (Rads)
1.96E+06	1.14E+08
2.01E+06	1.16E+08
2.59E+06	1.42E+08

Table 13: Integrated containment sump dose

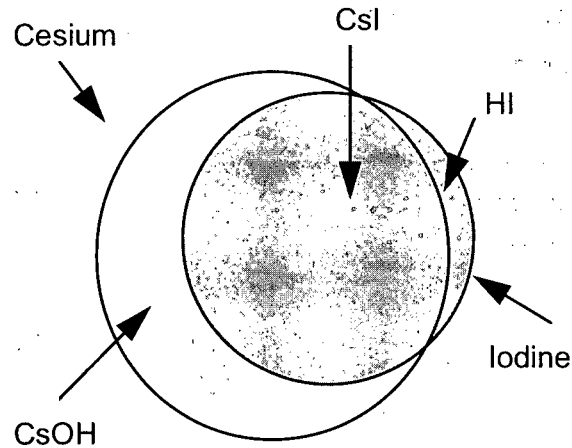
Time (sec)	Integrated Dose (Rads)
1.80E+01	1.94E+02
1.90E+01	2.16E+02
4.61E+01	6.05E+03
5.16E+01	8.51E+03
5.59E+01	1.08E+04
6.07E+01	1.38E+04
9.53E+01	4.73E+04
9.71E+01	4.94E+04
1.88E+02	1.88E+05
2.08E+02	2.24E+05
4.65E+02	6.56E+05
5.54E+02	7.85E+05
9.30E+02	1.26E+06
1.06E+03	1.41E+06
1.86E+03	2.16E+06
2.16E+03	2.39E+06
3.39E+03	3.25E+06
3.90E+03	3.56E+06
4.71E+03	4.00E+06
5.23E+03	4.26E+06
9.37E+03	5.93E+06
1.09E+04	6.42E+06
1.92E+04	8.62E+06
2.08E+04	8.97E+06
4.20E+04	1.26E+07

Time (sec)	Integrated Dose (Rads)
4.48E+04	1.30E+07
5.34E+04	1.41E+07
8.14E+04	1.71E+07
8.56E+04	1.75E+07
1.02E+05	1.89E+07
1.95E+05	2.61E+07
2.02E+05	2.66E+07
3.45E+05	3.56E+07
3.48E+05	3.56E+07
5.00E+05	4.42E+07
5.08E+05	4.47E+07
8.37E+05	6.20E+07
8.44E+05	6.22E+07
1.96E+06	1.15E+08
2.01E+06	1.17E+08
2.59E+06	1.43E+08

9.2.2 Production of Hydriodic Acid

Iodine is released from the core as fuel failure occurs. Table 2 of Reference [10.13] indicates that 5% of the core halogen inventory is discharged during the gap release phase while an additional 35% is discharged during the early in-vessel phase.

Consistent with Section 3.5 of Reference [10.13], the iodine exiting the reactor coolant system will be composed of 95% cesium iodide (CsI). This methodology will conservatively assume that all 5% of the remaining iodine release is in the form of HI in order to maximize the acid generation. This HI inventory is illustrated in the figure below.



This release process is assumed to occur at a constant rate over the release period (*i.e.*, 30 minutes and 1.3 hours for the gap and early in-vessel release phases, respectively). The core iodine inventory includes the stable I^{127} species to maximize the amount of acid produced. The following equations describe this release.

$$\frac{d}{dt} [HI] = \frac{0.05 * 0.05 m_I}{V_{sump} * 0.5 \text{ hr}} \quad (\text{Gap Release Phase})$$

$$\frac{d}{dt} [HI] = \frac{0.05 * 0.35 m_I}{V_{sump} * 1.3 \text{ hr}} \quad (\text{Early In-Vessel Release Phase})$$

where:

m_I = core iodine inventory (gram-mols), and

V_{pool} = volume of the suppression pool (liters).

This release can be integrated considering the 1/2-hour PWR gap release duration to yield the following equations during the gap and in-vessel release periods.

$$[HI](t) = \frac{m_I}{200 * V_{sump}} * (t - t_{gap}) \quad (\text{Gap Release Phase})$$

$$[HI](t) = \frac{m_I}{74.29 * V_{sump}} * [t - (0.5 + t_{gap})] + \frac{m_I}{400 * V_{sump}} \quad (\text{Early In-Vessel Release Phase})$$

where:

t = time into accident (hrs), and

t_{gap} = onset of gap release (hrs).

For HNP, the iodine and cesium inventories are provided in Curies in Table 2.0-1 of Reference [10.10] for only the radioactive isotopes included in the source term. These values are converted to moles and grams using the following relationships.

$$n(\text{atoms}) = \frac{A}{\lambda} = \frac{A(\text{Ci}) \cdot 3.7 \times 10^{10} (\text{atoms/s/Ci})}{\frac{0.693}{t_{1/2}}}$$

$$\text{moles} = \frac{n(\text{atoms})}{\text{Avogadro's Number}} = \frac{n}{6.02217E23 \text{ atoms/mole}}$$

$\text{mass in grams} = \text{moles} \times \text{molar mass}$

These relationships are implemented in the table below with half-life and molar mass information from Table A.1 of Reference [10.17] and Reference [10.1], respectively

Table 14: Radioactive Cesium and Iodine

	Ci	Half-life (sec)	Atoms	Mol	Grams
I-131	8.02E+07	6.947E+05	2.97E+24	4.94E+00	6.27E+02
I-132	1.16E+08	8.280E+03	5.13E+22	8.52E-02	1.08E+01
I-133	1.64E+08	7.488E+04	6.56E+23	1.09E+00	1.38E+02
I-134	1.80E+08	3.156E+03	3.03E+22	5.04E-02	6.39E+00
I-135	1.53E+08	2.380E+04	1.94E+23	3.23E-01	4.10E+01
Cs-134	1.53E+07	6.507E+07	5.32E+25	8.83E+01	1.17E+04
Cs-136	4.27E+06	1.132E+06	2.58E+23	4.28E-01	5.69E+01
Cs-137	9.17E+06	9.467E+08	4.64E+26	7.70E+02	1.02E+05

Using pages 18 through 20 of Attachment 4 of Reference [10.16], the grams of the stable isotopes I¹²⁷ and Cs¹³³ are estimated to conservatively include in the determination of CsOH and HI.

645/(1716-645) = 0.60, so the mass of the radioactive isotopes of Cesium will be increased by 60% to account for Cs¹³³. Note that stable Cesium-133 is not included in the determination of minimum pH, as not including the stable isotope of Cesium increases the amount of HI.

29.83/(136.3-29.83) = 0.28, so the mass of the radioactive isotopes of iodine will be increased by 28% to account for I¹²⁷. Note that stable Iodine-127 is not included in the determination of maximum pH, as not including the stable isotope of Iodine increases the amount of CsOH.

For HI, the total moles of radioactive iodine are increased by 28% to account for stable I-127 giving 1.82E+00 moles of I-127 and 8.3 total moles of iodine.

The table below presents the total HI added to the sump as a function of time based on the equations and data above.

Table 15: Integrated HI Added

Time(sec)	HI (gm-moles)
0	0.0000E+00
20	0.0000E+00
30	0.0000E+00
50	2.3062E-04
100	8.0718E-04
200	1.9603E-03
300	3.1134E-03
400	4.2665E-03
500	5.4196E-03
600	6.5728E-03
650	7.1493E-03
700	7.7259E-03
800	8.8790E-03
900	1.0032E-02
1000	1.1185E-02
1100	1.2338E-02
1200	1.3491E-02
1250	1.4068E-02
1300	1.4645E-02
1400	1.5798E-02
1500	1.6951E-02
1600	1.8104E-02
1973	2.5195E-02
2200	3.2242E-02
2400	3.8451E-02
2600	4.4660E-02
2800	5.0868E-02
3000	5.7077E-02
3500	7.2599E-02
4000	8.8121E-02
5000	1.1916E-01
6000	1.5021E-01
6480	1.6511E-01

9.2.3 NaOH Molarity

The NaOH molarity is taken from Reference [10.26] depending upon which train of containment spray is assumed operating. The NaOH molarity is minimized by assuming the NaOH solution is at a maximum temperature of 104 °F (per input 4.5 of Reference [10.15]) and the CSAT NaOH

concentration is 27 wt.%. The values for NaOH-molarity from Reference [10.26] are given in the following tables.

Table 16: NaOH Molarity – Train A operating

NaOH Molarity In Sump	
Time (sec)	Molarity (M)
0	0.0000
20	0.0004
30	0.0006
50	0.0009
100	0.0017
200	0.0028
300	0.0036
400	0.0042
500	0.0046
600	0.0050
650	0.0052
700	0.0053
800	0.0056
900	0.0058
1000	0.0060
1100	0.0061
1200	0.0063
1250	0.0063
1300	0.0064
1400	0.0065
1500	0.0066
1600	0.0067
1973	0.0070
2200	0.0078
2400	0.0085
2600	0.0092

NaOH Molarity In Sump	
Time (sec)	Molarity (M)
2800	0.0099
3000	0.0106
3500	0.0123
4000	0.0141
5000	0.0176
6000	0.0211
7000	0.0246
8000	0.0281
10000	0.0350
12000	0.0419
14000	0.0488
17538	0.0608
2.592E+06	0.0608*

* since the NaOH addition is complete at 17,538 seconds, there is no further increase in molarity after that point.

Table 17: NaOH Molarity – Train B operating

NaOH Molarity In Sump	
Time (sec)	Molarity (M)
0	0.0000
20	0.0004
30	0.0006
50	0.0010
100	0.0018
200	0.0031
300	0.0039
400	0.0046
500	0.0051
600	0.0055

NaOH Molarity In Sump	
Time (sec)	Molarity (M)
650	0.0057
700	0.0058
800	0.0061
900	0.0064
1000	0.0066
1100	0.0068
1200	0.0069
1250	0.0070
1300	0.0071
1400	0.0072
1500	0.0073
1600	0.0074
1973	0.0077
2200	0.0085
2400	0.0092
2600	0.0099
2800	0.0105
3000	0.0112
3500	0.0130
4000	0.0147
5000	0.0181
6000	0.0216
7000	0.0250
8000	0.0284
10000	0.0352
12000	0.0419
14000	0.0486
17742	0.0609
2.592E+06	0.0609*

* since the NaOH addition is complete at 17,742 seconds, there is no further increase in molarity after that point.

9.2.4 Water Inventory Boron Concentrations

Maximizing boron concentrations in the RWST, RCS, pressurizer and accumulator water inventory requires that more NaOH be added to the sump and minimizes sump pH. The maximum boron concentrations are 2000 ppm boron for the RCS and pressurizer and 2600 ppm boron for the accumulators and 2600 ppm boron for the RWST per Reference [10.26].

$$C_{\text{Boron, RCS, max}} = 2000 \text{ ppm}$$

$$C_{\text{Boron, RWST, max}} = 2600 \text{ ppm}$$

$$C_{\text{Boron, accumulator, max}} = 2600 \text{ ppm}$$

9.2.5 Cable Insulation Mass

The maximum cable insulation mass for Harris Nuclear Plant is assumed to be **20,000 lbm** based on Reference [10.14] giving a total of 17,350 lbm.

9.2.6 Sump Temperature for pH

Based on a sensitivity study for the Harris Nuclear Plant minimum sump pH inputs, a higher sump temperature is conservative for the pH calculation. It should be noted that Reference [10.26] maximizes the RCS, pressurizer and RWST liquid masses (by minimizing the temperature and maximizing the density), which consequently maximizes the associated boron masses; therefore, very conservative temperature biases are applied to the minimum sump pH cases. The temperature utilized for pH determination is 200 °F from Reference [10.26].

9.2.7 RCS Inventory in Sump

The maximum RCS inventory (including pressurizer) is given as 424,480 lbm in Reference [10.26]. Using the maximum inventory is conservative since it maximizes the mass of boric acid added to the sump from the RCS. This entire inventory is assumed to be deposited into the sump during the first second. This is accomplished using the following input table.

Table 18: Maximum RCS inventory profile

Time (sec)	Mass (lbm)
0	0
1	424480
2.592E+06	424480

9.2.8 RWST Inventory in Sump

The maximum RWST inventory delivered to the sump is given as 371,734 gallons from Reference [10.26]. The RWST temperature is assumed to be at the minimum value of 40 °F per Reference [10.26]. This inventory is added as per Reference [10.26] for the appropriate train.

This is accomplished using the following input tables for the A train and B train (note that the total injected RWST volume is conservatively higher than 371,734 gallons).

Table 19: Maximum RWST inventory profile – Train A

RWST Inventory In Sump	
Time (sec)	Mass (lbm)
0	0
20	16180
30	32387
50	64897
100	146237
200	308696
300	470798
400	632429
500	793566
600	954223
650	1034375
700	1114410
800	1274126
900	1433401
1000	1592262
1100	1750794
1200	1909081
1250	1988129
1300	2067115
1400	2224896
1500	2382425
1600	2539714
1973	3134251
2.592E+06	3134251*

* corresponds to 372,569 total gallons

Table 20: Maximum RWST inventory profile – Train B

RWST Inventory In Sump	
Time (sec)	Mass (lbm)
0	0
20	16167
30	32360
50	64842
100	146115
200	308437
300	470405
400	631905
500	792915
600	953448
650	1033539
700	1113514
800	1273112
900	1432273
1000	1591022
1100	1749445
1200	1907625
1250	1986621
1300	2065554
1400	2223233
1500	2380661
1600	2537851
1973	3131968
2.592E+06	3131968**

** corresponds to 372,569 total gallons

9.2.9 Accumulator/SIT Inventory in Sump

The accumulator/SIT mass is given as 197,871 lbs in Reference [10.26]. This value is input using the following table.

Table 21: Maximum Accumulator/SIT inventory profile

Time (sec)	Mass (lbm)
0	0
1	197871
2.592E+06	197871

9.3 Minimum Spray pH

For the minimum spray pH cases, the following input changes are made to the minimum sump pH inputs described in Section 9.2.

- The addition of the RCS, pressurizer and accumulator inventory/mass was shifted to happen in the time step after recirculation began to prevent any effect of this inventory on the sprays prior to the sprays taking suction from the containment sump. The inventories remained the same. The boron concentration, therefore, remains at 2600 ppm until recirculation begins.
- The sump temperature at which pH is determined is changed to the maximum RWST temperature of 125 °F prior to recirculation, since the RWST is the source of the spray water. The temperature remains at 200 °F after recirculation begins.
- The NaOH concentration/molarity is adjusted to the spray NaOH molarity from Reference [10.26] for the appropriate train until the time the appropriate CSAT low level is reached and delivery of NaOH ends.

Table 22: Spray NaOH Molarity - Train A

Time (sec)	Molarity (M)
0	0.0000
20	0.0452
30	0.0451
50	0.0449
100	0.0450
200	0.0450



Time (sec)	Molarity (M)
300	0.0452
400	0.0453
500	0.0454
600	0.0456
650	0.0456
700	0.0457
800	0.0458
900	0.0460
1000	0.0461
1100	0.0461
1200	0.0462
1250	0.0463
1300	0.0463
1400	0.0464
1500	0.0464
1600	0.0465
1973	0.0451
2200	0.0566
2400	0.0574
2600	0.0581
2800	0.0589
3000	0.0597
3500	0.0616
4000	0.0635
5000	0.0673
6000	0.0711
7000	0.0749
8000	0.0787
10000	0.0862
12000	0.0937
14000	0.1012
17538	0.1140

Table 23: Spray NaOH Molarity - Train B

Time (sec)	Molarity (M)
0	0.0000
20	0.0499
30	0.0497
50	0.0496
100	0.0496
200	0.0497
300	0.0499
400	0.0500
500	0.0502
600	0.0503
650	0.0504
700	0.0505
800	0.0506
900	0.0507
1000	0.0509
1100	0.0510
1200	0.0510
1250	0.0511
1300	0.0511
1400	0.0512
1500	0.0513
1600	0.0513
1973	0.0499
2200	0.0550
2400	0.0558
2600	0.0565
2800	0.0573
3000	0.0580
3500	0.0599
4000	0.0617
5000	0.0654

Time (sec)	Molarity (M)
6000	0.0691
7000	0.0728
8000	0.0765
10000	0.0838
12000	0.0910
14000	0.0981
17742	0.1110

- The hydrochloric, hydriodic and nitric acid concentrations from the containment atmosphere and sump are set to 0 prior to recirculation since these acids do not exist in the RWST.

9.4 Maximum Sump pH

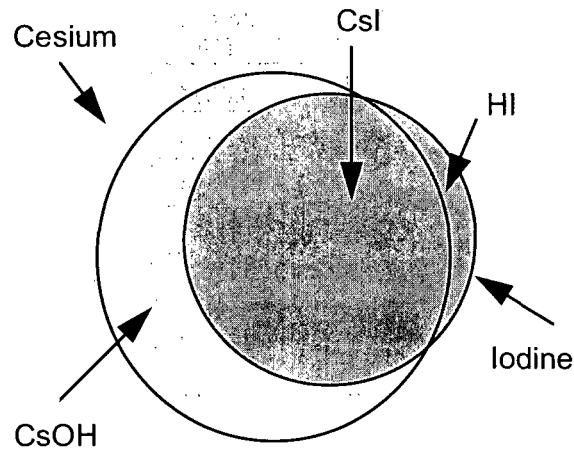
For the maximum sump pH case, the new maximum volume and the new maximum sodium hydroxide concentration for the CSAT are considered (3768 gallons and 29 wt.% NaOH). This increases the amount of base and increases the pH. The minimum boric acid concentration is considered for the RCS, pressurizer, accumulators and RWST. This decreases the amount of acid and increases the pH. The minimum volume/mass of the RCS/pressurizer and RWST are also utilized to decrease the amount of acid in the sump and increase the pH. To maximize the pH, the generation of hydrochloric acid, nitric acid and hydriodic acid is not considered in the maximum sump pH case. The generation of cesium hydroxide is conservatively considered in the maximum sump pH case.

Both trains of containment spray are credited to increase NaOH addition, so the minimum sump pH calculation is completed once.

9.4.1 Production of Cesium Hydroxide

Cesium is released from the core as fuel failure occurs. Table 2 of Reference [10.13] indicates that 5% of the core alkali metal inventory (including cesium) is discharged during the gap release phase while an additional 25% is discharged during the early in-vessel phase. For iodine, Table 2 of Reference [10.13] indicates that 5% of the core halogen inventory is discharged during the gap release phase while an additional 35% is discharged during the early in-vessel phase.

Consistent with Section 3.5 of Reference [10.13], the iodine exiting the reactor coolant system will be composed of 95% cesium iodide (CsI). The cesium that is not in the chemical form of CsI is assumed to exit the RCS in the form of cesium hydroxide (CsOH) and be deposited into the containment sump. This CsOH inventory is illustrated in the following figure.



This release process is assumed to occur at a constant rate over the release period (*i.e.*, 30 minutes and 1.3 hours for the gap and early in-vessel release phases, respectively). The core Cesium inventory includes the stable Cs^{133} species to maximize the amount of base produced. The following equations describe this release.

$$\frac{d}{dt} [CsOH] = \frac{0.05m_{Cs} - 0.95 * 0.05m_I}{V_{sump} * 0.5 \text{ hr}} \quad (\text{Gap Release Phase})$$

$$\frac{d}{dt} [CsOH] = \frac{0.25m_{Cs} - 0.95 * 0.35m_I}{V_{sump} * 1.3 \text{ hr}} \quad (\text{Early In-Vessel Release Phase})$$

where:

- m_{Cs} = core cesium inventory (gram-mols).
- m_I = core iodine inventory (gram-mols).
- V_{sump} = containment sump volume (liters)

This release can be integrated considering the 1/2-hour PWR gap release duration to yield the following equations during the gap and in-vessel release periods.

Gap Release Phase:

$$[CsOH](t) = \frac{0.1m_{Cs} - 0.095m_I}{V_{sump}} * (t - t_{gap})$$



Early In-Vessel Release Phase:

$$[\text{CsOH}](t) = \frac{0.19231m_{\text{Cs}} - 0.25577m_{\text{I}}}{V_{\text{sump}}} * [t - (0.5 + t_{\text{gap}})] + \frac{0.05m_{\text{Cs}} - 0.0475m_{\text{I}}}{V_{\text{sump}}}$$

where:

t = time into accident (hrs), and

t_{gap} = onset of gap release (hrs).

For HNP, the iodine and cesium inventories are provided in Curies in Table 2.0-1 of Reference [10.10] for only the radioactive isotopes included in the source term. These values are converted to moles and grams using the following relationships.

$$n(\text{atoms}) = \frac{A}{\lambda} = \frac{A(\text{Ci}) \cdot 3.7 \times 10^{10} (\text{atoms/s/Ci})}{\frac{0.693}{t_{1/2}}}$$

$$\text{moles} = \frac{n(\text{atoms})}{\text{Avogadro's Number}} = \frac{n}{6.02217 \text{E}23 \text{ atoms / mole}}$$

$$\text{mass in grams} = \text{moles} \times \text{molar mass}$$

These relationships are implemented in the table below with half-life and molar mass information from Table A.1 of Reference [10.17] and Reference [10.1], respectively.

Table 24: Radioactive Cesium and Iodine

	Ci	Half-life (sec)	Atoms	Mol	Grams
I-131	8.02E+07	6.947E+05	2.97E+24	4.94E+00	6.27E+02
I-132	1.16E+08	8.280E+03	5.13E+22	8.52E-02	1.08E+01
I-133	1.64E+08	7.488E+04	6.56E+23	1.09E+00	1.38E+02
I-134	1.80E+08	3.156E+03	3.03E+22	5.04E-02	6.39E+00
I-135	1.53E+08	2.380E+04	1.94E+23	3.23E-01	4.10E+01
Cs-134	1.53E+07	6.507E+07	5.32E+25	8.83E+01	1.17E+04
Cs-136	4.27E+06	1.132E+06	2.58E+23	4.28E-01	5.69E+01
Cs-137	9.17E+06	9.467E+08	4.64E+26	7.70E+02	1.02E+05

Using pages 18 through 20 of Attachment 4 of Reference [10.16], the grams of the stable isotopes I^{127} and Cs^{133} are estimated to conservatively include in the determination of CsOH and HI.

$645/(1716-645) = 0.60$, so the mass of the radioactive isotopes of Cesium will be increased by 60% to account for Cs^{133} . Note that stable Cesium-133 is not included in the determination of minimum pH, as not including the stable isotope of Cesium increases the amount of HI.

$29.83/(136.3-29.83) = 0.28$, so the mass of the radioactive isotopes of iodine will be increased by 28% to account for I^{127} . Note that stable Iodine-127 is not included in the determination of maximum pH, as not including the stable isotope of Iodine increases the amount of CsOH.

For CsOH, the total moles of radioactive cesium are increased by 60% to account for stable Cs-133 giving $5.15E+02$ moles of Cs-133 and 1373.40 total moles of cesium.

The CSOH is added in terms of molarity, so the sump volume in liters must be determined. The sump volume in liters that was used for the conversion of the moles of CsOH to molarity is in the following table. Once the pH case is run, the resultant sump volume in liters must be compared to the the following table for reasonableness.

Table 25: Sump Volume

Time(sec)	Sump Volume (liters)
0	0
20	290076
30	297917
50	313715
100	353319
200	432413
300	511293
400	589826
500	667987
600	745791
650	784565
700	823251
800	900363
900	977163
1000	1053682
1100	1130017
1200	1206264
1250	1244351
1300	1282415
1350	1320455
1400	1358470
1500	1434430
1557	1477690
1650	1477690

Time(sec)	Sump Volume (liters)
1660	1477690
1670	1477690
1680	1477690
1700	1477690
1800	1477690
2000	1477690
2500	1477690
3000	1477690
3500	1477690
4000	1477690
5000	1477690
6000	1477690
6480	1477690

The table below presents the CsOH added to the sump as a function of time based on the equations and data above.

Table 26: Integrated CsOH Added

Time(sec)	CsOH (M)
0	0.00E+00
20	0.00E+00
30	0.00E+00
50	2.42E-06
100	7.52E-06
200	1.49E-05
300	2.01E-05
400	2.38E-05
500	2.67E-05
600	2.90E-05
650	3.00E-05
700	3.09E-05
800	3.25E-05
900	3.38E-05
1000	3.50E-05
1100	3.60E-05
1200	3.68E-05
1250	3.72E-05
1300	3.76E-05
1350	3.80E-05
1400	3.83E-05
1500	3.89E-05
1557	3.92E-05
1650	4.16E-05

Time(sec)	CsOH (M)
1660	4.19E-05
1670	4.22E-05
1680	4.24E-05
1700	4.29E-05
1800	4.55E-05
2000	5.47E-05
2500	7.93E-05
3000	1.04E-04
3500	1.29E-04
4000	1.53E-04
5000	2.03E-04
6000	2.52E-04
6480	2.76E-04

9.4.2 NaOH Molarity

The NaOH molarity is taken from Reference [10.26]. The NaOH molarity is maximized by assuming the NaOH solution is at a minimum temperature of 60 °F (per input 4.5 of Reference [10.15]) and the CSAT NaOH concentration is 29 wt.%. The values for NaOH molarity from Reference [10.26] are given in the following tables.

Table 27: NaOH Molarity

NaOH Molarity In Sump	
Time (sec)	Molarity (M)
0	0.0000
20	0.0011
30	0.0017
50	0.0027
100	0.0047
200	0.0078
300	0.0099
400	0.0115
500	0.0127
600	0.0136
650	0.0140
700	0.0144



NaOH Molarity In Sump	
Time (sec)	Molarity (M)
800	0.0151
900	0.0156
1000	0.0161
1100	0.0166
1200	0.0169
1250	0.0171
1300	0.0172
1350	0.0174
1400	0.0175
1500	0.0178
1557	0.0179
1650	0.0190
1660	0.0191
1670	0.0192
1680	0.0193
1700	0.0196
1800	0.0207
2000	0.0229
2500	0.0286
3000	0.0342
3500	0.0398
4000	0.0454
5000	0.0565
6000	0.0677
7000	0.0787
8000	0.0898
8237	0.0924
2.592E+06	0.0924*

* since the NaOH addition is complete at 8,237 seconds, there is no further increase in molarity after that point.

9.4.3 Water Inventory Boron Concentrations

Minimizing boron concentrations in the RWST, RCS, pressurizer and accumulator water inventory requires that less NaOH be added to the sump and maximizes sump pH. The minimum boron concentrations are 15 ppm boron for the RCS and pressurizer and 2400 ppm boron for the accumulators and 2400 ppm boron for the RWST from Reference [10.26].

$$C_{\text{Boron, RCS, min}} = 15 \text{ ppm}$$

$$C_{\text{Boron, RWST, min}} = 2400 \text{ ppm}$$

$$C_{\text{Boron, accumulator, min}} = 2400 \text{ ppm}$$

9.4.4 Sump Temperature for pH

Based on a sensitivity study for the Harris Nuclear Plant maximum sump pH inputs, a lower sump temperature is conservative for the pH calculation. It should be noted that Reference [10.26] minimizes the RCS, pressurizer and RWST liquid masses (by maximizing the temperature and minimizing the density), which consequently minimizes the associated boron masses; therefore, very conservative temperature biases are applied to the maximum sump pH cases. The temperature utilized for pH determination is 77 °F, which is much lower than the expected post-LOCA sump temperature, particularly for 8237 seconds (the time it takes to add all of the NaOH).

9.4.5 RCS Inventory in Sump

The minimum RCS inventory (including pressurizer) is given as 416,768 lbm in Reference [10.26]. Using the minimum inventory is conservative since it minimizes the mass of boric acid added to the sump from the RCS. This entire inventory is assumed to be deposited into the sump during the first 20 seconds. This is accomplished using the following input table.

Table 28: Maximum RCS inventory profile

Time (sec)	Mass (lbm)
0	0
20	416768
2.592E+06	416768

9.4.6 RWST Inventory in Sump

The minimum RWST inventory delivered to the sump is given as 313,195 gallons from Reference [10.26]. The RWST temperature is assumed to be at the maximum value of 125 °F per Reference [10.26]. This inventory is added as per Reference [10.26] for the appropriate train. This is accomplished using the following input table.



Table 29: Maximum RWST inventory profile

RWST Inventory In Sump	
Time (sec)	Mass (lbm)
0	0
20	17007
30	34080
50	68481
100	154719
200	326949
300	498710
400	669718
500	839915
600	1009336
650	1093765
700	1178006
800	1345918
900	1513152
1000	1679773
1100	1845993
1200	2012023
1250	2094959
1300	2177843
1350	2260676
1400	2343455
1500	2508859
1557	2603059*
2.592E+06	2603059

* corresponds to 313,816 total gallons, which is 0.2% higher than 313,195 gallons. This is based on minor rounding differences for properties and flows in Reference [10.26].

9.4.7 Accumulator/SIT Inventory in Sump

The accumulator/SIT mass is given as 197,871 lbms in Reference [10.26]. This value is input using the following table.

Table 30: Maximum Accumulator/SIT inventory profile

Time (sec)	Mass (lbm)
0	0
20	197871
2.592E+06	197871

9.4.8 Additional Maximum Sump pH case for Initial pH

The initial pH for the RCS, pressurizer and accumulator prior to any addition of RWST or CSAT water is determined by running a single time step of the maximum sump pH case without the addition of NaOH or RWST water. This provides the event initiation/time 0 pH for use in precipitate determination.

9.5 Maximum Spray pH

For the maximum spray pH cases, the following input changes are made to the maximum sump pH inputs described in Section 9.4.

- The addition of the RCS, pressurizer and accumulator inventory/mass was shifted to happen in the time step after recirculation began to prevent any effect of this inventory on the sprays prior to the sprays taking suction from the containment sump. The inventories remained the same. The boron concentration, therefore, remains at 2400 ppm until recirculation begins.
- The NaOH concentration/molarity is adjusted to the spray NaOH molarity from Reference [10.26] for the appropriate train until the appropriate CSAT low level is reached and delivery of NaOH ends.

Table 31: Spray NaOH Molarity - Train A

Time (sec)	Molarity (M)
0	0.0000
20	0.0733
30	0.0727
50	0.0722
100	0.0722
200	0.0723
300	0.0726
400	0.0729
500	0.0733



Time (sec)	Molarity (M)
600	0.0736
650	0.0737
700	0.0739
800	0.0742
900	0.0745
1000	0.0747
1100	0.0748
1200	0.0748
1250	0.0749
1300	0.0749
1350	0.0749
1400	0.0750
1500	0.0750
1557	0.0750
1650	0.0934
1660	0.0935
1670	0.0936
1680	0.0938
1700	0.0940
1800	0.0953
2000	0.0978
2500	0.1040
3000	0.1103
3500	0.1165
4000	0.1228
5000	0.1352
6000	0.1475
7000	0.1597
8000	0.1717
8237	0.1745

Table 32: Spray NaOH Molarity - Train B

Time (sec)	Molarity (M)
0	0.0000
20	0.0682
30	0.0676
50	0.0671
100	0.0672
200	0.0673
300	0.0676
400	0.0679
500	0.0682
600	0.0685
650	0.0687
700	0.0688
800	0.0692
900	0.0694
1000	0.0697
1100	0.0697
1200	0.0698
1250	0.0698
1300	0.0699
1350	0.0699
1400	0.0700
1500	0.0701
1557	0.0701
1650	0.0841
1660	0.0843
1670	0.0844
1680	0.0845
1700	0.0848
1800	0.0861
2000	0.0886
2500	0.0950

Time (sec)	Molarity (M)
3000	0.1014
3500	0.1078
4000	0.1141
5000	0.1268
6000	0.1395
7000	0.1520
8000	0.1645
8237	0.1674

- The cesium hydroxide concentrations/molarities from the containment atmosphere and sump are set to 0 prior to recirculation since they do not exist in the RWST.

10. References

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