

CALCULATION TITLE PAGE

CALCULATION NUMBER: PSAT 3019CF.QA.04

CALCULATION TITLE: Post LOCA Suppression Pool pH for Vermont Yankee

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**Purpose**

The purpose of this calculation is to determine the pH of the suppression pool of the Vermont Yankee Nuclear Power Plant as a function of time following a severe core damage accident. This calculation is being performed using Polestar QA software STARpH 1.04 code [1] in accordance with references [2] and [3] procedures.

**Summary of Results**

The pH of the suppression pool in the Vermont Yankee Nuclear Power Plant remains above 8 for 30 days following a severe core damage accident, as shown in the table below.

**pH Results vs. Time**

<u>Time</u>	<u>pH</u>
1h	>8.0
2h	>8.0
5h	8.6
12h	8.6
1d	8.5
3d	8.4
10d	8.2
20d	8.1
30d	8.1

**Methodology**

- Calculate the  $[\text{HNO}_3]$  concentration in the suppression pool water as a function of time post-LOCA using the Radiolysis of Water model of the STARpH 1.04 code [1].
- Calculate cable jacket mass for the two types of chloride-containing cables from the cable lengths and dimensions.
- Calculate the  $[\text{HCl}]$  concentration in the suppression pool water as a function of time using the Radiolysis of Cable model of the STARpH 1.04 code [1].
- Manually calculate the  $[\text{H}^+]$  concentration added to the pool vs. time from the Radiolysis of Water model result and the sum of the Radiolysis of Cable model results for the two types of chloride-containing cable jackets.
- Determine the boron concentration added to the pool from the standby liquid control system (SLCS), the buffer dissociation constant, and the buffer starting pH.
- Calculate the pH of the water pool considering the concentration of boron and the  $[\text{H}^+]$  additions as a function of time using the Add Acid model of the STARpH 1.04 code [1].

**Assumptions**

**Assumption 1:** The fission product mass inventory is 1.33 times the mass inventory used in the pH calculation of the Oyster Creek Nuclear Generating Station (OCNGS) [4].

**Justification:** The Radiolysis of Water model in the STARpH 1.04 code uses mass inventories of fission product groups and energy deposition rates for each of those groups. Fission product inventories for Vermont Yankee are available in terms of curies of various isotopes per MWt at 102% power (1950 MWt) [5], whereas the inventory is available in terms of fission product group masses and curies of various isotopes per

MWt at 102% power (1969 MWt) for Oyster Creek Nuclear Generating Station [6]. Comparison of the curies per MWt of a large number of isotopes for the two reactors revealed a ratio with considerable variation, but generally the curies per MWt were higher for a given isotope for Vermont Yankee than for OCNGS, indicating a higher burnup in the Vermont Yankee core. The ratio of the curies per MWt for Cs-137 for Vermont Yankee to the value for OCNGS, 1.33, was chosen to adjust the fission product group masses from OCNGS to apply to Vermont Yankee. Cs-137 was chosen because it is a radiologically important long-lived isotope and the group represents a large mass. It is known from past studies with the ORIGEN2 code that the total decay power of fission products is no greater at higher burnup [1], so the application of a factor of 1.33 to the mass inventories of OCNGS for use in the Vermont Yankee calculation is conservative. The fission product group masses include a factor of 1.1 over and above the inventories for 102% reactor power.

**Assumption 2:** The fraction of aerosol source term in water pool is 0.90.

**Justification:** Previous Polestar QA calculations indicate that the fraction of the aerosol source term in an unsprayed drywell that settles in the sump pool is close to 90% (see for example reference [7] which calculates this fraction as 0.87 for the Perry Drywell). Given that the spray will tend to wash any aerosol that deposits on elevated surfaces into the sump, the actual fraction of aerosol in the water pool is expected to be essentially 100%. Thus use of 90% is conservative since it will overestimate the radiation level in the drywell vapor space and thus overestimate the [HCl] from radiolysis of chloride-bearing cable insulation.

**Assumption 3:** Proprietary information deleted

**Assumption 4: The pH effect of the increased pool temperature from the accident is very small in a strongly buffered system such as Vermont Yankee and can be neglected.**

**Justification: Proprietary information deleted**

**Assumption 5:** The SLCS is actuated and the sodium pentaborate is injected into the pool within several hours of accident initiation.

**Justification:** A core damage event large enough to release the substantial quantities of fission products in the time frame considered for the alternate source term in reference [16] will be very evident to the operators (e.g., core outlet temperature, radiation level in the drywell, pressure and temperature in the drywell, hydrogen level in the drywell) within minutes of the initiating event. Thus it is reasonable to assume for purposes of this calculation that the Vermont Yankee EOPs and SAMGs provide for SLCS actuation within ~1 hour of accident initiation.

If SLCS injection is into the pool (i.e., into the reactor vessel with the vessel communicating with the pool as in a recirculation line break), significant mixing will occur quickly, on the order of 1 hour based on drywell spray of 6650 gpm and a pool volume of ~590,000 gallons ( $=2.24E6$  L), see calculation of containment water pool volume in Calculation section.

If the reactor vessel is not immediately communicating with the pool, an additional few hours is assumed to transpire before the operators flood the vessel up to the break to assure communication with the pool or inject sodium pentaborate to the pool via an alternate pathway.

**Assumption 6:** The unbuffered pH of the pool should remain above 7 for at least several hours.

**Justification:** Proprietary information deleted

## References

1. PSAT C107.02, STARpH, A code for Evaluating Containment Water Pool pH During Accidents, Code Description and Validation and Verification Report, Revision 4, February, 2000.
2. PSAT 3019CF.QA.01, Project QA Plan for Design Basis Source Term Calculation of Vermont Yankee Nuclear Power Plant, April 11, 2003
3. PSAT 3019CF.QA.02, Rev.1, Implementing Procedure for Design Basis Source Term Calculation of Vermont Yankee Nuclear Power Plant, May 21, 2003.
4. PSAT 05201H.05, Suppression Pool pH for OCNGS Control Room Compatibility, Rev.2, April 13, 2001.
5. PSAT 3019CF.QA.03, Rev. 2, Design Data Base for Application of the Revised DBA Source Term to Vermont Yankee, July 26, 2003.
6. PSAT 05201U.03, Dose Calculation Data Base for Application of the Revised DBA Source Term to the Oyster Creek Nuclear Generating Station, Revision 3, September, 2000.
7. PSAT 04202H.12, Calculation of Fraction of Containment Aerosol Deposited in Water, April 1996.

8. Proprietary information deleted
9. J. Metcalf e-mail to R. Hobbins, "VY Coatings", July 23, 2003.
10. VY Engineering Record of Correspondence, ERC-2003-051, "Investigation of Primary Containment Coatings Vermont Yankee Nuclear Power Plant Vernon, Vermont", P. Perez, e-mail to J. Metcalf, July 23, 2003.
11. PSAT 05201H.01, "Thermal-Hydraulic Assessment for OCNGS Control Room Habitability," Rev. 0, March 1997.
12. Proprietary information deleted
13. Handbook of Physics and Chemistry, CRC Press, 1993, page 8-42.
14. Proprietary information deleted
15. Proprietary information deleted
16. "Alternative Radiological Source Terms for Evaluating Design Basis Accidents at Nuclear Power Reactors," Regulatory Guide 1.183, July, 2000.
17. Proprietary information deleted
18. Proprietary information deleted
19. Vermont Yankee Electric Company, Calculation No. VYC-1902, "SLC Boron Concentration Calculations", July 16, 1999.
20. A. E. Knowlton, Editor in Chief, Standard Handbook for Electrical Engineers, Ninth Edition, McGraw-Hill, 1957, page 490.
21. Proprietary information deleted
22. Proprietary information deleted

## Design Inputs

Design Input Data are from Reference 5 (Item numbers in brackets) with the exception of Input 6 from References 9 and 10, and Input 7 from Reference 9.

1. Reactor power = 1950 MWt [1.1]
2. Suppression pool volume = 68,000 ft<sup>3</sup> (min), 70,000 ft<sup>3</sup> (max) [3.3]
3. RCS Inventory = 397,989 lbm (min), 559,828 lbm (max) [6.7]
4. Conductivity limit for suppression pool = 5 µmho/cm [6.12]
5. Drywell is sprayed [3.9]
6. Torus was last painted with organic material in 1972, with the exception of 70ft<sup>2</sup> touchup in 1998
7. Drywell was last painted in 1972
8. Fission product inventories, see Assumption 1 and [1.1]
9. Drywell volume = 128,370 ft<sup>3</sup> (min) [3.1]
10. Torus airspace = 103,932 ft<sup>3</sup> (min) [3.2]
11. Length of PVC jacketed cable = 25,000 ft [6.2]
12. Length of Hypalon jacketed cable = 6,000 ft [6.2]
13. Average cable OD = 1 in [6.8]
14. Jacket thickness = 0.080 in [6.3]
15. 100% of chloride-bearing cable is in conduit [6.9]
16. Minimum boron injected as sodium pentaborate from SLCS = 600 lbm [6.4]
17. B-10 enrichment is 43% [6.4]

## Calculation

### Calculation of [OH<sup>-</sup>] and [HNO<sub>3</sub>] in Water Pool vs. Time

The BWR version of the Radiolysis of Water model in the STARpH 1.04 code [1] calculates the hydroxyl ion concentration, [OH<sup>-</sup>], from fission product cesium and nitric acid concentration, [HNO<sub>3</sub>], in the containment water pool generated by radiolysis. Per Assumption 3, organic acid from paints is neglected.

Inputs to the Radiolysis of Water model are based on the Design Inputs, Items 1 to 4 and Item 8, and Assumptions 1 and 2. The core inventories by radionuclide group are:

<u>Group Title</u>	<u>Elements in Group</u>	<u>Core Inventory (Kg)</u>
I	I, Br	29.8
Cs	Cs, Rb	401
Te	Te, Sb, Se	63.5
Sr	Sr	116
Ba	Ba	178
Ru	Ru, Rh, Mo, Tc, Pd	974
Ce	Ce	1510
La	La, Zr, Nd, Eu, Nb, Pm, Pr, Sm, Y	1400

Containment water pool volume = max. suppression pool volume + max. RCS volume

It turns out that the pH calculated is the same if one uses either the minimum or maximum water volumes because one is either maximizing the  $[H^+]$  and  $[B]$  for the minimum water volume or minimizing these same quantities for the case of the maximum water volume and they compensate each other. The maximum water volume is used to be consistent with Assumption 4 to ignore the suppression pool temperature increase following a LOCA, since the maximum RCS volume is evaluated at cold conditions [19].

$$\text{Max. RCS volume} = 559,828 \text{ lbm}/62.3 \text{ lbm/ft}^3 = 8,986 \text{ ft}^3,$$

where  $62.3 \text{ lbm/ft}^3$  is the density of water at  $70^\circ\text{F}$ .

$$\text{Containment water pool volume} = 8,986 \text{ ft}^3 + 70,000 \text{ ft}^3 = 7.90\text{E}4 \text{ ft}^3 \cdot 28.3 \text{ L/ft}^3 = 2.24\text{E}6 \text{ L}$$

The core inventory of fission products in the table above is entered in column F of the Radiolysis of Water model spread sheet and a burnup value of 33,000 MWd/t is used in cell K2 so that the fission product inventory is not modified when calculating values for HI and CsOH.

The initial pH of the water pool is evaluated based on the conductivity limit for the suppression pool of  $5 \mu\text{mho/cm}$  (Design Inputs, Item 4). The concentration,  $C$ , of either positive or negative ions (since they are equal) is determined by the conductivity,  $k$ , and a constant of proportionality,  $L$ , so that  $C = k/L$ . At low concentrations,  $L$  for  $H^+$  ions is  $349.6 \text{ mho}\cdot\text{cm}^2/\text{mole}$  and for  $OH^-$  ions it is  $199.1 \text{ mho}\cdot\text{cm}^2/\text{mole}$ . Moreover, at low concentrations these can be summed so that  $L_{\text{eff}} = v^+L^+ + v^-L^-$ , where  $v$  is an index based on the number of positive and negative ions that form upon dissociation. For water,  $v^+ = 1$  and  $v^- = 1$ . For pure water,  $C = 1\text{E}-10 \text{ moles/cm}^3$  ( $1\text{E}-7 \text{ moles/L}$  of either  $H^+$  or  $OH^-$ ); therefore, the conductivity is  $k = CL_{\text{eff}} = 1\text{E}-10 (3.49.6 + 1.99.1) = 5.5\text{E}-8 \text{ mho/cm}$  or  $0.055 \mu\text{mho/cm}$ . If one assumes that the conductivity limit of the pool,  $5 \mu\text{mho/cm}$ , is due entirely to  $H^+$  ions, one can calculate a maximum value for the  $H^+$  concentration of  $C = 5\text{E}-6 \text{ mho/cm} / 349.6 \text{ mho}\cdot\text{cm}^2/\text{mole} = 1.43\text{E}-8 \text{ moles/cm}^3 = 1.43\text{E}-5 \text{ moles/L}$ . The corresponding minimum pH is 4.84.

The output of the calculation with the Radiolysis of Water model in the form of net  $[OH^-]$  and  $[HNO_3]$  as a function of time is provided in the first and last columns of the output portion of Exhibit 1.

#### Calculation of [HCl] in Water Pool vs. Time

The concentration of HCl in the water pool as a result of radiolysis of electrical cable insulation is calculated using the Radiolysis of Cable model of the STARpH 1.04 code [1]. Inputs to the Radiolysis of Cable model are based on the Design Inputs, Items 1 to 3 and Items 9 to 17, and Assumption 2.

The containment free volume is sum of the minimum dry well and torus free volumes (Design Input, Items 9 and 10). The minimum free volume is used because this quantity is in the

denominator of the expression to calculate the quantity of HCl produced by radiolysis of the cable jackets.

Containment free volume = drywell volume + torus volume

$$\begin{aligned} &= 128,370 \text{ ft}^3 + 103,932 \text{ ft}^3 \\ &= 2.32\text{E}5 \text{ ft}^3 \times (12 \text{ in/ft})^3 \times (2.54 \text{ cm/in})^3 \\ &= 6.58\text{E}9 \text{ cm}^3 \end{aligned}$$

To account for gamma radiation leakage from the containment, the STARpH 1.04 BWR Mark 1 default value of 0.068 for one minus fraction of gamma leakage is used [1].

The masses of PVC and Hypalon jacket materials are calculated from the lengths of cable containing these materials (Design Inputs, Items 11 and 12), the average cable OD (Design Inputs, Item 13), the jacket thickness (Design Inputs, Item 14) and the jacket densities (1.4 g/cm<sup>3</sup> for PVC [20] and 1.55 g/cm<sup>3</sup> for Hypalon [21]).

$$\begin{aligned} \text{Mass of PVC} &= 25,000 \text{ ft} \cdot 12 \text{ in/ft} \cdot 2.54 \text{ cm/in} \cdot \pi/4 [(1.0 \text{ in})^2 - (0.84 \text{ in})^2] \cdot (2.54 \text{ cm/in})^2 \\ &\quad \cdot 1.4\text{g/cm}^3/454\text{g/lbm} = 3.50\text{E}3 \text{ lbm} \end{aligned}$$

$$\begin{aligned} \text{Mass of Hypalon} &= 6,000 \text{ ft} \cdot 12 \text{ in/ft} \cdot 2.54 \text{ cm/in} \cdot \pi/4 [(1.0 \text{ in})^2 - (0.84 \text{ in})^2] \cdot (2.54 \text{ cm/in})^2 \\ &\quad \cdot 1.55\text{g/cm}^3/454\text{g/lbm} = 9.31\text{E}2 \text{ lbm} \end{aligned}$$

The conversion factors,  $R_\gamma$  and  $R_\beta$ , found in cells H2 and I2 of the Radiolysis of Cable spreadsheet [1], are calculated for the cable geometry below. Separate calculations are made for the Hypalon and PVC cases.

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The inputs and outputs of the calculation with the Radiolysis of Cable model are provided for Hypalon in Exhibit 2 and PVC in Exhibit 3.

#### Calculation of [H<sup>+</sup>] Added to Pool

The net hydrogen ion concentration added to the pool is the sum of the Net [OH<sup>-</sup>] in Exhibit 1 and the total [HCl] from Exhibits 2 and 3. These data are combined in Table 1 below to give Net [H<sup>+</sup>] Added. The parenthetical values for Net [H<sup>+</sup>] Added mean that the values indicated are actually [OH<sup>-</sup>] since the Net [OH<sup>-</sup>] exceeds the [HCl]. The Net [OH<sup>-</sup>] is taken from the first column of Exhibit 1, and is the [OH<sup>-</sup>] concentration in mol/L which results from the [OH<sup>-</sup>] associated with CsOH less the [H<sup>+</sup>] from initial pH, HI, and HNO<sub>3</sub>. Also shown in Table 1 is the hydrogen ion concentration, [H<sup>+</sup>] Added, due to [HNO<sub>3</sub>] and [HCl] only (i.e., neglecting the [OH<sup>-</sup>] from CsOH, initial pH, and HI).

**Table 1. Calculation of [H<sup>+</sup>] added to pool**

Time	[HNO <sub>3</sub> ]	Net [OH <sup>-</sup> ]	[HCl]	[H <sup>+</sup> ] Added	Net [H <sup>+</sup> ] Added
1h	1.10E-5	2.40E-4	1.86E-5	2.96E-5	(2.21E-4)
2h	1.49E-5	2.37E-4	3.51E-5	5.00E-5	(2.02E-4)
5h	2.27E-5	2.29E-4	7.47E-5	9.74E-5	(1.54E-4)
12h	3.54E-5	2.16E-4	1.42E-4	1.77E-4	(7.37E-5)
1d	5.24E-5	1.99E-4	2.26E-4	2.78E-4	2.74E-5
3d	1.01E-4	1.51E-4	4.61E-4	5.62E-4	3.10E-4
10d	1.93E-4	5.87E-5	8.07E-4	1.00E-3	7.48E-4
20d	2.56E-4	(4.09E-6)	9.38E-4	1.19E-3	9.42E-4
30d	2.98E-4	(4.69E-5)	9.76E-4	1.27E-3	1.02E-3

Calculation of pH

The Add Acid model of STARpH 1.04 [1] is used to determine pH vs. time for the above system using the  $[H^+]$  Added values from Table 1 and the boron concentration in the pool in the form of sodium pentaborate injected from the SLCS system. The minimum boron injected is 600 lbm (Design Inputs, Item 16) and the B-10 enrichment is 43% (Design Inputs, Item 17) so the concentration of boron is calculated as follows:

$$\text{Molecular weight of boron} = 0.43 \cdot 10.01294 + 0.56 \cdot 11.00931 = 10.47 \text{ g/mol}$$

$$[B] = 600 \text{ lbm} \cdot 454 \text{ g/lbm} / 10.47 \text{ g/mol} / 2.24 \text{E}6 \text{ L} = 1.16 \text{E-}2 \text{ mol/L}$$

Proprietary information deleted

**Results**

Proprietary information deleted

For time points 1 hr and 2 hr, pH is indicated simply as >8.0 on the basis of Assumption 6. From 5 hours on, the effect of cesium is neglected and pH is obtained by applying the values of  $[H^+]$  added from Table 1 to Exhibit 4. The results are shown in Table 2.

**Table 2. pH Results vs. Time**

<u>Time</u>	<u>pH</u>
1h	>8.0
2h	>8.0
5h	8.6
12h	8.6
1d	8.5
3d	8.4
10d	8.2
20d	8.1
30d	8.1

**Conclusion**

The pH of the suppression pool in the Vermont Yankee Nuclear Power Plant remains above 8 for 30 days following a severe core damage accident.

Exhibits 1, 2, 3, and 4 are proprietary information deleted.

Thus, pages 16 thru 19 are not provided.