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1. INTRODUCTION

Energy Operations, Inc. requested NRC to amend their facility operating license for full-scope implementation of NUREG-1465 alternative source term at Grand Gulf Nuclear Station. In its submittal, Grand Gulf attached, among other things, three documents,¹⁻³ which relate to post-LOCA suppression pool water pH control and iodine re-evolution into the containment atmosphere.

This study constitutes an evaluation of these three documents for accuracy and rigor. Much of the work is based on previous NRC NUREG reports,⁴⁻⁶ and subcontractor publications, and where possible, these connections have been validated. However, some of the secondary references were not available, and it was beyond the scope of this review to investigate secondary references. The three principal documents are all related—ref. 1 sets out the basic methodology, which is applied in refs. 2 and 3. Thus, any flaw in one document will likely affect others as well.

In general, the Grand Gulf documents represent a thorough modeling of the suppression pool pH and iodine transport. The equations have been reviewed in detail and are generally correct. There are, however, a few assumptions and models which are nonconservative. These can be summarized as follows: 1) certain calculations do not consider temperature effects, and 2) acid generation in containment is underpredicted.

2. REVIEW OF ATTACHMENT 7, “SUPPRESSION POOL PH AND IODINE RE-EVOLUTION METHODOLOGY” (REFERENCE 1)

This document outlines the basic procedures for calculating pH in suppression pool water and iodine volatility as a result of pH changes following a design basis accident. The methodology is based in large part on previous work performed by the NRC and its contractors.⁴⁻⁶ The analysis is generally sound, although the results are different than those that have been drawn in similar studies.⁷⁻⁸ The primary discrepancies are the determination of pH from the water dissociation equilibrium at 25°C, and the handling of β -radiation in generating HCl from cable insulation. This section constitutes a thorough evaluation of parameter assignments and calculational procedures, especially those which have produced results different from previous NRC studies.

2.1 Evaluation of Calculational Procedures

As mentioned above, the basic methodology appears sound. It is discussed below, with notes about assumptions, etc.

- 1) Equation (3-0a) is approximately true at 25°C, but not at higher temperatures. The activity of free hydrogen ions increases with temperature, lowering the pH. For example, at 95°C, the pH of pure water is about 6.2, as compared to 7.0 at 25°C.
- 2) The authors assume HI inventory is 5% of iodine. Reference 4 indicates a maximum of 4% HI, although using the higher value is conservative for the acid generation. Equations (3-1a)-(3.1d) appear correct.
- 3) Nitric acid production requires presence of both N₂ and O₂. Equations (3-2) appear correct.
- 4) HCl Production. Equations (3-3a,b) appear correct, although see comment 9 below.
- 5) Effects of cable enclosures (p. 7). Undoubtedly, conduit or other metal enclosures would have some mitigating effect on both acid production and distribution. Production due to γ -radiolysis would continue, although β -radiolysis would be severely retarded. Diffusion out would take more time, but still could occur. Reaction with metal would depend on metal surface, much of which is painted. In addition, condensing steam may dissolve acid and drain it to sump.
- 6) Cesium Hydroxide. The assumption of CsOH is not unreasonable.
- 7) Iodine Re-evolution. The analysis in Section 5 is taken largely from ref. 8. All equations are correct. However, there is a discrepancy in applying pH determined from Eq. (3-0a) at any temperature other than 25°C.
- 8) Appendix A. The HCl model is similar to that of ref. 4. The primary difference is the use of absorbed dose (Mrad) rather than energy deposition (MeV). It is not shown how the actual dose itself is calculated from fission product decay, so this evaluation is necessarily incomplete (see Attachment 8, Section 3.4 in page 3). I have verified values in Table A-1, and Eqs. (A-1)-(A-6) are correct. The authors use each of the variables R and G to denote multiple quantities, which is confusing. Different variable names should be used (e.g., if R is in gmol/h, then \tilde{R} could be in gmol/s).
- 9) Appendix A. A.3 Sample Calculation. Reference to Fig. A-1 should be Table A-1. Variable “t” should be the thickness “th.” Quantity on p. 6 should be “4.055E-6 mols,” although use of this quantity in the final equation does result in the correct value of 5.55E-4 mols HCl/lb-Mrad.

2.2. Parameters and Calculations

The Sample pH Calculation (ref. 1, Sect. 4) utilizes all equations properly, although it produces quite different results from a similar analysis previously performed for Grand Gulf.⁷ A comparison of these two calculations is described below.

- 1) Nitric acid formation is neglected in ref. 7, since it is much smaller than the HCl production. However, in ref. 1 it appears to be applied only in the drywell sump and only resulting from γ -radiation in the sump. This phenomenon should occur in any air-water system (including the containment), and effects of β -radiation should also be included.
- 2) In ref. 7, both CsOH and CsI were released from the primary system into the drywell as aerosol, which subsequently deposited on drywell surfaces. Only CsI was assumed to wash into sump water, which was also connected to the wetwell. This is somewhat inconsistent, but was designed to maximize the volatility of iodine. In a best estimate, both CsI and CsOH would probably transport with equal likelihood to sump water, as has been done in ref. 1.
- 3) Fission product releases were obtained from a MELCOR calculation for ref. 7, whereas the present analysis uses the releases specified in ref. 4.
- 4) In ref. 7, HCl production was calculated directly from energy deposition due to released fission products. In the present analysis, dose rates are not explained. Comparison of other quantities involved in HCl productions are shown in Table 1.

The neglect of both HNO₃ and CsOH in ref. 7 offset each other in large part. Other calculations⁸ indicate that these two quantities are of similar magnitude. The major discrepancy between refs. 1 and 7 have to do with HCl production. Reference 7 adopts the model of Wing⁹ for HCl generation, which involves the radiative flux to the *surface* of the hypalon material. Reference 1 also adopts the same equation, but uses instead the *average* flux through the material. For γ -radiation, these two quantities are nearly the same. However, for β -radiation, the average is 11.2% of the surface value. Thus, the present study lowers the effects of β -radiation in acid production to only 11.2% of its legitimate value. As seen in Table 1 below, the two studies are similar in water volume and γ -absorption fraction, and ref. 7 considers about 4 times as much hypalon. However, the acid generation from ref. 1 is an order of magnitude lower—reflecting the lower amount of hypalon and the artificially low-dose effect. ***The model of Wing should be treated as a correlation based on surface flux as the independent variable, not as a mechanistic model based on first-principles absorption of radiant energy.***

Table 1. Comparison of HCl production

Quantity	Ref. 7	Ref. 1
Hypalon (lb)	1.8×10^5	5×10^4
Water volume (m ³)	3509	3500
γ absorption fraction	0.0179	0.0181
Cum. HCl produced at 10 h (mol)	654	46

2.3. Conclusions

The analysis is well-developed and generally correct, with the following exceptions: 1) calculation of pH from Eq. (3-0a) is incorrect if temperature is not 25°C, 2) HNO₃ is formed in all water that is exposed to air and is irradiated by β - or γ -radiation, and 3) It is incorrect to use average flux instead of surface flux in calculating dose rate to cable from β -radiation. All of these errors are significant and non-conservative. In addition, care should be taken in assigning the fraction of cable that is covered by conduit. The reliability of simply not including such cabling is beyond the scope of this evaluation. Also, calculation of dose itself should be explained more fully, so as to ensure consistency with the rest of the calculations.

3. REVIEW OF ATTACHMENT 8, SUPPRESSION POOL PH ANALYSIS

This document uses ref. 1 and applies the models to a realistic suppression pool pH analysis during a 30-day accident sequence. The developments appear generally sound, and the equations are used properly. If assumptions regarding parameters are correct, then the calculated values all appear correct. However, the errors discussed in the previous section would also apply here, rendering the results questionable. Additional issues that arise in this section are discussed below.

3.1. Irradiation of Hypalon

The cumulative dose rates in various locations are calculated elsewhere and fitted to empirical equations. Following are questions concerning these doses:

- 1) The Containment Airborne Gamma Dose rate is zero after 480-h, so the integrated dose is constant after this time. Is this dose rate realistic?
- 2) There is no Suppression Pool Beta Dose. Thus, formation of nitric acid is underpredicted.

- 3) There is no mention of a drywell sump, which might also be a repository for I, Cs, and containment acids.
- 4) Hypalon inventory and exposure. The report assumes that only cable, which is easily exposed should be considered. Perhaps this is true. However, under radiation and heating, it is possible that outer Hypalon sheaths could degrade, which would both expose other layers and facilitate release of acids. This certainly true if containment temperatures exceed 200°C.

3.2 Uncertainty

Several nonconservative assumptions have been previously discussed, which have yielded overly optimistic results. However, even if we assume that the calculations of acid production are correct as they stand, or at least represent a best estimate, the uncertainty in the calculations must be considered. This subject is addressed in ref. 3, although only with respect to addition of CsOH. We here undertake a more comprehensive discussion.

In Sect. 5.7 (ref. 2), the authors calculate additions over the 30-day period of $9.77 \text{ H } 10^{-5} \text{ M}$ and $10.48 \text{ H } 10^{-5} \text{ M}$, for acid and base, respectively. The base is slightly higher than the acid, resulting in a $\text{pH} > 7$. These numbers are quite close to each other, and a small increase in acid (or decrease in base) could completely reverse this effect. That is, within the uncertainty of the numbers, the resulting pH could easily be 5 or 6.

This effect is typical for unbuffered chemical systems—near neutrality, the pH can change very rapidly with only miniscule additions of acid or base. This pattern can be seen in the authors' own illustration: ref. 3, Fig. 6-1. Although the pH in the nominal case (ref. 2, Fig. 6-1) at 30 days is comfortably high, it is on the verge of a precipitous drop. Due to the uncertainty of the parameters, it is easily possible that such a drop could happen before 30 days, as demonstrated by the authors themselves in ref. 3. A comprehensive uncertainty analysis should consider all possible uncertainties (e.g., additional acid generation).

3.3. Conclusions

In addition to the objections mentioned for ref. 1, there are additional concerns in this implementation of the pH model. Additional nitric acid production could occur that was not calculated. In addition, the uncertainty of various parameters is quite important, since the suppression pool is not buffered—prediction of pH in the range 5-9 is highly uncertain.

4. REVIEW OF ATTACHMENT 9, DOSES FROM IODINE RE-EVOLUTION

The various equations and parameters have been reviewed, and appear to all be correct. This includes the derivations of differential rate equations and their analytic solutions. Terms and parameters that are primarily derived from references other than those mentioned in this review have not been verified. Specific comments follow:

1. Table 3-1 indicates that ^{132}I is ignored. Any initial source of this isotope would certainly be decayed within one day, however, the supply is continually renewed by decay of the tellurium precursor. Thus, deposition of Te in containment may continue to replenish ^{132}I supply.
2. Several equations in Section 5.2.1 [including Eq. (5-1)] involve mixing English and metric units, with no apparent conversion factors.
3. Uncertainty analysis involving temperature (Sect. 4.2) is largely irrelevant, unless all computational parameters are temperature dependent. (cf. Sect. 2 above)
4. Uncertainty analysis regarding the CsOH source is good. Such analysis should include additional quantities, such as acid generation, in order to be comprehensive.

5. CONCLUSIONS

The documents¹⁻³ represent methodology and calculations that are generally based on NRC-approved procedures. However, some of the usage is flawed, in that certain nonconservative assumptions have been made. A revision of the approach is warranted, especially with regard to generation of containment acids and temperature dependence of certain calculations. Furthermore, it is recommended that a more comprehensive uncertainty analysis be included, since moderate parameter changes can produce large pH changes.

6. REFERENCES

1. *Attachment 7, Suppression Pool pH and Iodine Re-Evolution Methodology*, Engineering Report No. GGNS-98-0039.
2. *Attachment 8, Suppression Pool pH Analysis*, Calculation XC-Q1111-98013.
3. *Attachment 9, Iodine Re-evolution*, Calculation XC-Q1111-98014.
4. L. Soffer et al, *Accident Source Terms for Light-Water Nuclear Power Plants*, NUREG-1465 (February 1995).
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6. E. C. Beahm, C. F. Weber, T. S. Kress, and G. W. Parker, *Iodine Chemical Forms in LWR Severe Accidents*, NUREG/CR-5732 (ORNL/TM-11861), U.S. Nuclear Regulatory Commission, Oak Ridge National Laboratory, April 1992.
7. C. F. Weber and E. C. Beahm, *Iodine Revolatilization in a Grand Gulf LOCA*, ORNL/M-6544, Lockheed Martin Energy Research Corp., Oak Ridge National Laboratory, January 1999.
8. E. C. Beahm, C. F. Weber, and T. A. Dillow, *Post-Accident pH of the Perry Containment*, ORNL/NRC/LTR-98/22, U.S. Nuclear Regulatory Commission, Oak Ridge National Laboratory, March 1999.
9. J. Wing, *Post-Accident Gas Generation from Radiolysis of Organic Materials*, NUREG-1081, U.S. Nuclear Regulatory Commission (September 1984).

APPENDIX A

GRAND GULF DISCUSSION ITEMS

QUESTIONS

Equation 3-0a in page 4 of 12 of Attachment 7 is approximately true at 25°C, but not at higher temperatures. The concentration of free hydrogen ions increases with temperature, lowering the pH. For example, at 95°C, the pH of pure water is about 6.2, as compared to 7.0 at 25°C. State the maximum expected suppression pool water temperature following a design basis accident and its corresponding calculated pH value.

In Section 3.3 of Attachment 7, you used the model provided in NUREG/CR-5950 for estimating the production of hydrochloric acid. This model utilizes the radiative flux to the *surface* of the Hypalon material rather than the *average* flux through the material. For γ -radiation, these two quantities are nearly the same. However, for β -radiation, the average is 11.2% of the surface value as you indicated. Thus, your evaluation may lower the effects of β -radiation in acid production to only 11.2% of its legitimate value. Explain the differences.

CLARIFICATIONS

In Section 3.3 of Attachment 7, you stated that cables in conduit or totally enclosed raceway will not contribute any hydrochloric acid to the suppression pool. Describe in more detail its construction for leak-tightness and potential diffusion of hydrochloric acid that may be produced into the containment.

In Section 4.0 of Attachment 7, it appears that nitric acid formation is applied only in the drywell, and only resulting from gamma radiation in the sump. This phenomena should occur in any air-water system (including the containment), and effects of beta-radiation should also included.

In Attachment 8, the containment airborne gamma dose is shown to be zero after 480 hours, so the integrated dose is constant after this time. Is this realistic?

(4) No suppression pool beta dose is shown in Attachment 8. Thus, formation of nitric acid is under predicted.

(5) In Attachment 8, there is no mention of a drywell sump, which might also be a repository for I, Cs, and containment acids.

Table 3-1 of Attachment 9 indicates that ^{132}I is ignored. Any initial source of this isotope would certainly be decayed within one day; however, the supply is continually renewed by decay of the tellurium precursor. Thus, deposition of Te in containment may continue to replenish ^{132}I supply.

- (7) Several equations in Section 5.2.1 of Attachment 9 [including Eq. (5-1)] involve mixing English and metric units, with no apparent conversion factors.
- (8) Uncertainty analysis in Attachment 9 involving temperature (Section 4.2) is largely irrelevant, unless all computational parameters are temperature dependent.
- (9) Uncertainty analysis in attachment 9 regarding the CsOH source is good. Such analysis should include additional quantities, such as acid generation, in order to be comprehensive.

TYPOGRAPHICAL ERRORS

- (1) Appendix A to Attachment 7. A.3 Sample Calculation. Reference to Figure A-1 should be Table A-1. Variable “t” should be the thickness “th.” Quantity on p. 6 should be “4.055E-6 mols,” although use of this quantity in the final equation does result in the correct value of 5.55E-4 mols HCl/lb-Mrad.

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