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Attachment 9

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CHLE-016: Calculated Material Release to Estimate Chemical Effects

PROJECT DOCUMENTATION COVER PAGE

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Title: Calculated Material Release to Estima	ate Chemical Effects	n (* 1949). En formen kenne het de sterne en e
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Summary/Purpose of Analysis or Calculation:

Time constraints required calculated values for material release and chemical product formation to be determined for use by CASA. This was done using WCAP-16530-NP material release equations with a wide matrix of conditions and solubility limits calculated using Visual MINTEQ.

None of the material release results obtained from cases evaluated under SBLOCA conditions with nominal temperature profiles produce concentrations that exceeded the solubility limits set for this analysis. However, the cases evaluated under MBLOCA and LBLOCA conditions with nominal temperature profiles did result in material release quantities that produce concentrations that exceed the set limits. Calcium phosphate is the dominant product predicted to exist in solution as a result of the larger break conditions.

Only the 6" break was evaluated with a maximum temperature profile. All cases evaluated using this profile resulted in material release quantities that produce concentrations that exceeds the solubility limits set for this analysis. The dominant product predicted to exist in solution is an aluminum product.

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1.0 Introduction

South Texas Project (STP) is pursuing a risk informed approach to resolve open issues related to Generic Safety Issue (GSI) 191. This approach uses the Containment Accident Stochastic Analysis (CASA) program to determine the probability and quantify uncertainty of the Emergency Core Cooling system (ECCS) pump performance for a full spectrum of Loss of Coolant Accident (LOCA) scenarios. CASA uses best estimate values for multiple parameters to generate these results. Material release and formation of chemical products resulting from a full spectrum of LOCA scenarios are two parameters that must be defined for successful application of CASA. While it is desirable to use a matrix of experimentally obtained values determined from the Chemical Head Loss Experiments (CHLE) test program, time constraints required calculated values for material release and chemical product formation to be obtained for the assessment of head loss bump up factors used by CASA.

2.0 Methods

A spreadsheet that incorporates the WCAP-16530-NP material release equations [1] was used to determine release rates for aluminum (AI), silicon (Si) and calcium (Ca). Although a zinc (Zn) product was observed to form under STP LOCA test conditions, Zn was excluded from the analysis. This exclusion provides conservatism within the obtained results since the presence of zinc material has been shown to markedly decrease actual material release as compared to the predicted release of those included in the analysis [2]. Also, the Zn product was determined to be crystalline and mainly adhere to structures within containment as opposed to traveling readily in solution [2]; therefore the head loss resulting from this product was estimated as a particulate source as opposed to a chemical source. The head loss related to the Zn product and the assessment of bump up factors determined from this analysis are explained elsewhere [3].

To obtain material release (Ca, Si, and Al) for a full spectrum of LOCA scenarios, break sizes were divided into small break (SB), medium break (MB), and large break (LB) LOCA categories. A small break size is any break between 0" inches and 2 inches, a medium break is any break larger than 2 inches up to 6 inches, and a large break is any break greater than 6 inches. The range of water volumes [4] and fiberglass quantities [5] used in this analysis are listed in Table 1. This analysis includes other materials existing at STP at a constant value as listed in Table 2. MELCOR/Relap-5 simulated temperature profiles and pH profiles determined under STP conditions [6] were also used in this analysis. Table 3 provides an overall matrix of conditions evaluated by this approach which are defined as Cases 1-8.

Category	Break Size (")	Min Fiberglass (ft ³)	Max Fiberglass (ft ³)	Min Water (L)	Max Water (L)
Small	1.5, 2	0	10	1,775,458	2,149,838
Medium	4, 6	10	60	1,880,546	2,254,923
Large	8, 15, DEG*	60	2,385	1,880,546	2,254,923

Table 1: Variables used in analyses

*DEG is a double ended guillotine break which measures 43.84"

Table 2: Existing	materials at	STP with	associated	surface	areas or	volume
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Fixed Variables	Value	
Aluminum Submerged (ft ²)	556.7	
Aluminum Not-Submerged (ft ²)	5010.3	90. 99 1
Fiberglass Insulation (ft ³)	12.5	
Microtherm (ft ³)	1.8	
Concrete (ft ²)	1447	

Table 3: Scenario matrix of all the different cases ran for all break sizes

Case #	рН	Fiberglass (ft ³)	Water (L)	Case #	рН	Fiberglass (ft ³)	Water (L)
1	min	min	min	5	max	min	min
2	min	min	max	6	max	min	max
3	min	max	min	7	max	max	min
4	min	max	max	8	max	max	max

2.1 Temperature Profiles

Nominal sump pool temperature profiles shown in Figure 1 were generated for all break sizes identified in Table 1. These profiles describe the temperature behavior of only about the first 10.3 hours of the 30-day scenario. A maximum sump pool temperature profile as shown in Figure 2 was generated for one break size (6" break).



Figure 1 - Simulated Nominal Sump Temperature Profiles



Figure 2 – Simulated Maximum Sump Temperature Profile During a 6-inch break

Since the MELCOR/Relap-5 simulation was only run for 10.3 hours, it was necessary to extrapolate the profiles from the available data to the full 30-day scenario duration. The simulated 10.3-hour profiles were extended to 30-day profiles for calculation of material release by linearly interpolating between the last simulated point and a 30-day temperature of 110 °F. Thirty-four temperature time steps from the 30-day profiles were used in the material release calculation. These time steps were chosen to describe the trends of the initial simulated temperature profile over time as shown by Figure 3. Once these features were defined using several of the thirty-four time steps, the remaining time steps were chosen to represent the linear portion of the profile. The final 30-day temperature profiles used in the analysis are shown in Figure 4 and the individual time/temperature steps associated with these profiles are presented in Appendix A.







Figure 3 – The initial period of the adjusted profile as estimated from the simulated profile

Figure 4 - Adjusted temperature profiles for different break sizes

The approach used to adjust the simulated profiles over the 30-day period results in varying degrees of conservatism (overestimated temperatures) when comparing the complete simulated models used in the MBLOCA [7] and LBLCOA [8] CHLE tests to the adjusted models as shown in Figure 5 for 6- and 15-

inch breaks. This is because the estimated portion of the profile (between 10.3 hours and 30 days) is not linear, yet adjustment was. The magnitude of conservatism associated with the adjusted model depends whether the final point of the simulated profile is in line with the general trend of the complete profile or on an upward path of a slight oscillation that exists early in the profile.





The 4" break adjusted temperature profile is a prime example of this phenomena and results in the most conservative estimate of all breaks evaluated. The simulated data for the 4" break did not allow the accident scenario to develop long enough for a close approximation of the full profile behavior, as seen in Figure 6. For the 4" break, the point at which the extrapolation to 30-days begins is on an increasing trend. Hence, applying the linear extrapolation to 110 °F at day 30 from that point will result in a greater overestimation of the temperature profile than for the other break cases. This scenario contrasts with the DEG adjusted profile because the short time period of the DEG simulated profile as seen in Figure 6 was able to establish the general trend of decreasing temperature over time.





2.2 pH

The bounding solution pH values of 7.0 and 7.3 were determined from an analysis of STP parameters which incorporates the range of trisodium phosphate (TSP) mass and boric acid concentrations for all categories of LOCA scenarios using Visual MINTEQ [6]. The values are consistent with those measured in the CHLE tests. Since the pH values of 7.0 and 7.3 reflect complete TSP dissolution, the pH as a function of a linear TSP dissolution during the first 80 minutes of the event had to be determined. The pH resulting from a partial dissolution of the TSP at several time steps was determined using Visual MINTEQ. Regression equations were fit to the time-dependent pH trends determined from linear TSP dissolution of the minimum and maximum TSP masses. These regression equations were used to estimate the pH for use in the material release calculations. This complete analysis is presented in Appendix A. After complete dissolution, 80 minutes, the pH value was held constant.

2.3 Chemical Product Formation

The material release rates were determined using the WCAP-16530-NP material release equations [1]. However, the total quantity of material released was not assumed to fully precipitate into chemical products. Instead, solubility limits of chemical products expected to form [1] were calculated as a function of temperature and pH using Visual MINTEQ to determine the lowest concentration of metal required for product formation from the range of selected conditions. Sodium aluminum silicate and aluminum oxyhydroxide are the aluminum products described as possible precipitates in WCAP-16530-NP; however only the aluminum hydroxide solubility limit (Log K of 10.8 [9]) was considered in this

analysis since it was determined as a suitable substitute for sodium aluminum silicate in head loss testing [1]. Calcium phosphate (Log K of -28.25 [9]) solubility limits were also evaluated.

The lowest concentration of metals required to form these chemical products were determined by identifying the lowest solubility over the pH range of 7.0 to 7.3 at a defined temperature. Different temperature bounds were required for this evaluation because a decrease in temperature results in a decrease of aluminum product solubility over the given pH range as seen in Figure 7; while it produces an increase in calcium product solubility over the same pH range as seen in Figure 8. The temperature bound for aluminum product solubility was set at 140 °F (60°C) since this temperature has been used by United States Nuclear power plants in past analyses. The temperature bound for the calcium product solubility was lower than the LOCA peak temperatures because these peaks occur over a very short duration (minutes) of a 30-day event and return to temperatures $\leq 185^{\circ}$ F (85°C) for appreciable durations before declining [2, 10]. Using this approach, the concentration of aluminum expected to result in formation of a chemical product is approximately 4.9 mg/L. The calcium concentration expected to result in the formation of a chemical product was 0.8 mg/L. These values were used to assess the presence of chemical product formation from the calculated material release.





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3.0 Results

The resulting material release concentrations obtained from the complete analysis using nominal temperature profiles are listed in Table 4. The resulting material release concentrations for the analysis using the maximum temperature profile for the 6-inch break are presented by Table 5. The change in material release as a function of temperature profile is listed in Table 6. Additional details associated with these results are present in Appendix A.

Case	Break (in)	Ca (mg/L)	Si (mg/L)	Al (mg/L)	Product	Case	Break (in)	Ca (mg/L)	Si (mg/L)	Al (mg/L)	Product
	1.5	0.2	1.7	1.3	-		1.5	0.2	1.7	1.6	-
	2	0.2	1.7	3.5	-	1	2	0.2	1.7	4.1	-
	4	0.3	2.8	4.3	-	1	4	0.3	2.8	5.0	Al only
1	6	0.3	2.8	1.7	-	5	6	0.3	2.8	2.1	-
	8	0.9	8.4	1.3	Ca only	1	8	0.9	8.4	1.5	Ca only
	15	0.9	7.2	1.1	Ca only	1	15	0.9	8.0	1.3	Ca only
	20	0.9	7.7	1.1	Ca only	1	20	0.9	8.4	1.3	Ca only
	1.5	0.1	1.4	1.1	-		1.5	0.1	1.4	1.3	-
	2	0.1	1.4	2.9	-]	2	0.1	1.4	3.4	-
	4	0.2	2.3	3.6	-]	4	0.2	2.3	4.2	-
2	6	0.2	2.3	1.5	-	6	6	0.2	2.3	1.7	
	8	0.8	7.0	1.1	-		8	0.8	7.0	1.3	-
	15	0.8	6.2	0.9	-		15	0.8	6.9	1.1	-
	20	0.8	6.6	0.9	-	1	20	0.8	7.0	1.1	-
	1.5	0.3	2.9	1.4	-		1.5	0.3	2.9	1.6	-
	2	0.3	2.9	3.6	÷]	2	0.3	2.9	4.1	
	4	0.9	8.4	4.5	Ca only		4	0.9	8.4	5.3	Ca and Al
3	6	0.9	8.4	1.8	Ca only	7	6	0.9	8.4	2.2	Ca only
	8	30.0	161.5	2.6	Ca only	1	8	30.0	173.1	2.9	Ca only
	15	25.0	41.6	1.5	Ca only	1	15	26.4	45.4	1.7	Ca only
	20	30.0	72.4	1.7	Ca only	1	20	30.0	78.6	2.0	Ca only
	1.5	0.3	2.4	1.1	-		1.5	0.3	2.4	1.3	-
	2	0.3	2.4	2.9	-	1	2	0.3	2.4	3.4	-
	4	0.8	7.0	3.8	-	1	4	0.8	7.0	4.4	
4	6	0.8	7.0	1.5	-	8	6	0.8	7.0	1.8	-
	8	25.0	154.5	2.3	Ca only]	8	25.0	167.3	2.6	Ca only
	15	25.0	37.5	1.3	Ca only	1	15	25.0	41.2	1.5	Ca only
	20	25.0	65.9	1.5	Ca only	1	20	25.0	72.0	1.7	Ca only

Table 4 - Nominal temperature profile material release results

Table 5 - 6" Max temperature profile material release results

Case	Ca (mg/L)	Si (mg/L)	AI (mg/L)	Product
1	0.3	2.8	37.0	Al only
2	0.3	2.3	30.8 AI	
3	0.9	8.4	37.6	Ca and Al
4	0.8	7.0	31.3	Al only
5	0.3	2.8	41.8	Al only
6	0.3	2.3	34.9	Al only
7	0.9	8.4	42.4	Ca and Al
8	0.8	7.0	35.4	Al only

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Case	Ca	Si	AI
1	1.1	1.0	21.2
2	1.1	1.0	21.2
3	1.0	1.0	20.3
4	1.0	1.0	20.3
5	1.1	1.0	20.4
6	1.1	1.0	20.3
7	1.0	1.0	19.6
8	1.0	1.0	19.5

Table 6 – Ratios of maximum to minimum material release results from both temperature profiles for a 6" break

4.0 Conclusion

None of the material releases quantities obtained from cases evaluated under SBLOCA conditions with nominal temperature profiles produce concentrations that exceeded the solubility limits set for this analysis of 0.8 mg/L for calcium and 4.9 mg/L for aluminum. Therefore, chemical products are not expected to exist in solution under these conditions. However, the cases evaluated under MBLOCA and LBLOCA conditions with nominal temperature profiles did result in material release quantities that produce concentration that exceed the set limits. Calcium phosphate is the dominant product expected to occur as a result of the larger break conditions. Aluminum material release results only produced concentrations that exceeded the set limit in analysis of the 4" break, Cases 5 and 7, and may be an artifact of the strategy for developing the adjusted simulated temperature profiles. Both the LBLOCA and MBLOCA conditions are expected to generate chemical products; although LBLOCA conditions are expected to generate the greatest quantities.

Only the 6" break was evaluated with a maximum temperature profile. All cases evaluated using this profile resulted in material release that produce concentrations that exceeds the solubility limits set for this analysis. However, the dominant product expected to exist in solution is an aluminum product. The use of maximum temperature profile in this analysis increased the calculated aluminum material release by 20X when compared to the results obtained using the nominal temperature profile. This increase in material release produces a shift in the dominant chemical product expected to exist in solution as compared to that generated using the nominal temperature profile.

5.0 References

- 1. Lane, A.E., et al., *Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191*, 2006, Westinghouse Electric Company: Pittsburge, PA.
- 2. UNM, CHLE-016 T2 LBLOCA Test Report, 2013, UNM: NM.
- 3. Sande, T.D., Letellier, B.C. and Zigler, G.L., South Texas Project Risk-Informed GSI-191 Evaluation, Volume 3, Casa Grande Analysis, 2013: Bay City, Texas.
- 4. Alion, *STP Post-LOCA Water Volume Analysis, Rev* 1, 2012, Alion Science and Technology: Albuquerque, NM.
- 5. LANL, CASA report for STP conditions, 2012.
- 6. UNM, *Chemical Addition Calculation*, 2012, University of New Mexico: Albuquerque, NM.
- 7. UNM, Test 1: Medium Break LOCA Tank Test Parameter Summary, 2012, University of New Mexico.
- 8. UNM, T2: Large Break LOCA Tank Test Parameter Summary, 2012, University of New Mexico.
- Gustafsson, J.P., Visual MINTEQ. <u>www.lwr.kth.se/English/OurSoftware/vminteq/index.html.</u>, 2010.
- 10. UNM, CHLE-012 T1 MBLCOA Test Report 2012, University of New Mexico: Albuquerque, NM.