Attachment 7

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CHLE-014: T2 LBLOCA Test Report

PROJECT DOCUMENTATION COVER PAGE

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Title: T2 LBLOCA Test Report								
Project: Corrosion/Head Loss Experiment (CHLE) Program Date:12 January 2013								
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Summary/Purpose of Analysis or Calculation: The Large Break (LB) Loss of Coolant Accident (LOCA) tank test is one experiment within the Chemical Head Loss Experiment (CHLE) test program created to assess the generic safety issue (GSI) 191 chemical effects at the South Texas Project Nuclear Operating Company (STP) facility. The LBLOCA tank test is specifically designed to evaluate aluminum corrosion and the presence of chemical products formed as a function of key material corrosion and dissolution under STP conditions resulting from a 15"								

Chemical products did form under the simulated STP LBLOCA test conditions but primarily were adhered to the submerged galvanized steel coupons. However, the abundant product formed was not in agreement with those predicted using the WCAP-16530-NP equations [1]. This product was a crystalline zinc material which closely matched hopeite, a hydrated zinc phosphate mineral. It is likely that the zinc product did not form in solution, but nucleated and deposited onto other test materials. However evaluation of in-line membrane filters suggest small fractions of this material may have been released into solution as evident by the sporadic occurrence of zinc-phosphorus based particles, suggest determined not to significantly influence chemical product formation [1], the release of aluminum, calcium and silicon was greatly over predicted. Evaluation of the in-line membrane filters showed the diffuse presence of particles with calcium, silicon and aluminum constituents.

Finally, an increase in head loss measurements was observed using both the NEI- and blenderprocessed fiber detector beds with similar 48-hour increases of 0.2 inches of water. The 30-day head loss detected across the NEI-processed fiber bed ranged from 0.3 to 2 inches of water and may have been a function of both raw material particulate and chemical product loading. Therefore, the detector beds response to resulting chemical products merits further investigation.

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1.0 Introduction

The Large Break (LB) Loss of Coolant Accident (LOCA) tank test is one experiment within the Chemical Head Loss Experiment (CHLE) test program created to assess the generic safety issue (GSI) 191 chemical effects at the South Texas Project Nuclear Operating Company (STP) facility. The LBLOCA tank test is specifically designed to evaluate aluminum corrosion and the presence chemical products formed as a function of key material corrosion and dissolution under STP conditions resulting from a 15" pipe break.

This 30-day tank test was conducted from October 4, 2012 to November 8, 2012 with the following characteristics [2]:

- 1. Temperature profile of a 15" cold leg LBLOCA predicted by MELCOR and Relap-5.
- 2. Fiberglass volume predicted by CASA for a 15" break with 41% of test fiber used in the columns to produce fiber beds equivalent to past testing [3, 4] and the remaining quantity submerged in the corrosion tank.
- 3. STP aluminum scaffolding as the source of aluminum corrosion material with 90% of the surface area in the tank vapor space and 10% submerged in the tank.
- 4. Submerged high purity zinc granules equivalent to the most conservative STP inorganic zinc estimate.
- 5. Submerged concrete aged longer than 28 days
- 6. Galvanized steel with 90% of the surface area in the tank vapor space and 10% submerged in the tank.
- 7. Material exposure to baseline chemicals of boric acid and lithium hydroxide from time zero with incremental additions of trisodium phosphate (TSP), hydrochloric acid and nitric acid.
- 8. Column approach velocity of 0.01 ft/s.
- 9. Two types of detector beds. The 30-day test was performed using the NEI-processed debris bed. On day 30, columns were isolated and blender-processed beds were installed. After base-line head loss measurements were obtained, tank solution was allowed to circulate through the blender-processed beds for 2 days.

2.0 Summary of Results

While the results of this test are detailed in the following sections, a summary of observations are presented below.

- 1. Differential pressure increased across all NEI-processed debris beds during the 30 day test.
- 2. All blender-processed debris bed head loss measurements increased from the 48 hour baseline measurements after exposure to the test solution for 2 days.
- 3. The final measured aluminum concentration was approximately 0.07 mg/L which is below the reporting limit of 0.2 mg/L but above the method detection limit (MDL) of 0.01 mg/L.
- 4. The calcium concentration increased to approximately 1.7 mg/L by day 7 and remained at approximately at that concentration duration of the test.
- 5. The silicon concentration gradually increased to 2.7 mg/L over 30 days of testing.

- 6. The zinc concentration peaked at 0.65 mg/L by day 9 and remained close to this concentration for the duration of testing.
- 7. Filtered and total concentrations of calcium, aluminum and silicon for days 1 through 30 were determined to be statically equivalent.
- Filtered and total concentrations of zinc days 1 through 30 were determined to be statically different.
- 9. Turbidity measurements peaked at the beginning of the test at approximately 0.7 NTU and gradually decreased about 0.5 units until the end of the test.
- 10. Chemical products were observed on the submerged galvanized steel, on the bottom of the tank, and slightly on the zinc granule mesh container.
- 11. Chemical products were observed on the in-line membrane filters.

3.0 Continuous Measurements

Many parameters required to simulate the 15" LBLOCA test under STP conditions were monitored continuously using a CompactRIO acquisition system and LabVIEW program. Head loss, temperature, and velocity measurements were continuously monitored and saved every minute to a spread sheet for analysis. Results and discussion associated with these continuously monitored parameters are presented in the following sub-sections.

3.1 Head Loss Measurements through the Fiberglass Debris Beds

Head loss measurements across two types of indicator beds are a tool from a suite of diagnostics used in the CHLE testing series [4] to assess the formation of chemical products. The first indicator bed used was the NEI-processed debris bed, which is thought to be more representative of what would occur during a LOCA. It served as a nucleation site for or a filter of possible chemical products that may form during the 30-day test, Figure 1A. Then a blender- processed bed was used at the end of testing. After thirty days of testing, test solution was filtered for 48 hours through a base-lined blender-processed debris bed which is thought to be highly sensitive but not as likely to form as a function of test conditions, Figure 1B.



Figure 1: NEI-processed (A) and blender-processed (b) debris beds used in this test.

Temperature affects density and viscosity which in turns affects the overall head loss measurement. The maximum head loss discrepancy due to density as a function of temperature and equipment mounting [4] is small, ~0.75 inches of water. However, the temperature effects on viscosity can have a significant impact on head loss. Head loss measurements were corrected for both viscosity and density using the equation listed below:

$$H_{L,c} = (DP_{raw} + (\rho_t - \rho_{rt})gh)(\frac{\mu_{std}}{\mu_t})$$
(1)

Where,

- *H_{l,c}* is the corrected head loss
- DP_{raw} is the instrument differential pressure measurement
- ρ_t and ρ_r are the densities at test temperature(t) and at room temperature (rt)
- g is the gravitational constant
- *h* is the length of the PTFE tubing connecting the column to the DP cell
- μ_t and μ_{std} . are the viscosity at test temperature(t) and at standard temperature (std) of 20 °C

It should be noted that the test temperature associated with density in the above equation is not measured but estimated to be equivalent to the column temperature. However, this temperature is likely lower due to equipment configurations [4]. Therefore, a negative differential pressure measurement at test initiation is not unexpected since this is the time period where the column temperature is likely to be much greater than the solution temperature used to determine a differential pressure measurement. As the test proceeds, the difference in the column temperature and the solution temperature used to determine a differential pressure measurements significantly decreases. It should also be noted that during the first thirty minutes of testing, the columns as shown by Figure 2. Once the equipment configuration was adjusted to ensure equal flow through columns, the column temperature became equivalent at approximately one hour.



Figure 2: Temperature plot of columns during the first hour.

As seen in Figure 3, all columns experienced an increase of head loss across the NEI-process debris bed as a function of time. Column 2 had the largest final head loss final value of approximately 2.5 inches of water, while column 1 had the smallest head loss value of about 0.4 inches of water. Column 3 had a final head loss measurement of approximately 1.2 inches of water.



Figure 3: Temperature-corrected head loss through NEI-processed fiberglass debris bed.

After 30 days of testing, the blender-processed beds were installed in the same manner as that was used during the MBLCOA test [4]. The base-line head loss measurements of all the columns experienced little to no change during the 2 days of isolation as shown in Figure 4. The baseline head loss measurements of columns 1 and 2 were equivalent,~ 0.65 inches of water, and approximately 0.3 inches of water less than the base-line measurements of column 3. After the columns were linked to the corrosion tank, the head loss measurements in all columns increased approximately 0.2 inches of water over two days.



Figure 4: Temperature corrected head loss measurements produced by the blender-processed beds.

The two detector beds used in testing are very different. While the magnitude of the 48 hour blenderprocessed bed head loss measurements were more than 2 times larger than the NEI-processed head loss measurments (neglecting column 3 results), it should be noted that both detector beds registered a similar increase, ~0.2 inches of water in 2 days, as a result of test solution filtering through the different beds as shown in Table 1. The magnitude of head loss detected may be associated with the baseline measurements of the detector beds and not with the response of the detector beds itself. Column 3 results were not in agreement with the trend indicated, but column 3 was inadvertently initially linked with a slightly different flow than columns 1 and 2. The thirty day increase in head loss measurements for the NEI-processed beds range from 0.4-2 inches of water which captures the variability associated the debris bed type.

	Head loss a	across NEI b	oed ("H ₂ O)	Head loss across blender bed ("H ₂ O)			
Time	C1	C2	C3	C1	C2	C3	
Baseline	-0.01	0.37	-0.15	0.68	0.65	0.93	
48 hour	0.21	0.58	-0.14	0.91	0.86	1.16	
30 day	0.36	2.44	1.15 N/A		N/A	N/A	
Magnitude of 48 hr	1				T.		
head Loss	0.22	0.21	0.01	0.23	0.21	0.23	

Table 1: Head loss measurements of the two detector beds

The increase of head loss is evident; however the source is not. Zinc granules enclosed in a stainless steel mesh envelope were used in testing. While every effort was made to eliminate granules smaller than the mesh, some granules escaped and were captured by the in-line membrane filter, Figure 5. Upon post-test analysis of the stainless steel mesh envelope, tears in the mesh were noted, Figure 6, which may have allowed granules larger than the mesh to also escape. While chemical products were observed and will be discussed further in later sections of this document, particulates (zinc granules) were circulating as early as test initiation and may have been caught in the debris beds influencing head loss measurements.



Figure 5: SEM image of zinc used in testing (left) and product captured in-line membrane filter taken after 24 hours of testing (right). EDX analysis of capture material indicates it is likely zinc granules



Figure 6: Small tears in zinc mesh bag along the seam.

3.2 Approach Velocity through Fiberglass Debris Beds

The approach velocity was maintained near 0.01 ft/s in all three columns throughout testing, Figure 7. Approach velocity for each column was adjusted by throttling a valve on the discharge side of the centrifugal pump followed by adjustment of the variable speed drive. This approach in velocity control prevents fiber buildup for occurring within the valve resulting in minimal disturbance of the velocity during testing.



Figure 7: Superficial filtration velocity through fiberglass debris beds used in this test

3.3 Temperature

The test was designed to simulate the temperature profile of a 15-inch cold leg LBLOCA event as determined by MELCOR and Relap-5 simulations [5]. The simulation predicts a large spike in temperature, 104.1°C (219.4°F) for approximately two minutes during the initial minutes of testing as seen in Figure 8. Before this initial high temperature spike, the solution temperature is predicted to be 48.7°C (119.6°F). After the two minute spike, the solution temperature returns to approximately 75.8°C (168.4°F) with a slight increase in temperature for a few minutes followed by a linear decrease. Since the initial behavior of the simulated profile cannot be experimentally achieved with the current configuration, it was decided to begin the test at the maximum equipment temperature of 85°C (185°F), followed by a controlled linear temperature decrease. During testing, it was observed that the test solution began to cool quicker than the simulated profile due to the insertion of room temperature test materials into the heated solution, the addition of 15-gallons of room temperature TSP solution, and linking of the room temperature columns. Therefore, the heaters were turned up to return the solution temperature to the temperature required by the simulated profile. Once the solution temperature was equivalent to the simulated profile required temperature, the heaters were operated to produce a slightly slower linear decrease in temperature than necessary during the spray phase to ensure the overall corrosion that occurred experimentally was greater than or equal to the corrosion expected to occur per the simulated profile.



Figure 8: Comparison of initial minutes of simulated and experimental temperature profile. Experimental temperature is measured in the center of the corrosion tank.

The WCAP-16530-NP calculations for predicting material release were used to evaluate whether the experimental deviation from the simulated temperature profile would affect the total material release. The results of this analysis determined that the calculated overall material release expected to occur under experimental conditions is slightly higher than the WCAP-16530-NP predicted material release as shown by Table 2. The material release expected to occur during the spray phase of both profiles were determined using the time periods and temperatures shown by Figure 9. The higher calculated release of material under experimental conditions is due to the higher starting temperature of 85°C (185°F) and the higher experimental temperature for approximately 300 minutes of the event as shown in Figure 8.

Table 2: WCAP	calculation of mater	ial release	during the	spray	phase of	testing

Case	Ca Release (kg)	Si Release (kg)	Al Release (kg)
Experimental	1.19	1.72	0.86
Simulation	1.12	1.47	0.72





Once the spray phase ended, the experimental profile linearly decreased to the simulated profile within hours and then traced the simulated profile for the duration of the test as shown in Figure 10. During day 28 to 34, the experimental temperature oscillates around the simulated profile temperature which is a result of non-optimized heater controller operation.



Figure 10: Comparison of simulated and experimental temperature profile.

The pool temperature appears to be slightly higher than the column as indicated by Figure 11. However the difference in temperature is only greater than 1° C for the first four days. As explained in previous

reports [4] the temperatures difference below 1°C are within the noise of the instrument and may not exist. Therefore, it is only certain that a slight temperature difference between the columns and the tank solution exist during the first few days of testing.

A difference between the tank solution temperature and tank vapor temperature of up to 4.5°C is also shown by Figure 11. The cycling associated with this difference (~0.5°C) is attributed to the change in room temperature from day to night since the cycling period is approximately 24 hours. The large spikes in temperature differences at day 30 and 34 are due to the removal of the tank lid for experimental needs.



Figure 11: Difference between pool and columns and pool and vapor space temperatures over the test.

4.0 Discrete Measurements

While many parameters were continually measured, some parameters such as soluble metal concentration, pH and turbidity were measured on discrete time frames. Samples for soluble metal concentration measurements were taken daily for the first ten days, followed by three times a week until the end of testing. The test solution pH was monitored both continuously with an in-line pH meter and at discrete times with a bench top pH probe to monitor for in-line pH meter drift. The discrete pH measurements were performed on the same sampling schedule as the soluble metal concentration measurements. Tank turbidity measurements were taken on the same sampling schedule as the soluble metal concentration inlet and outlet of the heat exchanger were taken on the same sampling schedule as the soluble metal inlet and outlet of the heat exchanger were taken on the same sampling schedule as the soluble metal in the soluble metal concentration measurements. Results and discussion associated with these parameters are presented in the following sub-sections.

4.1 Solution pH

The solution pH was measured by both in-line and bench top automatic temperature correction (ATC) pH meters. The in-line pH meter only calibrates with a two-point curve and was calibrated using the pH 7 and the pH 10 standards. This two-point calibration results in unreliable measurements below pH 7 for this test. Therefore the starting solution pH was obtained using the bench top meter which was calibrated using a three point calibration of standard 4, 7 and 10. Above pH 7, the bench top and in-line pH results were within 0.1 pH units of each other. As determined by the bench top pH meter, the solution pH at test initiation was 4.5 and increased to 7.3 during the addition of TSP. The solution pH remained at 7.3 ± 0.1 for the duration of the test as shown by Figure 12. Post-test evaluation of the in-line pH meter showed that the in-line pH meter was not functioning correctly which provides explanation for the erratic behavior observed in Figure 12.



Figure 12: T1 solution pH measurements.

4.2 Solution Turbidity

Turbidity measurements of the bulk test solution and solution from two locations in the heat exchanger loop (upstream and downstream of the heat exchanger) were collected. All turbidity measurements throughout the test were below the turbidity level which was shown to correlate well with 1 mg/L aluminum precipitate [3]. The turbidity was the highest on the first day of testing, ~0.7 NTU, and gradually decreased over the thirty days of testing to ~0.2 NTU, Figure 13. An increase in the tank turbidity measurement occurred when the blender beds were linked to the tank. This was likely due to loosely attached fiber and fiber-binder released from the new blender beds given that the tank turbidity measurements were constant during the new column isolation and no other source of particulate or chemical product was within the isolated columns. During the thirty days of testing, the solution

turbidity when cooled by the heat exchanger remained relatively similar to the test-temperature solution turbidity, Figure 13.



Figure 13: T2 solution turbidity measurements

4.3 Soluble Metal Concentrations

The total and filtered solution concentrations of aluminum, calcium, silicon and zinc were measured frequently during testing by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis. While total concentration samples were immediately acidified for analysis, the filtered concentration samples were run through a 0.45 μ m filter before acidification to remove particles larger than 0.45 μ m from solution. The filtered and total concentrations for the individual analytes taken from day 1 to 30 were subjected to statistical analysis using a t-test for both a 1-tail and 2-tail test with a p-value < 0.05 to determine whether the measurements were statistically equivalent. Finally, the predicted releases of these materials generated from the WCAP-16530-NP equations were compared to the experimentally obtained release. Zinc material release predictions are not generated in this analysis because it was previously determined that it does not contribute significant material release to the system [1].

The final measured aluminum concentration was approximately 0.07 mg/L and was present at this concentration by Day 1 as seen in Figure 14. The aluminum concentration reported is less than the reporting detection limit of 0.2 mg/L, but is above the equipment MDL. Therefore there is a degree of uncertainty associated with the absolute values in Figure 14. While the submerged aluminum surface area in this test (0.31 ft²) was about a third less than that in the MBLOCA test (0.47 ft²), there was much less aluminum detected in this test when compared to the MBLOCA test [4]. The T-statistic value listed in Table 3 was calculated from the analysis of the measured total and filtered aluminum concentration and is less than the T-critical value; therefore the total and filtered sample concentrations are



equivalent. Consequently, an aluminum product greater than 0.45 μ m is not expected to exist in solution.

Figure 14: T1 measured and predicted aluminum concentration over time

Т	ab	ble	e	3:	1	-test	results	for	а	luminum	measurements

	Al Total (mg/L)	Al Filtered (mg/L)	
Mean	0.0682	0.0661	
Variance	0.0001	0.0001	
Observations	20	20	
Pearson Correlation	0.6257		
Hypothesized Mean Difference	0.0000		
df	19		
t Statistic	1.1698		
P(T<=t) one-tail	0.1283		
t Critical one-tail	1.7291		
P(T<=t) two-tail	0.2565		
t Critical two-tail	2.0930		

Also, the measured 30-day aluminum concentration is approximately eleven times less than that predicted by the WCAP equations [1]. This difference between the predicted and experimental release is much larger than that obtained when evaluating the MBLCOA test results with the same predictive tool. While the difference between the experimental and predicted aluminum increased significantly in the presence of zinc material during the LBLOCA test, predictions for both the MBLOCA and LBLOCA overestimated the aluminum material release. Although the predictive and experimental releases were

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not in good numerical agreement, they were in agreement in that the release was to be very small, < 1 mg/L.

The calcium concentration after 30 days of testing was approximately 1.7 mg/L as shown by Figure 15. Although this test contained about 2.5 times more fiberglass than the MBLCOA test [4], this concentration was very close to that measured at the end of the MBLOCA test (1.8 mg/L). Statistically the filtered concentrations were equivalent to the total concentrations given that the T-statistic value was less than the T-critical value as listed in Table 4. Therefore it is likely that a calcium product greater than 0.45 μ m is not present in solution.



Figure 15: T1 measured and predicted calcium concentration over time

Table 4: T	-test results	for cald	cium meas	urements

	Ca total (mg/L)	Ca filtered (mg/L)
Mean	1.5850	1.5650
Variance	0.0108	0.0161
Observations	20	20
Pearson Correlation	0.8361	
Hypothesized Mean Difference	0.0000	
df	19	
t Statistic	1.2854	
P(T<=t) one-tail	0.1071	
t Critical one-tail	1.7291	
P(T<=t) two-tail	0.2141	
t Critical two-tail	2.0930	

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The experimentally obtained calcium concentration was approximately 70% of the predicted concentration obtained using the WCAP-16530 equations [1]. While the predictive equations under estimated the calcium release in the MBLOCA test [4], it over estimated the release of calcium in this test.

The measured silicon concentration was approximately 2.7 mg/L after 30 days of testing as shown by Figure 16. This concentration is approximately half of that measured at the end of the MBLCOA Test [4] even though there was approximately 2.5 times more fiberglass in solution. The silicon concentration increased continually over the 30 days of testing. Statistical evaluation of the total and filtered sample concentrations were equivalent given that the T-statistic value is less than the t-critical value. Therefore it is likely that a silicon product greater than 0.45 μ m is not present in solution. Also, the difference between the experimentally obtained and WCAP-16530 predicted [1]silicon concentration was large as opposed to the very small difference observed for the MBLCOA.





	Si tota	l (mg/L)	Si filtered (mg/L)	
Mean		2.2500		2.2400
Variance		0.1153		0.1278
Observations		20		20
Pearson Correlation		0.9844		
Hypothesized Mean Difference		0.0000		
df		19		
t Statistic		0.6980		
P(T<=t) one-tail		0.2468		
t Critical one-tail		1.7291		
P(T<=t) two-tail		0.4936		
t Critical two-tail		2.0930		

Table 5: T-test results for silicon measurements

The zinc concentration peaked to 0.65 mg/L by day 9 and remained close to this concentration for the duration of testing as seen in Figure 17. Statistically, the filtered concentrations were different than the total concentrations given the t-statistic value is greater than the t-critical value as listed in Table 6. This may indicate that a zinc product (raw material or in-situ formed product) greater than 0.45 μ m existed in solution. Zinc products were captured by the in-line membrane filters, but it is unknown whether this product was formed on a surface and brushed into solution or if this product is the result of a solubility limit existing in solution. It is also possible the product is a zinc granule that escaped from the mesh envelope.



Figure 17: T1 measured and predicted zinc concentration over time

	Zn total (mg/L)	Zn filtered (mg/L)	
Mean	0.5690	0.5560	
Variance	0.0071	0.0095	
Observations	20	20	
Pearson Correlation	0.9793		
Hypothesized Mean Difference	0.0000		
df	19		
t Statistic	2.5573		
P(T<=t) one-tail	0.0096		
t Critical one-tail	1.7291		
P(T<=t) two-tail	0.0193		
t Critical two-tail	2.0930		

Table 6: T-test results for zinc measurements

In conclusion, the total and filtered concentrations were statistically equivalent for calcium, silicon, and aluminum concentrations. However, there was a statistical difference in the total and filtered zinc concentrations. The analysis supports that only zinc chemical products or escaped granules > 0.45 μ m are expected to exist in solution. The predicted material releases for all materials were larger than the experimental release. The difference between the predicted material release and experimentally obtained material release was much larger than that observed under the MBLOCA test conditions. These results suggest that the presence of zinc in solution may have an effect on the overall release of material and therefore should be considered in future calculated predictions.

5.0 Post Test Sample Analysis

5.1 Aluminum Corrosion

Aluminum corrosion is the sum of the aluminum mass released into solution and the mass assimilated into the scale layer on the corroded material itself as defined by equation 2. Once in solution, the corroded aluminum can remain in solution, precipitate and be separated from solution by sedimentation or filtration, or form scale on other surfaces in the system as shown by equation 3. The concentration of material remaining in solution is easily obtained by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements. The mass of aluminum released into solution which does not remain in solution as a result of further chemical reaction can be estimated using a total aluminum mass balance of corroded aluminum. However, this mass balance requires the mass of corroded aluminum incorporated into the scale.

$$Al_{corroded} = Al_{scale} + Al_{released}$$
(2)

$$Al_{released} = Al_{soluble} + Al_{precipitated/scale}$$
(3)

To determine the mass of corroded aluminum that was incorporated into the scale layer on the material itself requires the knowledge of the original and final scale composition. Methods defined in the

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MBLOCA test [4] were used to evaluate this mass. The results obtained from X-ray photoelectron spectroscopy (XPS) of the pre-test scale was in agreement with the results obtained from the MBLOCA test [4] confirming that the original scale on the aluminum sample was a combination of aluminum phosphate (AIPO₄) and aluminum (Al₂O₃) as shown by Figure 18. However the distribution of the scale determined for the pre-test sample from the LBLCOA analysis was different than that determined from the pre-test MBLCOA sample. The analysis of the LBLOCA pre-test sample indicated that the initial scale was approximately 90/10 percent AIPO₄/ Al₂O₃ as opposed to the MBLOCA pre-test sample indication of approximately 55/45 percent AIPO₄/ Al₂O₃. Given that the samples analyzed were taken from the same source, further analysis on both samples were performed and it was determined that the MBLOCA results were erroneous due to charging issues. The original scale for the pre-test samples was confirmed to consist of approximately 90/10 percent AIPO₄/ Al₂O₃.





Given that the pre-test sample already had a notable presence of phosphate, a review of alloys was performed to obtain more insight into the previously undefined plant sample provided. It is assumed that the aluminum specimen obtained from STP may have been subject a phosphate conversion coating [6] which provides a mild wear resistance. However, the thickness of this coating is unknown. The XPS analysis of the LBLOCA post test samples showed a slight increase of the AlPO₄ within the scale composition. This the small increase, <2%, is less than the variability associated with multiple analyses of the same sample as seen in Table7. Since the change in scale composition is within the variability of the measurement approach and a pre-existing phosphate scale of unknown thickness exist, the attempt to determine aluminum corrosion converted to scale was abandoned. Therefore the final mass of corroded aluminum that occurred under these test conditions could not be estimated.

i and in the second sec	LBLOCA		MBLOCA	
Sample	Aluminum phosphate (%)	Alumina (%)	Aluminum phosphate (%)	Alumina (%)
Background Vapor	90.6	9.4	92.8	7.2
Background Submerged	93.1	6.9	100.0	0.0
Post Test Vapor	92.1	7.9	91.2	8.8
Post Test Submerged	94.6	5.4	90.1	9.9

Table 7: scale composition of pre- and post-test aluminum samples

5.2 Chemical product

During testing, white product was observed on discrete areas of the submerged galvanized steel as shown by Figure 19 and on the tank floor below the submerged galvanized steel coupons as seen in Figure 20. After testing, a similar product was observed on small areas of the mesh envelope which housed the zinc granules as well as on the zinc granules themselves as shown by Figure 21. This product was not overtly evident on the fiber beds, therefore debris captured by the beds are not explored in this section. It should be noted that these type of white deposits on the galvanized steel or inorganic zinc coated coupon have been seen in past testing done under similar conditions [7] as shown by Figure 22. However these deposits observed in past testing [7] were not subject of rigorous analysis.



Figure 19: Submerged galvanized steel coupons with white chemical deposit



Figure 20: White chemical product located mainly in the areas directly below the submerged galvanized steel coupons



Figure 21: White chemical product on the mesh envelope and on the zinc spheres it contained



Figure 4-8. GS-335 submerged, pre-test.



Figure 4-9. GS-335 submerged, post-test.



Figure 4-14. IOZ-79 submerged, pre-test.



Figure 4-15. IOZ-79 submerged, post-test.

Figure 22: White chemical product galvanized steel and inorganic zinc coated steel observed in past testing[7]

The white chemical product was taken from the galvanized steel plates and subjected to analysis by scanning electron microcopy (SEM) with Energy-dispersive X-ray spectroscopy (EDX), XPS, and ICP-AES after acid digestion. This product was also evaluated by X-ray diffraction (XRD) analysis. Samples taken from the tank floor were also analyzed by XRD to determine the composition and morphology of the substance.

As seen in SEM image of the chemical product in Figure 23, it appears with a flake like consistency and has constituents of zinc (~25 atomic %), phosphorous (~19 atomic %), and oxygen (~56 atomic %). The size and shape of the product range and is likely a result of scraping the product from a surface. SEM analysis of in-line membrane (discussed in detail in the upcoming section) did capture rod shaped particulate with very similar composition to that of the material scraped from the coupons. These capture particulate were <10 μ m long and a 1-2 μ m wide. An example of this product is shown by Figure 24 and may indicate the shape and size of such product that may be traveling within solution. The ICP-AES results obtained from analysis of the digested product are in agreement that the metal associated with this material is zinc (99.7%). XPS analysis determined that the material was also composed of zinc (18.3 atomic %), phosphorous (8.4 atomic %) and oxygen (73.3 atomic %) but could not determine a stoichiometric formula from the biding energies.



Figure 23: SEM image of white chemical product with a 50 μm scale bar



Figure 24: SEM image of rod shaped product captured on filter with equivalent composition as that scraped from coupons.

To further characterize the chemical product, it was evaluated by XRD analysis. The resulting diffraction patterns were analyzed using Jade 9.0 Plus software from by Materials Data, Incorporated. The Jade 9 software matches the diffractogram peaks obtained from the sample analyzed to standards found in the International Center for Diffraction Data (ICDD) database. It then assigns each match a Figure of Merit (FOM) value based on how well the experimental results compare to the standards. A FOM of zero indicates a perfect fit; while a FOM range of 0-20 is considered a close fit. The best FOM obtained from the analysis of the chemical product scraped from the submerged coupons was 9.6 and matched a synthetic Hopeite, $Zn_3(PO_4)_2$ ·4H₂O. As seen in Figure 25, the 2 Θ angle positions of the sample exactly match that of the standard and the sample intensity (indicated in black) slightly deviate from the standard intensities (indicated in green). This deviation in intensities is likely due to preferred particle orientation which explains why the FOM is not closer to 0. The stoichiometry of synthetic Hopeite, $Zn_3(PO_4)_2$ ·4H₂O, is also in close agreement with the percent atomic distribution determined by EDX analysis of the SEM image and the XPS results.



Figure 25: XRD result of chemical product obtained from submerged coupon

XRD analyses of samples taken from the north east, north west, and south west corners of the tank floor supports that the chemical product in these areas is equivalent to that found on the submerged coupons. It should be noted that the submerged galvanized steel coupons were located on the north side of the tank. The analysis of the product taken from the north east corner produced a diffraction pattern very close to synthetic hopeite (Figure 26) with a FOM of 9.6. The results obtained from the sample taken from the north west corner (Figure 27) also indicate that the product was hopeite. The best FOM of 2.9 determined from this match indicated that product was hopeite with a carbonate group, not the synthetic hopeite. However, the synthetic hopeite was also listed as a close match with a FOM of 4. The sample obtained from the south west corner was very close to the mass limit required for analysis and produced a FOM of 27.8. While this FOM indicates the match was between the sample and the identified standard was not very good, this was the best FOM obtained from the analysis and it identified the material as synthetic hopeite.







Figure 27: XRD result of chemical product obtained from submerged coupon End Test 2 NW Corner Precipitate



Figure 28: XRD result of chemical product obtained from submerged coupon End Test 2 SW Corner Precipitate

The results from multiple analyses on the white chemical product indicate that it is a crystalline form of a zinc phosphate solid. This compound, $Zn_3(PO_4)_2 \cdot 4H_2O$, also has a thermodynamic equilibrium dissolution coefficient (Log K) of -35.42 [8] which also supports that this compound is very insoluble. Consequently, the chemical product observed in abundance on the galvanized coupons under LBOCA conditions is a compound that has not been previously identified as a compound of concern for head loss tests.

5.3 Fiber bed

The NEI-processed fiber bed was collected on Day 30 and the blender-processed fiber bed was collected on Day 34. This test experienced a continually increasing head loss across the NEI-processed fiber bed which ranged from 0.4-2 inches of water and a head loss across the blender-processed fiber bed of approximately 0.2 inches of water. The appearance of the fiber beds at the end of testing were similar to that found at the end of the MBLOCA test [4] as shown by Figures Figure 29 and Figure 30. Both detector beds had a disperse collection of white, brown and greyish/black particulates on the tops of the beds. Particulate capture within the bed was not observed by the naked eye during dissection of the detector beds.



Figure 29: NEI-processed beds LBLOCA C3 (left) and MBLOCA C3 (right) beds after exposure to test solution



Figure 30: Blender-process beds LBLOCA C2 (left) and MBLOCA C3 (right) beds after exposure to test solution

The bottom of both detector beds have a similar pattern which has been observed in past testing as seen as seen in Figure 31. The pattern appears slightly more pronounced on the blender-processed fiber bed than on the NEI-processed fiber bed. When examining the bottom of the beds, areas of nodules appeared to have a slightly different texture than the others and in some cases small craters were noticed on the bottome of the bed as seen in Figure 32.



Figure 31: LBLOCA column 3 bottom of NEI-processed (left) and blender processed (right) beds after exposure to test solution



Figure 32: NEI-processed fiber bed bottom of column 1 (Left) and column 2 (right) with missing nodules

Representative sample areas of fiber with particulate were the taken from the top of the debris beds and evaluated with SEM. As seen in past testing [4], the particulate capture on top of the detector beds had constituents of probable chemical products derived from the solution chemistry. Images of the particle capture are presented by Figure 33. Further details for the SEM analysis of the fiber bed particle capture can be found in Appendix 1.



Figure 33: SEM images of a whitish (left), brownish (middle), and greyish particulate captured by the fiber beds

5.4 In-line Membrane Filters

Test solution was run through a $0.1 \,\mu$ m in-line membrane filter upstream and downstream of the heat exchanger to determine whether or not predicted temperature decreases caused precipitation to occur. Filtering of upstream solution occurred first to establish a baseline of particles existing before the simulated temperature drop. Once the upstream membranes were obtained, solution was then filtered downstream of the heat exchangers to capture precipitation, if it occurred. During SEM evaluation of these in-line membrane filters, a visual difference between the upstream and downstream membranes was not noticed. This could be a result of the heat exchanger design which allowed for a majority of heat loss at high temperatures to occur in the lines before the heat exchanger or it could be due to the fact nothing precipitated as a function of temperature.

Regardless of location, the debris captured on the inline membrane filters had constituents indicative of both possible chemical products and equipment debris, Appendix 1. Particles captured appeared both amorphous and defined as shown by Figure 34. Also, most of the membranes evaluated appeared coated with material as seen in Figure 35.



Figure 34: Examples of particles captured by the in-line membrane filters



Figure 35: Clean membrane (left) and example of coating observed on most membranes (left) evaluated from test

5.5 Zeta Potential and Size Distribution

Samples were stored at the end of the test for size distribution and zeta potential analysis. However, the samples were not run until approximately two months after testing. Therefore any results obtained from this analysis are not included in this report and were only for internal use due to unquantifiable uncertainties that are associated with the results.

6.0 Conclusion

Chemical products did form under the simulated STP LBLOCA test conditions but primarily were adhered to the galvanized coupons. However, the abundant product formed was not in agreement with those predicted using the WCAP-16530-NP equations [1]. This product was a crystalline zinc material which closely matched hopeite, a hydrated zinc phosphate mineral. It is likely that the zinc product did not form in solution, but nucleated and deposited onto other test materials. However evaluation of in-line membrane filters suggest small fractions of this material may have been released into solution as evident by the sporadic occurrence of zinc-phosphorus based particles, $\leq 10 \ \mu$ m. Not only was the abundant chemical product formed in this test derived from a material previously determined not to significantly influence chemical product formation [1], the release of aluminum, calcium and silicon was greatly over predicted. Evaluation of the in-line membrane filters showed the diffuse presence of particles with calcium, silicon and aluminum constituents.

Finally, an increase in head loss measurements was observed using both the NEI- and blenderprocessed fiber detector beds with similar 48-hour increases of 0.2 inches of water. The 30-day head loss detected across the NEI-processed fiber bed ranged from 0.3 to 2 inches of water and may have been a function of both raw material particulate and chemical product loading. Therefore, the detector beds response to resulting chemical products merits further investigation.

7.0 References

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