

Attachment 12

CHLE-020:

Test Results for 10-day Chemical Effects Test Simulating
LBLOCA Condition (T5), Revision 3

PROJECT DOCUMENTATION COVER PAGE

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Title: Test results for a 10-day chemical effects test simulating LBLOCA conditions (T5)		
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Summary/Purpose of Analysis or Calculation:

This report presents the results of CHLE Test T5 that was conducted to validate the conclusions of LBLOCA Test T2 conducted in 2012 and to compare it with other testing conditions. A 10-day chemical effect test with blender-processed bed under prototypical LBLOCA conditions was performed to (1) examine the release of chemical species (Al, Ca, Si, and Zn) into solution, (2) evaluate whether aluminum would precipitate under these conditions, and (3) evaluate the corrosion-induced chemical effects on head loss in blender-processed debris beds. In addition, the test results were combined with results from previous CHLE tests to develop a practical aluminum solubility boundary map. Test T5 contained aluminum scaffolding, zinc, galvanized steel, concrete, and fiberglass in the tank. The temperature profile was set according to prototypical LBLOCA conditions calculated by MELCOR and was identical with that of Test T2.

Based on a comparison between UNM's previous CHLE test results and the proposed precipitation map developed from thermodynamic calculations using Visual MINTEQ, aluminum precipitation would not occur in CHLE Tests T1, T2, or T5, and aluminum precipitation is predicted to occur on Day 7 in Test T3 and on Day 6 in Test T4, when the testing data points crossed over the proposed precipitation line. The predictions using the precipitation map also validated the turbidity measurement in Tests T3 and T4. Therefore, precipitation map analysis with turbidity measurement can be used as a reliable tool to predict the aluminum precipitation in CHLE testing.

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Contents

List of Figures	3
List of Tables	3
1.0 Executive Summary	4
2.0 Introduction.....	6
3.0 Experimental Methods and Materials.....	6
4.0 Experimental Test Conditions	8
4.1 Tank temperature.....	8
4.2 Solution pH.....	8
4.3 Approach velocity.....	9
5.0 Results and Discussion	10
5.1 Solution Turbidity.....	10
5.2 Metal (Al, Si, Ca, Zn) concentration in solution.....	11
5.3 Aluminum hydroxide precipitation map based on Visual MINTEQ.....	15
5.4 Normalized Head loss.....	19
5.5 Bed Examination.....	20
5.6 Corrosion product with SEM-EDS analysis	20
6.0 Summary and Conclusions	23
7.0 References.....	25

List of Figures

Figure 1: Experimental tank temperature profiles for Tests T2 and T5.....	9
Figure 2: T5 test solution pH measurements using bench-top pH meter	9
Figure 3: Turbidity measurements (a) at tank and room temperature for Test T5, (b) for Tests T5 and T2.	11
Figure 4: Test T5 measured silicon concentration for unfiltered (total) and filtered samples.....	13
Figure 5: Test T5 measured zinc concentration for unfiltered and filtered samples.....	14
Figure 6: Particle size of selected day samples in Test T5.	15
Figure 7: Test T5 aluminum concentration in solution and solubility curve for aluminum hydroxide $\text{Al}(\text{OH})_3$. Solubility of $\text{Al}(\text{OH})_3$ was calculated at $\text{pH}=7.20$ with the Test T5 temperature profile using Visual MINTEQ.....	15
Figure 8: Aluminum hydroxide precipitation map ($\text{pH}+\text{p}[\text{Al}]_{\text{T}}$ vs. temperature) with plotting UNM Test T5 data to identify Al precipitation.....	16
Figure 9: (a) Aluminum hydroxide precipitation map ($\text{pH}+\text{p}[\text{Al}]_{\text{T}}$ vs. temperature) with results from Tests T1, T2, T3, T4, and T5; (b) turbidity trend with corresponding aluminum concentration in Tests T3 and T4.	18
Figure 10: Normalized head loss measurements produced by all three columns for (a) Test T5 with blender-processed beds, and (b) Test T2 with NEI-processed beds.....	21
Figure 11: Columns 1 (left), 2 (center), and 3 (right) in Test T5 after exposure to 10-day test solution....	22
Figure 12: Scale formation on coupons. Two galvanized steel coupons are at the ends of the racks, the other coupons in the racks being zinc.	22
Figure 13: SEM of the deposited (zinc phosphate product) scale on the top surface of fiber beds from Test T5 with EDS results.....	23

List of Tables

Table 1: Differences between the conditions of Tests T5 and T2.....	6
Table 2: Chemicals added to the CHLE solution	6
Table 3: Quantities of materials used in Test T5.....	7
Table 4: Filtered and unfiltered (total) concentration of aluminum for Test T5	12
Table 5: Filtered and unfiltered (total) concentration of silicon for Test T5	13
Table 6: Filtered and unfiltered concentration of zinc for Test T5	14

1.0 Executive Summary

The Corrosion/Head Loss Experimental (CHLE) program is being conducted at the University of New Mexico (UNM) to investigate the effects of chemical precipitates on Emergency Core Cooling System (ECCS) strainer blockage under realistic conditions for the South Texas Project (STP) in support of the risk-informed resolution of Nuclear Regulatory Commission (NRC) Generic Safety Issue (GSI) 191. Three objectives within the CHLE program are to determine, for realistic conditions, (1) the rates of corrosion and release of chemical reactants and products from materials present in the containment building at a nuclear power plant (2) whether or not chemical precipitates can form in the post loss-of-coolant accident (LOCA) environment, and (3) the effect on ECCS strainer debris bed head loss from any observed chemical products. This report describes the results from one specific test in the CHLE program, designated Test T5.

Test T5 was designed to simulate the chemical effects that occur in a large-break LOCA using the prototypical temperature profile and chemistry conditions during a 15-inch cold leg break at STP. The objectives of the test were to (1) examine the release of chemical species (Al, Ca, Si, and Zn) into solution, (2) evaluate whether aluminum would precipitate under these conditions, and (3) evaluate the corrosion-induced chemical effects on head loss in blender-processed debris beds. One important factor in Test T5 was the selection of the debris bed. One debris preparation method, known as the NEI method, involves disaggregating a fiber blanket with a commercial pressure-washer. The NEI pressure-washed fiber, when introduced into a head loss column, results in a fluffy debris bed that does not generate as much head loss when collecting particles. The second method, known as the blender-processed method, involves chopping of fibers in a blender. The blender-processed fiber results in a denser bed, but was not used in most of the long-duration CHLE tank tests because it was not reproducible and did not produce predictable results when variables such as approach velocity or fiber quantity was varied. An earlier large break LOCA test was conducted in fall of 2012 using NEI debris beds. That test, designated as Test T2, found that zinc particles contributed to head loss but that chemical effects from the precipitation of aluminum did not occur. Test T5 results were compared with those of Test T2 to assess whether the use of blender-processed debris beds provides additional insight into chemical effects at STP. The main differences between Tests T5 and T2 were the use of a different debris bed, a shorter duration for Test T5 (10 days vs. 30 days), and the use of a different form of zinc.

The chemicals concentrations in solution (Al, Ca, Si, and Zn) in Test T5 were generally similar to Test T2. Aluminum and calcium were both below the commercial laboratory's reporting limits (except two samples of aluminum in Test T5, which were essentially at the detection limit). Silicon reached a maximum concentration of 2.8 mg/L in Test T5 and 2.7 mg/L in Test T2. Zinc reached a maximum concentration of 1.1 mg/L in Test T5 and 0.65 mg/L in Test T2. The turbidity followed the same trend in both tests, peaking early during the first day and declining gradually over the duration of the test. The zinc concentration and turbidity at the beginning of Test T5 were higher than in Test T2, and this result can be attributed to increased zinc release in Test T5 resulting from the use of a different zinc source material (zinc coupons as opposed to zinc granules). Nevertheless, the similarity between the metal concentration results in the two tests indicates that the tests are relatively reproducible when conducted under similar conditions, and that Test T5 was a reasonable replication of Test T2. No

precipitation of aluminum occurred in Test T5, a primary result that was consistent with the results in Test T2. Lack of precipitation was evidenced by steadily declining turbidity. In other tests (Tests T3 and T4, as well as preliminary tests involving the injection of aluminum nitrate), an increase in turbidity was well correlated with the precipitation of aluminum.

The normalized head loss in all three columns in Test T5 (blender-processed debris bed) started increasing rapidly at the beginning of the test, and then slowly leveled off over the remaining test period. Although the trends were similar in the three columns, the absolute value of head loss was different. Head loss appears to be related to the presence of zinc-containing particles in solution during the initial hours of the test. The presence of zinc particles was evidenced by a difference between total and filtered zinc concentrations, and turbidity. Under the conditions of the test, zinc particles appear to be released into solution from a zinc surface soon after the coupons were placed in the tank, and would be appearing in solution during the same time a debris bed was forming during an actual LOCA. Thus, it may be appropriate to treat the zinc as a particle source during bed formation rather than a chemical effect later in the accident scenario.

When compared to Test T2, the blender-processed debris beds produced significantly higher head loss than NEI-processed debris beds at similar conditions. Other than the higher head loss, the results are consistent with the results of Test T2. Zinc particles at the beginning of each test cause initial higher turbidity, which declined as the test progressed. Earlier tests (Tests T3 and T4, as well as additional preliminary tests) demonstrated that the blender-processed beds are highly sensitive to the presence of aluminum precipitates, even if the head loss is already relatively high from other sources. After the initial head loss increase caused by the zinc particles in Test T5, there was not a subsequent increase in head loss that might have been caused by a separate perturbation to the system. The absence of a significant increase in head loss during the second half of Test T5 is consistent with turbidity and aluminum concentration data that indicate that aluminum precipitation did not occur in Test 5. Thus, the head loss results of Test 5 are not inconsistent with the conclusion that aluminum precipitation did not occur in Test T2.

A solubility model that predicts aluminum precipitation as a function of temperature, pH, and aluminum concentration has been proposed. This "precipitation map" was founded on thermodynamic predictions from Visual MINTEQ, and then adjusted to account for variability and the complexity of UNM's CHLE testing conditions. The adjusted model predicts precipitation to occur sooner (at a higher temperature or a lower aluminum concentration) than predicted by Visual MINTEQ to provide for a more conservative prediction of chemical effects. The results of all completed CHLE tests (T1, T2, T3, T4, and T5) were mapped onto the adjusted precipitation map. From this analysis, the model correctly predicts that no aluminum precipitation occurred during Tests T1, T2, or T5 and that aluminum precipitation occurred on Day 7 in Test T3 and on Day 6 in Test T4. Tests T1, T2, and T5 were conducted under prototypical LOCA conditions, whereas Tests T3 and T4 were conducted under extreme conditions with nearly 100 times of aluminum source as that present in the STP containment. The model provides a consistent basis to conclude that precipitation of aluminum does not occur under conditions similar to a nominal LOCA at STP but will occur under the conditions of Tests T3 and T4.

2.0 Introduction

A 10-day chemical effect test (designated as Test T5) was conducted to simulate the chemical effects that occur in a LBLOCA using the prototypical temperature profile and chemistry conditions during a 15-inch cold leg break at South Texas Project Nuclear Operating Company (STP). The testing was part of a larger effort to resolve generic safety issue (GSI) 191 at STP using a risk-informed approach. The objectives of the test were to (1) examine the release of chemical species (Al, Ca, Si, and Zn) into solution, (2) evaluate whether aluminum would precipitate under these conditions, and (3) evaluate the corrosion-induced chemical effects on head loss in blender-processed debris beds. Test T5 results were compared with those of Test T2 [2], which was performed under similar LBLOCA conditions, to assess whether the use of blender-processed debris beds provide additional insight into chemical effects at STP. The primary differences between Tests T2 and T5 are shown in Table 1. In addition, the test results were combined with results from previous CHLE tests to develop a practical aluminum solubility boundary map. Test T5 was conducted from July 14, 2013 to July 24, 2013.

Table 1: Differences between the conditions of Tests T5 and T2

Condition	Test T5	Test T2
Zinc source	Zinc coupons (126 ft ² , submerged)	4.86 kg zinc granules (corresponding to 146 ft ² , submerged)
Bed preparation	Blender-processed beds	NEI-processed beds
Test duration	10 days	30 days

3.0 Experimental Methods and Materials

The experiments were conducted in the Chemical Head Loss Experiment (CHLE) system, which consists of a material corrosion tank connected to three parallel vertical head loss columns. The material corrosion tank is 4 ft x 4 ft x 6.6 ft and is partially filled with a solution simulating the fluid in the containment building during a LOCA. Additional details of the test equipment are described in CHLE-004 [3]. The solution chemistry used in these tests is presented in Table 2 [5]. The boric acid and lithium hydroxide were added prior to the beginning of the test, the trisodium phosphate (TSP) was pre-dissolved and injected over a period starting 15 minutes into the test and ending 80 minutes into the test, and the nitric and hydrochloric acids were added in batches between Days 5 and Day 9 of the test.

Table 2: Chemicals added to the CHLE solution

Chemical	Concentration (mmol/L)	Concentration (mg/L)	Total amount added to system
Boric acid (H ₃ BO ₃)	250.5	2,710 (as B)	17.59 kg
Lithium hydroxide (LiOH)	0.061	1.46	1.65 g
Trisodium phosphate (Na ₃ PO ₄ ·12H ₂ O)	8.87	3,370	3.83 kg
Nitric acid (HNO ₃)	0.229	14.4	16.55 mL of 15.7 M
Hydrochloric acid (HCl)	0.812	29.5	76.20 mL of 12.1 M

The corrosion coupons and materials listed in Table 3 were assembled onto racks and placed in the corrosion tank [5,10]. The tank is designed to contain racks of corrosion coupons in both the vapor space (above the solution pool) and submerged (in the solution pool). The quantities of materials used in the tests are presented in Table 3. The aluminum material was cut from scaffolding that was supplied by STP. The zinc and galvanized steel coupons were 1 ft x 1 ft x 1/16 inch metal sheets, and the concrete was a single block cast at UNM that was about 2 in x 4 in x 8.5 in. The material quantities represent prototypical amounts for a nominal 15-inch cold-leg LBLOCA. A portion of the fiberglass (58.5 g) was placed in the vertical head loss columns, and the remainder (74.4 g) was placed in a stainless steel mesh bag in the material tank.

Table 3: Quantities of materials used in Test T5

Material	Submerged Material	Non-submerged material
Aluminum scaffolding	0.31 ft ²	2.80 ft ²
Zinc coupons	126 ft ²	N/A
Galvanized steel coupons	16 ft ²	138 ft ²
Fiberglass	132.9 g	N/A
Concrete	0.81 ft ²	N/A

Test T2 used zinc granules to simulate a source of zinc from failed IOZ paint chips. During that test, some zinc granules escaped from its bag and may have contributed to head loss as a source of latent debris instead of as chemical products. To address this issue in Test T5, zinc coupons were used instead of zinc granules. In the STP containment, there is expected to be 372 lb of paint chips from failed qualified and unqualified IOZ coatings exposed to solution as a result of an LBLOCA [10]. For both Test T2 and Test T5, the zinc surface area was calculated to match the surface area of the zinc in failed paint chips based on the surface area of 10 µm particles and paint composed of 80% zinc. When calculations for the zinc granule surface area for Test T2 were performed, the density of the paint chips had been given as 208 lb/ft³, which corresponds to the density of qualified coatings. The calculations resulted in 146 ft² of zinc surface area in Test T2 [5]. For Test T5, a corrected paint density of 244 lb/ft³ corresponding to the density of unqualified coatings was used, which reduced the zinc surface area in Test T5 to 126 ft² [10]. Thus, Test T5 had 14 percent less zinc than Test T2, but the zinc coupons were more uniformly exposed to the solution than the granules used in Test T2.

The head loss columns consisted of three identical vertical head loss assemblies that are designed to run in parallel (connected to the corrosion tank) or individually (isolated from the corrosion tank). Each column has its own pump, flow meter, temperature sensor, and differential pressure transducer. The debris bed is supported on a perforated plate with the same hole size and pitch as that in the STP emergency core cooling system (ECCS) sump strainers. The portion of the column where the debris bed is formed is a 1/8-inch-thick polycarbonate tube with an inside diameter of 6.25 inches. Each debris bed consisted of 19.5 g of fiberglass debris (corresponding to an 18 g bed in a 6.0-inch-diameter column). The head loss columns contained blender-prepared debris beds. Debris preparation details are described in CHLE-007 [4]. The debris was added to the columns while the columns were isolated from the tank and solution was circulating at 0.1 ft/s; after the beds were formed, the approach velocity was

reduced to 0.01 ft/s (corresponding to the maximum velocity of the ECCS pumps at STP), where it remained for the duration of the test. Linking of the columns to the material tank constituted the initiation of the test. The non-submerged corrosion materials were subjected to a spray of recirculating tank solution during the first 6.5 hours of the test. The temperature profile was designed to simulate the first 10 days of a prototypical 15'' cold leg LBLOCA and was calculated by MELCOR and RELAP5. The actual temperature profile is shown in the results section. Additional details of the test protocol and procedures are described in CHLE-013 [5].

4.0 Experimental Test Conditions

Process parameters required to perform Test T5 under prototypical temperature conditions were monitored continuously using a Compact-RIO acquisition system and the LabVIEW program. Tank temperature, pH, and velocity measurements were continuously monitored and saved every minute to a spreadsheet for analysis. Results and discussion associated with these parameters are presented in the following sub-sections.

4.1 Tank temperature

The temperature profile for Test T5 was achieved using the heaters and temperature control system on the CHLE test apparatus. The water temperature was brought to 85°C, the coupons were promptly loaded, and Test T5 started when the columns were linked to the tank. The temperature profile in the CHLE control system closely approximated the prototypical temperature of containment during a LOCA. By the end of the 10 days, the temperature was below 40°C. Between set points, the temperature controller maintained a linear temperature decline by cycling the heaters on and off. The proportional controller caused the temperature to drift up and down with a sinusoidal pattern. This can be seen in Figure 1 as small peaks that occur three to four times per day. These peaks had larger amplitude the higher the temperature was; they can be seen very clearly through Day 6, but once the temperature neared 40°C, the sinusoidal pattern was decayed out. Figure 1 demonstrates that the temperature profiles during Tests T2 and T5 were nearly identical.

4.2 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 was calibrated prior to the test but the probe failed during the test, so all pH values reported in this report are from bench-top pH meter measurements. The bench top pH meter was calibrated daily using a three-point calibration with standard buffer solutions of pH 4.01, 7.00, and 10.01. The pH measurements were taken at approximately the same time each day. By Day 1, the pH was 7.27 and stayed close to this for the remainder of the test as shown in Figure 2. The solution pH measurement made with the bench top pH meter averaged 7.25 for Test T5 and 7.31 for Test T2.

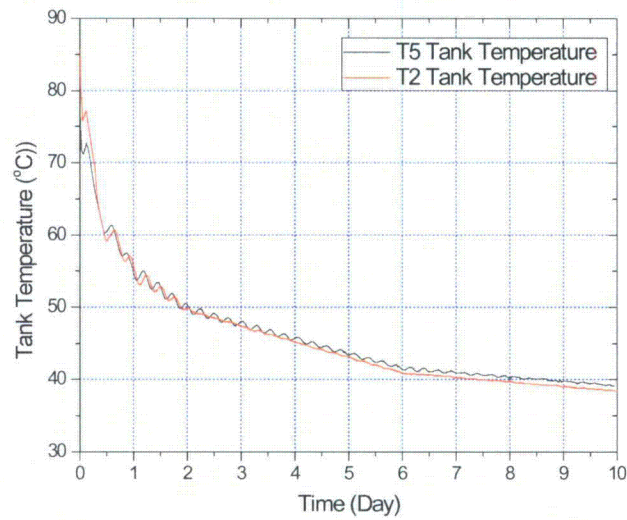


Figure 1: Experimental tank temperature profiles for Tests T2 and T5

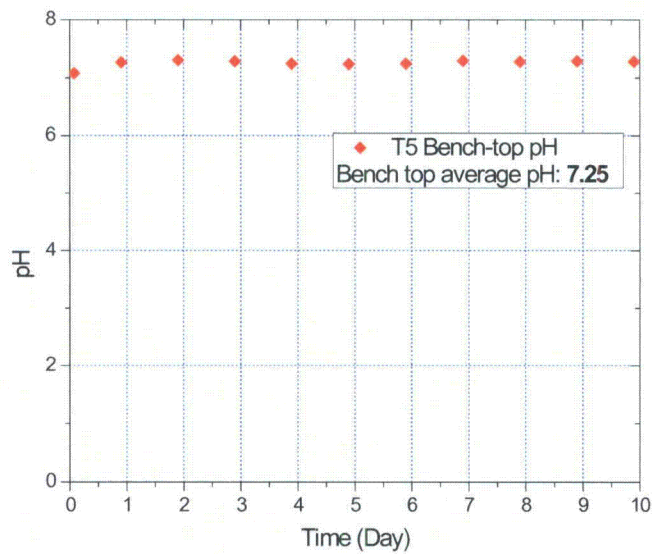


Figure 2: T5 test solution pH measurements using bench-top pH meter

4.3 Approach velocity

The approach velocity was maintained near 0.010 ft/s (to replicate the value used in Test T2) in all three columns. The initial flow rate was set approximately by throttling a valve on the discharge side of the centrifugal pump and then fine-tuned using the variable frequency drive (VFD).

5.0 Results and Discussion

Samples for soluble metal concentration measurements were taken at approximately the same time each day. Tank turbidity measurements were also taken daily at the same time. The head loss for each column was monitored continually.

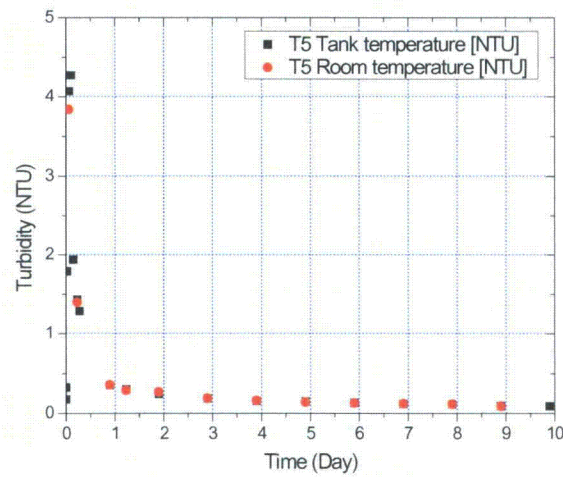
5.1 Solution Turbidity

Turbidity measurements of the bulk test solution were collected daily at room temperature and at tank temperature. Three turbidity measurements of each sample were taken and then averaged to obtain a mean value. In the previous ICET tests, rapid precipitation after samples were withdrawn from the tank could interfere with turbidity measurements. In Test T5, the similarity between the turbidity measurements at tank temperature and room temperature, as shown in Figure 3(a), indicated that precipitation did not occur after the solution was removed from the tank. Therefore, the turbidity measurements were a valid indication of the turbidity of the solution inside the tank.

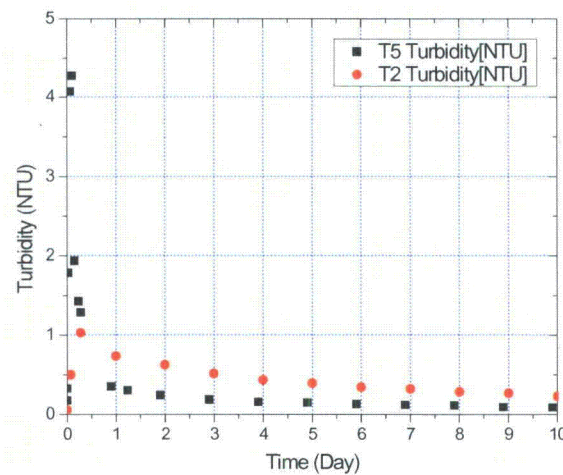
Figure 3(a) shows initial high turbidity prior to Day 1. The high turbidity reading (4.1 NTU) occurred at time 80 minutes, in which all metal coupons had been in the tank since time zero, columns had been linked to the tank, and TSP had been added to the boric acid solution. By Day 1 (24 hours of operation), turbidity had decreased to 0.31 NTU and temperature had decreased to 54.4°C. After Day 1, the turbidity continued to decrease. Particle size was measured using a Zetasizer Nano ZS (Malvern-ZPS). The particle size analysis showed the largest particle size (1.2 μm) on Day 0 (t=80 minutes), and the particle size decreased as time progressed.

The high turbidity at the beginning of Tests T5 and T2 shown in Figure 3(b) might be caused by detachment of zinc particles from the zinc coupons and galvanized steel coupons due to the high temperature during the first 80 minutes of the test. In Test T2, the turbidity was 1.0 NTU at t=1.5 hours, which is lower than the corresponding Test T5 value of 4.1 NTU. This difference might be attributed to the different type of zinc source (i.e., zinc granules in Test T2 versus zinc coupons in Test T5).

After Day 1, the turbidity was lower in Test T5 than in Test T2, as shown in Figure 3(b). The lower turbidity might be due to better filtration efficiency by the blender-prepared debris beds in Test T5 than the NEI-prepared debris beds in Test T2.



(a)



(b)

Figure 3: Turbidity measurements (a) at tank and room temperature for Test T5, (b) for Tests T5 and T2.

5.2 Metal (Al, Si, Ca, Zn) concentration in solution

The total and filtered solution concentrations of aluminum, calcium, silicon, and zinc were measured daily by inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. Total (unfiltered) concentration samples were immediately acidified for analysis; the filtered concentration samples were processed through a 0.10 μm filter before acidification to remove any particles larger than 0.10 μm from solution. The difference between filtered and total concentrations for the individual analytes (Al, Si, Ca, and Zn) taken from Days 1 to 10 were compared to determine whether the elements were in dissolved or particulate forms in the solution. A significant difference in concentration between filtered and

unfiltered samples indicates the presence of insoluble (solid) chemical products. The ICP-OES analysis has a separate report detection limit (RDL) for each analyte [6].

The aluminum concentration was somewhat below the laboratory's RDL of 0.20 mg/L except on Days 2 and 3, when it was essentially at the detection limit, as shown in Table 4. The relative standard deviation (RSD) for the aluminum measurements during this test was 4.8%, so the presence of two samples of aluminum at the detection limit followed by samples below the detection limit later in the test does not indicate a removal of aluminum over the course of the test. The result indicating a lack of aluminum in solution significantly above the detection limit was similar to Test T2, in which the aluminum concentration was also below the report detection limit.

With the quantity of aluminum scaled to the STP containment and the temperature profile of the LBLOCA, the aluminum concentration in solution never reached the saturation limit, even at the low temperatures (approximately 40°C) experienced at the end of Test T5. This explains why there was no increase in turbidity after the first couple of hours of the test.

Table 4: Filtered and unfiltered (total) concentration of aluminum for Test T5

Time mark	Total concentration (mg/L)	Filtered concentration (mg/L)	Absolute deviation (mg/L)
10 minutes	^l < 0.20	*--	--
80 minutes	< 0.20	< 0.20	0.0
Day 1	0.22	0.23	-0.01
Day 2	0.20	0.21	-0.01
Day 3	< 0.20	< 0.20	0.0
Day 4	< 0.20	< 0.20	0.0
Day 5	< 0.20	< 0.20	0.0
Day 6	< 0.20	< 0.20	0.0
Day 7	< 0.20	< 0.20	0.0
Day 8	< 0.20	< 0.20	0.0
Day 9	< 0.20	< 0.20	0.0
Day 10	< 0.20	< 0.20	0.0

*-- Filtered sample not taken

^l< Result is below report detection limit (RDL)

Silicon concentration remained fairly steady, as shown in Table 5 and Figure 4. The differences between filtered and unfiltered concentrations for silicon were insignificant, as shown in Table 5, with average deviation of 0.10 mg/L or less. The RDL was 0.80 mg/L for silicon [6]. Silicon has its lowest concentration (1.9 mg/L) at the beginning of the test and reached 2.9 mg/L by the end of the test. In Test T2, silicon concentration followed a similar pattern and reached 2.7 mg/L on Day 10. In this group of tests, the calcium concentration was far below the laboratory's report detection limit (RDL) of 10 mg/L [6]. Calcium was also consistently below the report detection limit of 10 mg/L in Test T2. Thus, there is no evidence of the presence of insoluble chemical products larger than 0.10 µm except for zinc, as discussed next.

Table 5: Filtered and unfiltered (total) concentration of silicon for Test T5

Day	Total concentration (mg/L)	Filtered concentration (mg/L)	Absolute deviation(mg/L)
10 minutes	1.9	*--	--
80 minutes	2.3	2.2	0.1
1	2.5	2.5	0.0
2	2.6	2.6	0.0
3	2.7	2.7	0.0
4	2.7	2.6	0.1
5	2.5	2.6	-0.1
6	2.8	2.8	0.0
7	2.8	2.8	0.0
8	2.8	2.8	0.0
9	2.9	2.9	0.0
10	2.9	2.9	0.0

*-- Filtered sample not taken

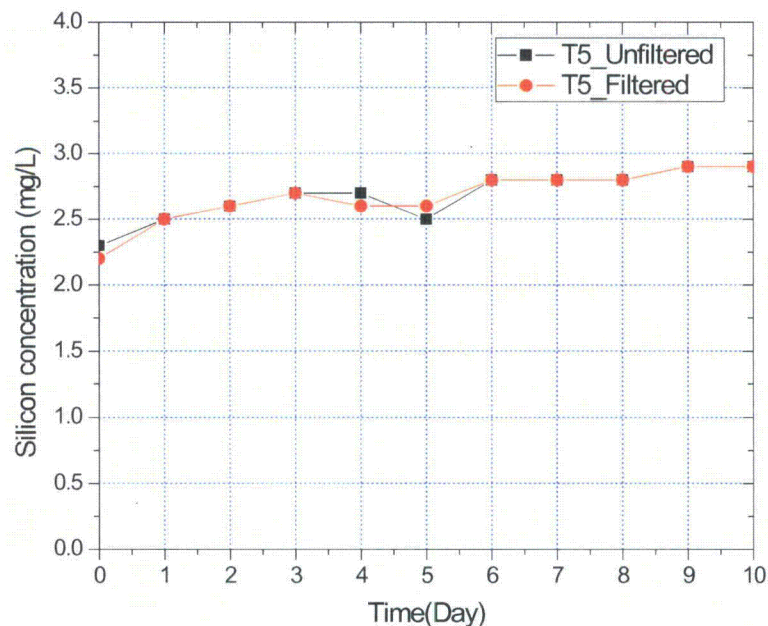


Figure 4: Test T5 measured silicon concentration for unfiltered (total) and filtered samples

Zinc reached its highest total concentration (3.5 mg/L) at 80 minutes; the corresponding filtered concentration (1.3 mg/L) was also the highest measured, as shown in Table 6 and Figure 5. This difference in concentration indicates that zinc-containing particles larger than 0.10 μm were in solution. By Day 1, the measured concentrations of zinc (total and filtered) decreased to 0.55 mg/L; on Day 2, these began to increase and reached 1.1 mg/L by Day 4 and remained constant for the remainder of the

test. The RDL was 0.10 mg/L for zinc. Test T5 indicated initial high turbidity (4.1 NTU), as shown in Figure 3, where the zinc had its highest concentration. The particle size for Test T5 at 80 minutes was measured at 1.2 μm , and then the size decreased, as presented in Figure 6. The correspondence between the initial turbidity peak, the particle size, and the total and filtered zinc concentrations indicates the presence of zinc particles (1.2 μm) that came from the zinc source material due to initial test conditions. In contrast, the initial turbidity peak in Test T2 was 1.0 NTU. The zinc concentration in Test T2 increased to 0.65 mg/L over about 10 days; however, the zinc concentration in Test T5 increased to 1.1 mg/L by Day 4 and then leveled off. Therefore, it appears that the zinc granules in the mesh bag were not as effective at releasing zinc as were the zinc coupons.

Table 6: Filtered and unfiltered concentration of zinc for Test T5

Day	Total concentration (mg/L)	Filtered concentration (mg/L)	Absolute deviation(mg/L)
10 minutes	4.60	*--	--
80 minutes	3.50	1.30	2.20
1	0.63	0.55	0.08
2	0.77	0.70	0.07
3	0.95	0.92	0.03
4	1.10	1.00	0.10
5	1.10	1.00	0.10
6	1.10	1.10	0.00
7	1.10	1.10	0.00
8	1.10	1.10	0.00
9	1.10	1.10	0.00
10	1.10	1.10	0.00

*-- Filtered sample not taken

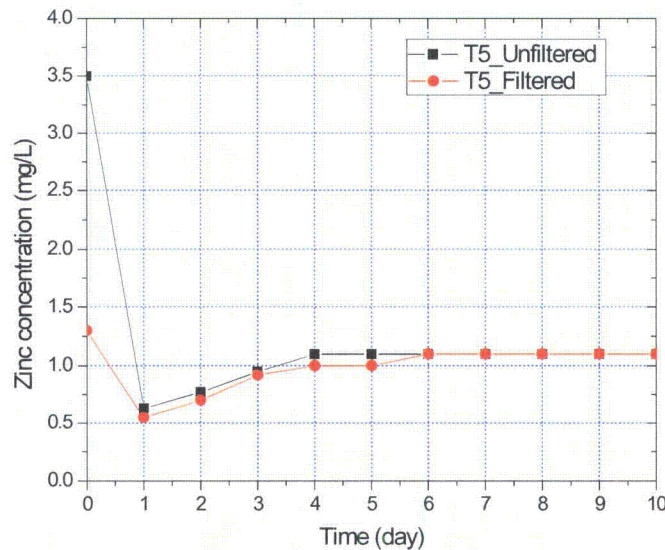


Figure 5: Test T5 measured zinc concentration for unfiltered and filtered samples.

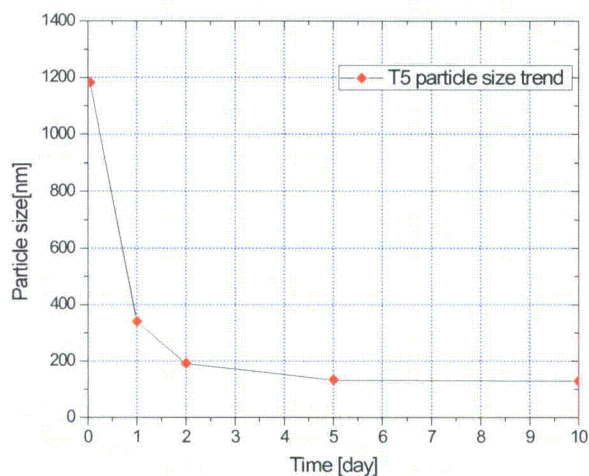


Figure 6: Particle size of selected day samples in Test T5.

5.3 Aluminum hydroxide precipitation map based on Visual MINTEQ

The aluminum concentration measured by ICP-OES was compared to the saturation limit (solubility) at equilibrium of aluminum hydroxide calculated by Visual MINTEQ. The measured aluminum concentrations were far less than the saturation limits throughout the test, as shown in Figure 7. As a consequence, aluminum is not predicted to precipitate. Some variability in the temperature dependence of aluminum solubility is expected due to complex reactions involving the many constituents of the solution. The relationship between the aluminum concentration in Test T5 and the $\text{Al}(\text{OH})_3$ solubility limit was further explored in the context of the thermodynamic model of Visual MINTEQ below [7].

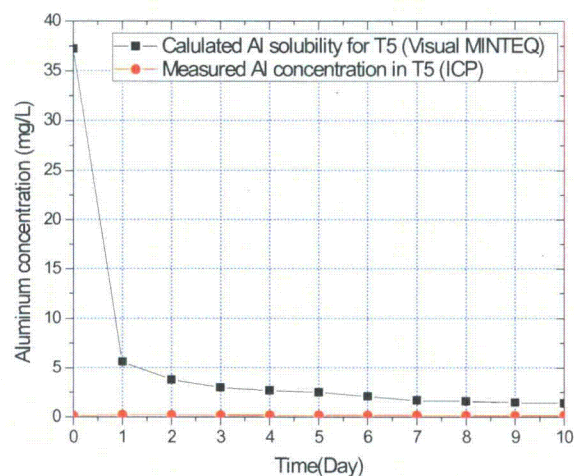


Figure 7: Test T5 aluminum concentration in solution and solubility curve for aluminum hydroxide $\text{Al}(\text{OH})_3$. Solubility of $\text{Al}(\text{OH})_3$ was calculated at pH=7.20 with the Test T5 temperature profile using Visual MINTEQ.

Because displaying $\text{pH} + \text{p}[\text{Al}]_t$ (the sum of the pH and the negative log of the molar total aluminum concentration) versus operating temperature facilitates a comparison of solubility and precipitation test results obtained under various test conditions [8], UNM's Test T5 results were incorporated into the $\text{Al}(\text{OH})_3$ precipitation map generated from Visual MINTEQ to differentiate the precipitation testing region and non-precipitation testing region. The boundary line between the precipitation region and the non-precipitation region corresponded to the solubility of $\text{Al}(\text{OH})_3$ determined by Visual MINTEQ, indicated by the red line in Figure 8. The plotted blue data points for Test T5 in Figure 8 were defined from the corresponding tank temperature at the fixed $\text{pH}=7.25$ and maximum aluminum concentration (0.22 mg/L). All of the data were located in the non-precipitation region, which leads to the conclusion that aluminum did not precipitate in Test T5. This analysis demonstrated consistency among the turbidity data, the aluminum concentration data, and the normalized head loss behavior in Test T5 as presented in following section.

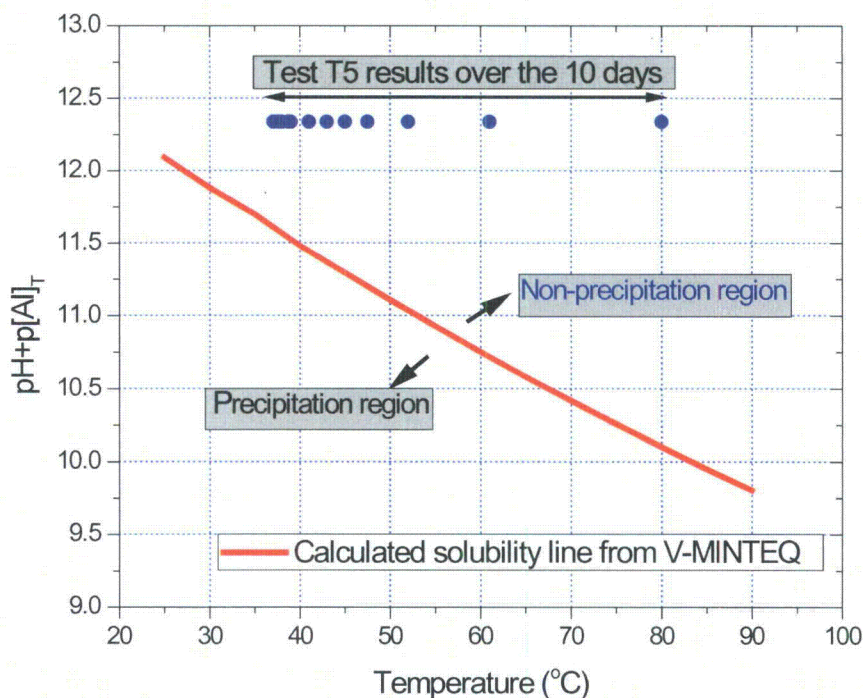
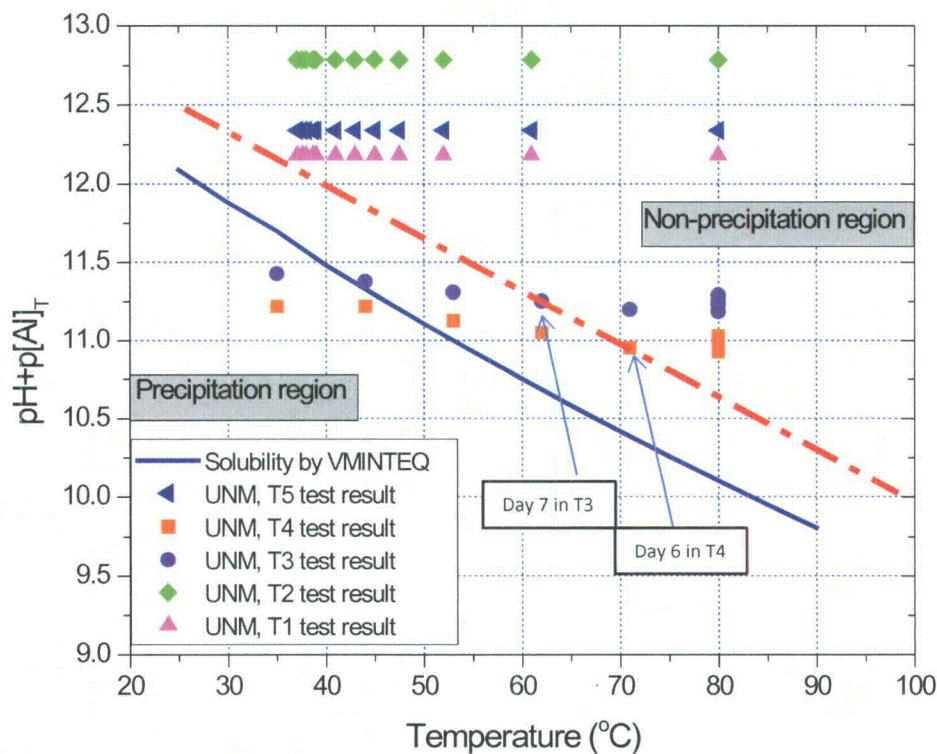


Figure 8: Aluminum hydroxide precipitation map ($\text{pH} + \text{p}[\text{Al}]_T$ vs. temperature) with plotting UNM Test T5 data to identify Al precipitation.

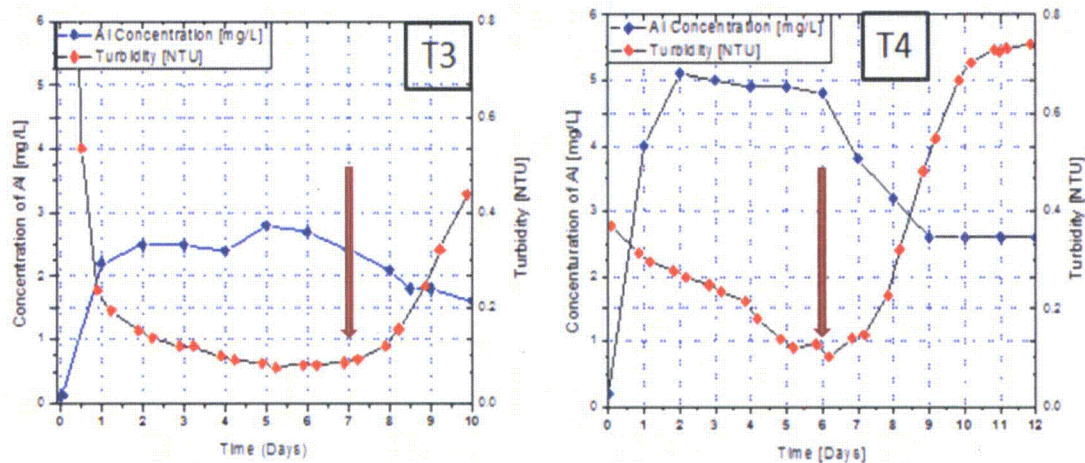
In addition, the aluminum precipitation map was augmented to incorporate the entire series of CHLE tests (T1, T2, T3, T4, and T5) and is presented in Figure 9. Fixed pH and maximum aluminum concentration with varying temperature profile were selected for each data point in the precipitation map. Although the solubility line (blue line) was calculated from Visual MINTEQ, the practical solubility boundary (red dotted line) was proposed in Figure 9(a) to identify the precipitation region and non-

precipitation region. The proposed solubility boundary in Figure 9(a) was located above the calculated solubility boundary based on the following reasons: (1) The chemical system present during a LOCA is a complex system containing a large number of aqueous species, each requiring thermodynamic constants. Inaccuracies or insufficient information regarding any of these constants can lead to uncertainties in thermodynamic predictions. Shifting the line accounts for uncertainties in the reported thermodynamic constants as well as variability in actual conditions such as pH and temperature. (2) The upward shift of the proposed solubility boundary provides for a more conservative precipitation prediction; i.e., precipitation is predicted to happen sooner (at a higher temperature or lower concentration) than would be predicted purely from calculations from Visual MINTEQ. (3) The data from the CHLE tests allowed us to determine the practical solubility boundary; i.e., the condition at which precipitation occurred in Tests T3 and T4 provides a basis for the extent of the upward shift. The degree of shift is also consistent with a large body of data from Bahn et al. [8] which found the majority of solubility data consistent with predictions by Visual MINTEQ, but a limited number of cases in which precipitation occurred above the Visual MINTEQ solubility boundary. The practical solubility boundary proposed here encompasses all of the solubility data from Bahn et al.

The modified precipitation map predicts that aluminum did not precipitate in CHLE T1, T2, or T5 and that aluminum precipitation was likely on Day 7 in Test T3 and on Day 6 in Test T4, when the testing data points crossed over the proposed precipitation boundary line. This prediction by the precipitation map also validated the turbidity and aluminum concentration measurements in Tests T3 and T4, as shown in Figure 9(b) [9].



(a)



(b)

Turbidity in tank resulting from the Al precipitation started increasing on Day 7 of Test T3 and Day 6 of Test T4.

Figure 9: (a) Aluminum hydroxide precipitation map ($\text{pH} + \text{p}[\text{Al}]_T$ vs. temperature) with results from Tests T1, T2, T3, T4, and T5; (b) turbidity trend with corresponding aluminum concentration in Tests T3 and T4.

5.4 Normalized Head loss

Due to the non-isothermal condition between testing apparatus (columns) and differential pressure measurement device, the head loss measurement needed to be normalized to a reference temperature, which in Test T5 was 20°C. Change in temperature will affect density and viscosity, which in turn affect the overall head loss. The maximum head loss discrepancy due to normalizing density as a function of temperature is small, a maximum of 0.75 inches of water at the temperatures used in this study. However, the temperature effects on viscosity have a significant impact on normalizing head loss. Normalizing to the reference temperature for both viscosity and density is done using the equation listed below:

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

where

- $H_{L,c}$ is the normalized head loss
- DP_{raw} is the instrument differential pressure measurement
- ρ_t and ρ_{rt} are the densities at test temperature (t) and at room temperature (rt)
- g is the gravitational constant
- h is the vertical height between the upper DP sample tap and the DP cell
- μ_t and μ_{std} are the viscosity at test temperature (t) and at standard temperature (std) of 20°C

In general, there was variation in normalized head loss for all three columns, but all three columns followed the same trend. They increased fairly rapidly for the first three days of the test, and then leveled off with slight gains over the next seven days, as shown in Figure 10(a). There were also random increases and decreases in head loss, but this was attributed to the sensitive nature of blender-processed fiber beds.

This normalized head loss trend can be explained as follows. Particles that cause the initial high turbidity readings were filtered out within the first 6 hours, according to the turbidity and particle size analysis. This caused the steep slope seen in the head loss increase at the beginning of Test T5, as shown in Figure 10(a). As the larger particles were collecting on the debris beds, the “pores” between individual fibers become clogged with these particles, causing rapid increase in head loss and causing the fiber beds to become denser. This particle capturing or clogging in the fiber bed was also observed in the SEM image in the following section. This increase in density causes progressively smaller “paths” for water and the medium and small particles to pass through, thereby trapping some of them. These particles cause less rapid increase in head loss because they are smaller, but they still caused some head loss increase. This logical concept (i.e., filling up the big “pores” and developing the small “paths”) could explain the continued increase in head loss even though the turbidity readings were fairly low in most of the previous CHLE tests. These small particles still caused head loss to increase over the next seven days but the concentration of particles was so small that the turbidity was low. The continued reduction in turbidity indicated that particles were still being filtered out of solution and deposited on beds. This helps to explain the continued slow increase in head loss in Test T5 as well as previous CHLE tests.

Turbidity was one of the key measurements for the previous CHLE tests. Because it detects particles in solution, it can provide information on particle release, head loss, and filtration. Turbidity was efficient at measuring the presence of large particles in the solution in the first hours of testing. Low turbidity readings of less than 1 NTU (from day 1 to day 10) indicate the presence of low concentrations of particles that contribute to a decreasing rate of head loss increase. This filtration continued until the test was ended and could be the reason for the normalized head loss trend in Test T5.

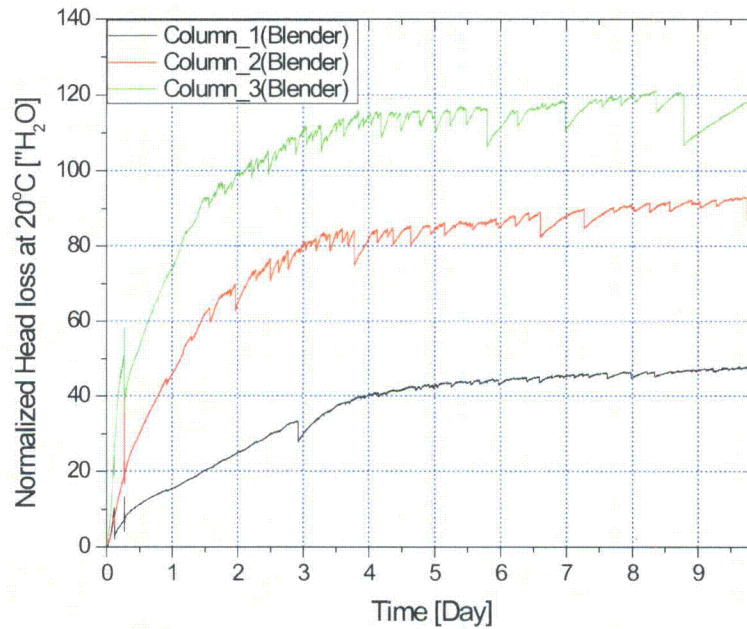
To compare the results of Test T5 and Test T2, the normalized head loss data for Test T2 is added in Figure 10(b). The general trend of head loss increase in Test T2 (NEI-processed bed) was quite similar to that in Test T5 (blender-processed bed); however, the magnitude of normalized head loss in Test T2 was significantly lower. Although the head loss exhibits some variability with repeated increases and decreases, the overall head loss remained relatively constant after Day 5 in Test T5. Previous experience with blender-prepared debris beds in this equipment setup indicates that they are highly sensitive to any perturbation, including particles, precipitation, and mechanical forces (i.e., jarring or vibrating the column). In Tests T3 and T4, head loss increased rapidly when the aluminum concentration decreased (indicating precipitation was occurring). The absence of a significant increase in head loss during the second half of both Test T2 and Test T5 is consistent with turbidity and aluminum concentration data that indicate that precipitation of aluminum did not occur in this test. Since this test was conducted at similar conditions to Test T2, this test validates the conclusion that chemical effects related to precipitation of aluminum did not occur in Test T2.

5.5 Bed Examination

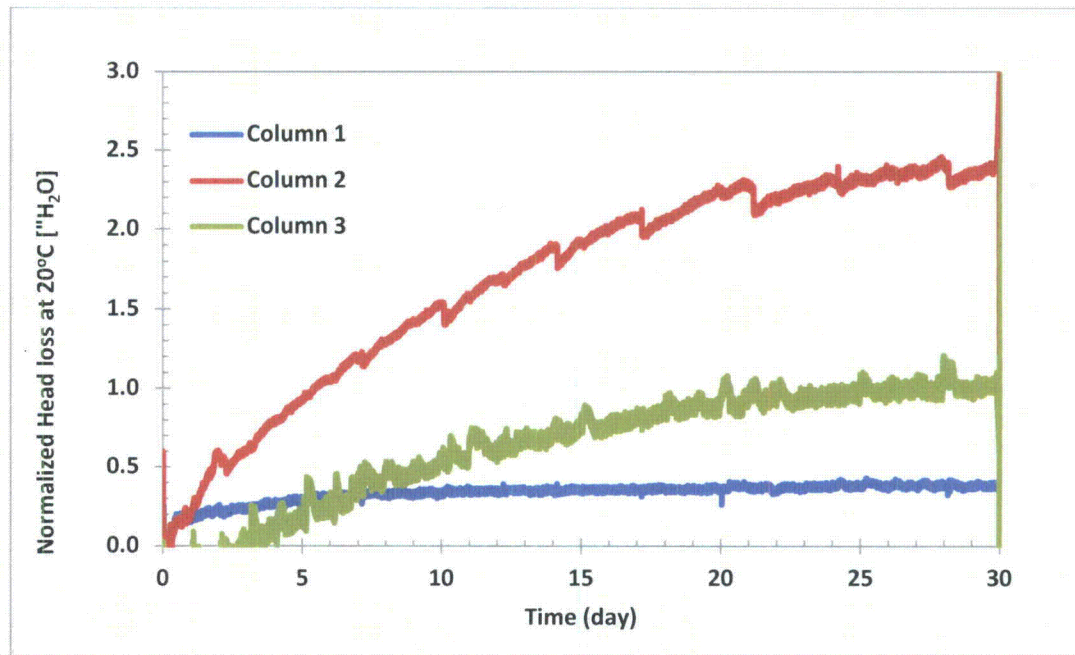
After Test T5 was complete, the fiber beds were removed from the columns for post-test analysis. Visual inspection showed that sparse white particles were present on the surface of all three beds. These particles were found in all three columns at the beginning of Test T5, they were found from the edge of each bed and propagated widely around the circle, as shown in Figure 11. Further post-bed visual inspection was not possible due to the particles' being too fine. The sample of fiber bed with obvious white particulate deposition was selected for SEM-EDS analysis to see what kind of particles were deposited and how the deposition appeared via an SEM image. The result of SEM-EDS is presented in the following section.

5.6 Corrosion product with SEM-EDS analysis

Metal corrosion is the sum of the metal mass released into solution and the mass assimilated into the scale layer on the corroded material itself. Once in solution, the corroded metal can remain in solution, precipitate and be separated from solution by sedimentation or filtration, or form scale on other surfaces in the system. The concentration of material in solution was measured by ICP-OES. The mass of corroded metal would be incorporated into the scale layer on the material itself. Thus, for all coupons (aluminum, zinc, and galvanized steel), the mass increased due to presence of the scale layer. This mass gain was also found for coupons in Test T3 [9].



(a)



(b)

Figure 10: Normalized head loss measurements produced by all three columns for (a) Test T5 with blender-processed beds, and (b) Test T2 with NEI-processed beds.

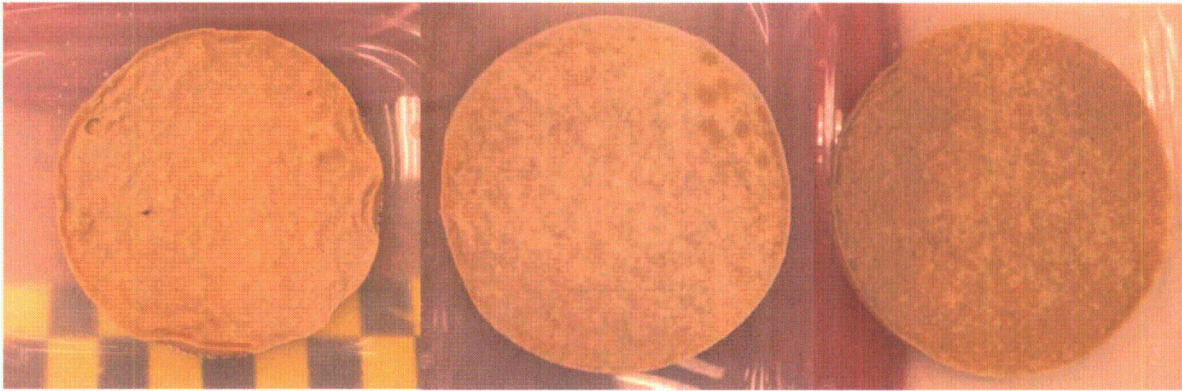


Figure 11: Columns 1 (left), 2 (center), and 3 (right) in Test T5 after exposure to 10-day test solution.

Previous SEM-EDS analysis performed on the Test T3 aluminum, zinc, and galvanized steel coupons indicated the presence of zinc and phosphorous. X-ray diffraction (XRD) conducted after Test T2 identified this material as zinc phosphate ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$). This particle was not detected on any of the aluminum coupons during Test T4. The distinction is due to the presence of zinc material in Test T3 and its absence in Test T4. The presence of zinc material along with the solution chemistry (borated TSP solution) caused the formation of the zinc phosphate. Zinc phosphate, present as white particles and scale, was also observed on aluminum, zinc, and especially on galvanized steel coupons in Test T5 (Figure 12), just as with Test T3.

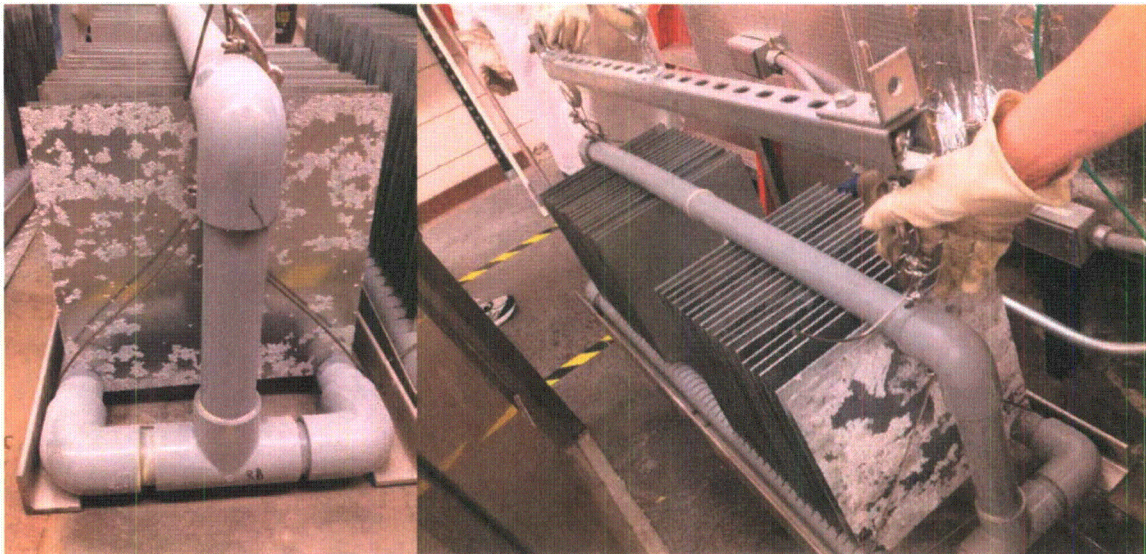


Figure 12: Scale formation on coupons. Two galvanized steel coupons are at the ends of the racks, the other coupons in the racks being zinc.

SEM and EDS analysis were performed on samples of the fiber bed in Test T5. An SEM image of the fiber bed can be seen in Figure 13. The SEM image with EDS analysis showed that the fiber bed contained deposited particles. The visual abundance of particles may help explain why the columns in Test T5 experienced head loss, as shown in Figure 10. It is expected that the amount of particles present in the solution will play a role in the amount of head loss experienced across a fiber bed. Based on EDS results, the particles found in the fiber beds of Test T5 contain zinc, phosphate, and a mixture of the solution chemistry, sodium, and fiberglass (Si) found in the tank. SEM-EDS analysis for Test T5 and the knowledge gained from Tests T2 and T3 indicated that zinc phosphate was present and deposited on all coupons and fiber beds. Zinc phosphate deposited significantly on galvanized steel, as shown in Figure 12; but as indicated in Test T3 SEM-EDS analysis, zinc phosphate was found on aluminum and zinc coupons as well, which in turn led to mass gain. SEM-EDS analysis also indicated that fiber beds had captured zinc phosphate product, which led to a zinc source effect in head loss increase during Test T5, as shown in Figure 10(a).

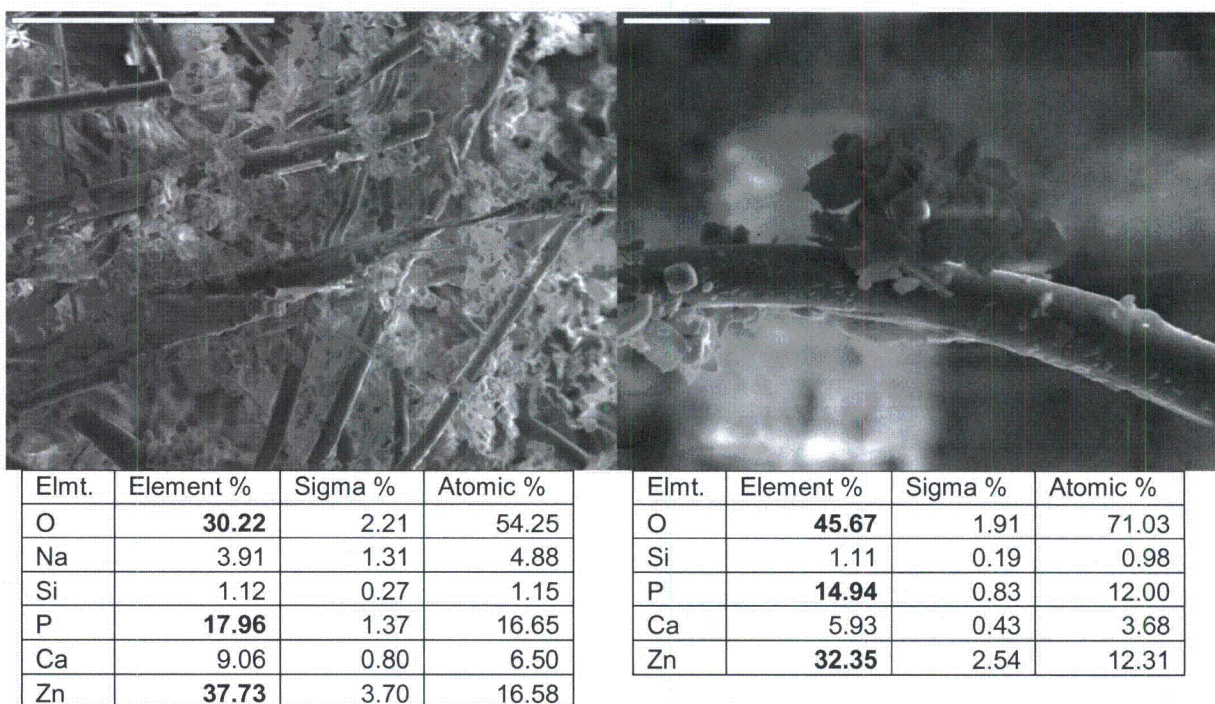


Figure 13: SEM of the deposited (zinc phosphate product) scale on the top surface of fiber beds from Test T5 with EDS results

6.0 Summary and Conclusions

The observations for Test T5 are summarized below.

1. The tank turbidity increased during the first 80 minutes of Test T5, and then decreased gradually over the remaining test period. The initial high turbidity appears to be due to detached zinc particles from the zinc source (zinc coupons, galvanized steel) at the high temperature and low pH. The results were similar to the results of Test T2 except that the initial peak of turbidity was higher in this test.

2. The aluminum, calcium, and silicon concentrations were generally consistent with the results of Test T2. In both tests, the aluminum was at or below the detection limit of 0.20 mg/L, and the calcium was below the detection limit of 10 mg/L. The turbidity and aluminum concentration results indicate that aluminum precipitation did not occur. The silicon was above the detection limit and reached about 2.8 mg/L in both tests.
3. The zinc concentration of filtered and unfiltered (total) samples demonstrated that zinc particles larger than filter size (0.10 μm) were in the sample taken at 80 minutes. The results suggest that the zinc particles were filtered or settled during the first day, because the filtered and unfiltered zinc concentrations were the same from Day 1 to the end of the test. After the zinc particles were removed, the zinc concentration increased slowly over the next several days due to corrosion. The gradual increase in zinc over several days is consistent with the results from Test T2, except that the maximum concentration of zinc was 1.1 mg/L in Test T5 and 0.65 mg/L in Test T2. Zinc phosphate was the only insoluble product identified in Test T5.
4. The initial turbidity spike in Test T2 (1.0 NTU) was not as high as in Test T5 (4.1 NTU), and the initial release of zinc particles was not as significant. That, combined with the higher concentration of zinc in Test T5, suggests that the zinc coupons were a greater source of zinc than the zinc granules in the mesh bag in Test T2.
5. The particle size analysis results showed that the size of particles on Day 0 ($t=80$ minutes) was 1.2 μm and that the size decreased to nearly 0.1 μm . The larger size of the initial particles is consistent with removal by settling or filtration.
6. The thermodynamic model from Visual MINTEQ was used to generate the aluminum hydroxide precipitation map that identified the aluminum precipitation and non-precipitation regions in the test operating domain of interest (pH, temperature, and aluminum concentration). Test T5 results were mapped out in the precipitation map and corresponded to the non-precipitation region, which supports the conclusion that there was no aluminum precipitation in Test T5.
7. A precipitation map with the precipitation boundary adjusted upward (which causes precipitation to occur sooner than predicted by Visual MINTEQ) to account for variability and the complexity of UNM's CHLE testing conditions was proposed in Figure 9. The results of all completed CHLE tests (T1, T2, T3, T4, and T5) were mapped onto the revised precipitation map. From this analysis, it was concluded that no aluminum precipitation occurred during Tests T1, T2, or T5 and that aluminum precipitation most likely occurred on Day 7 in Test T3 and on Day 6 in Test T4. Tests T1, T2, and T5 were conducted under prototypical LOCA conditions, whereas Tests T3 and T4 were conducted under extreme conditions with nearly 100 times of aluminum source as that present in the STP containment. Aluminum precipitation prediction by the precipitation map was validated with turbidity and aluminum concentration measurements in Tests T3 and T4 and showed good agreement with the prediction.
8. The normalized head loss in all three columns in Test T5 (blender-processed debris bed) started increasing rapidly from the beginning of the test to Day 3, and then slowly increased

over the remaining test period. Although the trends were similar in the three columns, the absolute value of head loss was different. Head loss appears to be related to the presence of zinc-containing particles present in solution during the initial hours of the test. When compared to Test T2, the blender-processed debris beds produced significantly higher head loss than NEI-processed debris beds at similar conditions.

9. SEM-EDS analysis was performed for Test T5 to identify deposited particles on the fiber bed. Based on the EDS analysis, the deposited particles appear to be zinc phosphate. The SEM image demonstrated that zinc phosphate was captured in the pores of the fiber beds, and those deposited particles are assumed to have caused the head loss increase in Test T5. As noted earlier, the zinc was released in particulate form during the initial minutes of the test. All of the CHLE tests used a pre-formed debris bed, but the debris bed in an actual LOCA would be forming in the same time frame as the release of zinc particles, which means that it may be appropriate to treat the zinc as a particle source during bed formation rather than a chemical effect later in the accident scenario.
10. The absence of a significant increase in head loss during the second half of Test T5 is consistent with turbidity and aluminum concentration data that indicate that aluminum precipitation did not occur in this test, and chemical effects related to aluminum precipitation did not occur in Test T2.

7.0 References

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