

PROJECT DOCUMENTATION COVER PAGE

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Title: Tests to assess chemical precipitate formation		
Project: Corrosion/Head Loss Experiment (CHLE) Program		Date: 3 April 2013
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Summary/Purpose of Analysis or Calculation:

The Corrosion/Head Loss Experiment (CHLE) program has been designed to acquire realistic material release and product formation results for use in Containment Accident Stochastic Analyses (CASA). The CHLE test parameters were derived from South Texas Project (STP) conditions for a spectrum of Loss of Coolant Accident (LOCA) scenarios and divided into three sections of testing: 30-day tank tests, bench tests, and short-term tank tests. Review of results obtained during 2012 has resulted in reassessment of the original test plan [1].

To continue progress on understanding the impact of chemical effects on the risk-informed resolution of GSI-191, a new test series has been developed. The objectives of this test series are to create conditions that promote the generation of insoluble chemical products from corrosion sources, characterize any insoluble products that form, evaluate the effect of zinc on the corrosion of aluminum, and evaluate the response of debris beds to the presence of supersaturated aluminum concentrations. The series consists of two 10-day tests as described in this document.

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1	3/04/2013	Initial draft
2	3/10/2013	Addressed internal review comments
3	3/21/2013	Streamlined document since a separate document on integration of chemical effects into CASA has been prepared
4	3/25/2013	Addressed additional internal review comments and changed the source of the zinc.
5	4/3/2013	Addressed additional internal review comments.

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1.0 Introduction

The Corrosion Head Loss Experiment (CHLE) program has been designed to acquire realistic material release and product formation results for use in Containment Accident Stochastic Analyses (CASA). The CHLE test parameters were derived from South Texas Project (STP) conditions for a spectrum of Loss of Coolant Accident (LOCA) scenarios and divided into three sections of testing: 30-day tank tests, bench tests, and short-term tank tests. Review of results obtained during 2012 has resulted in reassessment of the original test plan [1]. This reassessment has prompted a new tank test series and a better-defined path for incorporation of CHLE results into CASA.

The overall objective of the 30-day tank test series was to detect the formation of insoluble chemical products resulting from material corrosion or dissolution. These tests found that an insoluble chemical product formed on the galvanized steel coupons and produced other significant results. Initial testing revealed that the size of precipitates that formed when aluminum nitrate was added to the tank solution (in-situ formation) was an order of magnitude smaller than that of precipitates that formed in a concentrated suspension in a laboratory beaker (ex-situ formation). This concentrated suspension was added to the tank and allowed to circulate through the debris beds. The testing demonstrated that in-situ precipitates cause less head loss through a debris bed than do ex-situ precipitates, even when the concentration of the precipitates in the solution was the same [2]. The material release from corrosion and dissolution materials in the MBLOCA (medium break LOCA) test (T1) were less than that calculated, although the calculated release of materials did provide a reasonable estimate of the measured release of materials over 30 days [3]. However, the release of the materials was not large enough to determine whether products that formed as a result of corrosion or dissolution of materials would be similar to those formed in-situ from salt sources. The LBLOCA (large break LOCA) test (T2) generated an insoluble chemical product [4] derived from zinc material that has not been included in the list of precipitates considered in the WCAP-16530-NP protocol [5]. The material release calculated by WCAP-16530-NP also proved to greatly overestimate the actual release of aluminum, calcium, and silicon in the LBLOCA test, perhaps due to the presence of zinc [4].

2.0 New Tank Test Series

To continue progress on understanding the impact of chemical effects on the risk-informed resolution of GSI-191, a new test series has been developed. The purpose of this test series is to (1) address questions and issues identified by NRC staff following the 30-day MBLOCA and LBLOCA tests, and (2) continue gathering the data necessary to develop a model of chemical effects at STP. The MBLOCA test contained aluminum coupons as the only metallic source material to allow direct comparison to previous tests in which aluminum nitrate was injected at a slow rate to simulate the introduction of aluminum that might occur due to a corrosion process. In contrast, the LBLOCA test contained galvanized steel, zinc granules (99% pure, simulating zinc from paint chips), and concrete in addition to aluminum to evaluate a more integrated environment. The NRC staff requested information on how the results of the MBLOCA test may have been influenced by the selection of materials. In addition, both the MBLOCA and LBLOCA test were conducted with debris beds prepared with NEI-processed fiber in all three columns during the 30-day test period, after which blender-processed debris beds were placed in

the columns for 2 additional days. No increase in head loss occurred with either type of debris bed in the MBLOCA test, and only minor increases in head loss (less than 3 inches over 30 days) occurred with both types of debris beds in the LBLOCA test. The NRC staff questioned whether the NEI-processed debris bed may have removed chemical products from solution without exhibiting significant head loss, such that greater head loss would have been observed if the blender-processed debris beds had been in the columns during the 30-day period. This test series is designed to address both of these issues. Details associated with the tests are given below.

2.1 Test Objectives

The objectives of this test series are to create conditions that promote the generation of insoluble chemical products [5, 6] from corrosion sources; characterize any insoluble products that form with respect to product type, morphology, size, and formation location; evaluate the effect of zinc on the corrosion of aluminum; and evaluate the response of debris beds to the presence of supersaturated aluminum concentrations. Two tests will be performed. Test T3 will provide a more inclusive test that represents the mix of key materials expected to be present in containment, whereas Test T4 will more effectively assess the effect of supersaturated aluminum concentrations on the debris beds without the confounding effects of detached zinc product or other particulate debris that might be introduced into the tank in the more inclusive test. Although both tests will allow for characterization of chemical products, Test T3 will contain aluminum, galvanized steel, zinc plates (99.8% pure representing zinc from paint chips), fiberglass, and concrete. Test T4 will contain only aluminum and fiberglass because the presence of zinc may be responsible for the significant reduction in material release in the LBLOCA test, which might affect the quantity and/or properties of insoluble chemical products generated in the T3 test. The tests will contain blender-processed and NEI-prepared debris beds in a direct, side-by-side comparison of the response of the two beds to identical chemical conditions. The test duration will be 10 days.

2.2 Temperature Profile for 10-day Test Series

The temperature profile shown in Figure 1 was designed to maximize the potential for insoluble chemical product formation and is not representative of a specific LOCA scenario. The highest temperature in the 10-day test series, 80°C (176°F), is close to the CHLE equipment limits. This elevated temperature will be held for five days to stimulate aluminum corrosion that is predicted to exceed the solubility of amorphous aluminum hydroxide. After five days, the temperature will be reduced to 35°C (95°F). This temperature is slightly lower than the minimum yielded by a simulation of a 15" or 6" break, as shown in Figure 1. In addition, at the end of the 10-day test, the test solution will be stored and held agitated at 35°C (95°F) for an additional 20 days for further evaluation of any insoluble chemical product that may have formed.

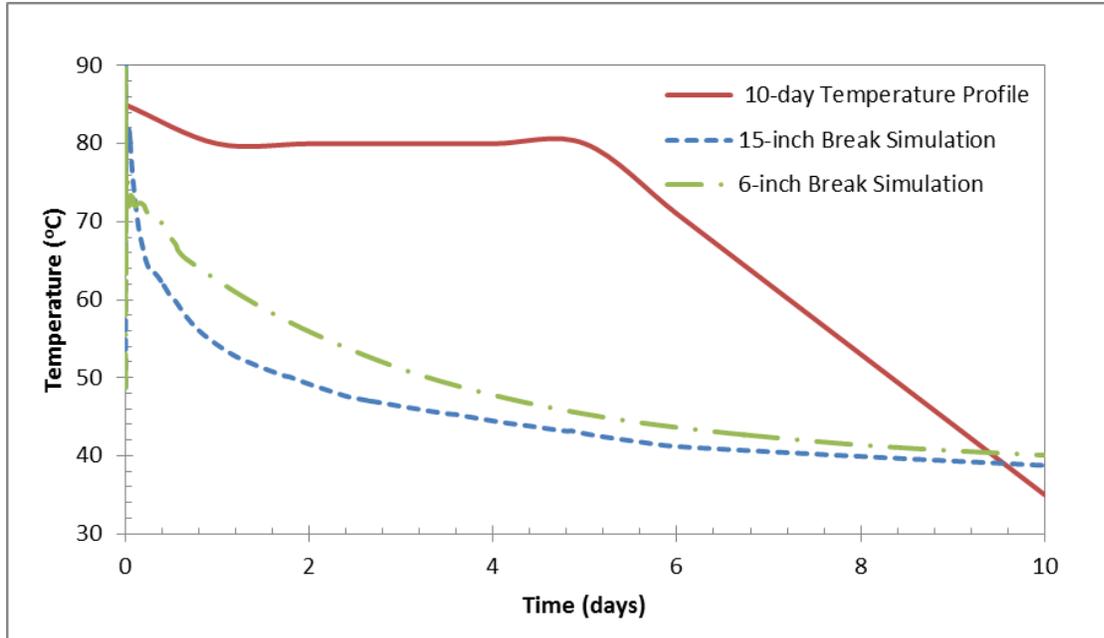


Figure 1: Temperature profile for the 10-day tank test and the simulated temperature profiles for a medium break (6") and large break (15") LOCA.

2.3 Tank Materials

To stimulate insoluble chemical product formation for capture and characterization of the resulting product, the two 10-day tank tests will contain previously identified key corrosion (metals) and dissolution (fiberglass and concrete) materials found in STP containment [7]. Table 1 presents a summary of the materials to be included in each test. The surface area or volume of each corrosion material and dissolution material (other than aluminum, as noted below) was determined from STP inventory using the nominal water volume of 71,778 ft³ [8], which was then scaled to a 300-gallon (40.1 ft³) test volume. Only submerged materials will be included in this test series; therefore, a spray phase is not necessary.

Table 1: Materials to be included (CHLE T2 LBLOCA proportions, except aluminum)

Materials	Test T3	Test T4
Aluminum ¹	Included	Included
Galvanized Steel	Included	-
Nukon Fiberglass	Included	included
Zinc ² (from paint chips)	Included	-
Concrete	Included	-

¹ASTM-209 B; Alloy 1100; ²99.8% pure zinc

2.3.1 Corrosion Materials

The aluminum surface area to be used in both tests will not be scaled to that found in STP containment. It is determined by the surface area that is predicted to release enough material into solution by the fifth day of testing to produce an aluminum concentration that exceeds the solubility of aluminum

hydroxide at a temperature of 80°C (176°F) and pH of 7.2 ± 0.1. Aluminum corrosion in the presence of phosphate is expected to be approximately one third [3, 9] of the calculated corrosion when using the equation generated by WCAP-16530-NP[5]. The calculated surface area predicted to produce the extent of corrosion in the presence of phosphate (53,800 ft² in the STP containment building), as determined by using previously identified corrosion equations [5], is approximately 97 times greater than that expected to be submerged in containment. As shown in Figure 2, the calculated release exceeds the solubility of aluminum on the fifth day of testing. At the end of testing, the calculated material release will be approximately 40 times the solubility limit.

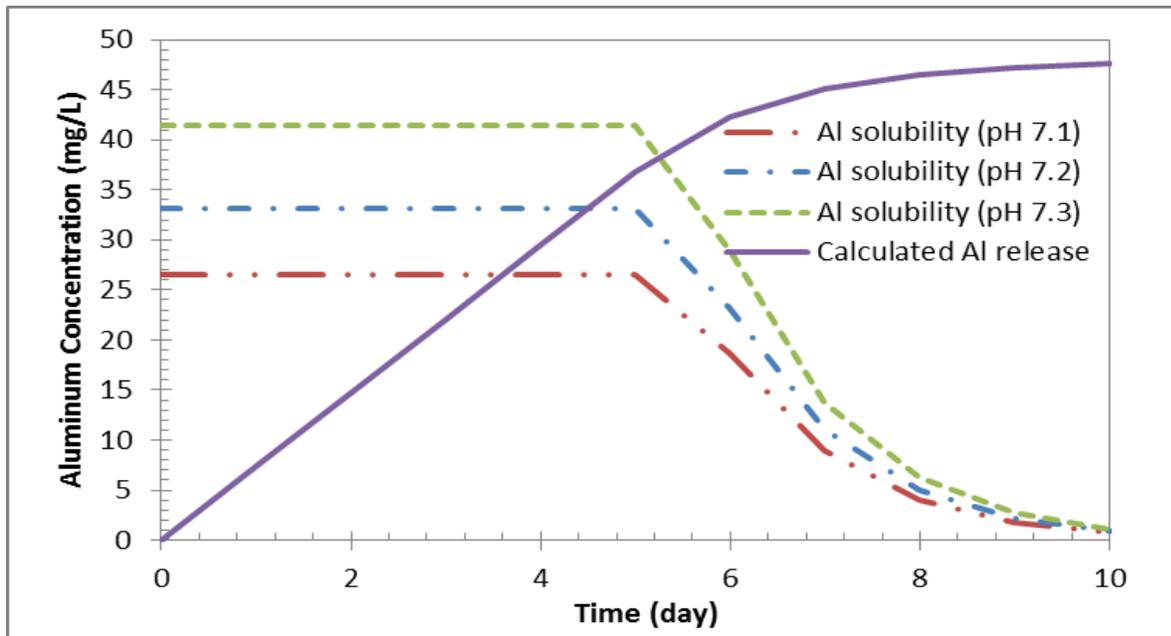


Figure 2: Aluminum solubility and the calculated material release as a function of time. Note that aluminum solubility depends on the temperature at each point in time (Figure 1)

Aluminum (Alloy 1100) will be the only corrosion material in Test T4 and will be present as 15 coupons (1 ft x 1 ft x 1/16 in). Test T3 will have galvanized steel and zinc plates (99.8% pure) that represent zinc components of paint chips expected to exist during a 15" LBLOCA scenario. In STP containment [7], there is expected to be 273,749 ft² of galvanized steel and 372 lb of paint chips exposed to solution as a result of an LBLOCA. This mass of paint chips is equivalent to 223,338 ft² of zinc, based on the surface area of 10 μm particles and paint composed of 80% zinc [10]. Only 10% of the galvanized steel would be expected to be submerged, yet all the paint chips would be submerged. Therefore, Test T3 will contain 30 ft² of aluminum (Alloy 1100) present as 15 coupons (1 ft x 1 ft x 1/16 in), 16 ft² of galvanized steel present as 8 coupons (1 ft x 1 ft x 1/16 in), and 126 ft² of zinc, present as 63 coupons, 99.8% pure, (1 ft x 1 ft x 1/16 in).

2.3.2 Dissolution Materials

The dissolution materials are based on a 15" break LBLOCA scenario. Fiberglass (Nukon) debris will be included in Tests T3 and T4. The Nukon fiberglass contribution is from two sources: latent debris and

insulation. To determine the fiberglass contribution from insulation, simulations were performed by Containment Accident Stochastic Analyses (CASA), which predicted that a 15" break generates 206 ft³ of Nukon debris [11]. To determine the fiberglass contribution from latent debris, a conservative value of 200 lb (170 lb of dirt and dust, 30 lb of fiber) [12] was used. Nukon fiberglass has been used as a substitute for latent fiber in past testing. Using the commercial density of Nukon (2.4 lb/ft³) and median STP sump volume (71,778 ft³) [8], the equivalent CHLE fiberglass debris quantity is 125.3 g generated from the 15-inch break, and 7.6 g due to the presence of latent debris, for a total of 132.9 g. The fiberglass will be distributed between the head loss section and the corrosion tank section of the CHLE tank apparatus. In the head loss section, the two columns will contain 36 g of fiberglass, distributed evenly on the two strainer sections of 6-inch diameter. In the corrosion tank section, 96.9 g of fiberglass in approximate 1-inch cubes will be contained in stainless steel mesh and submerged in the pool.

Concrete is included only in Test T3. It was determined that 1,446 ft² of concrete would be exposed to the containment pool solution during an LBLOCA [10]. Of the total area exposed, 67 ft² is expected to be in the vapor space and 1,379 ft² is expected to be submerged. For the CHLE tank experiments, these values correspond to 0.04 ft² of concrete in the vapor space and 0.77 ft² of submerged concrete. Since the quantity in the CHLE vapor space was very small, the total quantity of 0.81 ft² of concrete will be submerged in the CHLE tank. The concrete used in this test will be made using instructions obtained from STP and aged more than 30 days.

2.4 Fiber Beds

Both the NEI-processed and blender-processed debris beds will be used in these tests. The debris beds will be formed in the head loss columns at an approach velocity of 0.1 ft/s using room-temperature deionized water containing boric acid and trisodium phosphate (TSP) in concentrations reflective of the tank solution, resulting in a solution pH of approximately 7.2. Baseline head loss data will be collected. Then the solution will circulate through the columns at 0.01 ft/s for 48 hours to allow stabilization of the head loss due to bed formation [13-15]. After 48 hours, the rate of head loss increase will be assessed. If the head loss meets the acceptance criterion (rate of increase less than 0.025 ft in 6 hours), the columns will be linked to the corrosion tank, which will indicate the beginning of the 10-day test.

Once the linkage takes place, the temperatures of the tank and the columns will begin to converge, reaching equilibrium after several minutes. At the end of the 10-day test, the columns will be isolated and drained, and debris beds will be removed for post-test analysis. If the maximum head loss of 100 inches of water is reached in either column prior to the end of the 10-day test, the affected column will be isolated and the test will continue.

2.5 Chemicals

The concentrations listed in Table 2 are defined in supporting documentation [16]. Prior to test initiation, boric acid, lithium hydroxide, and TSP will be added to the tank and fully dissolved. The mass of boric acid and TSP added to the tank will be slightly less than the total specified in Table 2 because a small fraction will be retained for addition to the columns for debris loading. Hydrochloric and nitric acids will be added periodically over days 5 to 9 as indicated in Table 3, because the higher pH (without acid addition) during days 0 to 5 would encourage greater corrosion, and the slight reduction in pH (with

acid addition) would favor greater precipitation. The certified molarity of the acids shown in Table 4 was used in conjunction with data obtained from supporting documentation [17] to determine the volumetric quantities of nitric and hydrochloric acid to be added.

Table 2: Chemicals included in the 10-day tests

Chemical	Total Molar Concentration (mM)	Mass Concentration (mg/L)	Amount Added to Tank (total over 10 days)
Boric Acid	250.50 (as boron)	2,710 (as boron)	17.59 kg
Trisodium Phosphate	8.87	3,370	3.83 kg
Lithium Hydroxide	0.06 (as lithium)	1.46 (as lithium)	1.65 g
Nitric Acid	0.229	14.4	16.55 mL
Hydrochloric Acid	0.812	29.5	76.19 mL

Table 3: Incremental additions of acid over the 10-day test period

Simulated Generation Time (days) ^[17]	Cumulative [HNO ₃] (mM)	Cumulative [HCl] (mM)	Experimental Time of Addition	HNO ₃ (mL)	HCl (mL)
0.04	8.19E-03	2.70E-02			
0.08	3.09E-03	1.73E-02			
0.21	6.40E-03	3.58E-02			
0.50	1.05E-02	4.95E-02			
1.00	1.39E-02	5.50E-02			
3.00	3.92E-02	1.50E-01	Day 5	3.05	17.31
10.00	7.23E-02	2.76E-01	Day 6	2.84	14.05
20.00	4.57E-02	1.38E-01	Day 7	5.23	25.93
30.00	2.94E-02	6.38E-02	Day 8	3.30	12.92
			Day 9	2.13	5.99

Table 4: Manufacturer information associated with specific acid used in test

Acid Concentrate	Manufacturer	Lot Number	Molarity
Nitric Acid	EMD	NX0409P-5	15.7
Hydrochloric Acid	EMD	HX0603P-5	12.1

2.6 Methods of Chemical Product Detection

Filtered (0.1 μm) and unfiltered samples will be taken once per day for inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis for aluminum, calcium, silicon, and zinc. A difference in concentration between filtered and unfiltered samples may indicate the presence of an insoluble chemical product. Turbidity will be measured twice per day to monitor the formation of insoluble chemical products in solution. Given that insoluble chemical products are detected (i.e., turbidity is

greater than in the previous sample), samples will be collected for determination of particle size distribution and for zeta potential analysis.

The impact of supersaturated aluminum concentrations on the two types of processed-fiber debris beds will be assessed by monitoring the head loss across the beds. These tests are focused on assessing the impact that chemical precipitates have on head loss separate from the head loss from insulation and latent debris, which is accounted for in existing head loss correlations [18]. Changes in head loss can be due to multiple factors, including capture of particles, bed relocation, fiber shedding, changes in fluid viscosity, chemical precipitates, and other factors. It was observed in the LBLOCA test that zinc granules had escaped from the mesh bag in which they were contained, and may have contributed to the minor increase in measured head loss. To minimize this possibility in the current tests, the zinc granules will be replaced with zinc plates with equivalent surface area. As was done with previous CHLE testing, efforts will be taken to minimize the introduction of particles into the system by confirming tank cleanliness with conductivity and turbidity measurements and washing latent dirt and dust from materials before they are placed in the tank. Results from previous tests indicates that the turbidity in the tank solution (a sensitive measure of particulate matter in suspension) is highest at the beginning of a test, immediately after materials are placed in the tank and declines over time. The 48-hour startup period and initial head loss acceptance criterion will minimize the potential for substantial changes in head loss due to bed instabilities. An assessment of whether head loss is due to chemical precipitates or other factors will be determined by the nature of the head loss results in the context of the results of other diagnostics that are being measured. In addition, the test with only aluminum and fiberglass will minimize the potential for confounding effects from particles and will provide a separate measure of how supersaturated aluminum concentrations affect the debris beds.

2.7 Product Analyses

At the end of testing, test solution containing chemical products from the tank will be collected in 1-liter polyethylene or polypropylene containers and held agitated at test temperature. Aliquots of the stored test solution will also be subjected to sedimentation tests for a qualitative measure of particle size. Particle size and zeta potential will also be measured by a Malvern Zetasizer if the particles in solution are sufficiently concentrated. Other aliquots of solution will be centrifuged or filtered to obtain more than 1 gram of product for further analysis. Once the product is collected, it will be allowed to dry for more than 24 hours at room temperature for test analysis.

Collected chemical product will be analyzed by one or more of the following: x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), x-ray diffraction analysis (XRD), nuclear magnetic resonance (NMR) spectroscopy, or Raman spectroscopy. XPS will provide identification of elements in a scale found on corrosion materials and possibly indicate the stoichiometric formula of the compound. SEM will provide detailed images of the compound and will enable elemental identification of areas of interest that are captured in the image. XRD will indicate whether the product is amorphous or crystalline and may provide the stoichiometric formula of the compound. NMR and Raman spectroscopy will be used to examine the aluminum product, to evaluate whether the ligand bound to the aluminum is a silicate or a hydroxide group.

3.0 Conclusion

Evaluation of results from the CHLE 2012 program prompted a new tank test series designed to assess corrosion and dissolution chemical product morphology, to determine the effects of zinc on product formation, and to evaluate the response of debris beds to the presence of supersaturated chemical conditions. The experiments will generate data that will assist with the interpretation of results from previous 30-day tests, particularly with respect to the difference in corrosion rates in tests with and without the presence of zinc and the response of the debris beds to the chemical conditions. The experiments will also assist with continued progress toward understanding the importance of chemical effects on the risk-informed resolution of GSI-191, particularly by characterizing the morphology of any precipitates that form in sufficient quantities.

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