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Evaluation Guidance for the Review of GSI-191 Plant-Specific Chemical Effect Evaluations

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ENCLOSURE 3

ABSTRACT

The purpose of this document is to provide guidance to the Nuclear Regulatory Commission (NRC) staff on the important technical issues to be considered when reviewing plant-specific chemical effects evaluations of individual licensees in response to GSI-191, "Assessment of Debris Accumulation on PWR Sump Performance." It also provides guidance to licensees for the content of the chemical effects portion of their final supplemental responses to Generic Letter 2004-02. The fundamental issue that needs to be evaluated is whether or not plant-specific evaluations appropriately address the chemical effects that can occur following a postulated loss of coolant accident (LOCA).

This document consists of two main parts. The body of the document contains chemical effects evaluation guidance. Staff expectations for licensee chemical effect evaluations and Generic Letter 2004-02 supplement content are provided in this main body. A chemical-effects flow diagram is used to take the evaluator through the process of assessing potential concerns, formulating plans of testing, conducting tests, and evaluating test results. Staff expectations are provided in relation to the numbered figures in the flow diagram.

The second main part of the document is contained in Appendix B. Key results and observations from both NRC-sponsored testing and generic industry testing are provided in a summary "chemical effects knowledge base." The purpose of this section is to provide key results from chemical effects testing and to make observations based on the current state of knowledge that may not have been available to the authors of the original documents at the time they were prepared.

This document is being released as a **draft** since it may be useful to licensees that are currently performing chemical effects evaluations or will be performing chemical effects testing in the near future. The NRC staff continues to evaluate ongoing chemical effects testing and analyses and will update this document, as needed, based on additional information.

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Abbreviations and Acronyms

AECL…… ..... Atomic Energy of Canada, Limited
AES…… ..... Atomic Emission Spectroscopy
ANL…… ..... Argonne National Laboratory
CBS…… ..... Containment Building Spray
CRDM……..... Control Rod Drive Mechanism
CSS…… ..... Containment Spray System
ECCS……..... Emergency Core Cooling System
EDAX……..... Energy Dispersive X-ray Analysis
EPRI…… ..... Electric Power Research Institute
GSI…… ..... Generic Safety Issue
ICET…… ..... Integrated Chemical Effects Test
ICP…… ..... Inductively Coupled Plasma
LANL…… ..... Los Alamos National Laboratory
LOCA……..... Loss of Coolant Accident
NEI…… ..... Nuclear Energy Institute
NMR…… ..... Nuclear Magnetic Resonance
NTU…… ..... Nephelometric Turbidimetric units
NSSS……..... Nuclear Steam Supply System
PIRT…… ..... Phenomenon Identification and Ranking Table
PWR…… ..... Pressurized Water Reactor
RCS…… ..... Reactor Coolant System
RH…… ..... Relative Humidity
RHR……..... Residual Heat Removal System
RWST…… ..... Refueling Water Storage Tank
SEM……..... Scanning Electron Microscopy
SG…… ..... Sodium Gluconate
SMB……..... Sodium Metaborate
STB…… ..... Sodium Tetraborate
STPP…… ..... Sodium TripolyPhosphate
SwRI……..... Southwest Research Institute
TEM…… ..... Transmission Electron Microscopy
TLR……..... Technical Letter Report
TSP…… ..... Trisodium Phosphate
TSS…… ..... Total Suspended Solids
WCAP……..... Westinghouse Technical Report
XRD…… ..... X-ray Diffraction Analysis
ZOI…… ..... Zone of Influence

Vendor-Specific Materials[1]

Boraflex……..Absorber
CalSil……..……..Calcium Silicate Insulation
Durablanket…….…Alumina and Silica Woven Blanket Insulation
Kaowoo……Aluminosilicate Fiber Insulation
LEXAN…….....…Neutron Polycarbonate-based plastic
Microtherm……Silica, Mineral Oxide and Fiberglass Insulation
Min-K…….....Mineral Wool Insulation
NUKON……...Fiberglass Insulation
PVC…….Polyvinyl Chloride Plastic
RMI……....Reflective Metal Insulation
Temp-Mat ……..Fiberglass Insulation

[1] This listing of vendor materials is not an endorsement of their use. These materials are mentioned by name in various chemical effects test reports.

1. INTRODUCTION

Description of the Process

This evaluation guide seeks to provide a structured approach for NRC staff reviewing plant-specific responses to the chemical effects portion of GSI-191 "Assessment of Debris Accumulation on PWR Sump Performance." By providing NRC staff expectations in key technical areas, this document should be useful to licensees during preparation of the chemical effect part of their Generic Letter 2004-02 supplements. The PWR post-LOCA environment creates several challenges to material integrity based on temperature, chemical reactions, and effects from sprayed and pooled water. During a LOCA, materials in the zone of influence (ZOI) of the break can become debris that may transport to the sump area, where spray solution, spilled reactor coolant and borated water from other safety injection sources are accumulating. The combination of spray chemicals, insulation, corroding metals, and submerged materials creates a potential condition for the formation of chemical substances that may impede the flow of water through the sump strainers or affect downstream components in the emergency core cooling or reactor coolant systems.

Outstanding Issues from NUREG -1861

The NRC-sponsored testing that was performed to evaluate potential chemical effects was reviewed by a team of five independent experts in 2006. NUREG-1861, "Peer Review of GSI-191 Chemical Effects Program," provided the comments of the peer review panel. Several issues noted in NUREG-1861 are currently being evaluated by the Office of Nuclear Regulatory Research and are under consideration for inclusion in the evaluation guidance. These issues were evaluated using the Phenomenon Identification and Ranking Table (PIRT) Process, and additional scoping analysis is in progress. Depending on the outcome of the additional analyses, some of the peer review panel issues could affect future revisions to this document.

2. GENERAL APPROACH TO PLANT-SPECIFIC CHEMICAL EFFECTS EVALUATIONS

Plant-specific chemical effects evaluations should use a conservative analytical approach. In general, areas to be considered should include:

- Break selection and location
- Debris generation
- Latent debris
- Debris transport
- Chemical interactions prior to the sump screen
- Prolonged interaction (chemical) with recirculating liquid while materials are impinged on the sump screen
- Potential of debris to decompose and generate suspended particulates in the liquid flowing over the debris
- Head loss
- Potential chemical effects on components downstream of the sump strainer

These topics are further described in the sections that follow. The sequence of discussion follows the flow diagram shown in Figure 1.

The purpose of the flow diagram is to provide a logical sequence that outlines the paths of different plant-specific approaches to chemical effect evaluations. The diamonds in the flow diagrams represent decision points for testing that is to be performed. These decision points lead to different options that have been used in vendor testing. The description for the diamond identifies the different options that may be selected. The evaluation process flow path that is chosen by the licensee will affect the relevant technical issues to be addressed as part of the plant-specific evaluation.

Appendix A provides a sample of information that could be collected and used for a plant-specific materials evaluation.

Appendix B provides a Knowledge Base Review of chemical effects testing. This appendix summarizes the results of both NRC-sponsored tests and those nuclear industry sponsored tests that are intended for general industry use and are available to the public. Details regarding the conduct of the tests are to be found in the original referenced documents. The results summaries reference both the original documents where the detailed information can be found, and the step location in the Figure 1 flow diagram where this information is most applicable.

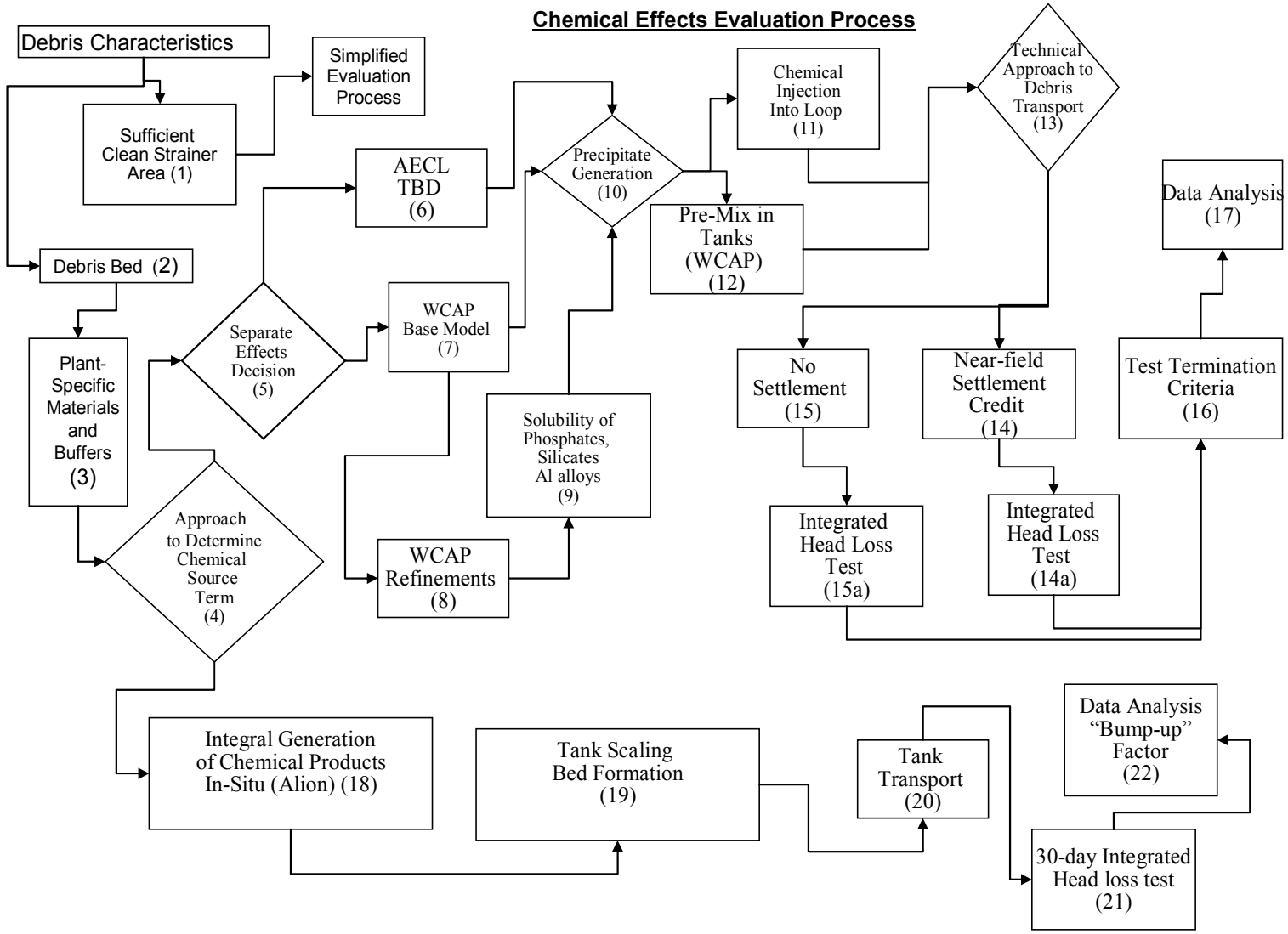


Figure 1.

Figure 1. Chemical Effects Evaluation Process Flow Diagram

3. EVALUATION PROCESS DESCRIPTION

The evaluation steps identified below are numerically identical to those in the Figure 1 flow diagram. Therefore, it may be helpful to print a copy of the flow diagram for reference while reviewing the remaining sections in the main body of this document. In the following sections, discussion for each numbered box in the flow diagram is subdivided into the following categories (some categories may be omitted from discussion of a given box if deemed inapplicable):

a. Knowledge Base- Lessons learned references are identified in the cited reports (see Appendix B for report details)

b. Technical Issues- This section identifies specific issues that can significantly affect the outcome of testing and which should be addressed.

c. NRC Staff Expectations

d. Generic Letter (GL) 2004-02 Supplement Content

Debris Characteristics

Plants should follow the NEI 04-07 Guidance Report, (ADAMS Accession No. ML041550332) as supplemented by the NRC Safety Evaluation (ADAMS Accession No. ML043280641) to determine the plant-specific debris characteristics. Consistent with the safety evaluation, the staff expects that licensee testing will simulate the debris from the break location that produces the maximum head loss.

(1) *Sufficient 'Clean' Strainer Area*

Plants that are able to demonstrate sufficient bare strainer area may use a more simplified chemical effects evaluation since chemical precipitates are expected to pass through a bare strainer. The methodology used to assess that there is sufficient clean strainer area should demonstrate that sufficient bare strainer area will remain available to support the design basis flow rate to the reactor core, considering all break locations within the uncertainties of debris generation and transport.

a. Knowledge Base
   i. NUREG/CR-6913

b. Technical Issues
   i. Strainer vendor head loss testing has shown that calculated debris beds substantially less than 1/8-inch thickness (e.g., 1/32 inch) can filter chemical products and cause significant pressure drops across the strainer. If sufficient microporous insulation, such as calcium silicate, is present, filtration of precipates has been demonstrated to occur with almost no fibrous debris other than that from the microporous insulation's fibrous binder.

   ii. Determining strainer coverage from non-chemical debris head loss tests can be difficult since test water may be cloudy and debris beds slump after the pump is stopped at the end of the test.

c. Staff Expectations
   i. Plants that plan to credit bare strainer area and perform a simplified chemical effect evaluation should demonstrate, for the maximum debris generation/transport break, that the screen design allows for chemical precipitates to pass unimpeded due to the excess available bare strainer area. For the purpose of this simplified analysis, strainer area with a very thin layer of debris that covers the strainer flow area is considered to be different from bare strainer area.

d. GL Supplement Content
   i. Those licensees performing a simplified chemical effects analysis should justify the use of this simplified approach by providing the amount of debris determined to reach the strainer, the amount of bare strainer area and how it was determined, and any additional information that is needed to show why a more detailed chemical effects analysis is not needed.

(2) Debris Bed Formation.

a. Knowledge Base
   i. NUREG/CR-6913
   ii.. NUREG/CR-6914, Vols. 1-6

b. Technical Issues
   i. ICET 3 test results indicate chemical precitates may form in representative post-LOCA environments.

c. Staff Expectations
   i. Licensees should follow the NEI 04-07 PWR Sump Performance Guidance report, supplemented by the NRC Staff Safety Evaluation, to determine the plant-specific debris bed characteristics. Chemical precipitate arrival sequence relative to non-chemical debris is discussed in later sections of this document related to strainer head loss testing.

d. GL Supplement Content
   i. Licensees should discuss why the debris from the break location selected for plant-specific head loss testing with chemical precipitate yields the maximum head loss. For example, plant X has break location 1 that would produce maximum head loss *without consideration of chemical effects*. However, break location 2, with chemical effects considered, produces greater head loss than break location 1. Therefore, the debris for head loss testing with chemical effects was based on break location 2.

(3) Plant-Specific Materials and Buffers.

In order to assess potential chemical effects, licensees need to identify the specific materials that are in their containment building that may react with the post-accident containment environment. Appendix A provides a sample of information that could be collected and used for a plant-specific materials evaluation. Plant materials should identify metallic and non-metallic items in the containment building including insulation types, concrete and coatings. Other considerations should include plant systems in containment that may contain chemicals (e.g., reactor coolant pump oil, thermal barrier system

corrosion prevention chemicals, air handling system drying materials such as molecular sieves, etc). The materials inventory should evaluate overall mass, location in containment and potential for being sprayed or immersed following a LOCA. Some items may have such a small mass or have such a small potential of being involved in the spray and containment sump liquid that they need not be considered. However, all specific materials should be noted and any assumptions for exclusion documented.

a. Knowledge Base
    i. NUREG-6913
    ii. SwRI (TLR IM 20.12130.01.001.320)
    iii. WCAP-16530
    iv. WCAP-16596-NP
    v. ANL Technical Letter Report on *"WCAP-16530-NP, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191"*

b. Technical Issues
    i. Each of the reports cited in Appendix B uses insulation materials and debris characteristic of those found at operating nuclear plants. However, each plant has different combinations of these materials, and may have others not included in any of the testing. Each licensee should thoroughly investigate plant-specific materials and include them in the proper proportion for strainer head loss testing.

    ii. Trisodium phosphate, sodium tetraborate and sodium hydroxide are the buffers currently used in plants. Certain buffer-materials combinations are particularly detrimental, and licensees should evaluate whether an alternate buffer would be beneficial from a chemical effects perspective.

c. Staff Expectations
    i. The licensee develops a thorough understanding of plant materials and the range of potential post-accident environments (e.g., temperatures, spray and pool pH values, spray durations), and uses this information to conservatively evaluate potential chemical interactions during the plant's ECCS mission time.

d. GL Supplement Content
    i. Licensees should provide their assumptions (and basis for the assumptions) used to determine chemical effects loading: pH range, temperature profile, duration of containment spray, and materials expected to contribute to chemical effects.

(4) *Approach to Determine Chemical Source Term*. *(Decision Point)*

This is the first decision point in the process of determining the method to be selected for plant-specific testing. The basic approach to determine chemical source term is determined by the strainer vendor that is selected by the licensee. To date, these involve:

(a) Single chemical effects tests which are later combined via a specific algorithm or,

(b) Integrated chemical effects tests where a plant-specific mixture of materials is tested in a representative post-LOCA environment to identify the specific chemical effects that will be observed in the plant. Only one vendor (Alion) has taken this approach to date.

Once all the materials have been identified, the major and minor constituents of each of these materials should be identified. These materials contain the "chemical source term" that was previously not considered during debris bed analysis. The evaluation should consider the chemical form of each of these materials and the potential for interaction with the environment during the LOCA and the subsequent ECCS mission time. Once again documentation of these considerations is important so that the final tests performed for the specific plant will be representative of the projected post-LOCA plant condition.

d. GL Supplement Content

i. Licensees should identify the vendor who performed plant-specific chemical effects testing.

(5) *Separate Effects Decision*. (*Decision Point*)

Within this part of the process flow chart two different methods of assessing the plant-specific chemical effects have been proposed. The WCAP-16530 study (Box 7 WCAP Base Model) uses predominantly single-variable test measurements. This provides baseline information for one material acting independently with one pH-adjusting chemical at an elevated temperature. Thus one type of insulation is tested at each individual pH, or one metal alloy is tested at one pH. These separate effects are used to formulate a calculational model which linearly sums all of the individual effects. A second method for determining plant-specific chemical effects that may rely on single-effects bench testing is currently being developed by one of the strainer vendors (Box 6, AECL).

(6) *AECL Model*.

[The AECL methodology for determining plant specific chemical effects has not yet been provided to the NRC staff. Therefore this section will be completed at a later date.]

a. Knowledge Base

b. Technical Issues

c. Staff Expectations

d. GL Supplement Content

i. Since the NRC staff is not currently aware of the testing approach, the NRC staff expects licensees using it to provide a detailed discussion of the chemical effects evaluation process along with head loss test results.

ii. Licensees should provide the chemical identities and amounts of predicted plant-specific precipitates.

(7) *<u>WCAP Base Model</u>*

a. Knowledge Base
   i. WCAP-16530
   ii. SwRI TLR, Dissolution Testing
   iii. ANL TLR on WCAP-16530
   iv. NUREG/CR-6913
   v. NUREG/CR-6914

b. Technical Issues
   i. WCAP-16530 provides useful information especially on a wide range of materials not included in ICET. However, care must be taken in interpreting the results as they are single-component effects. The model assumes that a linear combination of these single-effects tests can be summed to get a multiple effect result.
   ii. WCAP-16530 notes that none of the precipitated materials that formed settled rapidly.
   iii. The knowledge of which precipitates can form is not complete. The model in WCAP-16530 assumes that these precipitates are aluminum oxyhydroxide (AlOOH), sodium aluminum silicate ($NaAlSi_3O_8$) and calcium phosphate ($Ca_3(PO_4)_2$).
   iv In the presence of dissolved Si, the WCAP model assumes that $NaAlSi_3O_8$ precipitates before AlOOH. The model uses mass as a measure of the pressure drop experienced by the filter and does not consider volume of the highly hydrated precipitate.
   v. The WCAP model considers the surrogate precipitate to be an inert material and the filterability of AlOOH and $NaAlSi_3O_8$ to be equivalent. The NRC staff is currently sponsoring independent tests to confirm this assumption.
   vi. The aluminum release rate shown in Equation 6-2 under-of WCAP-16530 predicts aluminum corrosion rates observed in ICET 1 and ICET 5 <u>before</u> aluminum passivation occurred.
   vii. Relative comparison of WCAP-16530-NP conservative assumptions (e.g., all dissolved aluminum precipitates) and non-conservative aspects (e.g., does not account for RCS crud) will be provided in the staff safety evaluation of the topical report.

c. Staff Expectations
   i. Input of plant parameters (e.g., sump temperature, pH, and containment spray durations) into the WCAP-16530 spreadsheet will be done in a manner that results in a conservative amount of precipitate formation. In other words, plant parameter inputs selection will not be biased to lower the predicted amount of precipitate.
   ii. Analysis, using timed additions of precipitates based on WCAP-16530 spreadsheet predictions, will account for potential non-conservative initial aluminum release rates. *This comment is not applicable to tests with the projected 30-day chemical load added near the start of the test.*

d. GL Supplement Content
   i. For licensees proceeding from block 7 to diamond 10 in the Figure 1 flow chart, justify any deviations from the WCAP base model spreadsheet (i.e., any plant specific refinements) and describe how any exceptions to the base model spreadsheet affected the amount of chemical precipitate predicted.
   ii.. List the type (e.g., AlOOH) and amount of predicted plant-specific precipitates.

(8) *<u>WCAP Refinements</u>*

a. Knowledge Base
   i. WCAP-16785
   ii. WCAP-16530
   iii. NUREG/CR-6914
   iv. NUREG/CR-6913

b. Technical Issues
   i. The industry sponsored testing on submerged coupons. The timing of aluminum inhibition in a containment spray environment relative to termination of containment spray needs to be determined and factored into the plant-specific input.
   ii. Aluminum alloys corrode more slowly than Alloy 1100. WCAP-16785-NP considers that this difference in corrosion rate is negligible.
   iii. Westinghouse developed a multi-variate aluminum release rate equation for inhibition by silicate and a separate one for phosphate which is stated to be valid in the pH range of 4.5 to 9.0 and below 200 ^{0}F. Above pH 9.0 original aluminum release rate equation (from WCAP-16530) should be used.

c. Staff Expectations
   i. Conservative assumptions in the WCAP-16530 base model were intended to balance uncertainties in GSI-191 chemical effects knowledge. Therefore, when licensees use refinements to the base model they should demonstrate why their overall chemical effects assessment remains conservative when implementing these model refinements.

d. Supplemental Content

(9) *<u>Solubility of Phosphates, Silicates and Al Alloys</u>*

a. Knowledge base
   i. WCAP-16785
   ii. WCAP-16530
   iii. NUREG/CR-6914
   iv. NUREG/CR-6913

b. Technical Issues
   i. Silica and phosphate both inhibit the corrosion of aluminum. However, the corrosion rate still increases as pH increases (but more slowly in the presence of silicates and phosphates).

ii. Testing was performed on submerged coupons. The timing of aluminum inhibition in a containment spray environment relative to termination of containment spray needs to be determined and factored into the plant-specific input. This effect should be considered since the containment spray pH will vary in the first few hours.

iii. Use of the WCAP-16530 spreadsheet to determine leaching of silica from fiberglass is non-conservative for determining silica concentrations <u>for aluminum inhibition purposes</u>. Levels of dissolved silica in ICET Test 1 are much lower than would be predicted from tests on fiberglass in solutions with comparable pH values. Dissolved aluminum in solution can interact with fibers resulting in significantly lower silica in solution than predicted by single-effect tests.

iv. .Extrapolation of measured solubility values from WCAP-16785 bench testing to projected plant-specific post-LOCA environments will be difficult.

v. Mass balance of precipitate versus ionic input is performed in only one of the tests. The correlation between the two values was very poor.

vi. The precipitated materials from the tests (where particle size was measured) were found to be agglomerations of small particles (1-5 μm) built up into larger particles (>20 μm).

c. Staff Expectations

i. Credit for passivation of aluminum by phosphate or silica should be justified and thoroughly documented. If the silica or phosphate does not significantly contact the surface of aluminum for sufficient time during the event, passivation should not be credited.

ii. Conservative assumptions in the WCAP-16530 base model were intended to balance uncertainties in GSI-191 chemical effects knowledge. Therefore, when licensees use refinements to the base model they should demonstrate why their overall chemical effects assessment remains conservative when implementing these model refinements.

d. GL Supplement Content

i. Licensees should clearly identify any refinements (plant-specific inputs) to the base WCAP-16530 model and justify why the plant-specific refinement is valid.

ii. For crediting inhibition of aluminium that is not submerged, licensees should provide the substantiation for the following: (1) the threshold concentration of silica or phosphate needed to passivate aluminum, (2) the time needed to reach a phosphate or silicate level in the pool that would result in aluminium passivation, and (3) the amount of containment spray time (following the achieved threshold of chemicals) before aluminium that is sprayed is assumed to be passivated.

iii. For any attempts to credit solubility (including performing integrated testing), licensees should provide the technical basis that supports extrapolating solubility test data to plant-specific conditions. In addition, licensees should

indicate why the overall chemical effects evaluation remains conservative when crediting solubility given that small amount of chemical precipitate can produce significant increases in head loss.

iv. Licensees should list the type (e.g., AlOOH) and amount of predicted plant-specific precipitates.

(10) <u>Precipitate Generation</u> (Decision Point)

This is another decision point in the chemical effects flow chart process. Two basic methods of precipitate generation have been used in strainer head loss tests. Each of these methods has advantages and drawbacks. The first method involves the injection of chemicals into the flowing stream of the test flume. Both solutions initially contain no precipitates, and the combination of the two causes a precipitation reaction to occur (Flow diagram step 11). This leads to precipitation from a homogeneous solution. The second method creates a surrogate precipitate in a separate mixing tank. This surrogate solution is then injected into the flowing system to simulate the carrying of precipitated material to the sump screen area (Step 12). This leads to precipitation from a heterogeneous solution.

The testing done by the national laboratories performing the work described in the NUREG reports has shown significantly different amounts of boric acid incorporation into the precipitates that have formed, depending on the temperature of formation. The precipitate generation method will affect the reproducibility of such incorporation since metal borate compounds at the concentrations being examined are soluble.

c. Staff Expectations

i. Analysis of the water used for precipitate generation is performed to ensure spurious effects (from contaminants in the water) are not realized.

ii. Test parameters such as temperature, pH, and concentration of species are appropriately controlled such that precipitation processes are understood and are either representative or conservative.

(11) <u>Chemical Injection into the Loop</u>

a. Knowledge base

i. NUREG/CR-6915

ii. NUREG/CR-6914

iii. WCAP-16596-NP

b. Technical Issues

i. The time dependency effect of injection of the precipitate into the loop should be understood in terms of amount of chemical that transforms into precipitate and the timing of precipitation relative to test termination. In other words, the amount of precipitate that arrives at the strainer during the course of the testing interval should be known.

ii. Kinetics of aluminum hydroxide precipitation are complex. Solutions can maintain supersaturation for significant amounts of time (days), and then demonstrate a relatively rapid increase in head loss. The observed behavior in ANL loop tests and in ICET-1 (pH 9.6) tests is consistent with an ongoing

process of nucleation and growth of products too small to be detected visually.

iii. WCAP-16596 tests that added dissolved aluminum to a sodium tetraborate solution demonstrated a temperature related effect. When the aluminium was added at elevated temperature, a precipitate was formed as the solution cooled. There was no visible accumulation of precipitate when the same concentration of aluminium was added at room temperature.

c. Staff Expectations

i. Reactions that will occur during chemical injection into a test loop are sufficiently evaluated and understood to show how much and what type of precipitate is formed.

ii. Chemical matter is added in a manner that is representative with respect to the formation of the precipitate during the event chronology.

iii. Licensees should verify that the full loop chemistry test results for precipitates (mass and type) and aluminium (remaining in solution) match what was expected based on bench scale tests.

iv. Licensees should demonstrate that the settlement and filterability characteristics of the precipitates are representative of (or more conservative than) than those expected to be formed in the plant post-LOCA environment.

d. GL Supplement Content

i. Licensees should provide the one-hour settled volume (e.g., 80 ml of 100 ml solution remained cloudy) for precipitate prepared with the same sequence as with the plant-specific, in-situ chemical injection.

ii. For plant-specific testing, the licensee should provide the amount of injected chemicals (e.g., aluminium), the percentage that precipitates, and the percentage that remains dissolved during testing.

iii. Licensees should indicate the amount of precipitate that was added to the test for the head loss of record (i.e., 100 percent 140 percent).

(12) *<u>Pre-mix in Tank</u>*

a. Knowledge Base

i. WCAP-16530

ii. NUREG/CR-6914

b.Technical Issues

i. Pre-mix tank concentrations affect the precipitate agglomeration and settlement behaviour.

ii. A minimum one-hour mixing time is required by WCAP-16530 to allow for precipitate hydration and reaction completion.

iii. The surrogate precipitate has a defined shelf life. Potential changes to the precipitate as it ages make it important to measure settlement properties with 24 hours of testing.

c. Staff Expectations

i. Chemical precipitate is added in a manner that is representative or conservative (e.g., add predicted 30-day load early in the test) with respect to the formation of the precipitate during the event chronology.

ii. Chemical precipitate concentrations in the mixing tank do not exceed the recommended values in WCAP-16530 values (e.g., AlOOH is 11 g/L).

d GL Supplement Content

i. Licensees should discuss any exceptions taken to the procedure recommended for surrogate precipitate formation in WCAP-16530.

(13) *Technical Approach to Debris Transport (Decision Point)*

Debris transport represents another decision point in the flow chart. Plant-specific analysis determines the amount of debris that is generated and transported to the sump strainer. Test vendors have selected two basic debris transport approaches. Those licensees that attempt to credit settlement of debris away from the strainer surface, i.e., "near-field" settlement enter Box 14. Those licensees that use agitation or other means to keep debris suspended, such that essentially all debris analyzed to reach the strainer in the plant reaches the strainer in head loss testing, enter Box 15.

(14) and (14a) *Integrated Head Loss Test With Near- Field Settlement Credit*

a. Knowledge Base

i. NUREG-6913
ii. WCAP-16530-NP
iii. NRC Staff Review Guidance Regarding Generic Letter 2004-02 Closure in the Area of Strainer Head Loss and Vortexing (ADAMS Accession No. ML072600348)

b. Technical Issues

i. There are a number of non-chemical related technical issues related to "near-field" settlement. These are discussed outside the scope of this document (see NRC Staff Review Guidance Regarding Generic Letter 2004-02 Closure in the Area of Strainer Head Loss and Vortexing (ADAMS Accession No. ML072600348)).

ii. Since the objective of tests with near field settlement include settling chemical precipitate, it is critical that the precipitate used in these tests settle no more rapidly than would be expected in the projected plant environment.

c. Staff Expectations

i. Precipitate settling rate will not exceed the settling rate of the 2.2 g/L surrogate aluminum solution shown in Figure 7.6-1 of WCAP-16530.

d. GL Supplement Content

i. Licensees should provide the one-hour or two-hour precipitate settlement values measured within 24 hours of head loss testing.
ii. Licensees should provide a best estimate of the amount of surrogate chemical debris that settles away from the strainer during the test.

(15) and (15a) *Head Loss Testing Without Near Field Settlement*

Tests performed using this methodology introduce prepared plant-specific debris materials and chemical precipitates into a test tank or flume and keep the material in suspension to enable it to reach a strainer segment. The objective is to have all material eventually reach the strainer surface.

a. Knowledge Base

i. ANL Technical Letter Report on WCAP-16530
ii. NUREG/CR-6914
iii. NUREG/CR-6913

b. Technical Issues

i. The amount of debris added to the test loop is at least the amount that is analyzed to reach the strainer surface.
ii. Solutions of aluminum of ≥ 100 ppm (with no apparent, visual precipitate) at pH 9.6 and 75 ^{0}F showed pressure drops in the loop that were greater than could be predicted based on changes in viscosity. Testing indicated that the particulate size in this case was likely less than 0.2 µm.
iii. Thin filter beds (≤ 1/8 inch) can produce much higher head loss than thicker filter beds.

c. Staff Expectations

i. Licensees who are not crediting settlement of debris should keep surrogate chemical debris suspended in solution until it is able to deposit on the test strainer's surface. Low-flow areas of test tanks and flumes should be agitated mechanically of hydraulically so that debris is not able to settle out before reaching the strainer surface.

d. GL Supplement Content

i. Licensees should provide an estimate of the amount of debris and precipitate that remains on the tank/flume floor at the conclusion of the test and justify why the settlement is acceptable.
ii. Licensees should provide the one-hour or two-hour precipitate settlement values measured and the timing of the measurement relative to the start of head loss testing (e.g., within 24 hours).

(16) *Test Termination Criteria*

a. Knowledge Base

b. Technical Issues

All measurement objectives that determine test termination should be stated prior to the commencement of the test. Factors that should be considered in these measurement objectives:

i. Has all the material that will yield an effect had the opportunity to get into solution?
ii. Do the test termination criteria represent a point in time where formation of further significant impediments to flow will not occur?
iii. For precipitates formed by chemical injection into the test loop, measurement of the test solutions at various times in the event sequence

is needed to show that the precipitation is completed prior to test termination.

iv. Have the overall chemical effects stopped, or slowed to the point that any further changes will be insignificant?

c. Staff Expectations

i. Licensees have high confidence that tests are terminated in a conservative manner such that additional test duration would not alter the measured or projected maximum head loss considering factors such as completion of precipitation, transport of chemical material to the screens, etc.

d. GL Supplement Content

Provide the test termination criteria.

(17) *Data Analysis*

a. Knowledge Base

i.WCAP-16596

ii.WCAP-16785

b. Technical Issues

c. Staff Expectations

i. Licensees should consider a number of items such as debris/ precipitate settlement, the presence of debris bed bore holes, test repeatability, pressure drop across the bed as a function of time, and other factors when evaluating head loss test results.

d. GL Supplement Content

i. Licensees should provide a copy of the pressure drop curve(s) as a function of time for the testing of record.

ii. Licensees should explain any extrapolation methods used for data analysis.

(18) *Integral Generation (Alion)*

The objective of this vendor's test approach is to assess the head loss resulting from chemical effects by performing 30-day, integrated tests with plant-specific debris in a representative plant-specific environment.

a. Knowledge Base

i. NUREG/CR-6914

ii. NUREG/CR-6913

iii. NUREG/CR-6915

iv. WCAP-16596-NP

b. General Technical Issues

i. Determining the combination of plant parameters (e.g., temperature, pH) that results in a conservative chemical effects test is challenging. For example, within a range of plausible pH values for a postulated plant

LOCA, the higher pH favors more rapid dissolution of aluminium, while the solubility of aluminium is lower (i.e., a higher probability of precipitation for a given aluminium concentration) at the low end of the pH range.

ii. Potential influences of temperature cycling, such as occurs as fluid in the ECCS passes through a heat exchanger and into the reactor vessel or out a pipe break, should be understood.

iii. Integral tests assume solubility limits observed in the test are applicable to the prototypical situation, although there may be some significant differences.

c. Staff Expectation

i. A sufficient technical basis is developed to support selecting plant-specific test parameters that produce a conservative chemical effects test.

ii. Inability to reach peak sump temperatures is offset by extended testing at highest loop temperatures.

d. GL Supplement Content

(19) *<u>Tank Scaling/Bed Formation</u>*

a. Knowledge Base

b. Technical Issues

i. The NRC Staff is currently interacting with the strainer vendor to resolve non-chemical effects related scaling questions.

c. Staff Expectations

i. Scaling factors for the test facilities are representative or conservative relative to plant-specific values.

ii. Bed formation is representative of that expected for the size of materials and debris that is formed in the plant specific evaluation.

d. GL Supplement Content

(20) *<u>Tank Transport</u>*

a. Knowledge Base

b. Technical Issues

c. Staff Expectations

i. Transport of chemicals and debris in testing facility tanks should be representative or conservative with regard to the expected flow and transport in the plant-specific conditions.

d. GL Supplement Content

(21) *<u>30-day Integrated Head Loss Test</u>*

a. Knowledge Base

b. Technical Issues

c. Staff Expectations

d. GL Supplement Content
   i. Licensees should provide the plant-specific test conditions and the basis for why these test conditions and test results provide for a conservative chemical effects evaluation.
   ii. Licensees should provide a copy of the pressure drop curve(s) as a function of time for the testing of record.

(22) *<u>Data Analysis Bump Up Factor</u>*

At the time of this draft guidance development, the staff is working with the vendor to resolve technical issues related to the validity of using a “bump-up” factor from these tests.

a. Knowledge Base

b. Technical Issues

c. Staff Expectations

a. GL Supplement Content
   i. Licensees should provide the details and the technical basis that show why the bump-up factor from the particular debris bed in the test is appropriate for application to other debris beds.

4. ADDITIONAL TECHNICAL INFORMATION

The information provided in the previous sections resulted from vendor and NRC-sponsored research on the chemical effects in the PWR post-LOCA environment. Additional technical information is available that may assist licensees in the preparation of their responses and potential plant specific changes. These are general areas of chemical knowledge that were not intended for the chemical effects testing but are related to the effects that have been measured. This information is not listed in any specific order.

A. Solubility of Sodium Aluminum Silicate

It is known that sodium aluminum silicate is insoluble in certain environments. However the solubility limit and the effects of different ratios of sodium, aluminum and silica on that solubility are not clear. Research done by DOE at the Hanford site [Reference 1] identified that crystallized sodium aluminum silicate may be assisting in the precipitation of uranyl ions from some of the storage tanks. The calculated value for the K_{sp} of aluminum silicate that they determined was ~$4x10^{-4}$. Their observation was that, in solutions of excess aluminum sodium aluminosilicate precipitated rapidly (minutes). These researchers also found that the form of sodium aluminosilicate changed slightly under conditions of higher temperature. The precipitate was found to be depleted in silica concentration.

B. Passivation Effects of Silica and Phosphate

Both silicate and phosphate are used routinely in closed cooling water systems to minimize general corrosion. The ERPI Closed Cooling Water Guidelines [Reference 2] identify concentrations of silica that can passivate the surface of aluminum metal as 20-200 ppm. Phosphate as an inhibitor is used in formulations that are glycol-based and usually is adequate for passivation in the 500 ppm range.

It is important to note that it is an acceptable conservatism to minimize the amount of dissolved aluminum based on the corrosion rate in silica solution. However, the short term corrosion rate of aluminum should be used for determination of final aluminum concentration and potential for precipitation.

C. Sources of Silica in PWRs Other Than Insulation

Spent fuel at PWR facilities is stored in the spent fuel pool system. This system is in a separate building and isolated from the reactor coolant system, except during each refueling outage. During the refuel cycle the spent fuel pool water the reactor coolant water and the water in the refueling water storage tank all become one system. Over the past ~20 years, PWRs have been using additional neutron absorbing material known as Boraflex in the spent fuel pools so that fuel assemblies can be placed closer together optimizing storage space. A few years after the introduction of Boraflex to the spent fuel system, it was observed that Boraflex was undergoing radiolytic and chemical decomposition yielding reactive silica in the spent fuel pool water. Concentration of silica in some spent fuel systems has been greater than 100 ppm. Fuel manufacturers have specifications for silica concentration in the reactor coolant system. These specifications have been described in the EPRI guidelines [Reference 3] for the reactor coolant system.

D. References

1. “Sodium Diuranate and Sodium Aluminosilicate Precipitation Testing Results,” R. A. Peterson and R. A. Pierce, Westinghouse Savannah River Company, Aiken, SC 29808. This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy (October 2000).

2. “Closed Cooling Water Chemistry Guideline,” Revision 1, EPRI TR-1007820 (April 2004).
3. “Pressurized Water Reactor Primary Water Chemistry Guidelines,” Revision 5, EPRI TR-1002884 (September 2003, updated 2005).

APPENDIX A

BASIC INFORMATION TO BE COLLECTED BY LICENSEE TO SUPPORT THE EVALUATION

The licensee should have documentation to support the performance of the containment materials assessment. One example method for collecting materials information is shown below. This listing of information is intended to be as complete as possible to support a plant-specific baseline evaluation. However, plant-specific features may result in different approaches to collecting containment materials information or require that additional information be collected to performance a baseline evaluation.

1. General containment design information
    - Plan view of containment and its components at each level
    - Piping isometric drawings
    - Process diagrams for flows in different systems within the containment
    - The most current Accident Analysis data and the licensing basis for post-LOCA recirculation. This information should include information such as emergency core cooling flows, containment building spray flows, linear velocity through the RHR piping and across the containment floor at various accident stages, spray sequence following a large break LOCA and flows, length of time between discrete post LOCA events, sump water temperature profile, RCS and RHR temperature profiles etc.
2. Insulation details
    - Manufacturer, batch and chemical composition of all insulation used inside containment (insulation specifications)
    - Volume or mass of insulation material installed
    - Where it was used on equipment, in penetrations, on piping, etc. (drawings)
    - How it was installed; encapsulated, banded, etc. (drawings)
    - Inspection records, if appropriate or available
    - Design changes that may have changed insulation used (specifications and 26 drawings)
3. Piping Penetration details
    - Penetration plan (elevation and azimuth)
    - Drawings of insulation material used in penetrations
    - Any materials used for bracing or cushioning of piping in the penetrations or against piping supports.
4. Fire barrier details
    - Major and minor chemical composition of material used inside containment (e.g., Bisco Seal®)
    - Where it was used inside containment (drawings)
    - How it was installed (drawings)
    - Inspection records, if appropriate or available
    - Design changes that may have changed fire barrier material or location inside containment
5. Containment (specifications and drawings)
    - Protective coatings details (area covered)
    - Chemical composition of the coatings applied (qualified and unqualified)
    - Where they were applied
    - Coatings application specification(s)
    - A copy of the “Exempt” or “Unqualified” coatings log, if used at the site
6. Location and identification of other potential debris sources
    - Foreign materials exclusion program documentation
    - Latent debris observed to be inside containment

- Tagging and labeling procedures or technical instructions
- References for use of cable ties inside containment
- Permanent shielding devices installed (e.g., lead blankets with plastic sheathing).

7. Location and identification of other potential sources of chemicals in the containment building
    - Chemicals in systems other than the RCS and CBS systems (e.g., component cooling water corrosion inhibitors)
    - Oil reservoirs for pumps
    - Hydraulic fluids for valve actuators, polar crane, and other mechanical devices
    - Lubricants used within the containment building on a routine basis
    - Desiccants for instrument air system
    - Secure storage locations within containment where expendable products may be stored between outages (tool cages, gang boxes, etc)

APPENDIX B

Knowledge Base Review of Chemical Effects

The purpose of this appendix is to summarize the important facts resulting from all of the technical reports and research regarding chemical effects testing. In some cases, additional observations have been made based on the current state of knowledge that may not have been available to the author(s) when the original documents were prepared.

The Knowledge Base is organized according to the individual documents such as NUREGs or topical reports. Each report section is then divided into the following sub-categories:

1. Description of Tests and Procedures
2. Summary of Important Results
   2.1. Overview
   2.2. Solution Chemistry
   2.3. Precipitation
   2.4. Passivation
   2.5. Chemical Model (this section is added when modeling was used in the report)
3. Comments and Observations

Since all reports do not address all of the sub-sections of category 2 above, only the applicable subsections are shown.

In the Summary and Comments sections each item has a number or numbers in brackets at the end, such as [2, 3, 6]. These numbers refer to the numbered boxes in the flow diagram in Appendix B of this document.

Each numbered item in these two sections may also have an additional qualifier denoted with {section 1.2.5, p. 13}. This refers to the section number and page number in the Adobe version of the document where the information supporting this conclusion or comment may be found.

This Appendix is divided into two parts. Part A contains documents related to nuclear industry testing. Part B contains National Laboratory test reports and reviews

Part A
Nuclear Industry Test Report Reviews

A. WCAP-16530-NP "*Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191*"

1. Description of Tests and Procedures

The Westinghouse report describes their approach to the effect of containment post-LOCA spray chemicals on debris generated and, metal and nonmetal surfaces in containment during the early phases of the event.

Westinghouse developed a questionnaire that was sent to the US PWR fleet. The questionnaire asked for information about the types of insulation in containment, the approximate percentages of each type, the types of metallic components and if they were coated, and several other questions related to the types of materials in containment that potentially could react with spray solution chemicals. In addition, they requested specific information about the chemicals being used in the containment building spray solution. Sixty-nine (69) responses were received and the responses tallied. Although there were a wide variety of materials identified, testing focused on those materials that were present in the highest percentages and in the greatest numbers of plants.

Three different types of chemicals are used in PWRs to adjust post-LOCA pool pH: sodium hydroxide, trisodium phosphate and sodium tetraborate. These provide different values for the final equilibrium pH in the containment sump. The tests were performed at three different pH values so that the pH values generated during a post-LOCA event would be bounded by the tests.

Eleven different materials were selected for testing at pH values of 4.1, 8.0 and 12.0, in solutions that contained boric acid (4400 ppm B) with added trisodium phosphate (TSP), sodium tetraborate (STB) and sodium hydroxide. These tests were conducted at temperatures of 190^0F and 265^0F and were monitored during three different time periods (30, 60 and 90 minutes). Table 4.2-1 of the document identifies the combination matrix of test materials, pH, buffering agents and temperatures tested.

The tests were divided into several categories:

- Measuring the dissolution of ions or ionic compounds from the fifteen materials tested
- Measuring the precipitation resulting from the dissolved ions and the containment spray media
- Determination of the type of precipitates formed and their settling rates
- Ability to reduce the flow through filtration media
- Effect of temperature on the precipitate formation
- Effect of pH on the precipitate formation
- Measurement of the pressure drop across a filtration medium
- Development of a chemical model that was subsequently tested using a "particle generator."

The testing described in this WCAP was intended to complement the testing done as reported in the "Integrated Chemical Effects Test Project: Consolidated Data Report," NUREG-CR-6914.

The insulation materials tested were NUKON, Interam, CalSil, Temp-Mat (fiberglass), Mineral Wool, Durablanket and Min-K. The remaining materials tested were galvanized steel, uncoated carbon steel, aluminum, and concrete (powdered).

Several different analytical techniques were used to determine the identity of dissolved and precipitated materials: Inductively Coupled Plasma (ICP), Scanning Electron Microscopy (SEM), and Energy Dispersive X-Ray Analysis (EDAX).

2 Summary of Important Results and Conclusions

2.1 Overview

The tests performed in this study were aimed at the settling of precipitates and their filterability. The basic interactions of individual materials or precipitates were observed and mathematical models to assess how these individual materials affect filterability were developed. The materials examined and the solution chemistry conditions were, to a large extent, based upon feedback from the aggregate answers to a questionnaire sent out by Westinghouse. Not all materials were tested, but the major contributors to those materials that would contribute to debris in the post-LOCA environment were tested.

2.2 Solution Chemistry

2.2.1 Ten (10) different containment materials were dissolution tested; 7 different insulation materials, aluminum metal, zinc metal, carbon steel and crushed concrete. The total time for this test was 1.5 hours at either 190^0 or 265^0F.
[3], {Section 5.2.2, p.65}

2.2.2. Elemental analysis was performed using inductively-coupled plasma (ICP) for Al, Fe, Zn P, S, Si, Ti, Mg, Ca on all materials tested. The ionic material of greatest concentration after the equilibration tests was aluminum followed by silica and calcium, as shown in the table below.

Table 5.2-1: Comparison of Total Mass Release in Dissolution Testing by Element

Element	Total Mass Released into Solution (mg)
Fe	3
Zn	3
S	25
Ca	110
Si	393
Al	1634

For this table, “The total mass of each element release in the design matrix dissolution tests was calculated by summing the releases for all times, temperatures, and pH levels.” This particular method of comparing the mass of precipitates generated is internally consistent to this research effort but cannot be compared directly to other efforts. Additionally, the study summed the dissolution of materials from each of the individual materials tested as seen in this figure:

Table 5.2-2: Comparison of Total Mass Release from the Tested Materials

Material	Total Mass Released into Solution (mg)
Carbon Steel	6
Galvanized Steel	8
Mineral Wool	18
Interam	31
Durablanket	34
Nukon Fiberglass	55
MIN-K	69
High Density Fiberglass	92
CalSil	177
Concrete	376
Aluminum	1580

The materials were tested in proportion to their containment surface area except for the crushed concrete that had a surface area greater than would be representative of a PWR. The significant elemental contributions based on this relationship are aluminum> calcium > silicon. [7, 8], {Section 4.2.2, p. 37; Section 5.1.1, p. 45}

2.2.3 The dissolution of aluminum increases with increasing pH while the dissolution of calcium decreases with increasing pH. [7],{Section 5.2.3, p. 74}

2.3 Precipitates

2.3.1 None of the 13 precipitates (out of 60 solutions tested) that formed settled rapidly and thus all of the precipitates are of concern for sump screen performance. [9, 10], {Section 4.2.1, p. 36; Section 4.2.3, p. 41; Section 5.2.4, p.75 and Table 5.3-1}

2.3.2 The total mass of precipitates that were measured did not correlate well with the total mass of material dissolved from the substrates tested. [3,9], {Section 5.2.4, p.75}

2.3.3 SEM analysis of the 13 precipitated materials identified the agglomerated particle size as $\geq$ 20 microns, but individual particle sizes vary in size down to sub-micron level. [9], {Section 5.3.2, p. 85}

2.3.4 Precipitate filterability was assessed in this study by calculating filter cake coefficients. These coefficients were used to form a mathematical model for pressure drop across the screen. [9], {Section 5.4, p 88}

2.3.5 The major chemical species identified as precipitates in these studies were: aluminum oxyhydroxide, sodium aluminum silicate and calcium phosphate. The report indicates that, based on this testing, their chemical model needs only to consider the ionic materials that form these compounds. [7], {Section 6.1, p. 92}

2.3.6 Using the WCAP model for precipitate formation, CalSil substantially dissolution was greatest at pH values between 5.6 and 8.5, and decreases above 8.5. However this is offset by a reverse effect with pH seen by aluminum corrosion. [9]{Section 6.5.4, p.112}

2.3.7 The WCAP presents a ‘particle generator’ model for use in testing of containment sump screens or filters. The WCAP tests the efficacy of this model and identifies it as suitable for the purposes of design testing. Using different precipitates [12],{Section 7.5, p. 122-125}

2.4 Passivation

2.4.1 For all the materials tested, the materials that yielded the greatest dissolution mass were aluminum metal, concrete (calcium as the major contributor) and CalSil (both calcium and silicate as major contributors). [7], {Section 4.2.2, p. 37-41; Section 5.2.2-5.2.3, p. 65-75}

2.4.2 Galvanized steel and carbon steel had relatively low release rates compared to aluminum, and were not considered to be of significance in the modeling process.[8], {Sections 6.2.2 and 6.2.3, p. 97-99}

2.4.3 Aluminum release was highest at pH 12.0 (in NaOH) and lowest at pH 4.1 (no buffer material added).[7, 8, 9], {Section 6.2.1, p. 93}

2.5 Chemical Model

2.5.1 The WCAP presents a mathematical model based on the chemical data from the tests runs in this study. The base case is a simple mix of containment materials and TSP as the buffer chemical. The materials that comprise the greatest precipitate mass from this model are calcium phosphate and sodium aluminum silicate. {Section 6.5, p. 106-110}

3. Comments and Observations

3.1 The effects of an hydraulic transient induced release of corrosion products was considered negligible. Although the WCAP provides a graph that indicates that the release may be small, this graph is based on a controlled plant shutdown under conditions of constant pressure, temperature and flow rate. The thermal, hydraulic, pressure and chemical transient that occurs post-LOCA would likely release more corrosion products than what the WCAP estimates. [7,8], {Section 5.1.2, Figure 5.1-1, p. 46}

The measurement of precipitate-induced pressure increase across a filter, in this study, is not reliable since the model used to calculate the filter cake coefficient is determined by calculating a precipitate mass measured after drying. These calculations assume the same degree of hydration between different batches of precipitate and between different precipitates. This may not be a valid assumption. {Section 5.4, p 88}

B. *"SUPPLEMENTARY LEACHING TESTS OF INSULATION AND CONCRETE FOR GSI–191 CHEMICAL EFFECTS PROGRAM,"* Center for Nuclear Waste Regulatory Analyses San Antonio, Texas. Technical Letter Report IM20.12130.01.001.320

1. Description of Tests and Procedures

These NRC-sponsored tests focused on a more detailed evaluation of the dissolution characteristics of specific insulation materials and concrete resulting form post-LOCA solutions. It also had the objective of attempting to reproduce the results of the Westinghouse tests. Original models used by Westinghouse assumed that dissolution rates for the same material classes (e.g., different types of fiberglass insulation) had similar dissolution characteristics. The CNWRA tests used different materials (than in the Westinghouse tests) from the five different insulation classes, recorded their dissolution rates, and then compared them to the assumptions made in the Westinghouse Report. A test was done for a concrete coupon in this test. This should be contrasted with a concrete 'powder' that was used in the WCAP testing regime. The concrete surface area used in the SwRI report is representative of the upper bound of uncoated concrete in U.S. PWRs.

Each of the materials was soaked in 4,400 ppm boric acid solutions at pH values of 4.1, 8 and 12 at both 265^0F and 190^0F for 90 minutes. The solutions at pH 8 and 12 were adjusted to their respective pH values using NaOH.
The test vessels were allowed to cool for approximately two hours prior to making chemical and scanning electron microscopy (SEM) measurements and visual observations on the solutions. Additional visual observations of the solutions were made after equilibration at room temperature continued for 1 day and 85 days.

There were no settled precipitates visually observed at the end of the cool down phase of test. However the CalSil solutions were cloudy. Only one chemical compound was positively identified. This was Na_2CO_3 on the surface of the Microtherm material. The exact chemical identity of the specie(s) creating the cloudy solutions could not be ascertained.

2. Summary of Important Results

2.1 Overview

The SwRI tests were a repeat of some of the WCAP methodology tests and also some new tests to complement the WCAP studies. Both groups performed tests at the same temperatures and at the same three pH values (4.1, 8.0 and 12.0). It is important to note and contrast the results of these tests.

2.2 Solution Chemistry

Solution Cooling

The first of these differences is the cooling rates afforded to the solutions in contact with the simulated containment materials. The WCAP methodology maintained the solutions in equilibrium with the separate test materials at the test temperature (either 190^0 or 265^0F) while performing *in situ* filtration through a 0.7 micron filter. The first sets of tests were to determine the concentration of various compounds leached from the test materials. Once these samples were taken at 0.5, 1.0 and 1.5 hours, another volume of liquid was transferred into settling cones at a temperature of 80^0F. This second test was to determine the precipitation rate of the cooling solutions. It is important to note that these solutions *did not have* the containment materials in contact with them either when sample aliquants were removed or when they were in the cooldown phase. The total contact time of the materials with the solutions was 90 minutes. [9] {Section 2, p. 2-1}

In the SwRI tests the materials were brought to test temperature (either 190^0 or 265^0F) for 90 minutes. The cooldown was achieved by equilibration of the sample containers with ambient laboratory temperature. These solutions remained in contact with the simulated containment materials during the cooldown process. The cooldown took approximately 2 hours, yielding a total contact time of the solution with the materials of ~3.5 hours. At the end of the cooldown period a one mL aliquant was withdrawn through a 0.45 micron filter. The remainder of the leachate solution was then decanted from the test vessel and put into separate vessels to observe settling rates at day 1 and day 85.

Physical Conditions
The WCAP used Teflon containers at 190^0F and stainless steel containers at 265^0F, as there were container integrity problems with Teflon at 265^0F.
The SwRI tests were performed in poly-tetrafluorethylene vessels at both temperatures; no container integrity problems were noted with this material.

The WCAP methodology attempted to provide mixing effects by having the reaction vessel placed on a shaker table during the 1.5 hour equilibration period. Additionally the WCAP tests fully submerged the materials in the solutions at the start of the tests. The SwRI tests allowed the samples to sink to the bottom of the test vessel based on material wetting and gravity. The SwRI tests also *did no*t include any device to enhance mixing or stirring. [8] {Section 2, p. 2-1}

The WCAP methodology employed ground, aged concrete for their tests. The SwRI methodology used solid blocks of concrete. There was no attempt in the SwRI studies to use materials identical to the ones in the WCAP studies. In fact different materials of the same insulation class were specifically chosen to see if the tests would bear out the hypothesis that all classes of materials in the same insulation type would react the same way. [3] {Section 2, p. 2-1}

2.3 Precipitates

2.3.1 No precipitates were observed in *any* of the test vessels after the two-hour cooling period. Plant specific materials were used in all of these solutions. However the solutions with CalSil in them were cloudy due to the presence of 'disaggregation' of the insulation, although there was no visual evidence of physical change to the solid material. [9], {Section 3.1, p. 3-1}

2.3.2 Following an equilibration period of 85 days, none of the solutions had precipitates in them. The CalSil solutions were still cloudy and the only 'solid' materials on the bottom were small pieces of the insulation. [9], {Section 3.1, p. 3-1}

2.3.3 For the amorphous silica class of insulation materials significant quantities of silica are released from the pH 8 and 12 solutions vs. the pH 4.1 solutions. [7, 8, 9], {Section 3.3.3, p. 3-4}

2.3.4 For the E-glass classes of insulation materials greater amounts of silica were dissolved at pH 12 than at pH 4.1.[7, 8, 9], {Section 3.2.1, p.3-3}

2.3.5 For aluminum silicate class of insulation materials, higher concentrations of silica were observed in the pH 12 than in the pH 4.1 solutions. [7, 8, 9], {Section 3.2.1, p. 3-3}

2.3.6 The two insulation materials from the aluminum silicate class, Kaowool and Durablanket, reacted to the chemical leaching tests the same way. [7, 8, 9], {Section 3.2.1, p. 3-3}

2.3.7 Na_2CO_3 is formed in high pH solutions of Microtherm insulation. It was only found in the pH 12 solution, but the time of formation is not known because the hydrated from of the solid is transparent. It was discovered during the Energy Dispersive X-ray Spectroscopy (EDS) analysis of the Microtherm surface due to very high sodium concentration. This was not identified in any of the other samples. [9], {Section 3.3, p.3-13}

2.4 Passivation

2.4.1 Calcium silicate materials demonstrated higher solubilization of calcium at pH 4.1 than pH 8 or 12, and higher concentrations of potassium and silica at pH 8 and 12 than at pH 4.1. [9], {Section 3.2.4, p. 3-8}

2.4.2 Concrete dissolution tests showed that calcium is significantly solubilized at pH 4.1, whereas at pH 12 the principal materials solubilized were silica and potassium. All three pH solutions had sulfur identified in the ppm range (chemical specie was not determined). [9],{Section 3.2.5, p. 3-8}

3 <u>Comments and Observations</u>

It is important to note the differences in the SwRI and WCAP test methodologies. Each of these methodologies provides information regarding the solution chemistry. The slower cooling in the SwRI tests better represents cooling of a post-LOCA containment pool while the more rapid cooling in the WCAP tests better represents cooling that may occur in a RHR heat exchanger. In the WCAP tests, the removal of the containment materials from the solution prior to cooldown is a non-conservatism as it does not represent what happens to the material on the sump screens where the debris will have cooled in the presence of the post-LOCA pool. Although materials of the same manufacturer were used for both tests, the materials were not of the same production batch. This is of some importance as the insulation is made from mined materials with very little chemical treatment to remove natural impurities. These impurities would not affect the insulating properties of the material but may make their chemical composition slightly different.

3.1 SEM measurements of the fibers from all the solutions (except Microtherm) after the test showed no difference with the images of the same materials taken before the test. Specifically no evidence of dissolution of the material or precipitation of other substances could be detected by SEM. [3], {Section 3.3, p. 3-13}

3.2 No information on how quickly the turbidity in the solutions from CalSil were formed is available in the report with the exception that the cloudy appearance of the CalSil solutions was present after the 2 hour cool down and remained even after 85 days. These materials were ‘disaggregation’ of the bulk insulation and not a precipitate. There were no tests performed on the filterability of these solutions. [9]

3.3 No measurements were made of pressure drop during the testing period of this report. [13]

3.4 The chemical tests of the Microtherm solution and the SEM of the material indicated that a significant amount of silica had dissolved and an apparent outer layer was formed on the surface of the fibers. Additionally at pH 12, the Microtherm had a deposit which was determined by x-ray diffraction (XRD) to be Na_2CO_3. However it is unclear if this material formed during the 'dry-out' of the insulation or if it was formed *in situ* from solution. [3, 7, 8, 9]

C. WCAP-16596-NP, "*Evaluation of Alternative Emergency Core Cooling System Buffering Agents*"

1. Description of Tests and Procedures

The two most common buffering agents in PWRs are sodium hydroxide (NaOH) and trisodium phosphate (TSP). Sodium tetraborate (STB) is mostly used in ice condenser plants although several plants with other designs have recently switched to STB due to calculated reductions in post-LOCA precipitates with this buffer. Both NaOH and TSP can be easily employed as pH control agents for the post-LOCA environment. Both form precipitation products in this environment that can lead to clogging of containment sump strainers. These tests examined the feasibility of using other buffering agents which would not have the deleterious effects of screen clogging.

The buffering agents that were compared during this testing regime were:

- Trisodium Phosphate (TSP)
- Sodium metaborate (SMB)
- Sodium tetraborate (STB)
- Sodium gluconate (SG)
- Sodium tripolyphosphate (STPP)

The stated objectives of the test program were:

- Quantity of material required to adjust pH to target value
- Dissolution rate of the material in water at post-LOCA sump temperatures
- Affordability and ready availability
- No demonstrated deleterious effects, e.g., corrosion to key containment structural materials
- Does not adversely affect the solubility of boric acid, or lead to an increase in boric acid precipitation on structures
- Resistant to degradation from radiation, elevated temperatures and humidity, i.e., long storage life in containment environment
- Non-hazardous material, i.e., does not create habitability concerns during storage or handling
- Will not cause significant release of metal oxide deposits from the fuel or primary coolant system surfaces

These objectives were tested using seven steps that attempt to ascertain the properties of the buffering agents under a variety of conditions in the post-LOCA environment.

The seven steps were (numbered as they are in the Westinghouse Report):

4.1 Dissolution of the buffering agent at 150°F in demineralized water.
4.2 Adjustment of the pH of boric acid solutions of several different concentrations using the buffering agent.
4.3Dissolution of the buffering agent at 100^{0}F in 2500 ppm boric acid solution.
4.4 Assessment of calcium and aluminum effects on a solution of 2500 ppm boron with enough of the buffering agents to bring pH to 8.5.

4.5 Corrosion test (2 week trial) of the effects of each of the candidate buffer solutions (2500 ppm boron adjusted to pH 8.0) on pure aluminum and A508 steel (carbon steel).
4.6 Long term (30 days) test at elevated (150^0F) temperature and 100% or 30% relative humidity of candidate buffer solid stability.
4.7 Boric acid solutions are tested for solubility stability at boiling by adding each of the candidate buffers.

The performance goal for Test 4.1 on these buffering agents was that the final simulated post-LOCA solution would have a pH above 8.0. Although the regulatory position on this issue is that the minimum acceptable pH is 7.0, Westinghouse decided to make the requirements for pH control more stringent to account for any acidic materials that may form from radiolysis of organics (such as cable wrap materials that may contain chlorides) in containment.

2 Summary of Important Results and Conclusions

2.1 Overview

Six different buffering agents were identified at the start of this project. The important characteristics were solution stability, pH buffering capacity, low probability of forming insoluble precipitates or gels, and cost.

The overall conclusion of this study is that sodium tetraborate is the best alternative to TSP for plants with appreciable calcium containing materials. TSP is recommended for plants with very little contribution from calcium containing materials. Sodium metaborate (SMB) was identified as a suitable replacement for NaOH, although the SMB would need to be in solution due to its solubility characteristics.

2.2 Solution Chemistry

2.2.1 Sodium Gluconate was eliminated as a possible buffering agent as it did not met the Test 4.1 requirements for final pH. {Section 5.1, p. 25}

2.2.2 All buffering agents dissolved between 2 hours and 21 minutes and 5 hours and 20 minutes. As a comparison, the TSP dissolution took place in 2 hours and 20 minutes. [3], {Section 5.1, p. 25}

2.2.3 TSP, SMB and STB all used similar mass quantities to achieve pH values > 8.0 in 2500 ppm boron solutions. NaOH took much less, and STPP could not achieve a pH of greater than ~7.5 regardless of mass added. [3, 10], {Section 5.2, p. 25-26}

2.2.4 STB, TSP, SMB and STPP all achieved solubility in 2500 ppm boric acid solution at temperatures of 100^0 F, 150^0 F and 200^0F, without any precipitation of boric acid. [3], {Section 5.3, p. 27}

2.2.5 The results of the environmental testing on the solid materials can be seen in the summary table below. This was done to determine the effect of long term storage at high temperature and humidity on the dissolution or pH control of these compounds. [3, 9], {Section 5.6, p. 34}:

Buffering Agent	Condition of Solid at 150^0F + 30% RH[1]	Condition of Solid at 150^0F + 100% RH[2]	Dissolved In water after 30% RH test
STB	Solid clump- Removable from beaker	Solid clump	Y
SMB	Crystalline appearance, not easily removed from beaker, volume reduced	Dissolved into a clear solution	Y
STPP	Solid clump- Removable from beaker	No Data	Y
TSP	Clumped but Granular	Dissolved into a clear solution	Y

[1]30-day test
[2]14 day test

2.2.6 All recommended buffers increased the solubility of boric acid. [9], {Section 7, p. 44; Section 5.7, p. 36}

2.2.7 A formal calculation is provided to allow plants to accurately estimate the SMB or STB concentration required in the final volume of post-LOCA liquid to achieve an acceptable pH. [17], {Section 8.2.2, p. 47}

2.2.8 The buffering agents tested are rated as excellent, good or poor for each of the testing areas (sections 4.1 to 4.7) and dependant upon the environmental conditions within the containment building. [8], {Section 6.0, p. 37-38}. The table shown here summarizes this result:

2.3 Precipitates

2.3.1 For all the buffering agents tested, TSP caused the least amount of combined corrosion with A508 carbon steel and aluminum coupons. [9], {Section 5.5, p. 33-34}

2.3.2 Calcium addition to all solutions containing the individual buffer in 2500 ppm boron yielded a precipitate or suspended floc (except NaOH).[9],{Section 5.4.1-3, p. 27-30}

2.3.3 Aluminum addition to all solutions containing the individual buffer in 2500 ppm boron yielded a precipitate or suspended floc (except for STPP). [9],{Section 5.4.1-3, p. 27-30}

2.3.4 Testing at elevated pH (initial value of 8.5) and lower concentrations of calcium and aluminum showed that precipitation did not occur before threshold values of >177 ppm (STB) or 75 ppm (SMB) for aluminum, and >254 ppm for calcium (in both STB and SMB).[9], {Section 5.4.3, p. 30-31}

2.3.5 Values of pH less than 8.0 for SMB and STB showed no evidence of precipitation with calcium (of up to 700 ppm Ca).[9],{Section 5.4.2, p. 30}

Table 6.1 Summary of Characteristics of Candidate ECCS Buffering Agents

Criterion	Buffering Agent					
	NaOH	TSP	STB	SMB	STPP	SG
Precipitate Formation	P(1)	G(2)	E	G	E	No Data
Quantity required to adjust pH>8.0	E	G	G	E	P	P
Dissolution Rate	N/A(3)	G	G	G	G	G
Affordability/Availability	E	E	E	G	G	G
Corrosiveness	G	E	G	G	P	No Data
Effect on Boric Acid Solubility	G	G	G	G	G	No Data
Environmental Stability	G	G	G	G	G	No Data
Habitability Concern	G	E	G	G	E	E
Oxide/CRUD Release	G	G	G	G	P	P

(1) NaOH rated P due to elevated Al production
(2) TSP rated P under elevated calcium conditions
(3) NaOH provided as a 50% solution
(4) SMB rated P based on behavior
(5) E =excellent, G = good, P = poor

2.3.6 STB is recommended for use at plants that will have high calcium concentrations in the post-LOCA environment. TSP is recommended for plants that will have low calcium concentrations in the low post –LOCA environment. SMB solution could replace sodium hydroxide in any plant that currently uses sodium hydroxide. [17], {Section 7, p. 44}

2.3.7 Calculation of the filter cake coefficients is presented as a means of assessing pressure drop across a filter from these materials. [15, 17], {Section 5.4.3, p. 31-2}

2.4 Passivation

2.4.1 The corrosion rates for both aluminum and carbon steel in STPP solution (at pH 7.5) were very high relative to other buffering agents. The solution from the carbon steel test was yellow from the high level of dissolved Fe^{+3}. [9, 10], {Section 5.5, p. 33}

3 Comments and Observations

3.1. Threshold values for precipitate formation from dissolved aluminum in STB (177 ppm) are significantly higher than those observed during longer term bench testing and head loss testing at Argonne National Laboratory and ICET Test 5 (about 50 ppm).

3.2. Testing of the radiolytic stability of the compounds and their solutions was not performed. This was an objective of the program. The two recommended buffers, SMB and STB, were not tested under conditions of a radiolytic field. It is likely that in the presence of gamma radiation sodium metaborate would become sodium tetraborate or mono-borate anion although, this needs to be tested.
[3], {Section 2.3 p.16}

3.3. For Test 4.1 it is not clear if the dissolution testing was performed under static conditions (i.e., no mixing) which would best simulate the effect in containment. Most likely the solution was heated using a hot plate which would have caused convection currents. In the post-LOCA environment the opposite effect would be occurring because sump water would be cooling down (from contact with concrete below the material) and no upward convection would occur. Actual simulation of the dissolution based on plant design should be a *major* consideration in the actual testing of any material. If the water is to flow over the solid buffer material any test should also simulate this effect. [8, 9, 10], {Section 4.1, p.19 and Section 5.1, p.26}

3.4. Sodium gluconate is the product of a strong base (sodium hydroxide) and a weak acid (gluconic acid). The measured pH of 10 g SG in 1 Liter of demineralized water was 6.93. The K_b for gluconate anion is $4x10^{-9}$ which should have yielded a pH of about 9.1 in demineralized water. This result indicates that another factor was present in this test that was not considered. [3, 4], {Section 5.1, p.25}.

3.5. Test 4.4 did not add calcium and aluminum together, but separately. Thus no potential synergic effect of the mixture can be assessed from this data. [3], {Section 5.4, p. 27-31}

3.6. Silica was not used in any of these tests. The positive or negative effect of silica or silicates on these test results is unknown. [3]

3.7. The results of the precipitation settling tests and coefficients of filter cake formation tests are reported as: “These results do not provide an accurate measure of the precipitate contribution to sump screen head loss”. Thus there is no quantitative fashion in which these results can be used. {Section 5.4.3, p. 30-31}

3.8. The test performed in 2.3.4 is contradicted by ANL work that found that concentrations of aluminum at 60-70 ppm yielded precipitate and at 80-100 ppm plugged filters.

3.9. While investigating the effects of aluminum concentration on precipitate formation in STB, WCAP tests showed that the formation of precipitates is dependent on the temperature of the solution at the time of the addition of the metal solution. Less precipitate was formed when the same amount of dissolved aluminum was added at room temperature compared to addition at 60 ^{0}C. This effect was not studied so it is not known if this is related to precipitation kinetics.

D. WCAP-16785-NP, "*Evaluation of Additional Inputs to the WCAP-16530-NP Chemical Model*"

1. Description of Tests and Procedures

The chemical dissolution model developed in WCAP-16530-NP was intended to be generic for all PWRS. In this follow-on report, Westinghouse describes the results of tests which further evaluate the inhibition of aluminum and aluminum alloys corrosion in the presence of silicates and phosphates at temperatures of 100 and 200 ^{0}F. The specific areas chosen for testing were: silicate and phosphate inhibition of aluminum corrosion, the variability in corrosion rates between aluminum alloys, and the solubility of key precipitates containing aluminum, silica and phosphate.

This study first uses the generic Westinghouse chemical model and applies to it the ICET program parameters to predict the amount of chemical precipitates that will form. This computed result is then compared to the results of the ICET tests.

Task 1 tested the passivation of aluminum corrosion by silica (at concentrations of 0, 50, 75, 100 and 125 ppm) at a pH of 8.0 and 200 ^{0}F. The passivation concentration minimum is then tested at various pH values (6.0, 8.0, and 11.0) and temperatures (150 and 200 ^{0}F). This task also tested the effect that silica had on the passivation of aluminum in the presence of phosphate.

Task 2 tested the corrosion rates of various aluminum alloys at pH 8.0.

Task 3 measured the passivation of aluminum and its alloys by phosphate at pH 8.0 and 200^{0}F.

Task 4 measured the solubility of calcium and aluminum precipitates at various pH values and temperatures and in the presence of silica.

2 Summary of Important Results and Conclusions

2.1 Overview

The WCAP investigated the solubility of aluminum silicate, aluminum oxyhydroxide and calcium phosphate precipitates over the range of temperature and solution chemistry anticipated in the post-LOCA environment. It also investigated the inhibition of corrosion (i.e., passivation) of aluminum metal in environments containing TSP and silica.

The investigation was very focused on aluminum as the major contributor to ionic component of the post-LOCA environment as a result of aluminum corrosion. Aluminum as the major contributor to dissolved ionic species following a LOCA is supported by WCAP-16530-NP as well as the ICET work documented in NUREG/CR-6914.

2.2 Solution Chemistry

All tests were conducted in solutions of 2500 ppm boron. This was used as the primary 'test solution:'

> "The range of temperatures and pH conditions tested were selected to bound the long-term equilibrium conditions under which the bulk of the material release and subsequent precipitate formation occurs."

With this as the test objective, the pH of test solutions was adjusted to the following values: 4.5, 6.55, 8.0 or 11.0 at the onset of the measurement process.

The lowest pH value (pH 4.5) occurs in the test solution when a small amount of TSP is added (Task 3). The pH value of 6.5 is realized when sodium silicate is added such that the silicon concentration is 75 ppm (Task 1). The pH of ~8.0 is realized when TSP is added to the solution of boric acid (Task 3). The solutions for this test only used TSP for pH adjustment (i.e., no NaOH was added to these solutions).

For tests of passivation a separate test solution was adjusted to each of the test pH values (using NaOH or TSP) and the temperature was adjusted to either 150^0F or 200^0 F prior to inserting test coupons. These were used in Tasks 1, 3 and 4.

2.3 Precipitates

2.3.1 Task 4 measured the solubility of sodium aluminum silicate, aluminum oxyhydroxide and calcium phosphate

2.3.1.1 Sodium Aluminum Silicate. In the absence of TSP, and a concentration of 60 ppm aluminum and 178 ppm silica, a precipitate formed at both 80^0 and 140^0F at pH 8.0. Solutions containing 99 ppm aluminum and 294 ppm silica, with TSP used as a buffer, formed precipitates at pH 8.0 and 200^0F.

2.3.1.2 Aluminum and silica were added to solution of 2500 ppm B (pH 8.0 using NaOH) at a temperature of 200 ^{0}F. The precipitate solubility was calculated by incremental additions of the aluminum and silica solutions until precipitation occurred. The limit of solubility for $NaAlSi_3O_8$ at 80 ^{0}F is between 40 and 60 ppm aluminum with 119-178 ppm silica. [11], {Section 3.4.1 to 3.4.3, p. 21-22, Section 5.4.1, p. 33}

2.3.1.3 Aluminum oxyhydroxide. At a solution temperature of 200 ^{0}F and a maximum aluminum concentration of 98 ppm, no precipitates were observed for 30 days at any pH value. No precipitate was observed in the 140 ^{0}F test solution at 40 ppm aluminum for up to 30 days at pH 8.0 [10], {Section 3.4.4 to 3.4.6, p. 21-23 ; Section 5.4.2, p. 34-35}

2.3.1.4 Solutions of AlOOH just below the solubility limit were cycled between 200 and 80 ^{0}F over a four day period. No details were provided concerning the rate of temperature change during cycling. No precipitation occurred. Additionally the pH was varied from 8.0 to 7.0 and from 8.0 to 9.0 at constant temperature (200 ^{0}F) and no precipitate formation occurred. [9], {Section 5.4.2, p. 34}

2.3.1.5 Calcium Phosphate. Calcium phosphate was found to be insoluble at all pH, concentrations and temperatures tested. [10], {Section 3.4.7 to 3.4.9, p.23-25; Section 5.4.3, p. 34}

2.4 Passivation [The corrosion coupons were immersed for a total of either 12 or 24-hours].

2.4.1 Task 1 in this study showed the 24-hour corrosion rate of aluminum was lower than the 12-hour corrosion rate of aluminum (this is a usual circumstance in corrosion rate measurements) in both solutions adjusted with the different buffers. The aluminum corrosion rate *decreased* over the concentration range of 0 to 75 ppm silica from 9.5 $mg/m^2/min$ where it leveled off at <2.0 $mg/m^2/min$ after a 24-hour period. [9], {Sections 3.1.1 and 3.1.3, p. 17-18; Sections 5.1.1 and 5.1.2, p.25-27}

2.4.2 Similar passivation of aluminum by silica is observed using the same test conditions as above with TSP added as the buffer (bringing the solution to pH 8.0). This task also demonstrated that the corrosion rate of aluminum in silica solution *increased* greatly with increasing pH for both 150^0 and 200^0F tests. [9], {Sections 3.1.4, 3.2.3 and 3.3, p. 19-21; Section 5.1.3, p.27-29}

2.4.3 Task 3 tested the ability of only phosphate to passivate aluminum alloy 1100. At pH 8.0 and at 200 ^{0}F, the amount of aluminum dissolved decreased by a factor of 3.6 using TSP. Reductions in corrosion were realized at a pH 9.0 as well as at higher temperatures when compared to solutions with no phosphates. [9], {Section 5.3, p. 30-31}

2.4.4 Based on the results, for 2.4.1 and 2.4.2 above, Westinghouse developed a multi-variate aluminum release rate equation for inhibition by silicate and one for phosphate which they claim to be valid in the pH range of 4.5 to 9.0 and below 200^0F. Above pH 9.0, the original aluminum release rate equation should be used. [17], {Section 5.3, p. 31}

2.4.5 Additional tests in Task 1 identified that the Westinghouse model for aluminum corrosion in WCAP-16530 was more conservative than the actual measured corrosion rate at both temperatures evaluated. [7], {section 5.3.1, p31-32}

2.4.6 Task 2 measured the corrosion rates of three aluminum alloys: 3003, 5005 and 6061. The corrosion tests were performed for 12 hours and 24 hours at a temperature of 200 ^{0}F in 2500 ppm boron solution adjusted to pH 8.0 using NaOH. The corrosion rates were compared to the rate of aluminum alloy 1100 corrosion. The table below from the report compares the relative corrosion rates of the aluminum alloys tested.

Table 5-3: Summary of Corrosion Results for Aluminum Alloy Corrosion Scoping Test

Coupon	Exposure Time (hours)	Corrosion (μm)		Dissolved Aluminum (ppm)	Percentage of Alloy 1100 Corrosion	Percentage of Alloy 1100 dissolved Aluminum
		Scaled	De-scaled			
1100-1	12	4.47	5.92	202	NA	NA
1100-2	24	4.09	7.57		NA	
3003-1	12	3.02	5.33	160	67.6	79.2
3003-2	24	3.09	5.55		75.6	
5005-1	12	3.68	6.05	186	82.3	92.1
5005-2	24	4.43	7.03		108	
6061-1	12	3.45	5.50	182	77.2	90.1
6061-2	24	3.80	6.05		92.9	

The conclusion presented in the report is that the *difference* in corrosion rate of aluminum *alloys* (as compared to aluminum metal) under identical conditions as in Task 1 was negligible. Additionally, due to the variety of aluminum alloys used in

plant applications, it was concluded that the net reduction in aluminum generated precipitates would be low. [7], {Section 3.2, p. 19-20; Section 5.2, p.29-30}

2.4.7 Task 3 tested the passivation of aluminum in TSP-buffered boric acid solution without added silica. The aluminum corrosion with silica was 1/54th of thatwithout silica. The tests also showed that there is a significant decrease in passivation when the TSP solution is brought to pH 9.0. Westinghouse again developed a multi-variate equation to model the corrosion as a function of pH and temperature. This model, as before, showed that there is significantly less passivation from the model than from actual testing. [9, 17], {Section 5.1, p.25-28 ; Section 5.3, p. 30-32}

3 Comments and Observations

3.1 Additional testing has been performed to study TSP and silica inhibition of aluminum corrosion. Based on the overall application of inhibition and alloy specific corrosion rates it may be possible for an individual plant to use these results to demonstrate a lower aluminum release rate compared to the WCAP-16530-NP base model.

3.2 During corrosion testing, the aluminum coupons were placed on the bottom of the Erlenmeyer flask. This affects the surface area of the coupon exposed to the bulk solution and could introduce variability in results.

3.3 The temperatures and pH values at which measurements were made were not exactly the same as those of other studies and within this study itself. It was very difficult to make direct comparisons of different corrosion rates for aluminum for this reason. As an example the silicate inhibition tests were run at 150 and 200 ^{0}F and at pH values of 6.55, 8.0 and 11.0. The pH of 6.55 resulted from the addition of basic sodium silicate. Other passivation tests were performed at pH 4.5. The pH of all the solutions was measured after precipitation and was at the target pH (with the exception of the 6.55 value). This indicates that TSP was not the limiting reagent in the precipitation reactions.

3.4 No confirmatory analyses (e.g., XRD) were performed on the precipitates. It was assumed that sodium aluminum silicate, aluminum oxyhydroxide and calcium phosphate were the precipitates that formed in those tests, and no others.

3.5 As a preliminary affects study, this is a good basis. However, there is a tacit assumption that the effects of *other* materials that will be present will have no effect on the results of these measurements. Based on the experimental evidence here identifying that the theoretical model originally used overestimates the mass of precipitates formed, the assumption of no synergic effects is *not* justified.

Part B
National Laboratory Test Report Reviews

E. *"Technical Letter Report on WCAP-16530-NP, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191,"* Preparation of Surrogate Precipitates Evaluation by W. J. Shack, Argonne National Laboratories

1. Background and Report Description

This report[1] is a review of WCAP-16530-NP, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191[2] by staff at the Argonne National Laboratory. It includes some criticisms of the release equations for Al developed in the WCAP and some comments and observations on the surrogates for $Al(OH)_3$ produced by the procedures described in WCAP-16530-NP. It also summarizes literature results on the solubility of $Al(OH)_3$ in various crystalline and amorphous forms.

2. Summary of Important Results

2.1 Overview

For the most part the calculations of releases proposed in WCAP-16530-NP seem appropriate. The model for calcium release includes a saturation term that is not relevant if phosphate is present, but this has little practical impact for the levels of calcium that would be experienced in the post-LOCA environment.

2.2 Solution Chemistry

The release rate models in WCAP-16530-NP are based on "one–material–at–a–time" dissolution tests and thus may miss important interactions that can occur in more complex environments. For example, straightforward application of the silica release equation in WCAP-16530-NP would greatly overestimate the release of silica in ICET–1.

There is excellent agreement between the results of the WCAP-16530-NP aluminum dissolution tests and the observed dissolution rate in ICET–1 for days 1–15. However, when comparing predictions of the release rate models with data from ICET–1, the average value of dissolution rate over the whole 30 days of the test is used[2]. The recommended Al release model in WCAP-16530-NP (Equation 6-2) significantly underestimates releases in ICET–1 over the first 15 days of operation (predicted 11.5 mg/L/day and observed 20.8 mg/L/day) and underestimates the dissolution data in the tests reported in WCAP-16530-NP. It also underestimates somewhat the release rates in ICET–5 (predicted 2.4 mg/L/day and observed 4.1 mg/L/day).

2.3 and 2.5 Precipitation and Chemical Model

An alternate release model is given in WCAP-16530-NP (Equation 6-1) that seems to better reflect the available data. It should be noted that the coefficients for this equation in Rev. 0 of the report are incorrect. Corrected coefficients are given in the Technical Letter Report that give excellent agreement with the WCAP-16530-NP dissolution data and ICET–1 day 1–15 data. This release model seems to over-predict releases in sodium tetraborate environments (predicted 9.4 mg/L/day and observed 4.1 mg/L/day).

The assumption in WCAP-16530-NP that all dissolved calcium in TSP environments form precipitates is reasonable. The assumption that all dissolved aluminum forms precipitates is quite conservative in Al/NaOH and Al/STB environments (ICET-1 and 5 respectively). Some crystalline forms of $Al(OH)_3$, such as gibbsite, have very low solubilities, but the solubility of amorphous forms in the pH range of interest for sumps is significant. However, accurate prediction of solubility limits is difficult since they are sensitive to the choice of the solubility constant and pH. For amorphous materials, literature citations on Al/NaOH solubility have values ranging from 14–54 ppm at 25°C and pH 9.5.

Confirmatory tests at ANL show that the surrogate $Al(OH)_3$ produced by the procedures described in WCAP-16530-NP produces very fine precipitates that produce high head loss in loop tests. The ANL report notes that WCAP-16530-NP does not provide other information such as solubility under changing pH or temperature conditions that might provide information on whether the products are crystalline or amorphous.

3. Comments and Observations

   a. WCAP-16530-NP provides useful data/information especially on a wide range of insulation materials not included in ICET. However, care must be taken in interpreting the results as they are single component effects. [7]

   b. The study only tests single effect dissolution; in most cases only one material in the alkaline NaOH/boric acid solution. [7]

   c. The Equation 6-1 release rate in WCAP-16530-NP (with corrected coefficients) gives conservative rates for Al release in all stages of ICET-1 and ICET-5. [7]

   d. The Equation 6-2 release rate in WCAP-16530-NP (with corrected coefficients) gives non-conservative rates for Al release in ICET-1 and ICET-5 prior to passivation of the aluminum. [7]

   e. The assumption in WCAP-16530-NP that all dissolved calcium in TSP environments form precipitates is reasonable. [7, 8, 9]

   f. The assumption that all dissolved aluminum forms precipitates is quite conservative in Al/NaOH and Al/STB environments. [7, 8, 9]

References

1. W. J. Shack, Technical Letter Report on WCAP-16530-NP, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191, 2007.

2. A. E. Lane, T. S. Andreychek, W. A. Byers, R. J. Jacko, Edward J. Lahoda, and Richard D. Reid, Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191, WCAP-16530-NP, Westinghouse Electric Company LLC, 2006.

3. J. Dallman, B. Letellier, J. Garcia, J. Madrid, W. Roesch, D. Chen, K. Howe, L. Archuleta, and F. Sciacca, F. Integrated Chemical Effects Test Project: Consolidated Data Report, NUREG/CR-6914, Volume 1, U.S. Nuclear Regulatory Commission, Washington, D.C., 2006.

1. Background and Test Description

The U.S. Nuclear Regulatory Commission (NRC) and the nuclear utility industry undertook a joint series of tests, the Integrated Chemical Effects Test (ICET) project, to simulate the chemical environment present inside the sump after a LOCA. Five different insulation materials/environment combinations were studied in the tests.[4] Large amounts of chemical products were observed to form in the ICET–1 and ICET-3 tests. In ICET–1 with NaOH for pH control and NUKON fiberglass insulation, the product was due to dissolution of aluminum metal and subsequent formation of aluminum hydroxides. In ICET–3 with a trisodium phosphate (TSP) buffer and NUKON fiberglass and CalSil insulation, the product was due to the formation of calcium phosphates due to the reaction of Ca leached from the CalSil insulation with the TSP. The ICET–3 environment appeared to have the most potential for significant head loss, because the product formed very early in the test, corresponding to a time when the need for cooling would be greatest in an accident situation.

2. Summary of Important Results

2.1 Overview

A test loop was constructed at Argonne National Laboratory to study the effects of the chemical products observed in the ICET tests on head loss.[5] In addition to considering a CalSil loading of 19 g/L (ICET-3), consideration was given to the effect on head loss of much lower CalSil loadings (0.5 g/L and less), which would be more representative of most plant situations.

Most of the tests in the ICET-3 environments were integrated tests in which the chemical products were formed by the dissolution and reaction of actual containment materials. In the ICET-1 and ICET-5 environments, the tests used surrogate chemical products. Use of the surrogate forms was justified by comparisons with the chemistry and other physical characteristics such as the amorphous structure of the products formed in the integral ICET tests.

A schematic of the ANL test loop is shown in Figure 1. The piping in most of the loop is chlorinated polyvinyl chloride (CPVC); the clear test section containing the test screen was either LEXAN or clear PVC. LEXAN has better high temperature strength; polyvinyl chloride (PVC) is more resistant to NaOH solutions. The heater and cooler sections are stainless steel. During operation temperatures around the loop are typically ±0.6°C (1°F). Loop velocities can be controlled over the range from 0.02 to 2 ft/s. The inner diameter of the LEXAN section is 6.5 in.; the inner diameter of the PVC section is 5.625 inches. The fluid volume in the loop is 119 liters (4.2 ft^3). At 0.1 ft/s, the transit time around the loop is about 4 minutes. The sump screen in these tests is a flat perforated plate. Two different perforated plates have been used. Differential pressure transducers measure the differential pressures across the screen and bed.

In scaling results from the ANL test facility, the mass of chemical product and physical debris per unit area of screen must be considered. The mass of chemical product produced scales with fluid volume while the potential for head loss is characterized by the product mass per unit screen area. A 15 g loading of debris in the LEXAN section corresponds to a loading of

0.7 kg/m^2. To maintain the same loading per unit area in the PVC section requires 11.5 g of debris.

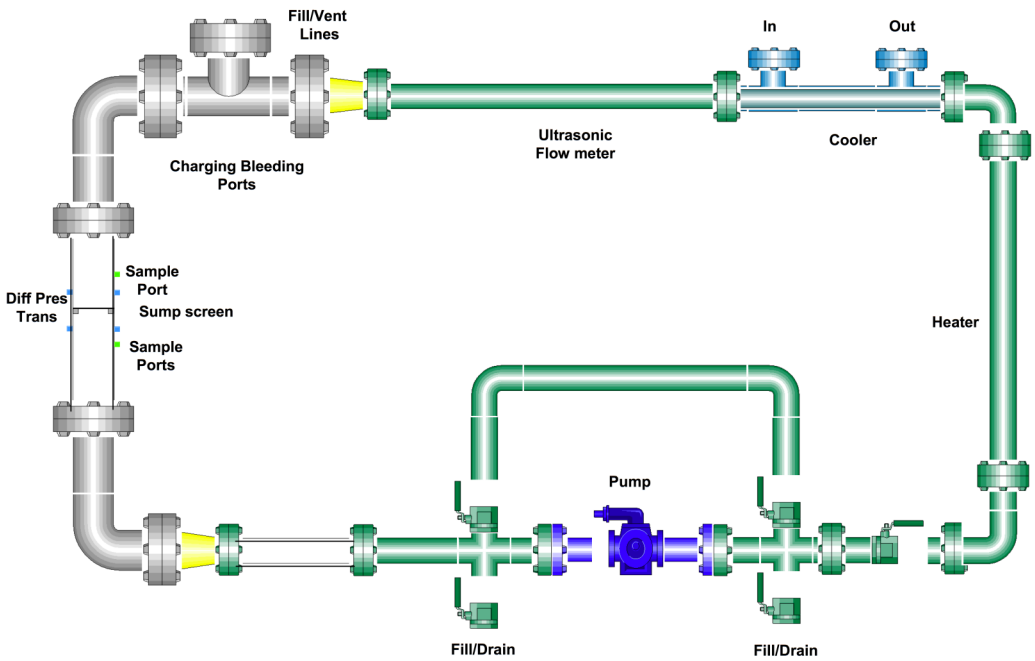


Figure 1. Schematic of the test loop

Physical debris and chemicals are introduced to the loop through a charging port at the top of the loop. The horizontal configuration of the screen is not intended to reflect a realistic screen configuration, but rather to permit the development of uniform beds with well–defined characteristics. The head loss behavior for such beds would characterize the local head loss behavior of more complex, non-uniform beds that might form on realistic screen geometries.

In the basic test procedure, test the loop was filled with deionized water and heated to 130°F. Boric acid, LiOH, and a pH control chemical (NaOH, TSP, or STB) were added to reach desired concentrations and pH. The loop was held at temperature overnight to deaerate the liquid. NUKON and CalSil were used to create the physical debris bed. The insulation materials were added as slurries. The NUKON was shredded and processed in a blender; the CalSil was ground with a mortar and pestle. Liquid was added to form a slurry. In some cases, the slurry was held at temperature for some time before being added to the loop. Pressure drop across the bed, flow velocity, and temperature were monitored continuously. In ICET-1 type tests, aluminum nitrate solutions were added to the loop after the physical debris was formed. The pressure drop across the bed prior to addition of the aluminum nitrate solution provided a baseline value for pressure drop without chemical effects. In the ICET-3 environments, tests were run without TSP additions to get baseline values for the pressure drop due to the physical debris alone.

2.2 Solution Chemistry

ICET-3 Tests

A series of tests (ICET-3-1 to ICET-3-11) were performed to evaluate the potential for head loss due to chemical effects in a TSP-buffered environment. The conditions in the tests are

summarized in Table1. The tests were designed to explore conditions corresponding to a range of debris amounts, containment sump residence times, and TSP dissolution times. The two basic physical parameters that are affected by these variables are the degree of CalSil dissolution that will occur prior to the formation of the debris bed and the interaction between the chemical products and the physical debris during bed formation. Unlike the ICET-3 integrated test, these tests have excess phosphate available, i.e., the amount of calcium phosphate that can form is limited by the amount of calcium available from dissolution of the CalSil.

Bench Top CalSil dissolution tests

Bench top, small–scale dissolution test of CalSil were performed to identify the potential effects of the TSP dissolution rate on the dissolution of CalSil and the subsequent formation of calcium phosphate precipitates. Three different histories of TSP addition were studied, which were intended to encompass the range of histories of TSP dissolution expected within an actual containment sump:

1. Add TSP before CalSil addition (instantaneous dissolution of TSP).
2. Titrate TSP over 1 hr period into solution after CalSil addition (nominal case).
3. Titrate TSP over 4 hr period into solution after CalSil addition (very slow addition of TSP).

ICET-1 and ICET-5

Surrogate solutions for ICET–1 environments were developed using aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$. Since in ICET–1 the solutions arise from the dissolution of aluminum in a basic solution containing boric acid, the surrogate solutions were prepared by dissolving commercial aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ powder in a base solution containing 2800 ppm B added as boric acid, 0.7 ppm Li as LiOH, and NaOH sufficient to get a pH of 9.6.

Aluminum hydroxides, nominally $Al(OH)_3$, are the principal chemical product with potential to cause head loss observed in ICET–1 and 5 environments. The most stable form of $Al(OH)_3$ is the crystalline form gibbsite, although other crystalline and amorphous forms can also form. However, detailed characterization of the products formed in ICET-1 showed that the products are amorphous.[6] The solubilities of the crystalline forms are smaller by a factor of ≈100–500 than that of the amorphous form.[7,8]

Table 1. ICET-3 Environment head loss tests

Test No.	NUKON (g)[a]	CalSil (g)	30 min Presoak	TSP[b]	Additional dissolved Ca (ppm)	Comment
ICET-3-1	15	15	No	Initially in loop	200	Simulates initial conditions in ICET-3; precipitates arrive after bed forms
ICET-3-2	15	15	No	Initially in loop	10, 25, 50 ppm Ca[d]	Parametric test starting with 1/20th dissolved Ca of ICET-3: precipitates arrive after bed forms
ICET-3-4	7	25	Yes	1/8th initially in loop; 7/8th metered in	None	Minimal CalSil dissolution prior to initial bed formation; continued dissolution as test continues
ICET-3-5	7	25	Yes	None	None	Baseline physical debris only
ICET-3-6	15	15	Yes	1/8th initially in loop; 7/8th metered in	None	Minimal CalSil dissolution prior to initial bed formation
ICET-3-7	15	15	Yes	None	None	Baseline physical debris only
ICET-3-8	15	0	No	Initially in loop	43.5[c]	$CaCl_2$ & NUKON added simultaneously; Maximum CalSil dissolution prior to bed formation
ICET-3-9	15	0	No	Initially in loop	9, 18, 27 ppm Ca[d]	$CaCl_2$ added after NUKON bed stabilizes maximizes arrival time of precipitates to bed; Maximum CalSil dissolution prior to arrival at the bed
ICET-3-10	15	15	Yes	1/2 metered presoak; 1/2 metered	None	Intended to represent a "typical" degree of CalSil dissolution prior to bed formation
ICET-3-11	Replicates ICET-3-7					
ICET-3-12	15	5		1/2 metered presoak; 1/2 metered	None	Lower CalSil loading
ICET-3-13	15	5	Yes	None	None	Baseline for ICET-3-12
ICET-3-14	Replicates ICET-3-7 & 11					
ICET-3-15	15	10	Yes	None	None	Baseline physical debris only
ICET-3-16-A1	15	10	Yes	1/2 metered presoak; 1/2 metered	None	Lower CalSil loading
ICET-3-17-A1	Replicates ICET-3-10					
ICET-3-18-A1	5	10	Yes	1/2 metered presoak; 1/2 metered	None	Thinner NUKON bed
ICET-3-19-A2	–	25	Yes	1/2 metered presoak; 1/2 metered	None	CalSil/calcium phosphate precipitate only debris

[a] 1 g of debris corresponds to a screen loading of 47.6 g/m^2

[b] The total amount of TSP in each test where TSP was added was always 3.4 g/l. Some fraction was either dissolved initially in the test loop or metered in during the presoak period. The remaining fraction was metered in during a 30-60 minute period after the debris was added to the loop.

[c] Calcium equivalent to full dissolution of 15 g CalSil.

[d] Calcium additions added incrementally to sequentially reach values of dissolved Ca listed.

Samples of surrogate solutions containing 100, 200, and 375 ppm Al are shown in Fig. 2. In all the samples, precipitates form at room temperature. For simple aluminum nitrate/NaOH solutions, the equilibrium solubility of amorphous $Al(OH)_3$ at pH 9.6 and 20°C is ≈ 60 ppm.[7] The precipitates are too fine and too dilute for direct measurement of structure. However, when samples were taken through heating and cooling cycles, the sediments would re-dissolve at high temperatures. This together with measurements of the Al level in the supernate suggests that solubility behavior is similar to that expected for amorphous $Al(OH)_3$, which suggests that the sediments are amorphous or at least act like amorphous $Al(OH)_3$.

The tests performed in ICET-1 and ICET-5 like environments are summarized in Table 2. For the ICET-1 environments the dissolved Al levels ranged from 100 to 375 ppm. For the ICET-5 environment where the pH is lower a dissolved Al level of 50 ppm was used (for the final portion of this test, this value was raised to 100 ppm).

Figure 2 shows solutions formed from $Al(NO_3)_3$ of 100, 200, and 375 ppm as surrogates. The photo on left was taken without flash to heighten the contrast between sediment and supernate. The photo on the right characterizes better the semi–translucent nature of the sediment. The bottles on the far left in each photo have no aluminum added to them.

Figure 2. $Al(NO_3)_3$ Solutions Containing Concentrations of Al^{+3}.

Table 2. Summary of the Head Loss Tests: NaOH and STB

Test	Description	Test section	Screen
ICET-1-3	NUKON 15.0 g; NaOH; 375 ppm Al	A	1
ICET-1-1-B2_100ppm	NUKON 15.0 g; NaOH; 100 ppm Al	B	2
ICET-1-2-B2_200ppm	NUKON 11.6 g; NaOH; 200 ppm Al	B	2
ICET-1-3-B2_375ppm	NUKON 11.6 g; NaOH; 375 ppm Al	B	2
ICET-1-1-B2_100ppm repeat	NUKON 11.5 g; NaOH; 100 ppm Al	B	2
ICET-1-1-B2_100ppm repeat2	NUKON 11.5 g; NaOH; 100 ppm Al	B	2
ICET-5-1-B2_042606	NUKON 11.5 g; STB 1248g; 50 ppm Al	B	2
ICET-3-STB1-A2	NUKON 15.0 g; CalSil 15.0 g; STB 1248g; 50 ppm Al	A	2

A LEXAN test section.
B PVC test section.
1 Perforated plate with 51% flow area and 3/16 in. holes with 1/4 in. staggered centers.
2 Perforated plate with 40% flow area and 1/8 in. holes with 3/16 in. staggered centers.

2.3 Precipitation

Significant effects on head loss due to chemical products were observed in environments with CalSil and TSP buffer (ICET-3) and in environments with significant dissolved aluminum and NaOH for pH control (ICET-1).

In ICET–3 environments, the head losses associated with purely physical debris beds of NUKON and CalSil are generally much smaller than those that occur across debris beds in which some of the CalSil has been replaced with a corresponding amount of calcium phosphate precipitate. For a thin NUKON bed (≈ 3 mm), very large pressure drops were observed for the lowest tested CalSil loading, 0.47 kg/m^2. However, with thicker NUKON beds (≈ 12 mm), little chemical effect could be observed for CalSil loadings ≤ 0.47 kg/m^2. These results show that the relation between head loss and fiber loading for a given particulate loading is highly nonlinear and not monotonic. Beds in which no NUKON was present were also examined. In this case, a significant portion of the screen remains open for the highest screen loading of CalSil tested, 1.2 kg/m^2. The pressure drops are very low with this open area.

The dissolution of CalSil and hence formation of calcium phosphate would be retarded if all TSP could be dissolved prior to the CalSil addition (i.e., simulating instantaneous TSP dissolution). However, even with instantaneous TSP dissolution, the equivalent dissolved Ca will exceed 75 mg/l after a few hours for CalSil concentrations as low as 0.5 g/l. Such an equivalent dissolved Ca concentration was shown to produce pressure drops on the order of 5 psi at an approach velocity of 0.1 ft/s across a 0.71 kg/m^2 NUKON debris bed.

The chemical products in the ICET–1 environment that can have significant effects on pressure drop are amorphous aluminum hydroxides. Pressure drops much larger than what would be expected from corresponding debris beds in an inert environment have been observed in

environments with NaOH buffer for dissolved Al levels of 375 and 100 ppm. These high pressure drops can occur with no visible precipitates.

To form the chemical products that can result in large pressure drops across sump screen debris beds, the dissolved Al concentration (which is controlled by the amount of Al in containment) must exceed a solubility limit. Literature data suggest that for a temperature of 4°C (40°F) and a pH of 9.2, this is ≈ 30 ppm.[7,9] However, because of the complexity of the sump environment, it is difficult to justify the applicability of literature data to this situation.

Sodium tetraborate buffers seem more benign than NaOH or TSP. A submerged aluminum area and sump volume that results in a 375 ppm dissolved Al concentration in a NaOH environment, results in a 50 ppm dissolved Al concentration with a sodium tetraborate buffer. No significant head loss was observed in a test that lasted ≈ 11 days with 50 ppm aluminum and a STB buffer. A test with a NUKON/CalSil debris mixture and STB buffer produced much lower head losses than observed in corresponding tests with TSP, although tests were not performed over the full range of CalSil loadings of interest.

Head Loss in ICET-3 Environments

Pressure drops across the bed for tests with physical debris of 15 g NUKON/15 g CalSil and TSP present (ICET-3-6 and ICET-3-10) are compared with the baseline test ICET-3-11, which had 15 g NUKON/15 g CalSil but no TSP, in Figures 3a and b, respectively.

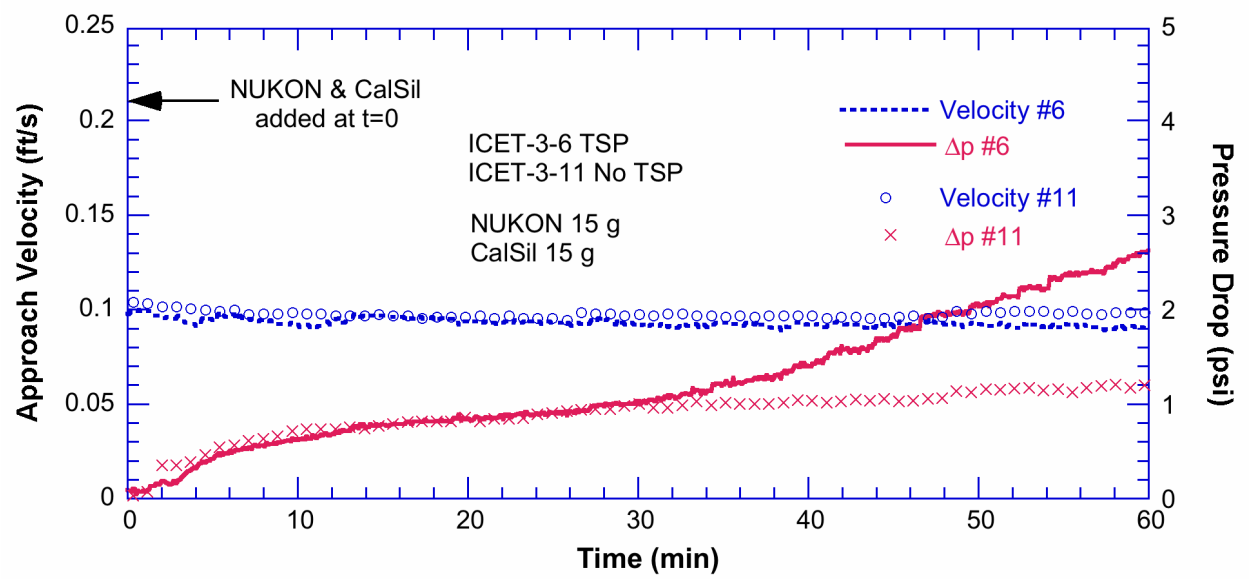
In ICET-3-6, no TSP was added to the presoak in order to limit the possible dissolution of the CalSil. This scenario was intended to give a lower bound for the amount of calcium phosphate precipitate arriving as the debris bed is formed. As expected, the initial pressure drop behavior in ICET-3-6 is very similar to the baseline case ICET-3-11 in which no chemical precipitates are present (Figure 3a). However, a comparison of the maximum pressure drops reached in ICET-3-6 and -11 shows that the difference in the pressure drop increases with time. The increase of the pressure drop with time in ICET–3-6 is attributed to the continuing dissolution of CalSil and additional formation of calcium phosphate precipitates.

Test ICET-3-10 some TSP was added during the presoak. This test was intended to give a more “typical” amount of calcium phosphate precipitate arriving as the debris bed is formed. This results in a much more rapid increase in head loss than in ICET-3-6 (Figure 3b), although the pressure drop in ICET-3-6 eventually approaches the steady state value obtained in ICET-3-10.

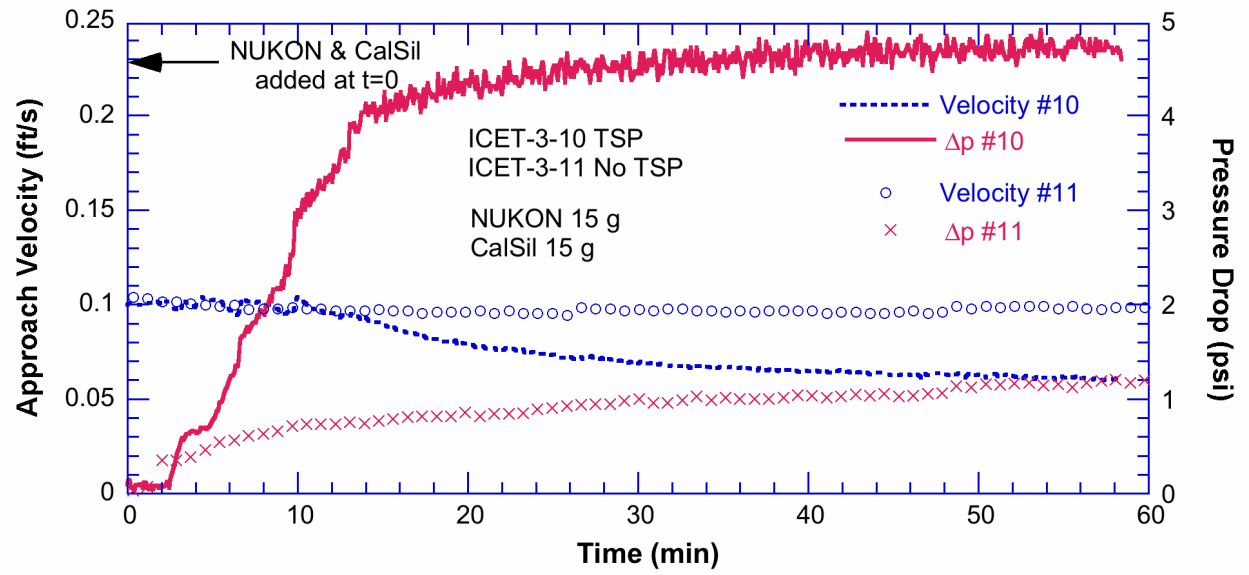
The pressure drop across a 15 g NUKON bed at 0.1 ft/s is about 0.2 psi. With the addition of 15 g of CalSil, but no chemical reaction, the pressure drop at 0.1 ft/s is about 1.2 psi. With the addition of TSP, the pressure drop across the bed increases to greater than 5 psi even though the velocity is decreasing to less than 0.05 ft/s.

The degree of dissolution that would occur before the debris reached the sump screen in a prototypical situation would presumably be bounded by the ICET-3-6 and ICET-3-8 limiting cases, and may be most similar to the ICET-3-10 case. The test results suggest that variability in the degree of CalSil dissolution is likely to have a relatively small effect on chemical effects on head loss in this system. Differences in debris transport time would probably have a much large effect on the rate at which the pressure drop increases. The actual amount of head loss for a plant specific case is also dependent on many additional factors such as the sump screen debris loading, uniformity of the screen debris loading, propensity for flow bypass (i.e., jetting)

through the debris bed, debris bed screen approach velocity, and transport of chemical precipitate not addressed in these tests.



(a)



(b)

Figure 3. (a) Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-6 & 11; (b) Bed approach velocities and differential pressures across the screen as a function of time for test ICET-3-10 & 11 (15 g load = 0.7 kg/m^2).

ICET-3-18 used a debris loading of 5 g NUKON and 10 g CalSil. This resulted in a thin debris bed about 3–4 mm thick. The bed approach velocity and differential pressure across the screen

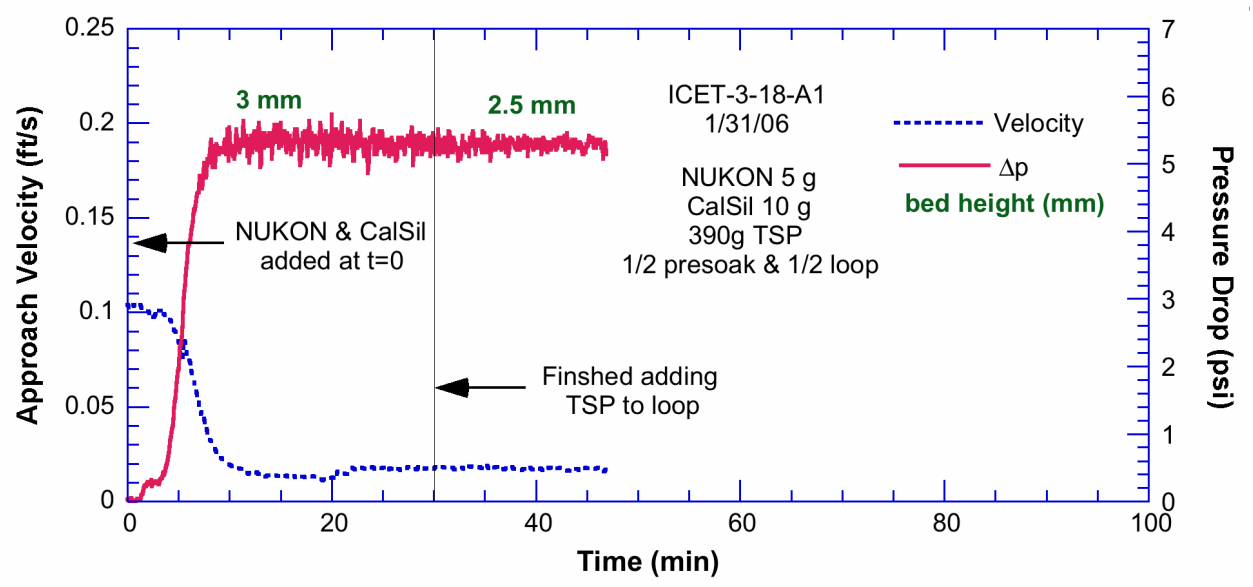


Figure 4. Bed approach velocity and differential pressure across the screen as a function of time for test ICET-3-18.

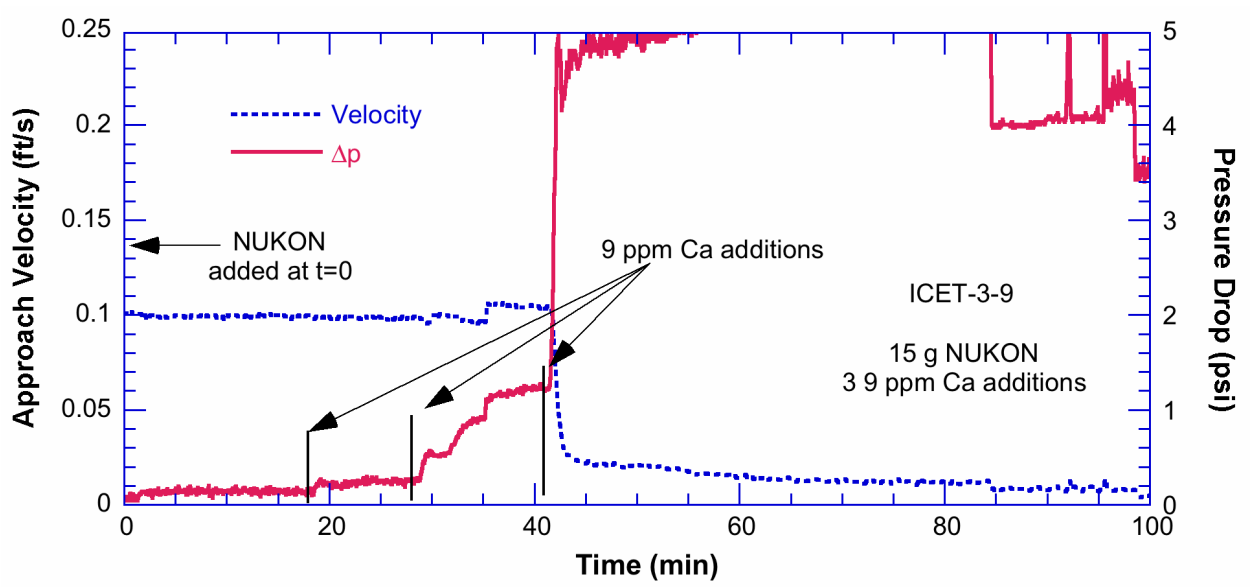


Figure 5. Bed Approach Velocities and Differential Pressures: ICET-3-8 and 9.

as a function of time for test ICET-3-18–A1 are shown in Figure 4. This test resulted in a rapid buildup of head loss. After 10 minutes, the flow velocity could not be maintained at 0.1 ft/s and the flow velocity gradually decreased. The thinner bed plugged more rapidly than in either ICER–3–10 or ICET–3–17, which had 15 g NUKON and 15 g CalSil and was about 12 mm thick. This test result is consistent with the classic thin–bed head loss behavior observed elsewhere (i.e., a thin fiber bed that becomes saturated with particulate can result in high head loss).

Test ICET-9 was performed with $CaCl_2$ additions. The pressure drop history in ICET-3-9, shown in Fig. 5, suggests a strongly nonlinear relationship between the amount of the calcium phosphate precipitate and the pressure drop. The first two additions of $CaCl_2$ in ICET-3-9

produced relatively small increases in pressure drop. The third addition resulted in a very rapid increase in pressure drop. The total inventory of dissolved Ca added in ICET-3-9 is equivalent to complete dissolution of 9 g of CalSil or a CalSil loading of 0.4 kg/m^2 of screen. However the results from ICET-18 (Figure 4) show that the loading that results in high pressure drops will also depend on the thickness of the fiber bed.

A test was also run with a debris loading of 25 g CalSil with no NUKON. The 25 g of CalSil used in this test corresponds to a screen loading of 1.2 kg/m^2, which is probably conservative for most plants after their sump screens are updated. The debris bed that formed on the screen is shown in Figure 6. Although a portion of the flow area is blocked by the CalSil, a significant portion of the screen remains open with this loading. The pressure drops are very low as expected with a significant open area. It appears even with a heavy loading of CalSil, another source of fiber is necessary to form a bed that can trap the CalSil particulate and the associated chemical product.

Figure 6. Plan view of debris bed formed by pure CalSil loading (ICET-3-19-A2).

2.3 CalSil Dissolution and $Ca_3(PO_4)_2$ Settling Tests

Because the dissolution rate of CalSil is pH dependent (dissolution is more rapid at lower pH), it will depend on the rate at which TSP is added to the system. Tests were performed with TSP dissolved in the solution before any addition of CalSil ("instantaneous" dissolution of TSP), and with TSP metered in over 1-h and 4-h periods. The TSP dissolution history had a larger effect

at a CalSil loading of 1.5 g/L than at 0.5 g/L. It took substantial time (approximately 4 days) to achieve full dissolution for the 1.5 g/L CalSil loading while dissolution of the 0.5 g/L loading appears to be complete within approximately 1–3 days. However, for both CalSil concentrations, substantial Ca dissolution (> 75 mg/l) has occurred within a few hours regardless of the TSP addition rate.

In the head loss loop tests, virtually all the calcium phosphate precipitates that form are transported to the bed. In an actual sump, there is a potential for the precipitates to settle before they reach the sump screen. Settling tests were performed to determine settling rates for calcium phosphate under conditions with no bulk directional flow. Tests were performed in a settling tower with an effective height of 71.5 cm. The tower was filled with a solution containing LiOH (0.7 ppm Li) and boric acid (2800 ppm B) and TSP (3.4 g/L). $CaCl_2$ solution was then added to the tower. The dissolved Ca reacts with the TSP in the solution to form calcium phosphate precipitate. The solution is stirred to get a uniform mixture and then the precipitates are allowed to settle. Two different $CaCl_2$ concentrations were tested. One produced a dissolved Ca inventory equivalent to 300 ppm and the other an inventory equivalent to 75 ppm. The 300 ppm inventory is roughly equivalent to full stoichiometric dissolution of a 1 g/L concentration of CalSil; the 75 ppm inventory is roughly equivalent to full stoichiometric dissolution of a 0.25 g/L concentration of CalSil. The settling rate was dependent on concentration. For the 75 ppm calcium test, which is more representative of the concentrations of interest, the settling velocity was estimated to be 0.8 cm/min.

Head loss in ICET-1 and ICET-5 Environments

Pressure drops much larger than would be expected from corresponding debris beds in an inert environment have been observed in environments with NaOH buffer for dissolved aluminum levels of 375 and 100 ppm. These high pressure drops can occur with no visible precipitates. The increases in pressure drops are much larger than those expected due to the small changes in bulk fluid properties like viscosity for these solutions.

In short–term laboratory testing with surrogate solutions, the kinetics of the formation of chemical products can lead to substantial test–to–test variability. Both tests with 375 ppm dissolved Al concentrations resulted in large pressure drops. No high head losses were observed in two short, 8–10-h tests with 100 and 200 ppm Al in solution, respectively. However, two longer, 6–8 day tests with 100 ppm Al did result in large pressure drops. The pressure drop history in one of these tests is shown in Figure 7.

Samples of the solutions from all the loop tests formed emulsions that settled to the bottom of the sample containers when allowed to remain at room temperature for some time. ICP measurements were made to determine the Al content of the clear supernate solutions above the emulsions. Although the solutions appeared perfectly clear, this does not preclude the possibility that some fine precipitates remain. Thus the measurements may somewhat overestimate the solubility of amorphous $Al(OH)_3$ at room temperature at nominally pH 9.6 in sump solutions. The measured values ranged from 32–63 ppm. The variability in the results is probably due primarily to small variations in pH. Literature estimates of the solubility at room temperature give values of 37–59 ppm for pH values 9.4–9.6, which are reasonably consistent with the results from the loop tests.[7]

The observation that the solutions in the head loss loop can remain supersaturated for a substantial period is consistent with results from the ICET–1 test.[4] Although the concentration

of aluminum in the test remained constant over the 10–15 days of the test, precipitates formed more rapidly and in greater volume as the solution was cooled as the test progressed.

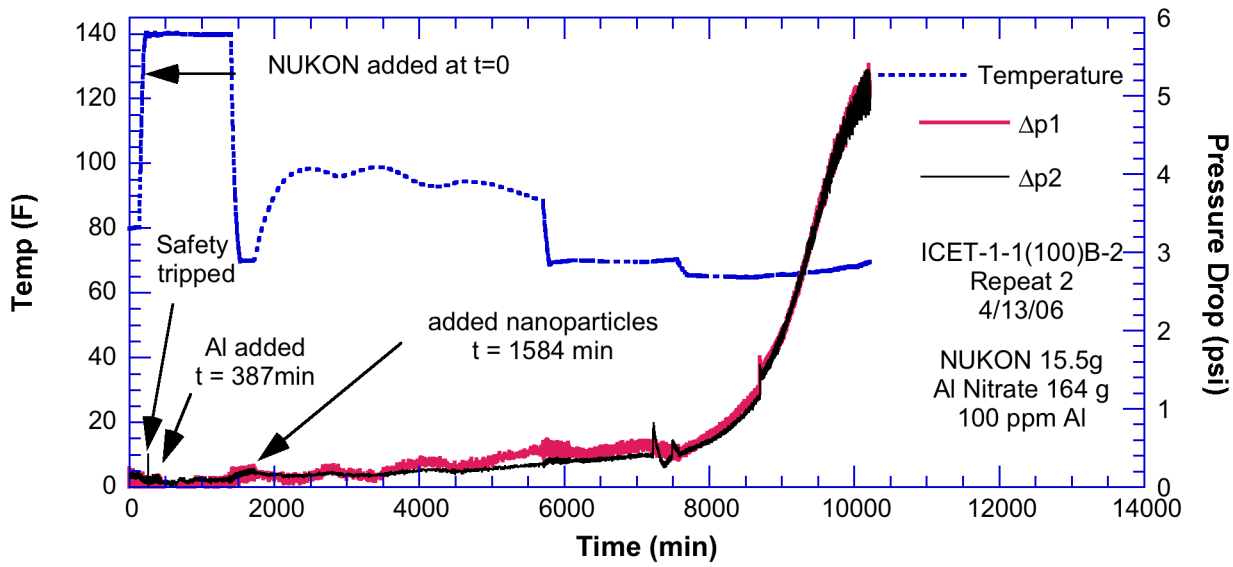


Figure 7. Pressure and Velocity History in test ICET-1-1-B2_100ppm repeat 2.

The head loss test in the ICET-5 environment was conducted for ≈ 11 days. No increase in head loss due to precipitate formation was observed. Sodium tetraborate buffers seem more benign than NaOH or TSP. A submerged Al area and sump volume that results in a 375 ppm dissolved Al concentration in a NaOH environment, results in a 50 ppm dissolved Al concentration with a sodium tetraborate buffer. The 375 ppm concentration resulted in high head loss in 0-2 h. Interaction with NUKON/ CalSil debris mixtures produced much lower head losses than observed in corresponding tests with TSP, although tests were not performed over the full range of CalSil loadings that might be of interest.

2.5 Chemical Modeling

<u>Relationship of ICET–1 environments to plant environments</u>

Although the final level of dissolved Al in ICET–1 was ≈ 375 ppm, actual plant levels of dissolved Al for the same environments would “scale” with the amount of Al exposed, which is plant specific. In addition, the ICET–1 test was run isothermally at a temperature of 60°C (120°F), whereas the actual temperatures will vary considerably over the whole course of the accident. The amount of Al exposed to the environment depends strongly on whether the sprays are on. In most plants, the amount of submerged Al is a small fraction of the total Al in containment.[9] To obtain a better estimate of the range of Al that may be expected in the recirculating water, calculations were performed using more realistic thermal histories for 17 plants for which estimates of the amount of Al in containment were available in Ref. (10).

The results suggest that the dissolved Al concentration in ICET-1 is conservative, and most plants with NaOH buffering would be expected to have dissolved Al concentrations at 30 days below 100 ppm. Because of the large amount of aluminum that is exposed to sprays but not submerged, one plant, based on the survey results and the preliminary calculations, could have a concentration 65 ppm after one day, rising to 80 ppm after 30 days. Although comparable

time–temperature–dissolution history calculations were not performed, the dissolved Al concentration in ICET-5 is probably similarly conservative. Based on the corrosion rates inferred from ICET–5 and the relative amounts of Al in containment compared to ICET–5, most plants with STB buffering would be expected to have dissolved Al concentrations at 30 days below 15 ppm.

3. Comments and Observations

   a. Significant effects on head loss due to chemical products were observed in environments with CalSil and TSP buffer (ICET-3) and in environments with significant dissolved aluminum and NaOH for pH control (ICET–1). [4, 15a, 15b]

   b. ICET-3 Environments

      - CalSil dissolves quickly in prototypic environments. Dissolved calcium concentration was greater than 75 ppm within a few hours even with concentrations of CalSil of 0.5 g/L. [3]
      - Uncertainties in TSP dissolution rates and degree of dissolution of CalSil prior to bed formation have relatively small impacts on dissolution rate of CalSil for CalSil loadings of interest. [3] (Ref. 5, p 40)
      - Solubility of calcium phosphate is low over temperature and pH ranges of interest in the sump. Thus, precipitate will occur simultaneously with dissolution of CalSil and TSP. Significant amounts of precipitate are likely to occur in a relatively short time for TSP plants that have sufficient amounts of dissolved calcium in a post-LOCA containment pool. [9]
      - Tests with the vertical head loss loop tests showed that dissolved calcium levels of 10-20 ppm (corresponding to 0.03–0.06 g/L of CalSil) had significant increases in head loss due to precipitation of calcium phosphate. These test results are consistent with the test results of WCAP-16785-NP regarding the highly insoluble nature of calcium phosphate. [14a, 15a]
      - The level of dissolved Ca required for high head loss in environments with TSP depends strongly on fiber bed thickness, sump volume, and screen area. Thin fiber beds (≤ 3 mm) show a much higher head loss. [14a, 15a]
      - In the results from a test facility are scaled up to plant-specific parameters, the mass of chemical product and physical debris per unit area of screen must be considered. The mass of chemical product produced should be proportional to the fluid volume while the potential for head loss is characterized by the product mass per unit screen area. [15a, 15b]
      - Even with a heavy loading of CalSil, a source of fiber is necessary to form a bed that can trap the CalSil particulate and the associated chemical product. [14a, 15a]

   c. ICET-1 Environments

      i. ICET-1 environments gave high losses in tests with Al concentrations down to 100 ppm. Post-test measurements suggested that approximately 50 ppm remained in solution at ≈ 75°F, pH ≈ 9.6. [9]

      ii. No visible precipitate was observed in tests with 100 ppm aluminum in solution even though high head loss was observed. This is consistent with results from ICET–1 that precipitates are very small. [9]

iii. ANL measurements on filtered/unfiltered solutions in bench tests with 0.2-µm filters showed no differences in aluminum concentration. [9]

iv. $Al(OH)_3$ precipitates are difficult to characterize. (Exact form of Al precipitates is unclear. ANL and LANL generally refer to $Al(OH)_3$, which is the crystalline form gibbsite, but is also used to refer to an amorphous material. WCAP-16530 refers to AlOOH, which is boehmite. The forms differ chemically only by the addition of water and for the present purposes can be used interchangeably). [9]

v. TEM suggests precipitates consist of agglomerations of 30 nm particles.[6] ANL measurements gave 19 µm without ultrasonic deflocculation and 2 µm with deflocculation consistent with the LANL observations of agglomerates. High hydration of products increases effectiveness in plugging of debris bed formed on screen. [9]

vi. Kinetics of $Al(OH)_3$ precipitation are complex. Solutions can maintain a significant amount of supersaturation for significant amounts of time (days), and then a relatively rapid increase in head loss can occur. The behavior of precipitated aluminum in ANL loop tests and in ICET-1 is consistent with an ongoing process of nucleation and growth of products too small to be detected visually. [9]

vii. In these tests, a large amount of aluminum was removed from solution (more than 50 ppm). Later ANL tests with surrogate product (AlOOH)[11] corresponding to 5 ppm aluminum in solution also showed high head loss.[12] However, a later loop test with a STB buffer suggested somewhat large amounts of product (10–30 ppm) were required to get high head loss.[12] [14a, 15a]

viii. Although all the tests were run with the thickness of NUKON bed, it is expected that level of dissolved aluminum required for high head loss depends strongly on fiber bed thickness, sump volume, and screen area. Thin fiber beds could produce a much higher head loss for the same mass of chemical product than a thicker bed. [15a, 15b]

d. ICET-5 Environments [sodium tetraborate buffer (STB)]

i. ICET-5 environment head loss tests showed no measurable increase in head loss due to chemical effects with 50 ppm dissolved Al for tests of 12-20 days. [14a, 15a]

ii. An increase of dissolved aluminum to 100 ppm resulted in high head loss.[14a, 15a]

iii. A test with a NUKON/CalSil + STB resulted in a head loss characteristic of NUKON/CalSil without chemical effects. The head loss slowly decreased with time consistent with dissolution of the CalSil (thus reducing its effectiveness as a physical particulate) with no formation of a precipitate product (at a concentration of CalSil of 0.12 g/L). [14a, 15a]

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G. "Integrated Chemical Effects Test Project: Consolidated Data Report," NUREG-6914
Prepared by J. Dallman, B. Letellier, J. Garcia, J. Madrid, W. Roesch, Los Alamos National Laboratory

1. Background and Test Description

The Integrated Chemical Effects Test (ICET) project was a joint effort by the U.S. NRC and the nuclear utility industry. The ICET tests attempted to simulate the chemical environment present inside a containment water pool after a loss-of-coolant accident (LOCA) and monitored the chemical system for 30 days to identify the presence, composition, and physical characteristics of chemical products that formed during the tests. The ICET test series was conducted by Los Alamos National Laboratory at the University of New Mexico. The primary objectives were (1) to determine, characterize, and quantify chemical-reaction products that may develop in the containment sump under a representative post-LOCA environment, and (2) to identify and quantify any chemical precipitates that might be produced during the post-LOCA recirculation phase. No measurements of head–loss were made in the tests.

All of the ICET tests were conducted in an environment that attempted to simulate containment pool conditions during recirculation. The tests included an initial 4-hour spray phase to simulate containment spray interaction with the unsubmerged materials. The materials present in this environment included representative amounts of submerged and unsubmerged aluminum, copper, concrete, zinc, carbon steel, and insulation samples. Representative amounts of concrete dust and latent debris (dirt) were also added. Insulation samples consisted of amounts of NUKON fiberglass and calcium silicate (CalSil) material. Water was circulated through the bottom portion of the test chamber during the entire test to achieve representative flow rates over the submerged specimens.

The amounts of material in the test were scaled to the liquid volumes of the test chamber and the containment sump volume. For most materials, the scaling was in terms of the surface area of material to the sump volume, but for insulation materials, the scaling was in terms of the volume of material to the sump volume. The relative amounts of material were based on an informal survey of a number of plants.[6] More detailed plant survey information available after testing indicated the amount of insulation (e.g., CalSil) in these tests may have been too high to be representative. The ratios of material to sump volume are in most cases larger than would be expected for a typical plant, although the values are not necessarily bounding. The ratios of the material quantities to sump water volume are summarized in Table 3.[14]

The physical and chemical parameters that defined the tank environment are summarized in Tables 4, 5, and 6.[14] Note that of the chemical parameters listed, only boric acid, lithium hydroxide, and hydrochloric acid were present in all five tests. Boric acid is present in the reactor coolant system (RCS) and the refueling water storage tank (RWST) for reactivity control. Lithium hydroxide is present in the RCS for pH control; during a fuel cycle the Li levels could range from 0 to 3.5 ppm. Because of the additions from the RWST, the levels of Li in the sump recirculation are considerably lower than those typical of the RCS. Hydrochloric acid (HCl) can be formed from the degradation of cable insulation material. The addition of 100 ppm of HCl test was intended as a conservative estimate of the potential of this degradation. The initial test solution pH was different in each test, and it varied from ~7.3 in Test 2 to ~9.8 in Test 4. The pre-determined amounts of chemicals were added for each test, and no attempt was made to control or alter the resulting pH during the test.

Table 3. Material Quantity/Sump Water Volume Ratios for the ICET Tests

Material	Ratio Value (ratio units)	Submerged Material (%)	Unsubmerged Material (%)	Comments
Zinc in galvanized steel	8.0 (ft^2/ft^3)	5	95	Accounts for grating and duct work that might be submerged.
Inorganic zinc primer coating (non–topcoated)	4.6 (ft^2/ft^3)	4	96	Addresses both non-topcoated zinc primer applied as well as zinc primer exposed as a result of delamination of a topcoat.
Inorganic zinc primer coating (topcoated)	0.0 (ft^2/ft^3)	–	–	Epoxy-based topcoats prevent interaction of the zinc primer with sump and spray. Exposure of zinc primer to sump and spray fluids due to local failures of epoxy-based topcoats is accounted for in the non-topcoated zinc coatings.
Aluminum	3.5 (ft^2/ft^3)	5	95	Aluminum is generally not located at elevations inside containment where it may be submerged.
Copper (including Cu-Ni alloys)	6.0 (ft^2/ft^3)	25	75	Majority of surface area associated with CRDM coolers and instrument air lines.
Carbon steel	0.15 (ft^2/ft^3)	34	66	Majority of surface area associated with containment fan coolers.
Concrete (surface)	0.045 (ft^2/ft^3)	34	66	The submerged value accounts for limited damage to floor and wall surface areas that will be submerged due to primary RCS piping being elevated above the containment floor.
Concrete (particulate)	0.0014 (lbm/ft^3)	100	0	
Insulation material (fiberglass or calcium silicate)	0.137 (ft^3/ft^3)	75	25	The submerged value accounts for most of the fiberglass to remain in areas where it will wash down into the sump pool.

Table 4 Physical Parameters for the ICET Tests

Physical Parameter	Test Value	
Tank water volume	949 L	(250 gal.)
Circulation flow	100 L/min	(25 gpm)
Spray flow	15 L/min	(3.5 gpm)
Sump temperature	60°C	(140°F)

Table 5 Chemical Parameters for the ICET Tests

Chemical	Concentration
Boric acid (H_3BO_3)	2800 mg/L as boron[a]
Trisodium phosphate (TSP—$Na_3PO_4 \cdot 12H_2O$) [Tests 2 & 3]	As required to reach pH 7 in the simulated sump fluid
Sodium hydroxide (NaOH) [Tests 1 & 4)	As required to reach pH 10 in the simulated sump fluid
Sodium tetraborate [Borax] (STB—$Na_2B_4O_7 \cdot 10H_2O$) [Test 5]	As required to reach boron concentration of 2400 mg/L in Test #5
HCl	100 mg/L[a]
LiOH	0.7 mg/L[a]

[a]Concentrations applicable to Tests #1–#4. Concentrations for Test #5 were 2400 mg/L boron, 43 mg/L HCl, and 0.3 mg/L LiOH.

Table 6 Test Series Parameters

Test	Temp (°C)	pH Control	pH[a]	Boron (mg/L)	Notes
1	60	NaOH	10	2800	100% fiberglass insulation test. High pH, NaOH concentration as required by pH.
2	60	TSP	7	2800	100% fiberglass insulation test. Low pH, trisodium phosphate (TSP) concentration as required by pH.
3	60	TSP	7	2800	80% calcium silicate/20% fiberglass insulation test. Low pH, TSP concentration as required by pH.
4	60	NaOH	10	2800	80% calcium silicate/20% fiberglass insulation test. High pH, NaOH concentration as required by pH.
5	60	STB	8 to 8.5	2400	100% fiberglass insulation test. Intermediate pH, sodium tetraborate (Borax) buffer.

[a]Values shown were the target pH for Tests #1–#4. The value for Test #5 is in the expected range.

The materials described in Table 3 were introduced to the tank as 373 flat–metal coupon samples (40 submerged) and 1 submerged concrete sample. Recirculation flow rate, test solution temperature, and pH were monitored online. Flow rate and temperature were controlled to maintain target values of 25 gpm and 60°C. The value of 25 gpm was chosen to yield fluid velocities over the submerged coupons from 0–3 cm/s. Daily water samples were obtained for measurements of pH, turbidity, total suspended solids, kinematic viscosity, shear-dependent viscosity, and for chemical analyses. In addition, microscopic evaluations were conducted on water-sample filtrates, precipitates, fiberglass, CalSil, metal coupons, and sediment.

Upon reaching the desired temperature, test-specific chemicals were dissolved into the heated water. Latent debris, concrete, test coupons, and insulation samples were then placed in the tank. Once the solution temperature reached the required test temperature of 60°C, the test commenced with initiation of the tank sprays. During the 4-hour spray period, additional chemicals were added if required. The tests ran for 30 days. Water samples, insulation samples, and metal coupons were analyzed after the test. Sampling and analyses were conducted in accordance with approved project instructions.

2. Summary of Important Results

2.1 Overview

Solution samples from Tests 1 and 5 produced precipitates upon cooling to room temperature, whereas samples from Tests 2, 3, and 4 did not. A precipitate formed at the test temperature in Test 3. The Test 1 precipitates occurred much more quickly and were present in greater quantities than the Test 5 precipitates. Except for precipitates seen on the first day of Test 3, no precipitates were visible in the test solutions at the test temperature of 60°C. Turbidity measurements were taken at 60°C and 23°C. In Tests 2, 3, and 4, measurements at both temperatures produced similar results, consistent with the assumption that the turbidity is due to physical particulate and independent of temperature. During the first 4 hours of Test 3, a large increase in turbidity was seen, which corresponded to the visible precipitates in that test. In Tests 1 and 5, the turbidity at 23°C rose higher than the 60°C values, consistent with the presence of a precipitate at the lower temperature.

The precipitates in Tests 1 and 5 are primarily amorphous forms of $Al(OH)_3$.[15] The precipitates are difficult to characterize, and the exact form of the precipitates is unclear. The ICET reports generally refer to $Al(OH)_3$, which is the crystalline form gibbsite, but is also used to refer to an amorphous material. WCAP-16530 refers to AlOOH, which is the crystalline form boehmite. They differ chemically only by the addition of water and for the present purposes can be used interchangeably.

The precipitate in Test 3 is a calcium phosphate.[14] Calcium phosphate is the name given to a family of minerals containing calcium, phosphorus, and oxygen (and sometimes hydrogen). They are all highly insoluble in the moderately alkaline solutions of interest. Although the actual precipitate represents a mixture of these forms, the precipitate is probably predominantly $Ca_3(PO_4)_2$, tricalcium phosphate.

Elemental chemical analyses with Inductively Coupled Plasma—Atomic Emission Spectroscopy (ICP-AES) were performed similarly for each test. Daily samples were analyzed for aluminum, calcium, copper, iron, magnesium, nickel, silica, sodium, and zinc. The solution samples were completely mixed before the ICP-AES measurements. Thus, the results are representative of the solution plus any precipitate present. Boron, lithium, potassium, lead, and chloride (analyzed using ion chromatography) were evaluated at the beginning of the tests, at the midpoint, and at the end of the tests. In Test 1, aluminum and sodium were present in greater concentrations than were all other tested elements. In Test 2, silica and sodium were the dominant elements in solution. Silica, sodium, and calcium were present in the greatest concentrations with the Test 3 solution. In Test 4, silica, sodium, calcium, and potassium were

present in solution in the greatest concentrations. Sodium, aluminum, calcium, and silica were the elements of highest concentration in the Test 5 solution.

Turbidity measurements were made as a measure of suspended solids. In all of the tests, turbidity peaked within the first few hours of testing and decreased to lower values within 24 hours. By the second day of testing the turbidity decreased to very low values. The turbidity measurements remained at these low values for the duration of the tests. Tests 3 and 4 had higher values of turbidity early in the test than the other tests because CalSil particulate was added to the tank before test initiation. There was a very high peak in turbidity early in Test 3 due to the formation of a chemical precipitate ($Ca_3(PO_4)_2$).

Total suspended solids (TSS) were also measured in each test by filtering a volume of approximately 500 mL through an in-line, 0.7-µm, glass microfiber filter directly at the sample tap and drying and weighing the filter paper to determine what was collected. A baseline TSS concentration was measured after the coupons, fiberglass, concrete dust, and latent debris were introduced to the tank. With the exception of Test 5, all tests reached a maximum TSS value by the first day and decreased to a value relatively close to the baseline measurement for the duration of the test. Test 5 TSS measurements varied between the baseline and the maximum value throughout the test.

Insulation debris, which was composed of fiberglass or a mixture of fiberglass and CalSil, was analyzed after completion of each test. Three types of deposits were found on the fiberglass samples: flocculants, films, and webbing. Particulate deposits were confined to the exteriors of the samples and were physically attached or retained. Flocculent deposits were found throughout the samples and were more prevalent on the fiberglass interior. It is likely that film or webbing deposits that were observed in Tests 1 and 4 were caused by chemical precipitation during the drying process. The amounts of deposits seen on the fiberglass insulation varied from test to test because of differing solution chemistry. The largest amount of deposition occurred in Test 3, followed in order by Tests 1, 4, and 2. Test 5 samples had the fewest deposits.

Test 1 experienced the largest amount of corrosion on the submerged coupons. No significant corrosion of the submerged coupons was observable in Tests 2–5, except for the aluminum coupons in Test 5.[14] None of the tests showed significant corrosion on the unsubmerged coupons. The sediment on the tank bottom at the end of the tests also varied. Tests 3 and 4 had the most sediment, most of it attributable to the large amount of crushed CalSil added to the tank. In Test 3 there were also significant amounts of chemical precipitate. Tests 1, 2, and 5 produced the smallest amount of sediment, which was composed largely of materials from the insulation used (fiberglass) and debris added to the tank.

2.2 Solution Chemistry

Each test had a target pH that was attributable to specific chemical requirements as given in Table 6. The actual measured pH values are shown in Figure 8 and are relatively constant throughout the tests except for Test 3. In Test 3, the pH increased from the initial pH by approximately 0.8 units. In this test, the formation of $Ca_3(PO_4)_2$ removed phosphate from the solution early in the test which diminished the buffering capacity of the system. Without adequate buffering, the system pH could be more easily affected as varying chemical reactions occurred.

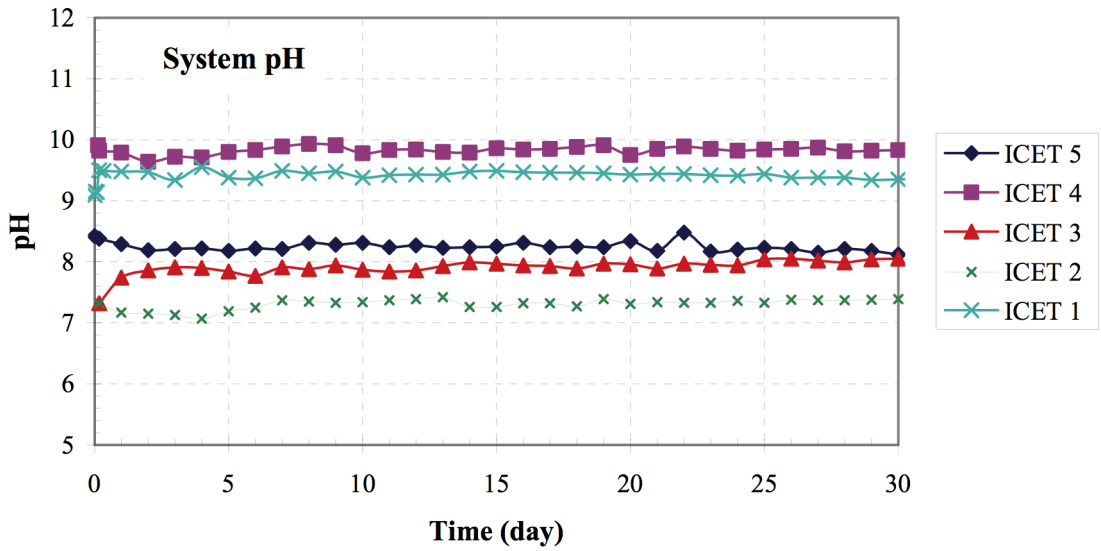

Figure 8. Measured pH During the ICET Tests

The only metal coupons that showed significant corrosion in any of the tests were the aluminum coupons in Tests 1 and 5 and the uncoated carbon steel coupons in Test 1. The measured aluminum concentrations during Tests 1 and 5 are shown in Fig. 9. The results for Test 5 are re-plotted with an expanded scale in Fig. 10. Aluminum concentrations in the other tests were below the detection limit of the ICP measurements. The pH in both tests was in range of high aluminum solubility. Test 1 had a higher pH which is consistent with the higher observed corrosion rate. In both Tests 1 and 5, the aluminum levels increased fairly steadily for about 15 days, and then stayed relatively constant for the remainder of the test. Although the pH in Test 4 was also high, the aluminum levels in solution were less than 1 mg/L. As will be discussed later, this low level of corrosion is probably due to the presence of high amounts of Si in solution from dissolution of the large amount of CalSil insulation in Test 4. The pH in Test 2 corresponds to a solubility minimum for $Al(OH)_3$ which is consistent with the very low levels of dissolved aluminum in this test.

The concentrations of zinc and copper were very low compared to the concentrations of aluminum in Tests 1 and 5. Neither zinc nor copper appeared as either adsorbed or precipitated species in these tests. Calcium levels were high in Tests 3 and 4 due to the addition of large amount of CalSil in those tests. The solubility of CalSil (mostly calcium silicate $CaSiO_3$) decreases with increasing pH. This may partly explain why the dissolved Ca levels at long times are lower in Test 4 than in Test 3. However, the higher pH in Test 4 may also lead to increased dissolution of fiberglass and the resulting increase in dissolved silica levels (Fig. 12) may also result in a decrease in dissolved Ca level. The dissolved calcium in the tests without CalSil additions is probably due to leaching from concrete dust and other concrete sources. The drop in the calcium level early in Test 3 is due to the removal of Ca from solution by precipitation of $Ca_3(PO_4)_2$. The amount of TSP added in Tests 2 and 3 is about 4g/L. Fully dissolved this would give P levels greater than 300 mg/L. For CalSil loadings greater than about 2 g/L, the amount of $Ca_3(PO_4)_2$ that can be formed is limited by the amount of phosphate that is available. Thus in Test 3, the measured phosphate levels from day 1 to day 30 were less than 1 mg/L—all the phosphate has been removed from solution by precipitation of $Ca_3(PO_4)_2$. Although the precipitation of $Ca_3(PO_4)_2$ removed Ca from solution early in Test 3, because of

the large amount of CalSil present in the test (19 g/L), dissolution of the CalSil continued until the equilibrium solubility limit corresponding to the pH was reached.

The measured silica concentrations are shown in Fig. 12. They are high in Tests 3 and 4 as expected from the large amounts of CalSil in those tests. The silica concentration is also high in Test 2 which has only fiberglass insulation and a TSP buffer. It is extremely low in Tests 1 and 5. This was somewhat unexpected. Fiberglass solubility increases with pH and separate effects testing[11,17] would suggest significant dissolution of fiberglass in Test 1 and somewhat less in Test 5. It appears that dissolved aluminum quickly reacted with the fiberglass to coat the fiberglass with a sodium aluminum silicate that inhibited further corrosion of the fiberglass.[18]

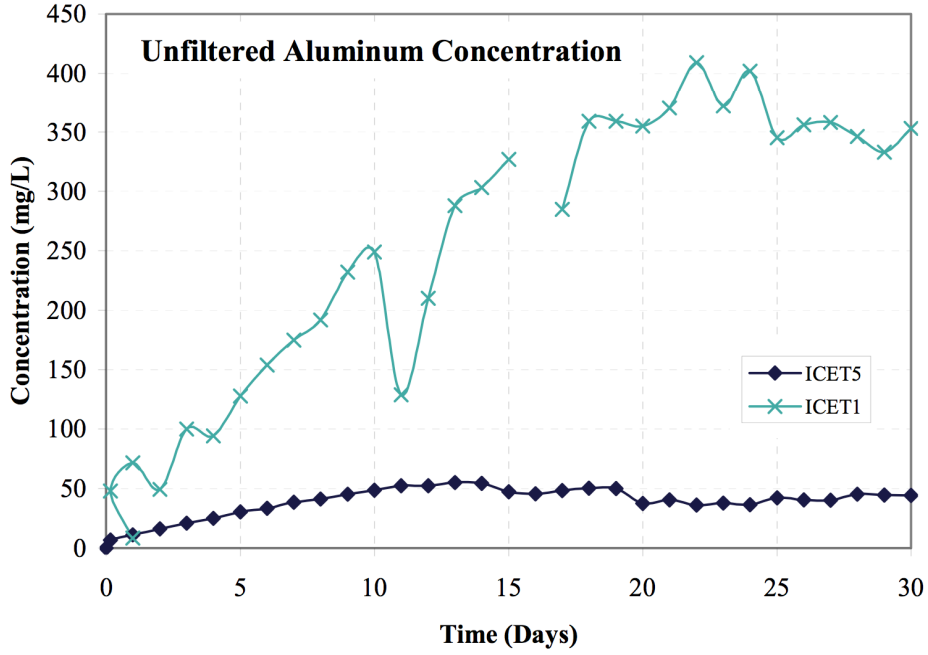

Figure 9. Measured Aluminum Concentrations in Tests 1 and 5

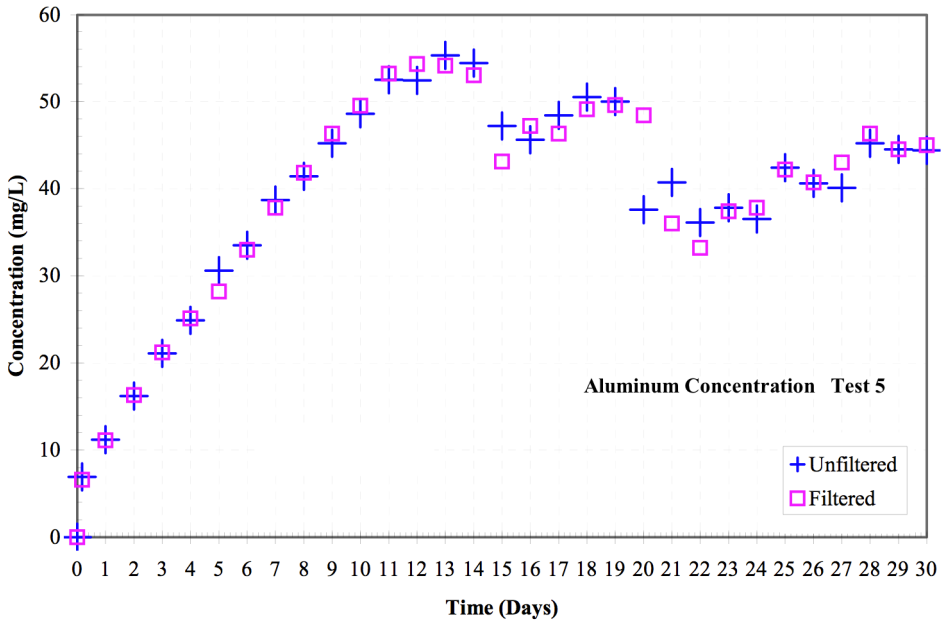

Figure 10. Measured Aluminum Concentration in Test 5

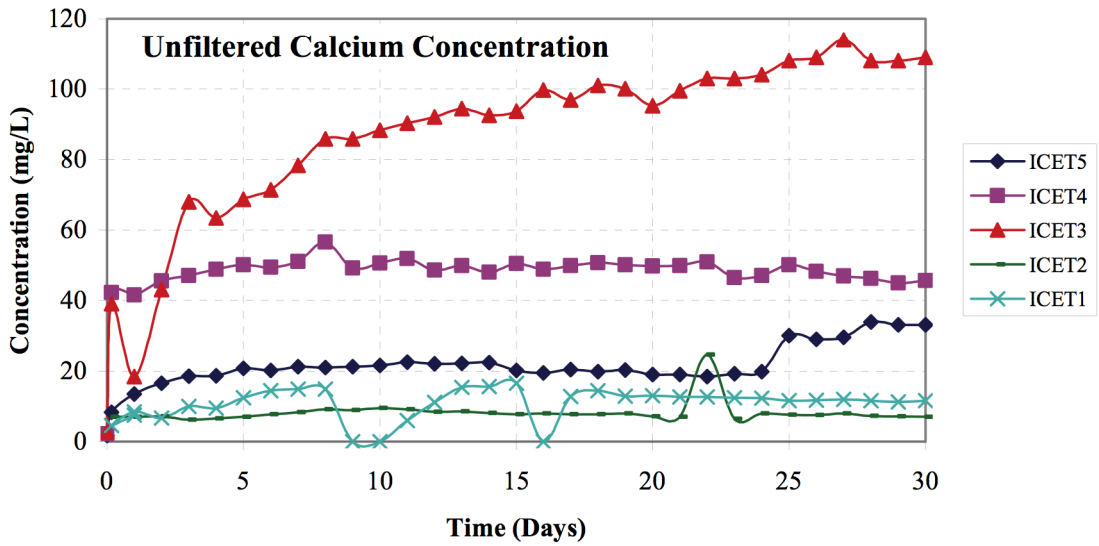

Figure 11. Measured Calcium Concentrations in Tests 1–5

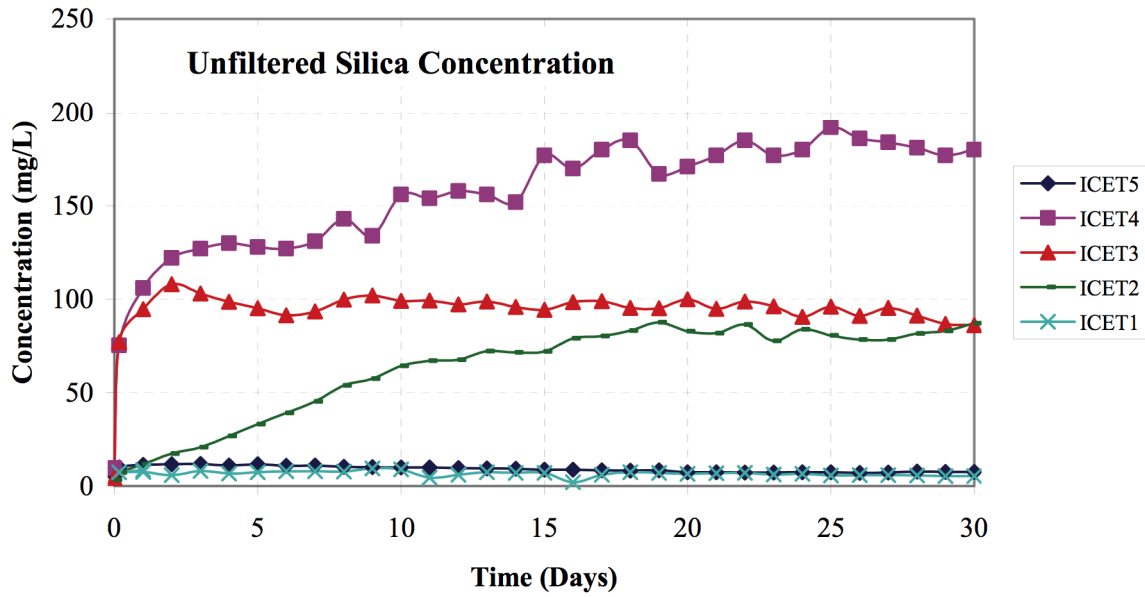

Figure 12. Measured Silica Concentrations in Tests 1–5*

2.3 Precipitates

The two major chemical precipitates observed in the ICET tests are $Ca_3(PO_4)_2$in Test 3 and some form of $Al(OH)_3$ in Tests 1 and 5. The formation of the $Ca_3(PO_4)_2$ precipitate in Test 3 occurred very quickly with the addition of TSP through the sprays and is easily replicated in separate effects tests when phosphates are added to solutions that contain dissolved calcium. No precipitates were observed in Test 2, which also used TSP, but had no CalSil. Concrete would be a potential source of dissolved calcium. Figure 11 shows that the dissolved calcium level in Test 2 is lower than that in Test 5. Since leaching of calcium from concrete increases with decreasing pH,[11] this is somewhat unexpected. It is possible that some of the calcium was removed from solution by formation of $Ca_3(PO_4)_2$. Because this would form almost immediately as calcium was leached from the concrete, it would probably not be visible as a precipitate in the solution, but would add to the sediment.

The behavior of the precipitates in Tests 1 and 5 is more complicated. White precipitates were observed in Tests 1 and 5 test solution samples as the solutions cooled to room temperature. No precipitates were observed at 60°C. In Test 1, precipitates became visible after the first 8 hours of testing, when the test solution was cooled to room temperature. The amount of visible precipitation at room temperature increased, and the precipitates formed more quickly during cooling as the test progressed. In Test 5, the precipitates took longer to form (several days at room temperature), and the quantities were much smaller than in Test 1. In addition, the quantity of Test 5 precipitates was relatively unchanged throughout the test.

ICP-AES results indicated that the precipitates were composed largely of aluminum and boron. Calcium and sodium were also present in smaller amounts. ICP analysis cannot detect the presence of either oxygen or hydrogen in materials. The precipitates from Tests 1 and 5 have

* Although expressed in NUREG/CR-6914 as silica concentration, it is probably Si concentration since that is what would be directly measured by ICP.

similar chemical compositions. The precipitate in Test 1 may have a somewhat greater proportion of aluminum than in Test 5. The precipitate in Test 5 appears to have a larger concentration of calcium. These results are consistent by the relative amounts of aluminum and calcium in solution (Figures 7 and 11). Transmission electron microscope (TEM) analysis of the precipitates from Test 1 indicated that they were primarily amorphous rather than crystalline, and the fundamental particle size was ~10 nm. However, much larger agglomerations of these basic particles were observed.[19]

Table 7. Distribution of Main Elemental Components of Precipitates from Tests 1 and 5

Precipitate Sample	Al (%)	B (%)	Ca (%)	Na (%)	Other
Test 1					
Day 7	62	24	7	7	0
Day 29	41	46	2	10	1
Average	51	35	5	8	0.5
Test 5					
Day 7	43	36	13	8	0
Day 29	39	40	13	7	0
Average	41	38	13	8	0

Comparison of the observed concentrations of dissolved aluminum with observations of precipitate formation at room temperature early in the tests suggests that the equilibrium concentration of dissolved aluminum at room temperature is about 50 ppm at pH ≈ 9.6 (Test 1) and less than 30 ppm at pH ≈ 8.3 (Test 5).

The presence of a precipitate could not be detected visually at the test temperature, 60°C, at any time during Test 1. However, the increase in the rapidity and the volume of precipitate formed upon cooling argues for the occurrence of some kind of nucleation and ripening process involving precipitate products in the Test 1 solution. As noted, post–test measurement of the precipitate product indicates a fundamental particle size of ~10 nm. Such particles and even significant agglomerations of such particles could not be observed visually.

The turbidity measurements shown in Figure 13 are supportive of an ongoing ripening process in the Test 1 solution. As the solution cooled from 60°C to 23°C, the turbidity was observed to increase in a 10–minute period from 0.3 NTU at 60°C to significantly higher values at 23°C becoming more than 133 NTU during the later stages of the test

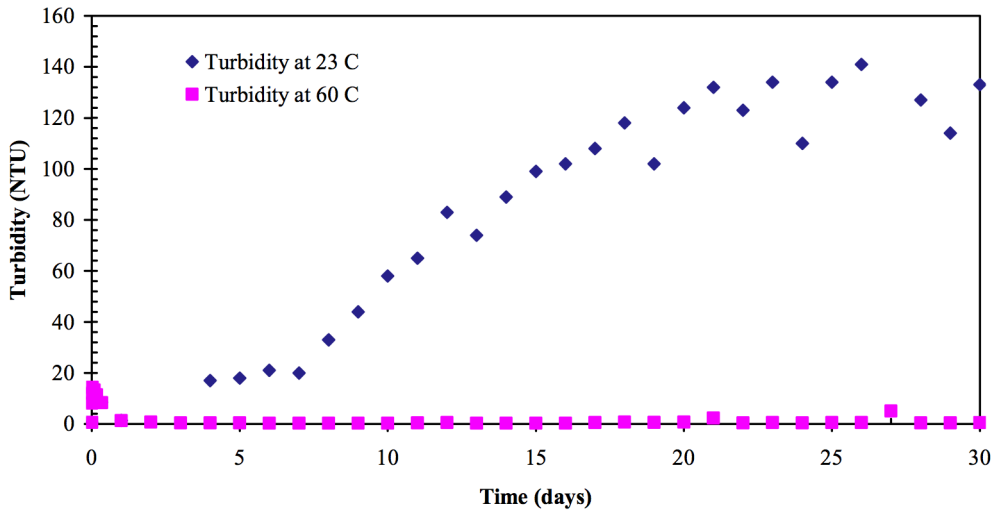

Figure 13. Turbidity in Test 1 at 23°C and 60°C

A surrogate precipitate was produced by titrating aluminum nitrate solution with pH 9.5 containing 2800 mg/L boron and sodium hydroxide at 25°C. Nuclear magnetic resonance analysis was performed on this surrogate precipitate, which indicated that a complexation between aluminum and boron occurred when the solution cooled below 40°C. Thus the description of the precipitate as $Al(OH)_3$ or AlOOH is a simplification of a more complex situation.

2.4 Passivation of Aluminum in ICET Solutions

In both Test 1 and Test 5, the dissolved aluminum concentrations increased approximately linearly with time during the initial part of the test, but then reached pseudo–steady–state values (Figures 9 and 10). Such behavior could be associated either with reaching a solubility limit or passivation of the metal coupons. However, other evidence suggests that it is passivation that is occurring.[20,21]

Hydrogen is generated as part of the corrosion reaction of aluminum with water. Generation of hydrogen is an indication of an ongoing corrosion process. There were some problems with the hydrogen measurements during Test 1. However, the data from day 20 until the end of the test are at least qualitatively accurate. The hydrogen generation decreased from day 21 to day 26, which corresponds to the leveling off of aluminum concentration on day 25 in Test 1. Similarly, the decrease in the hydrogen generation associated with Test 5 around day 17 is consistent with the leveling off of aluminum concentration in that test. These measurements thus support an argument for passivation, not a solubility limit as the mechanism that produces the leveling off of the dissolved aluminum concentration in these tests.

The mechanism and conditions for passivation in these environments is not clear. The results in Test 4 suggest passivation by aluminum silicates. Despite the high pH which would favor high aluminum dissolution as in Test 1, the presence of a large amount of soluble CalSil led to high dissolved silicate levels, and minimal dissolution of the aluminum coupons occurred.

Passivation by aluminum silicates requires a source of soluble silicates. In Test 4 considerable leaching of Si from the fiberglass appears to have occurred, but the presence of dissolved aluminum in Tests 1 and 5 appears to significantly inhibit leaching from the fiberglass. The initial dissolved silica levels of 100 mg/L Test 4 seemed to rapidly produce passivation of the aluminum. At the dissolved silica levels of ≈ 8 mg/L seen in Tests 1 and 5, it takes many days for passivation to occur and it is possible that these low levels of silica may not have affected aluminum passivation in these tests.

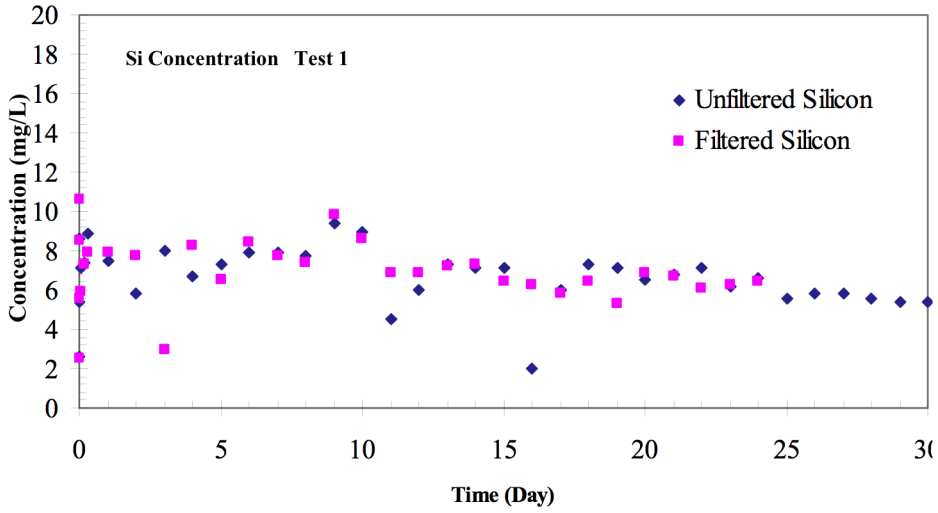

Figure 14.Silicon Concentration in Test 1

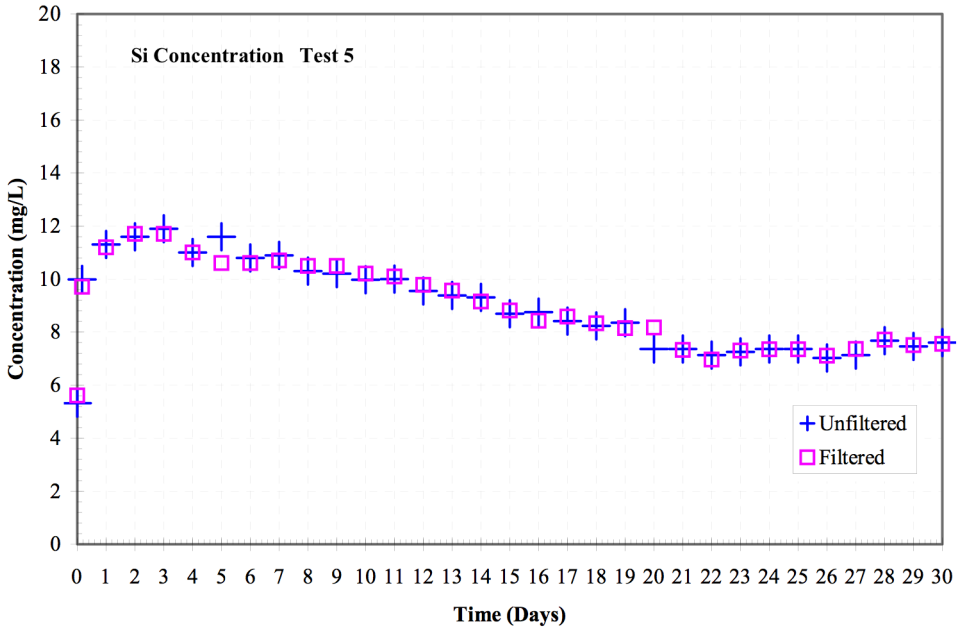

Figure 15. Silicon Concentration in Test 5

3.Comments and Observations

- Aluminum hydroxides, $Al(OH)_3$ or related forms, and calcium phosphates are the primary chemical precipitates in the ICET tests. [7, 8, 9]
    - Significant dissolution of aluminum was observed in solutions with pH of 8.0 or greater.
    - Isothermal nature of the ICET tests results in non-conservative estimates of the potential corrosion of non–submerged materials in containment and the corrosion that occurs early in the accident.
- Calcium phosphates formed in solutions with TSP and CalSil. [7, 8, 9]
    - Concrete and other insulation materials are another potential sources of dissolved Ca that could react with TSP to form calcium phosphate.
    - No visible precipitates were observed in the Test 2 fluid, which had TSP but no CalSil. The measured Ca levels suggest that some calcium phosphate may have formed.
- Rapid formation of calcium phosphate precipitate may be especially detrimental, since pump net positive suction head (NPSH) margins are typically at a minimum near the switchover to emergency core cooling system (ECCS) recirculation. [9]
- A nucleation and ripening process involving precipitate product occurred in Test 1. [9]
    - As the test progressed, precipitates formed more rapidly and in greater volume when the solution was cooled, although the concentration of aluminum in the test solution at temperature remained relatively constant.
    - No visible precipitates formed at 60°C in Tests 1 and 5.
- The isothermal nature of the test could underestimate the time required for nucleation and ripening of aluminum hydroxide precipitate products. [7]
    - In the plant, the recirculated water is cooled by the shutdown cooling heat exchangers. Formation of the precipitate product would be more rapid at the lower temperature.
    - ANL work indicates precipitates would redissolve readily at higher temperature.[23]
- The initial aluminum precipitation product is amorphous. Eventually it will transform to the more stable, much less soluble, crystalline form.[24] The crystalline form is much less soluble than the amorphous form, and any portion of the precipitate that transforms would be much less likely to redissolve at higher temperatures. [9]
- ICET results show solution chemistries observed in complex multi-component environments are not always consistent with those predicted based on tests in simpler environments. [7, 8, 9]

- Levels of dissolved silica in Test 1 are much lower than would be predicted from tests on fiberglass in solutions with comparable pH value.[11,17] Aluminum in solution inhibits the dissolution of fiberglass. [7, 8, 9]
- Low levels of dissolved aluminum in Tests 3 and 4 provide strong evidence for the potential for passivation of aluminum in solutions with large amounts of silica in solution. In this respect, the large amount of CalSil in the ICET tests is non-conservative. [9]
- PWROG data indicate a 75 ppm threshold silica inhibition level for passivation with a marked decrease in aluminum corrosion at a 50 ppm concentration[5]. [8]
- Aluminum phosphates are also highly insoluble making phosphates a candidate inhibitor (if no CalSil is present). [9]
- Passivation also occurred in Tests 1 and 5. At the low levels of dissolved silica in these tests (≈ 8 ppm), it not clear that the mechanism of passivation in these tests was in any way related to the formation of aluminum silicates. It is not clear how to "credit" passivation in such environments based on different ratios of aluminum surface area, fiberglass volume, pH, other materials, etc. [9]
- When passivation occurs, use of the average corrosion rate over the whole test period gives non-conservative estimates of the amount of corrosion that will occur during active dissolution, before the material becomes passivated. [7]

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1. Background and Report Description

This report describes the results of an extensive literature search and bench-scale experiments that were performed to gain a better understanding of the corrosion of aluminum and the formation of precipitation products in environments similar to ICET-1 and ICET-5. It also includes a comprehensive examination of both the test solutions and precipitates from ICET-1 and ICET-5. The precipitates were visually examined using both SEM and transmission electron microscopy (TEM). Supplemental analytical measurements were performed using x-ray diffraction (XRD), nuclear magnetic resonance (NMR) (both liquid and solid state), and light-scattering.

2. Summary of Important Results

The morphology of the precipitates that form as the ICET–1 and ICET–5 solutions cool are agglomerations of nanometer–sized particles. The size of the agglomerations grows with time. The precipitate is highly hydrated consisting of about 90% water by mass.

X-ray diffraction (XRD) and transmission electron microscopy (TEM) analyses of the precipitates of ICET Tests 1 and 5 indicate that the precipitates were largely composed of amorphous aluminum hydroxide, with a substantial quantity of boron adsorbed onto the surface. The amorphous form is to be expected because of the high concentration of anions in the solution. Such high concentrations of anions are known to retard crystallization at temperatures below 60°C. Chemical analysis results indicate that up to 35% of the boron from the initial solution may have been adsorbed onto the amorphous aluminum hydroxide precipitate. Nuclear magnetic resonance (NMR) measurements showed complexation between aluminum and boron. This corroborates the hypothesis that complexation was responsible for impeding the crystallization of aluminum compounds.

This conclusion that the solid phase controlling precipitation of the aluminum in solution is an amorphous aluminum hydroxide is also consistent with the measurements of the aluminum in solution in ICET-1, ≈ 375 mg/L. It is estimated that at 60°C and a pH of 9.6 (ICET-1 conditions), the solubility of amorphous $Al(OH)_3$ is ≈ 1300 mg/L, while the solubility of the crystalline form gibbsite is ≈ 48 mg/L. The solubility models predict that cooling of ICET Tests 1 and 5 solutions to ambient temperature would produce precipitation, as observed in practice.

Light scattering measurements of particle sizes in surrogate solutions simulating ICET–1 showed that the solutions contain particles with a bimodal modal size distribution peaking at ≈ 30 and ≈ 500 nm. Thus, although at 60°C and pH 9.6, the estimated solubility limit for amorphous aluminum hydroxide is much larger than the ≈ 375 mg/L measured in ICET-1, the solution is a colloid with tiny particles dispersed in solution rather than a true solution containing only aluminate ions ($Al(OH)_4^-$).

In acidic solutions, aluminum in solution can exist as: Al^{3+}, $AlOH^{2+}$, and $Al(OH)_2^+$. In alkaline solutions, aluminate ions ($Al(OH)_4^-$) are the only stable form of aluminum. The solubility is a function the solid hydroxide phase present (amorphous or crystalline) and increases with pH in alkaline solutions. The presence of some organics and inorganics can increase the aluminum solubility. The solubility can also be affected by the particle size presented in the solution.

A review of the literature shows that sodium silicates have been found to be an effective inhibitor of corrosion of aluminum, with an inhibition efficiency of almost 100%. The inhibition is due to the formation of an amorphous aluminosilicate film on the metal surface. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis was performed on the Tests 1 and 4 aluminum coupons. The EDS results indicate that the major components are aluminum, oxygen, silicon, sodium, and calcium, with small amounts of carbon and magnesium. Silica was present to a much larger degree in ICET-4 than in ICET-1. Thus, in ICET Test 4, the corrosion of aluminum was inhibited by the dissolution of calcium silicate.

A bench scale test was performed that provided a direct comparison between aluminum corrosion in a boric acid/NaOH solution and a boric acid/NaOH with silicates. The silicate addition produced virtually instantaneous passivation of the aluminum and no measurable corrosion could be detected. The concentration of the silicate inhibitor is cited as 88 mg/L, but it is not clear whether this is the concentration of Si or silica.

3. Comments and Observations

   a. The amorphous forms of $Al(OH)_3$ are more highly hydrated than crystalline forms. The rate of transformation to the more crystalline form is controlled by the rate at which hydroxyl anions replace water in the amorphous solid. This may mean that per mole of aluminum, an amorphous precipitate may be more effective in producing head loss than a crystalline precipitate. [9]

   b. Because aluminum in solution exists in different forms in acidic and alkaline solutions, it is not clear that the process for producing surrogates such as outlined in WCAP-16530-NP, that starts from an acid solution, will produce precipitates comparable to those that could potentially form in an alkaline sump environment. [7] (Ref.26, p 53)

   c. The presence of silica in solution can lead to inhibition of the corrosion of aluminum. The large amount of CalSil in ICET-4 probably produced a concentration of dissolved silica that was *not* representative of what would be found in the post-LOCA environment. Passivation needs to be demonstrated for conditions representative of plant-specific conditions. [9]

   d. Complete inhibition of aluminum corrosion was demonstrated in a bench test with a concentration of silicate inhibitor at 88 mg/L. This is in reasonable agreement with WCAP-16785-NP values.

   e. The solubility of aluminum in ICET-1 environments (pH control by NaOH) is reasonably consistent with literature data, although there is uncertainty in the solubility data that results in differing estimates of the solubility in this report and in Ref. 6. For example, at 60°C and pH 9.6, the solubility

limit for amorphous solid is reported as ≈ 1300 mg/L in this report and 854 mg/L in Ref. 6. [9]

f. Because these solutions can exist as colloids, the aluminum content of a solution is not a complete measure of the likelihood of the formation of precipitates as a solution is cooled. Although the aluminum concentration in ICET-1 remained relatively constant from Day 15 to Day 30, precipitates formed much more readily as the solution cooled during the later part of the test. [9]

g. The long term solubility of aluminum in ICET-1 solutions that was stored at ambient temperature was 49 mg/L after 4 months (Ref. 26, p 54). This is consistent with the measured concentration of aluminum in solution at the end of ANL head loss tests.[5] [9]

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I. "*Technical Letter Report on Follow–on Studies in Chemical Effects Head-Loss Research; Studies on WCAP Surrogates and Sodium Tetraborate Solutions,*" C. B. Banh, K. E. Kasza, and W. J. Shack, Argonne National Laboratory

1. Background and Report Description

In this study the procedure given in Westinghouse report WCAP-16530-NP[30] for preparing precipitates representing several insoluble aluminum[*] precipitates was used to prepare aluminum oxyhydroxide surrogate product and the properties of this product was studied. Only limited characterization of the product was actually performed, since a head loss test demonstrated that it is very effective in producing head loss. Small scale tests were also performed to determine the solubility of aluminum in sodium tetraborate (STB) solutions as a function of temperature at a pH of approximately 8.3. A long–term (35 days) head loss test with STB buffer was performed to confirm earlier test results.

The solubility of aluminum in NaOH solutions has been studied extensively. Although the crystalline forms such as gibbsite are thermodynamically more stable, experience with ICET–1 suggests that over the time frames of interest, the solubility is controlled by the formation of amorphous products.[31] This is also supported by studies in the literature.[32]

For the pH range of interest the most significant soluble aluminum specie is aluminate ion, $Al(OH)_4^-$. The equilibrium reaction between the solid phase and its supernatant solution is given by:

$$Al(OH)_{3\,(s)} + H_2O_{\,(aq)} \rightarrow H^+_{\,(aq)} + Al(OH)_4^{-1}{}_{(aq)} \qquad (1)$$

The $Al(OH)_4^-$ concentration at equilibrium is a function of pH:

$$\log Al(OH)_4^- = \log K - \log H^+ = \log K + pH \qquad (2)$$

Values of the solubility product constant log K are given by Van Straten et al.[32] and Langmuir[33] and can be inferred from experiments by Klasky[31] at LANL and Park at ANL and the ANL loop tests.[34] The data cited in Van Straten and Langmuir is for aluminum/NaOH systems with no other added chemcials. The data from Klasky, Park, and the ANL loop tests are for systems with 2800 ppm B and LiOH. The "best estimate" value for log K based on experiments in environments containing boron (present as boric acid) is about -12.2. Data on the solubility as a function of temperature are given by Benezeth et al.[10] These suggest that the variation of K with temperature can be expressed as

$$K = K_O \exp(-6969/T)$$

where T is in degrees Kelvin.

[*]In this report, $Al(OH)_3$ is used a short–hand for a family of aluminum oxyhydroxides that could form in a variety of crystalline and amorphous forms.

The LANL ICET–5 test suggests that at a pH of 8.4 the solubility of aluminum in sodium tetraborate solutions is about 50 ppm at room temperature (70°F). This value is also consistent with the result of ICET-5-1-B2 (the initial ANL loop test with STB buffers) in which no head loss was observed with 50 ppm after about 12 days of operation at 70°F. These concentrations are much higher than suggested by the literature data under these conditions (≈ 4 ppm) and this anomaly provides motivation for the current small–scale tests on solubility.

2. Summary of Important Results

2.1 Solution Chemistry (Studies on the WCAP Surrogates)

The procedure in WCAP-16530-NP[30], in particular the limitations on the concentrations and the requirements on the settling rates, does seem effective at producing fine precipitates. However, the concentrations in the mixing vessels are still very high compared to the concentrations expected in the post-LOCA sump, in the ANL 100 ppm loop tests, or ICET–1 tests. No arguments or data are available to show that they are in any physical sense equivalent to the suspensions that would be produced under conditions more representative of those that might occur in a post-LOCA sump. Limited x–ray spectra on surrogates similar to those developed by the WCAP process, suggest that they are probably crystalline.

A head loss test was conducted using the WCAP aluminum oxyhydroxide surrogate. The amount of surrogate precipitate added to the test loop would be equivalent to an original concentration of aluminum of 5 ppm and having it completely precipitate from the 119 liter test loop. The pressure increase during the test was extremely rapid, starting just after the few seconds necessary for transport of the injected surrogate solid from the mixing tee to the plate with the NUKON bed. The pressure drop capacity of the system was exhausted almost immediately. No precipitate was visible (~595 mg was added as solid) in the water approaching the bed and no buildup of precipitate was visible on the bed.

Studies with Sodium Tetraborate Buffers

Two series of small–scale tests were performed. Both started with initial solutions of sodium tetraborate (STB). In the first test series, $Al(NO_3)_3$ was added periodically to solutions held at constant temperature resulting in nominal aluminum concentrations ranging from 10 to 90 ppm. The solutions were carefully examined visually for evidence of the formation of precipitates. In the second test series, sufficient $Al(NO_3)_3$ was added to the solution to cause precipitation and have solid material in equilibrium with the supernatant solution. If all the aluminum added would have stayed in solution, this would have yielded a nominal aluminum concentration of 400 ppm. The solutions were then held under isothermal conditions for over 22 days. If the solution reaches equilibrium with the precipitate during the test, the dissolved aluminum concentration will be equal to the solubility of $Al(OH)_3$ under the given conditions.

In the solubility tests at 80°F, visual observation suggests that precipitation began to occur at concentrations of aluminum in the range of 55 to 66 ppm. The amount of precipitate at these levels was very small and difficult to observe. At levels of 80 ppm and greater, the precipitate was easy to see and clearly evident. In the solubility tests at 100°F, visual observation of precipitation was observed at a concentration of 77–80 ppm. Although precipitates were observed in the 80°F test at 55–66 ppm of Al, the measured concentration in the supernate increased as the nominal concentration was increased. This finding suggests that either the kinetics of precipitation is sluggish or the precipitate particles are initially smaller than the 0.22

μm filter used to filter the supernate. In the solubility tests at 100°F, the increase in the measured concentration as the nominal concentration was increased was smaller than in the case of the test at 80°F; this may indicate that the kinetics of precipitation are faster at the higher temperature.

2.3 Precipitation

In the precipitation kinetics tests, all the test solutions were cloudy at the beginning of the tests, but the sample at 120°F looked less cloudy than the samples at 80 and 100°F. After 9 days, the sediment in 80 and 100°F had largely settled, but the 120°F test was still cloudy with no sedimentation. The 120°F test did not show visible sedimentation until 20 days after the test started. The solution pH was 8.3-8.4 for all the tests. ICP analysis of samples from the tests at the three temperatures shows that after 22 days the solutions have not reached equilibrium concentrations.

The tests were shut down after ≈104 days, but unfortunately, the last samples were taken at 22 days. Because room temperature is not too different from the test temperature for the 80°F test, a sample was taken at 134 days from this solution. Since the higher temperature solutions were allowed to cool, no long-term data were available. Therefore, the concentrations at 100° and 120°F at 134 days were estimated assuming an exponential decrease in the supernate concentrations. The measured values of the aluminum concentration at 22 days for the 80, 100, and 120°F tests, and the measured value at 104 days for the 80°F test and the extrapolated long-term data for the 100 and 120°F tests are plotted as a function of temperature in Figure 16. The predicted aluminum solubility based on data in NaOH and boric acid solutions is also plotted in Figure 16. The measured results are much higher than the predicted results. The reasons for these differences are not clear. Previous small-scale tests with NaOH and boric acid at the pH ranges of 9.5-10.0 indicated good agreement with the predicted aluminum solubility data.[34]

The predicted results show a monotonic increase of aluminum solubility with increasing temperature, but the measured aluminum concentrations in the supernates after 22 days showed the highest concentration at the lowest temperature. Rather than a difference in solubilities, it is likely that the STB solutions can be highly supersaturated at 80°F because the precipitation kinetics are slow. For the 100 and 120°F solutions, the kinetics would be faster so that the observed aluminum concentration in the supernate could be lower than at 80°F. The solubility tests also suggested that the precipitation kinetics are slower at 80°F than at the higher temperatures. The processes could also be made more complex by changes in the kinetics of the transformation of the precipitates from their initial amorphous form to crystalline forms.

Because of the slow kinetics, longer–term tests would be needed to get better quantitative estimates of aluminum solubility by this approach.

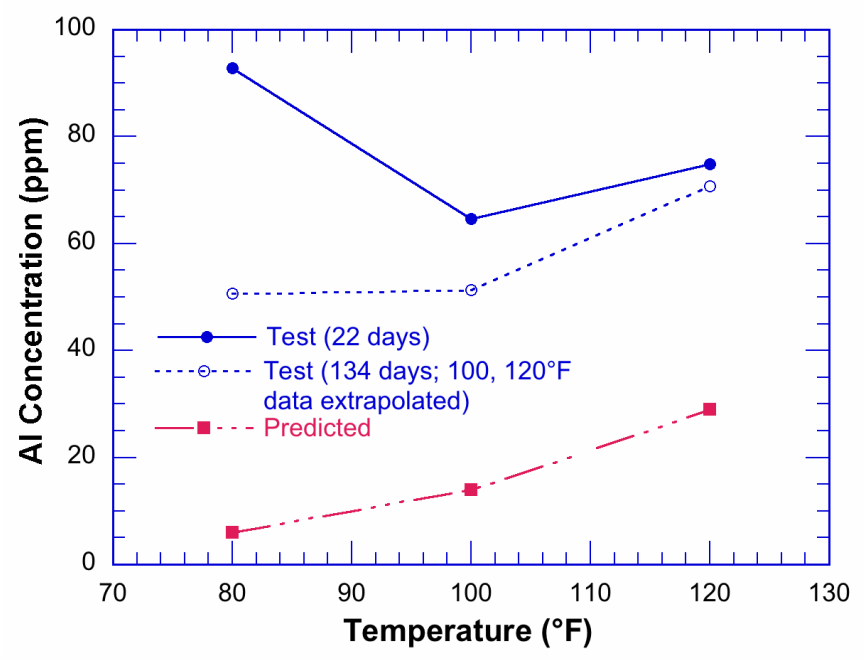

Figure 16.
Measured Al concentrations in the supernate after 22 days from the 80, 100, and 120°F precipitation kinetics tests, 134 day values, and predicted solubility.

Since initial head loss tests with STB buffer showed no pressure drop at 50 ppm dissolved aluminum and a large pressure drop at 100 ppm dissolved aluminum, a second head loss test with a STB buffer (ICET–5–2–B2) was performed to evaluate interim concentrations. The temperature and pressure history during the test is shown in Figure 17. The test was run with 50 ppm aluminum at approximately 80°F for ≈ 21 days. No increase in pressure drop in was observed in the initial test period. After ≈21 days, $Al(NO_3)_3$ was added to increase the nominal dissolved aluminum concentration to 60 ppm. The test was continued for about a day. Then additional $Al(NO_3)_3$ was added to increase the nominal dissolved aluminum concentration to 70 ppm. At the 70 ppm dissolved aluminum concentration, a notable pressure increase occurred even at 120°F. The pressure drops increased as the temperature was dropped to 100°F and then 80°F. The significant increase in pressure drop between 120 and 80°F with 60 ppm is consistent with that expected due to the change in viscosity (≈50%). The initial increase in pressure drop between 120 and 100°F with 70 ppm (≈20%) is also consistent with the change in viscosity (≈20%). However, the continued increase in pressure drop with time at 100°F and 70 ppm is indicative of precipitate formation. The increase in pressure drop as the temperature is decreased from 100 to 80°F (≈30%) is consistent with that expected from viscosity alone (≈30%). The growth in pressure drop with time at 120°F with a nominal 80 ppm Al is clearly faster than with nominal 70 ppm aluminum. The jump in pressure drop as the temperature is decreased from 120 to 100°F with a nominal 80 ppm aluminum (≈40%) is somewhat greater than would be expected from viscosity alone (≈20%). The jump in pressure drop as the temperature is decreased from 100 to 80°F with a nominal 80 ppm aluminum (≈40%) is again somewhat greater than would be expected from viscosity alone (≈30%). The pressure drop increased from ≈0.2 psi at 80°F with a nominal 50 ppm Al to 1.3 psi with 80 ppm Al and the difference was still increasing when the test was terminated.

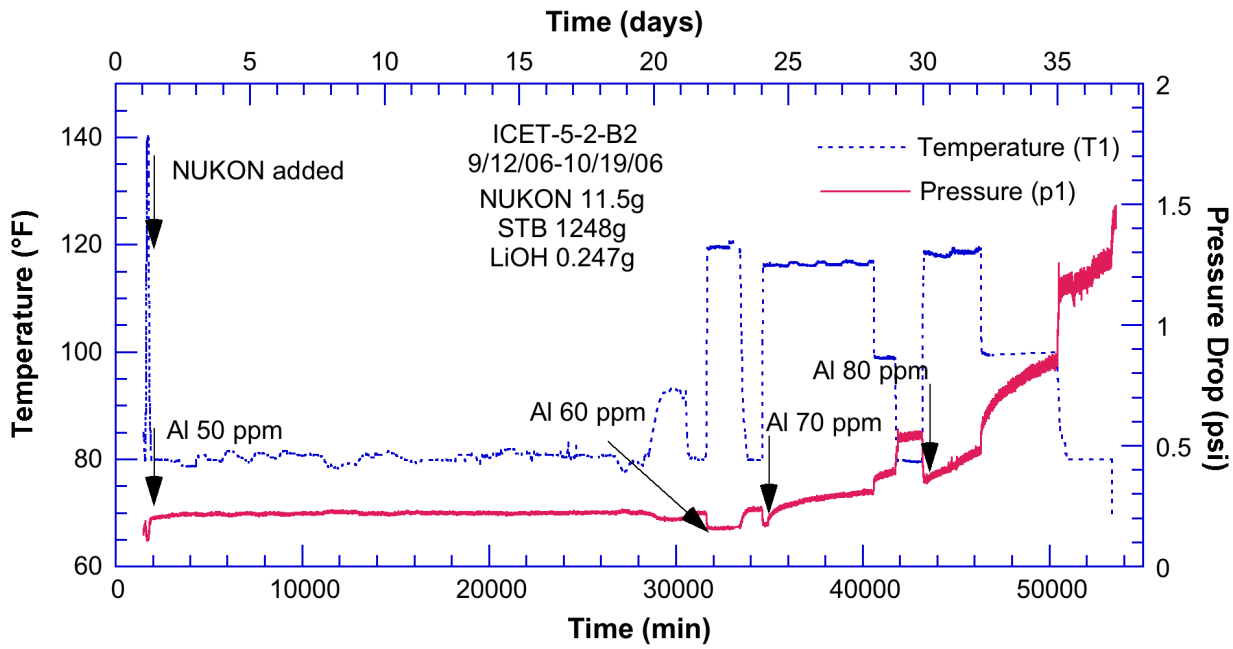

Figure 17. Pressure/Temperature Time History During Loop Test ICET–5–2–B2

3. Comments and Observations

a. ANL prepared $Al(OH)_3$ surrogate according to the WCAP-16530 procedure. It was tentatively concluded that the precipitate had a fine crystalline structure rather than being truly amorphous. However, regardless of structure, the aluminum oxyhydroxide surrogate that was produced was very effective in producing head loss. An amount of surrogate equivalent to the precipitation of 5 ppm dissolved aluminum resulted in immediate blockage of the vertical head loss loop. Results are consistent with industry test results from vertical head loss testing. [15a]

b. ICET-5 Environments [sodium tetraborate buffer (STB)]

- A head loss test with STB (pH ~8.3) with 50 ppm dissolved aluminum showed no measurable head loss increase after 20 days of testing at 80°F. An increase to 70 ppm resulted in the first measurable increase in head loss and an increase to a dissolved aluminum level of 80 ppm produced more significant head loss. Tests confirm results seen in an earlier head loss test at ANL. [15a]
- Equilibrium solubility limit for aluminum in STB and boric acid solutions with pH ≈ 8.3 is less than ≈ 50 ppm, but kinetics of precipitation are very sluggish, especially at temperatures as low as 80°F.[9]

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