

WCAP-16785-NP  
Revision 0

May 2007

# **Evaluation of Additional Inputs to the WCAP-16530-NP Chemical Model**



**WCAP-16785-NP, Revision 0**

## **Evaluation of Additional Inputs to the WCAP-16530-NP Chemical Model**

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**This work performed under PWROG Project Number PA-SEE-0354.**

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## EXECUTIVE SUMMARY

The PWR Owners Group (PWROG) has commissioned this program to evaluate additional plant-specific inputs to the chemical effects model developed in WCAP-16530-NP. The results of this evaluation provide guidance for reducing the precipitate generation through consideration of these additional inputs in the chemical model. Reducing the chemical precipitate formation supports resolution of Generic Safety Issue (GSI) 191 and responses to the Nuclear Regulatory Commission (NRC) Generic Letter (GL) 2004-02.

### *Identification of Plant-Specific Inputs*

For this program, conservatisms were identified in the generic chemical model which could be addressed through the inclusion of more plant-specific inputs. The conservatisms expected to provide the greatest benefit in precipitate reduction were selected by comparing the Integrated Chemical Effects Test (ICET) program results to the model predictions using the ICET conditions. Based on this comparison, the 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.

### *Summary of Test Results*

A phased test plan was developed in which initial scoping tests were performed to estimate the potential benefit of each plant-specific input. Follow-on parametric testing was conducted to fully quantify the effects over the range of temperature and chemistry conditions if the established criteria were met in the scoping tests. The temperature and pH ranges tested were selected to bound the long-term equilibrium conditions applicable for the participating plants. This approach was taken since the majority of the precipitates are formed under these conditions. The specific lower bound values used were selected to enable direct comparison to previous test results.

Significant benefit was observed in the testing of the silicate and phosphate inhibition of aluminum metal corrosion. The presence of 75 ppm silicate was shown to reduce the aluminum release over the range of pH and temperature conditions considered. Similarly, the presence of phosphate from the trisodium phosphate (TSP) buffer reduced the aluminum metal release. However, the reduction in aluminum metal corrosion through consideration of the specific aluminum alloy was shown to be minor, so the parametric testing was not conducted.

Finally, solubility testing of the sodium aluminum silicate and aluminum oxyhydroxide precipitates demonstrated aluminum and silicon concentrations at which these precipitates remained soluble for the range of temperature and chemistry conditions tested. The calcium phosphate precipitate was confirmed to be insoluble even at very low concentrations over the range of temperature and pH evaluated.

### *Conclusions*

Aluminum release rate equations have been provided for reduction of the aluminum metal release due to either the presence of silicate or phosphate in the sump solution. Guidance on the use of these equations has also been provided. Credit may be taken for the silicate and phosphate inhibition effects on both submerged aluminum metal and aluminum metal exposed to the spray. Silicate inhibition occurs in any of the currently used

buffering agents, as well as the alternative buffering agents identified in WCAP-16596-NP; while phosphate inhibition occurs in the presence of the trisodium phosphate buffer.

Guidance is also provided for implementing the solubility limits of the sodium aluminum silicate and aluminum oxyhydroxide precipitates in the determination of precipitate formation. The concentrations of aluminum and silicon available to form precipitate may be reduced according to these solubility limits at the applicable sump temperature.



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## 1.0 REPORT OVERVIEW

The purpose of this report is to evaluate additional plant-specific inputs to the WCAP-16530-NP chemical model. By including certain attributes that are specific to individual plants, the chemical precipitate formation may be decreased by addressing these conservatisms in the generic model. The information contained in this report supports the resolution of GSI-191 through reduction of the potential chemical precipitate formation following a Loss of Coolant Accident (LOCA).

Section 2 of this report presents an introduction to the testing performed to evaluate the additional plant-specific inputs, the background of the concern for chemical effects, and also provides the objective of the program.

Section 3 outlines the Test Plan for evaluating the additional plant-specific inputs to the chemical model, including the scoping tests, criteria which must be met to proceed with additional testing, and the parametric tests.

Section 4 describes changes or additions made to the original Test Plan as outlined in Section 3.

Section 5 presents a summary of the test results performed according to Sections 3 and 4.

Section 6 provides conclusions and recommendations as determined from the testing performed. This section includes guidance on implementation of the test results in using the generic chemical model with the addition of applicable plant-specific inputs.

Finally, Appendix A contains the detailed testing steps and results.

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## 2.0 INTRODUCTION

A chemical model was developed under PWROG PA-SEE-0275 (Reference 2.3-1) and reported in WCAP-16530-NP (Reference 2.3-2) to provide a methodology for predicting plant-specific precipitate formation for use in sump screen performance testing. The model was generated to be applicable to all US Pressurized Water Reactors (PWR). As a consequence, the model does not include certain attributes that are specific to individual plants. The PWROG approved PA-SEE-0354 (Reference 2.3-3) for performance of testing to evaluate the degree of conservatism introduced by these plant-specific conditions. The specific attributes that were evaluated during this program are silicate and phosphate inhibition of aluminum corrosion, the variability in corrosion rates between aluminum alloys, and the solubility of key precipitates.

In order to estimate the degree of conservatism in the generic model, the test conditions used during the individual Integrated Chemical Effects Tests (ICET) program runs (Reference 2.3-4) were used as inputs to the WCAP-16530-NP chemical model, and a comparison of the model predictions to the ICET results was performed. This evaluation demonstrated that under some test conditions the chemical model provides a high degree of conservatism for aluminum corrosion. The results indicate that the high degree of conservatism may be a result of the inhibition of aluminum corrosion by the presence of silicates, as determined from a comparison to the ICET 4 results, or phosphates, as identified by comparing the model predictions to the ICET 2 and 3 results. The production of silicate is a result of dissolution of insulating materials, and thus silicate inhibition is applicable to plants with high fiber loading. Phosphate is present only in plants that use trisodium phosphate as a buffering agent.

Testing performed at Oak Ridge National Laboratory demonstrated that the corrosion rates of aluminum alloys, and the subsequent release of corrosion product, may vary based on the particular aluminum alloy (Reference 2.3-5). Aluminum corrosion rates used in the WCAP-16530-NP model are based on measured corrosion of commercially pure aluminum, Alloy 1100. Thus, inclusion of alloy-specific corrosion rates in the WCAP-16530-NP model may result in lower predicted aluminum releases.

A fourth conservatism relates to the solubility limits for key precipitates. Currently the WCAP-16530-NP model assumes that 100% of the available aluminum forms precipitates and 100% of the available calcium forms precipitates if phosphate is present. In reality, solubility limits dictate the quantity of species remaining in solution. Consequently, some fraction of the dissolved species may not actually form precipitates as conservatively assumed, but may remain in solution. Inclusion of solubility limits in the model could reduce the predicted quantity of precipitates generated.

Solubility limits were not included in the original model since available solubility data on the precipitates suggested they were essentially insoluble over the range of chemistry and temperature conditions of interest. However, this literature data was not developed for the specific chemistry conditions which exist in the Emergency Core Cooling System (ECCS) following a LOCA. Observations of dissolved material remaining in solution from the ICET program support consideration of solubility limits under more prototypical conditions.

## 2.1 BACKGROUND

The conditions in PWR containment buildings are designed to both contain radioactive materials releases and facilitate core cooling in the event of a LOCA. The cooling process requires water discharged from the break and containment spray to be collected in a sump for recirculation by the ECCS and Containment Spray System (CSS). Typically, a containment sump contains one or more screens in series that protect the components of the ECCS and CSS from debris that could be washed into the sump. Fibrous and particulate debris generated by the break could form a debris bed on the screen that would collect particulates, including chemical precipitates. There is a concern that this particulate material could plug the debris bed to an extent that recirculation of coolant to the core would be impeded, leading to inadequate core cooling.

The NRC opened Generic Safety Issue (GSI) 191 (Reference 2.3-6) to address these sump screen plugging concerns. Generic Letter (GL) 2004-02 (Reference 2.3-7), issued in September 2004, identified actions that utilities must take to address the sump blockage issue. The NRC's position is that plants must be able to demonstrate that debris transported to the sump screen after a LOCA will not lead to unacceptable head loss for the recirculation pumps, will not impede flow through the ECCS and CSS, and will not adversely affect the long-term operation of either the ECCS or the CSS. Generic Letter 2004-02 also identifies that plant modifications and associated analyses demonstrating acceptable head loss be implemented by the end of December 2007.

A major difficulty in predicting the pressure drop across a sump screen is presented by the chemical reactions occurring within the post-LOCA environment. Containment materials will dissolve or corrode when exposed to the reactor coolant and spray solutions. Corroded materials can release oxide particulates, and dissolved material can precipitate due to changes in temperature or reactions with other dissolved materials. The effects of precipitated material on head loss are the most difficult to predict. This type of material cannot be currently analyzed using the methodology for head loss calculations provided in NUREG / CR-6224 (Reference 2.3-8).

The ICET program (Reference 2.3-4) and PWROG-sponsored Chemical Effects Bench Testing, documented in WCAP-16530-NP (Reference 2.3-2), evaluated the potential for chemical precipitation given a set of plant conditions post-LOCA. The NRC has performed head loss testing at Argonne National Laboratory (ANL) (Reference 2.3-9) which indicates that these chemical products may contribute significantly to head loss across simulated sump screen debris beds. In addition, ongoing plant-specific replacement sump screen head loss testing has raised a concern for the quantity of chemical precipitates predicted using the WCAP-16530-NP chemical effects spreadsheet.

## 2.2 PROGRAM OBJECTIVE

This program has been developed to evaluate plant-specific inputs for incorporation in the WCAP-16530-NP chemical model spreadsheet. Areas to be considered include the aluminum alloy type, inhibition of aluminum corrosion by either silica or phosphate, and solubility limits for the key chemical precipitates. This program is not intended to change the methodology developed in WCAP-16530-NP, but to provide supplemental information to allow utilities to

reduce conservatisms through the incorporation of plant-specific inputs. As a result, the chemical debris load for sump screen performance testing will be reduced for plants which address these conservatisms. This information is intended to support verification of the adequacy of replacement sump screen designs to provide sufficient flow post-LOCA to maintain core cooling.

## **2.3 REFERENCES**

- 2.3-1 PWROG PA-SEE-0275, "Method for Evaluating Post-Accident Chemical Effects in Containment Sump Fluids," October 2005.
- 2.3-2 WCAP-16530-NP, Revision 0, "Evaluation of Post-Accident Chemical Effects in Containment Sump Fluids to Support GSI-191," February 2006.
- 2.3-3 PA-SEE-0354, "Incorporation of Additional Plant Inputs in the Chemical Effects Spreadsheet," December 2006.
- 2.3-4 J. Dallman, et al., NUREG / CR-6914 / LA-UR-06-3673, "Integrated Chemical Effects Test Program Consolidated Data Report," December 2006.
- 2.3-5 J.C. Griess and A.L. Bacarello, Oak Ridge National Laboratory Report ORNL-TM-2412, Part III, "Design Considerations of Reactor Containment Spray Systems – Part III. The Corrosion of Materials in Spray Solutions," December 1969.
- 2.3-6 Generic Safety Issue 191 (GSI-191), "Assessment of Debris Accumulation on Pressurized Water Reactor (PWR) Sump Performance."
- 2.3-7 NRC Generic Letter 2004-02, "Potential Impact of Debris Blockage on Emergency Recirculation During Design Basis Accidents at Pressurized-Water Reactors, September 13, 2004.
- 2.3-8 NUREG / CR-6224, "Parametric Study of the Potential for BWR ECCS Strainer Blockage due to LOCA Generated Debris," October 1995.
- 2.3-9 J. H. Park, et al., NUREG / CR-6913, "Chemical Effects Head Loss Research in Support of Generic Safety Issue 191," December 2006.

## **3.0 TEST PLAN**

A test plan was developed to evaluate the additional plant-specific inputs to the chemical model spreadsheet (Reference 3.5-1). The purpose of this evaluation is to quantify the reduction in aluminum corrosion for each of the conservatisms identified in the model and to identify the conditions at which inhibition of the aluminum corrosion occurs for implementation in the spreadsheet. Additionally, another intention of this evaluation is to determine the solubility limits for key precipitates under specific chemistry conditions as a function of temperature and pH.

The testing outlined in the test plan below is divided into separate tasks to determine the effects of the four attributes: the aluminum alloy type, inhibition of aluminum corrosion by either silica

or phosphate, and solubility limits for the key chemical precipitates. Initial scoping tests were performed under each task to gauge the degree of influence for each effect. Based on the results of the scoping tests, parametric testing of the attributes was performed to fully quantify the effects over a range of temperature and chemistry conditions.

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. The lower bound temperature for corrosion testing under Tasks 1, 2 and 3 (150°F) was selected to enable direct comparison to results of corrosion tests performed during the alternative buffer program, as reported in WCAP-16596-NP (Reference 3.5-2). Based on the observed temperature dependence of corrosion, the material release rate equations developed from the test data are applicable at all temperatures below 200°F. This approach is consistent with the approach taken in the original WCAP-16530-NP chemical model development.

The lower-bound pH value used for Task 1 was selected as the lowest achievable in 2500 ppm boron with 75 ppm silicon added as sodium silicate (6.5). Similarly, the lower bound pH value used for Task 3 was selected as the lowest value achievable with 2500 ppm boron and a small amount of trisodium phosphate (4.5). The upper bound pH value of 11.0 for Tasks 1 and 2 was selected to bound reported values for all plants, regardless of buffering agent used. The upper bound for Task 3 (phosphate inhibition) was selected to bound reported values for plants using trisodium phosphate buffering.

A temperature of 140°F was selected for solubility testing to provide for direct comparison to the results of testing performed under the ICET program. Based on the observed temperature dependence of solubility for the materials evaluated, the solubility limits determined at 80°F are applicable from 80°F to 140°F, the solubility limits determined at 140°F are applicable from 140°F to 200°F, and the solubility limits determined at 200°F are applicable at any temperature above 200°F.

All testing was performed in the presence of 2500 ppm boron, added as boric acid. This value was selected as prototypical for most plants, and for consistency with previous test programs. Consistent with the approach taken in the original WCAP-16530-NP chemical model, the ICET program and the alternative buffer program, the results from this test program are not considered to be a function of boric acid concentration.

### **3.1 TASK 1: SILICATE INHIBITION OF ALUMINUM CORROSION**

#### **3.1.1 Scoping Test: determination of silicate inhibition threshold at pH 8.0**

1. Prepare 2 liters of stock 2500 ppm boron test solution by adding 28.5735 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 1750 ml of deionized water. Adjust final volume to 2.0 liters.
2. Measure and record the initial mass and dimensions of 10 Aluminum Alloy 1100 coupons (commercially pure aluminum).
3. Perform the following steps for silicon concentrations of 0, 50, 75, 100, and 125 ppm:

- a. Transfer 200 ml of stock boron solution to an Erlenmeyer flask. Add sufficient 40% sodium silicate solution to achieve the desired silicon concentration. Adjust pH to 8.0 as required using sodium hydroxide. Measure and record the pH and final solution volume.
- b. Heat the solution to  $200 \pm 5^\circ\text{F}$  ( $93 \pm 3^\circ\text{C}$ ). Maintain temperature for the duration of the test.
- c. Insert two Alloy 1100 coupons.
- d. After 12 hours, remove one coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
- e. After 24 hours, remove the second coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
- f. Measure and record the pH and aluminum concentration of the final solution.

### **3.1.2 Scoping Test Acceptance Criterion**

Using the chemical model and plant input data from WCAP-16530-NP, develop a histogram for dissolved silicon concentration in operating plants. To generate predicted silicon values, use sump chemistry and temperature conditions expected at 24 hours after event initiation and a six-day (144 hour) run duration. If the model predicts that the silicon threshold determined in the scoping test will be exceeded within one week for a sufficient number of operating plants (as determined by the test engineer), perform parametric testing as described below.

### **3.1.3 Parametric Testing 1.1: determination of silicate inhibition as a function of temperature and pH**

1. Measure and record the initial mass and dimensions of 16 Aluminum Alloy 1100 coupons (commercially pure aluminum).
2. Perform the following steps at  $150^\circ\text{F}$  for pH 8.0, and at  $150^\circ\text{F}$  and  $200^\circ\text{F}$  for pH 6.0 and 11.0:
  - a. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water.
  - b. Add sufficient 40% sodium silicate solution to achieve the threshold silicon concentration determined during the scoping test. Adjust to the desired pH using sodium hydroxide, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
  - c. Heat the solution to the desired temperature. Maintain temperature for the duration of the test.
  - d. Insert two Alloy 1100 coupons.
  - e. After 12 hours, remove one coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale

the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.

- f. After 24 hours, remove the second coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
- g. Measure and record the pH and aluminum concentration of the final solution.

### **3.1.4 Parametric Testing 1.2: determination of effect of phosphate on silicate inhibition**

4. Prepare 2 liters of stock 2500 ppm boron test solution by adding 28.5735 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 1750 ml of deionized water. Adjust final volume to 2.0 liters.
5. Measure and record the initial mass and dimensions of 10 Aluminum Alloy 1100 coupons (commercially pure aluminum).
6. Perform the following steps for silicon concentrations of 0, 50, 75, 100, and 125 ppm:
  - a. Transfer 200 ml of stock boron solution to an Erlenmeyer flask. Add sufficient 40% sodium silicate solution to achieve the desired silicon concentration. Adjust pH to 8.0 as required using trisodium phosphate. Measure and record the pH and final solution volume.
  - b. Heat the solution to  $200 \pm 5^\circ\text{F}$  ( $93 \pm 3^\circ\text{C}$ ). Maintain temperature for the duration of the test.
  - c. Insert two Alloy 1100 coupons.
  - d. After 12 hours, remove one coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
  - e. After 24 hours, remove the second coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
  - f. Measure and record the pH and aluminum concentration of the final solution.

## **3.2 TASK 2: CORROSION RATES OF VARIOUS ALUMINUM ALLOYS**

### **3.2.1 Scoping Test: determination of corrosion rates at pH 8.0**

1. Prepare 1 liter of stock 2500 ppm boron test solution by adding 14.2868 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 900 ml of deionized water. Adjust pH to 8.0 using sodium hydroxide, and then adjust final volume to 1.0 liter. Measure and record the pH of the final solution.
2. Perform the following steps for Aluminum Alloys 3003, 5005 and 6061:
  - a. Measure and record the initial mass and dimensions of two (2) coupons.
  - b. Transfer 225 ml of stock boron solution to an Erlenmeyer flask.

- c. Heat the solution to  $200\pm 5^{\circ}\text{F}$  ( $93\pm 3^{\circ}\text{C}$ ). Maintain temperature for the duration of the test.
- d. Insert two coupons of the desired alloy.
- e. After 12 hours, remove one coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
- f. After 24 hours, remove the second coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
- g. Measure and record the pH and aluminum concentration of the final solution.

### **3.2.2 Scoping Test Acceptance Criterion**

If the corrosion rate for the tested alloy is less than 25% of the rate determined for Alloy 1100 under Task 1 with 0 ppm silicon, perform parametric testing as described below.

### **3.2.3 Parametric Testing: determination of corrosion rates as a function of temperature and pH**

Repeat the steps described for the Task 2 Scoping Test at  $150^{\circ}\text{F}$  for pH 8.0, and at  $150^{\circ}\text{F}$  and  $200^{\circ}\text{F}$  for pH 4.5 and 11.0.

## **3.3 TASK 3: PHOSPHATE INHIBITION OF ALUMINUM CORROSION**

### **3.3.1 Scoping Test: determination of phosphate inhibition at pH 8.0 and $200^{\circ}\text{F}$**

1. Measure and record the initial mass and dimensions of two (2) Aluminum Alloy 1100 coupons.
2. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using trisodium phosphate, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
3. Heat the solution to  $200\pm 5^{\circ}\text{F}$  ( $93\pm 3^{\circ}\text{C}$ ). Maintain temperature for the duration of the test.
4. Insert two Alloy 1100 coupons.
5. After 12 hours, remove one coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
6. After 24 hours, remove the second coupon; rinse with deionized water and allow the coupon to cool to room temperature. Measure and record scaled mass. De-scale the coupon and measure and record descaled mass. Note the formation of any precipitates in the flask.
7. Measure and record the pH and aluminum concentration of the final solution.



### 3.3.2 Scoping Test Acceptance Criterion

If the corrosion rate in the presence of phosphate at pH 8.0/200°F is less than 25% of the rate determined for Alloy 1100 under Task 1 with 0 ppm silicon, perform parametric testing as described below.

### 3.3.3 Parametric Testing: determination of corrosion rates as a function of temperature and pH

Repeat the steps described for the Task 3 Scoping Test at 150°F for pH 8.0, and at 150°F and 200°F for pH 4.5 and 9.0.

## 3.4 TASK 4: SOLUBILITY OF ALUMINUM AND CALCIUM PRECIPITATES

Testing under this task will be performed at 140°F and 200°F to bound equilibrium sump temperatures at which the precipitates are likely to be slightly soluble. Limited testing will be performed at ambient temperature (80°F) to confirm the precipitates are essentially insoluble at low temperature.

### Solubility of sodium aluminum silicate

#### 3.4.1 Scoping Test: sodium aluminum silicate solubility

1. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using sodium hydroxide, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
2. Prepare 100 ml concentrated aluminum solution by adding 13.9900 grams of aluminum nitrate nonahydrate to 90 ml of water. Adjust the pH to 5.0 by careful addition of 50 percent sodium hydroxide solution. No precipitates should be present in the resultant solution. Adjust final volume to 100 ml. This solution will contain 10 mg/ml aluminum.
3. Prepare 100 ml concentrated silicon solution by adding 49.1481 g (41 ml) of 40% sodium silicate solution to 50 ml of water. Adjust the pH to 9.0 by careful addition of 8 molar nitric acid. No precipitates should be present in the resultant solution. Adjust final volume to 100 ml. This solution will contain 31.22 mg/ml silicon.
4. Heat boron solution to 200°F, with stirring.
5. Maintain temperature at 200°F. Simultaneously add concentrated aluminum solution and concentrated silicate solution in 0.5 ml increments until a precipitate is noted. Allow 10 minutes between additions for precipitate formation. Record volume of aluminum and silicon solution added ( $V_a$  and  $V_s$ , respectively). Measure and record pH.

- Determine concentration of sodium aluminum silicate (NAS) at the point of precipitate formation as:

$$\text{NAS}_{\text{pop}}, \text{ ppm} = 9.719 * [(V_a - 0.5) * 10] / [(250 \text{ ml} + (V_a - 0.5 \text{ ml}) + (V_s - 0.5 \text{ ml})) / 1000]$$

### 3.4.2 Scoping Test Acceptance Criterion

If the concentration of NAS at the point of precipitate formation is greater than 25 ppm, perform long term solubility testing at 200°F as described below. Repeat scoping test at 80°F and 140°F, and perform long term solubility testing at 140°F. Also repeat scoping test at 200°F using trisodium phosphate to adjust pH in place of sodium hydroxide in step 1.

### 3.4.3 Long Term Solubility Test: sodium aluminum silicate

- Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using sodium hydroxide, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
- Heat the boron solution to 200°F.
- Add 0.5 ml less than the volume of concentrated aluminum solution and 0.5 ml less than the volume of concentrated silicon solution determined in the scoping test (i.e.,  $(V_a - 0.5)$  ml aluminum solution and  $(V_s - 0.5)$  ml silicon solution). Visually verify that no precipitates are present. Measure and record the pH of the final solution.
- Maintain solution temperature at 200°F for one week (168 hours). Observe the solution daily for precipitate formation. Slowly add demineralized water as necessary to maintain solution volume.

### Solubility of aluminum oxyhydroxide

### 3.4.4 Scoping Test: aluminum oxyhydroxide solubility

- Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using sodium hydroxide, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
- Prepare 100 ml concentrated aluminum solution by adding 13.9900 grams of aluminum nitrate nonahydrate to 90 ml of water. Adjust the pH to 5.0 by careful addition of 50 percent sodium hydroxide solution. No precipitates should be present in the resultant solution. Adjust final volume to 100 ml. This solution will contain 10 mg/ml aluminum.
- Heat boron solution to 200°F, with stirring.
- Maintain temperature at 200°F. Add concentrated aluminum solution in 0.5 ml increments until a precipitate is noted. Allow 10 minutes between additions for precipitate formation. Record volume of aluminum added ( $V_a$ ). Measure and record pH.
- Determine concentration of aluminum oxyhydroxide at the point of precipitate formation as:

$$\text{AlOOH}_{\text{pop}}, \text{ ppm} = 2.22 * [(V_a - 0.5) * 10] / [(250 \text{ ml} + (V_a - 0.5 \text{ ml})) / 1000]$$

### 3.4.5 Scoping Test Acceptance Criterion

If the concentration of  $\text{AlOOH}$  at the point of precipitate formation is greater than 25 ppm, perform long term solubility testing at 200°F as described below. Repeat scoping test at 80°F and 140°F and perform long term solubility testing at 140°F. Also repeat scoping test at 200°F using trisodium phosphate to adjust pH in place of sodium hydroxide in step 1.

### 3.4.6 Long Term Solubility Test: aluminum oxyhydroxide

1. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using sodium hydroxide, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
2. Heat the boron solution to 200°F.
3. Add 0.5 ml less than the volume of concentrated aluminum solution determined in the scoping test (i.e.,  $(V_a - 0.5)$  ml aluminum solution). Visually verify that no precipitates are present. Measure and record the pH of the final solution.
4. Maintain solution temperature at 200°F for one week (168 hours). Observe the solution daily for precipitate formation. Slowly add demineralized water as necessary to maintain solution volume.

#### Solubility of calcium phosphate

### 3.4.7 Scoping Test: calcium phosphate solubility

1. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using trisodium phosphate, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
2. Prepare 100 ml concentrated calcium solution by adding 4.3960 grams of calcium acetate to 90 ml of water. Adjust the pH to 5.0 by careful addition of 50 percent sodium hydroxide solution. No precipitates should be present in the resultant solution. Adjust final volume to 100 ml. This solution will contain 10 mg/ml calcium.
3. Heat boron solution to 200°F, with stirring.
4. Maintain temperature at 200°F. Add concentrated calcium solution in 0.5 ml increments until a precipitate is noted. Allow 10 minutes between additions for precipitate formation. Record volume of calcium added ( $V_c$ ). Measure and record pH.
5. Determine concentration of calcium phosphate at the point of precipitate formation as:

$$\text{CaPO}_{\text{pop}}, \text{ ppm} = 2.58 * [(V_c - 0.5) * 10] / [(250 \text{ ml} + (V_c - 0.5 \text{ ml})) / 1000]$$

### 3.4.8 Scoping Test Acceptance Criterion

If the concentration of calcium phosphate at the point of precipitate formation is greater than 25 ppm, perform long term solubility testing at 200°F as described below. Repeat scoping test at 80°F and 140°F, and perform long term solubility testing at 140°F.

### 3.4.9 Long Term Solubility Test: calcium phosphate

1. Prepare 250 ml of 2500 ppm boron test solution by adding 3.5717 grams boric acid ( $\text{H}_3\text{BO}_3$ ) to about 200 ml of deionized water. Adjust pH to 8.0 using trisodium phosphate, and then adjust final volume to 250 ml. Measure and record the pH of the final solution.
2. Heat the boron solution to 200°F.
3. Add 0.5 ml less than the volume of concentrated calcium solution determined in the scoping test (i.e.,  $(V_c - 0.5)$  ml calcium solution). Visually verify that no precipitates are present. Measure and record the pH of the final solution.
4. Maintain solution temperature at 200°F for one week (168 hours). Observe the solution daily for precipitate formation. Slowly add demineralized water as necessary to maintain solution volume.

## 3.5 REFERENCES

- 3.5-1 LTR-CDME-06-197, "Test Plan: Evaluation of Additional Inputs to the WCAP 16530-NP Chemical Model," January 2007.
- 3.5-2 WCAP-16596-NP, Revision 0, "Evaluation of Alternative Emergency Core Cooling System Buffering Agents," July 2006.

## 4.0 CHANGES TO TEST PLAN

Changes to the original test plan described in Section 3 are outlined below. These changes were made to obtain additional information or as adjustments in the testing approach due to problems encountered in implementation of the original test methods.

1. Several minor changes were made to the original test plan to further elucidate the solubility behavior of surrogates in Task 4. These changes included:
  - Increased observation time from 7 days to 30 days in the long-term solubility tests.
  - Added sensitivity tests to evaluate the effect of perturbations in pH and temperature on precipitate solubility.
  - Performed tests in which inert material (stainless steel powder) was added to aluminum-containing solutions to determine whether addition of nucleation sites would encourage precipitation. Also performed test in which aluminum oxyhydroxide precipitate was added to an aluminum containing solution to determine whether seed material would encourage precipitation.
2. Based on the initial results of long-term solubility tests for aluminum oxyhydroxide and sodium aluminum silicate in trisodium phosphate, it was determined that the ten minute observation period was not sufficient to gauge the short-term solubility of these

precipitates. The test plan was revised to determine short-term solubility by preparation of solutions with varying concentrations of aluminum or aluminum plus silicon.

3. It was determined that adequate control of pH could not be maintained using aluminum nitrate as the aluminum source for the aluminum oxyhydroxide solubility tests. Therefore, sodium aluminate was substituted as the aluminum source.
4. The lower pH value for testing of silicate inhibition in Tasks 1.1 and 1.2 was changed to 6.5 since it was not possible to achieve a pH of 6.0 using sodium silicate to achieve a 75 ppm silicon concentration in 2500 ppm boron added as boric acid.

## **5.0 SUMMARY OF TEST RESULTS**

Tests to evaluate the additional plant-specific inputs to the WCAP-16530-NP model were performed at Fauske & Associates, Inc. from January to March 2007 (Reference 5.5-1) according to the Test Plan presented in Sections 3 and 4 above. An interim report was issued providing initial results from this testing (Reference 5.5-2). The results of the tests performed for each of the tasks are presented below.

### **5.1 TASK 1: SILICATE INHIBITION OF ALUMINUM CORROSION**

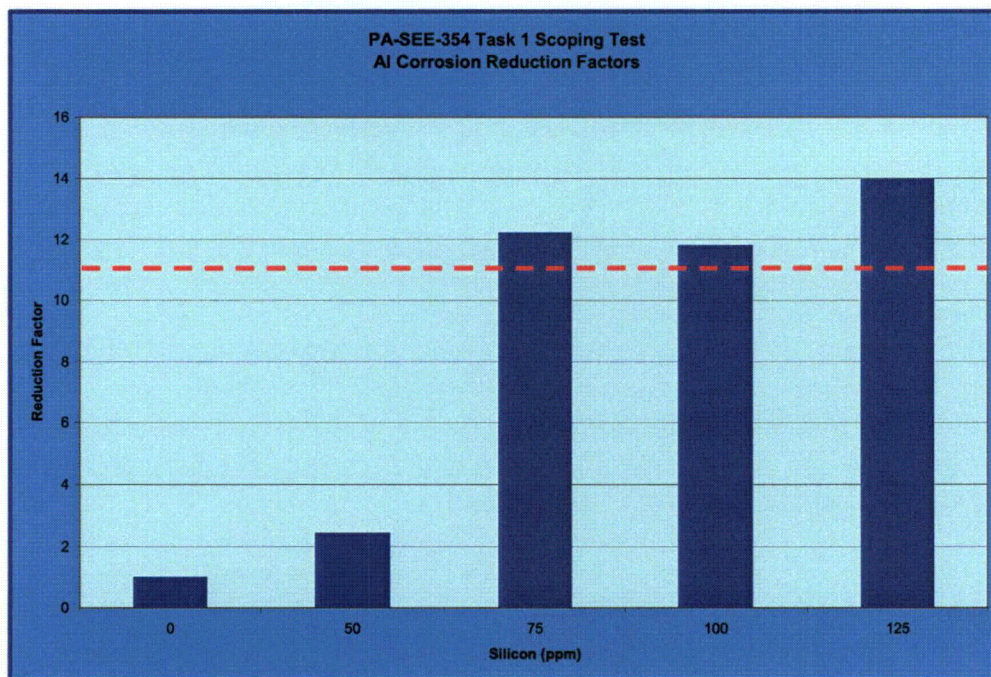
#### **5.1.1 Task 1.0 Scoping Test Results**

In the scoping test for Task 1, Silicate Inhibition, aluminum Alloy 1100 coupons were exposed to sodium hydroxide-buffered boric acid solutions containing silicon at concentrations of 0, 50, 75, 100 and 125 ppm. Silicon was added as sodium silicate. The initial solution pH was adjusted to 8.0, the boric acid concentration was 2500 ppm (as boron), and the solution temperature was maintained at 200°F for the duration of the exposure. Coupons were removed after 12 hours and at the end of the 24-hour test exposure. The coupons were evaluated for weight loss before and after removal of the deposit developed on the coupon surface during the exposure. The test solutions were analyzed for pH and dissolved aluminum.

The results of the Task 1 scoping test confirm that silicate inhibits corrosion of aluminum (Table 5-1). Dissolved aluminum was reduced from 202 ppm in the no silicon case to 1.6 ppm with 75 ppm silicon, or a reduction factor of 126. Figure 5-1 provides a summary of the reduction factors based on weight-change data for the coupons. The reduction factors based on coupon data are lower due to formation of a protective silicate corrosion film on the coupons. Thus, reduction factors based on dissolved aluminum values would be expected to be much higher. The test results also show that limited inhibition of aluminum corrosion is obtained at 50 ppm silicon (corrosion reduction factor of 2.4 and aluminum release reduction factor of 1.7).

**Table 5-1: Summary of Corrosion Results for Silicate Inhibition Scoping Test**

Silicon (ppm)	Exposure Time (hr)	Corrosion ( $\mu\text{m}$ )		Corrosion ( $\text{mg}/\text{m}^2/\text{min}$ )		Dissolved Aluminum (ppm)
		Scaled	De-Scaled	Scaled	De-Scaled	
0	12	4.47	5.92	17.04	22.58	202
	24	2.52	4.98	4.80	9.51	
50	12	1.84	2.55	7.01	9.73	116
	24	0.67	3.20	1.27	6.08	
75	12	0.37	1.72	1.39	6.54	1.6
	24	0.02	0.88	0.03	1.66	
100	12	0.38	1.28	1.44	4.87	0.3
	24	0.05	0.93	0.09	1.76	
125	12	0.32	1.14	1.21	4.28	0.3
	24	0.21	1.00	0.39	1.90	

**Figure 5-1: Reduction Factors as a Function of Silicon Concentration Determined from Scaled Corrosion Coupons during Silicate Inhibition Scoping Test**

### 5.1.2 Task 1.1 Test Results

Under Task 1.1, the degree of silicate inhibition obtained at the 75 ppm threshold value was determined over a range of pH values at temperatures of 150 and 200°F. In all cases, pH was adjusted with sodium hydroxide and the solutions contained 2500 ppm boron, added as boric acid. The results of these tests, summarized in Table 5-2, show that silicate inhibits aluminum corrosion over the range of temperatures and pH values evaluated. Figures 5-2 and 5-3 show the aluminum release measured in the presence of 75 ppm silicon relative to that predicted by the WCAP-16530-NP chemical model.

Based on the corrosion and aluminum release measured in Task 1.1, a silicate-inhibited release rate equation may be obtained using the methodology presented in WCAP-16530-NP. This equation was developed using a multivariate regression analysis to determine the constants by fitting the aluminum release data in Table 5-2 to the functional form shown below. This equation is valid over a pH range of 6.55 to 11.0 and at temperatures below 200°F. Extension of the results to temperatures below 150°F is justified by the fact that corrosion rates are lower and more predictable at more moderate temperatures. The original WCAP-16530-NP aluminum release equation must be used outside these conditions.

$$\text{Log}_{10}(\text{RR}) = 51.15271 - 12.8577 * (1000/T) + 0.260448 * (\text{pH})^2 - 11.3727 * (\text{pH} * T/1000)$$

Where RR is the aluminum release rate in mg/m<sup>2</sup>/min, pH is corrected to 25°C and T is the temperature in Kelvin.

**Table 5-2: Aluminum Corrosion and Aluminum Release in 75 ppm Silicon Determined in Task 1-1**

pH	12-Hour Descaled Corrosion (μm)		Dissolved Aluminum (ppm)		Aluminum Release (mg/m <sup>2</sup> /min)	
	150°F	200°F	150°F	200°F	150°F	200°F
6.55	0.90	1.35	0.71	6.44	0.55	0.38
8.0	0.86	1.72	0.05	1.6	0.16	0.51
11	39.07	125.47	1414	1200	91.50	193.01

### 5.1.3 Task 1.2 Test Results

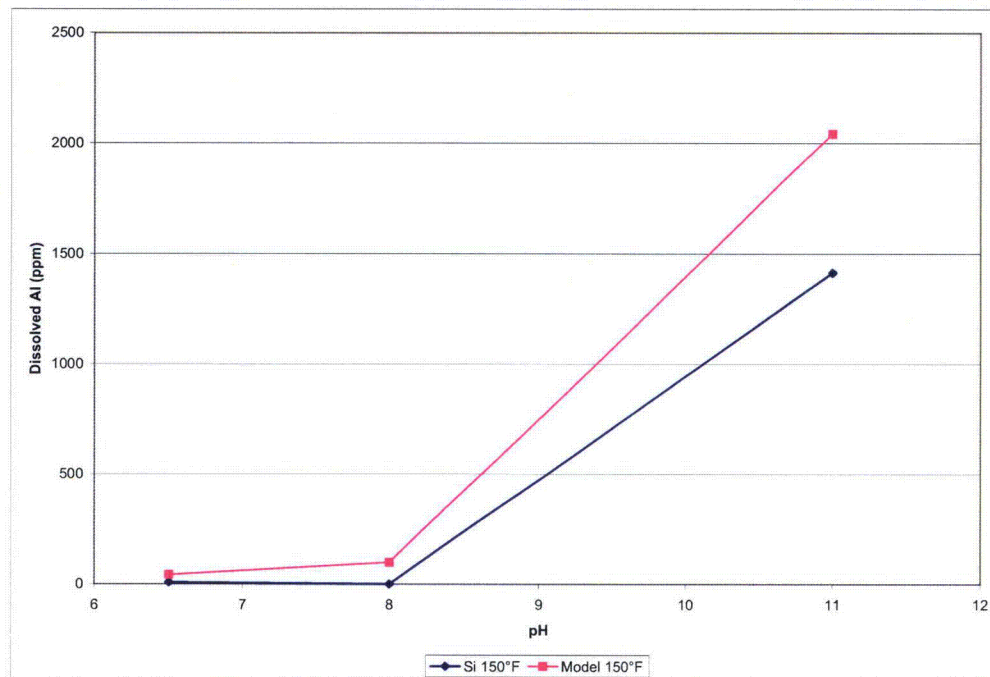
Under Task 1.2, the effect on silicate inhibition from using trisodium phosphate for pH adjustment was evaluated. In the test, aluminum Alloy 1100 coupons were exposed to trisodium phosphate-buffered boric acid solutions containing silicon at concentrations of 0, 50, 75, 100 and 125 ppm. The initial solution pH was adjusted to 8.0, the boric acid concentration was 2500 ppm (as boron), and the solution temperature was maintained at 200°F for the duration of the exposure.

The results of these tests showed that silicate inhibition of aluminum corrosion occurs to the same degree, and at the same 75 ppm threshold value, when trisodium phosphate is used as the



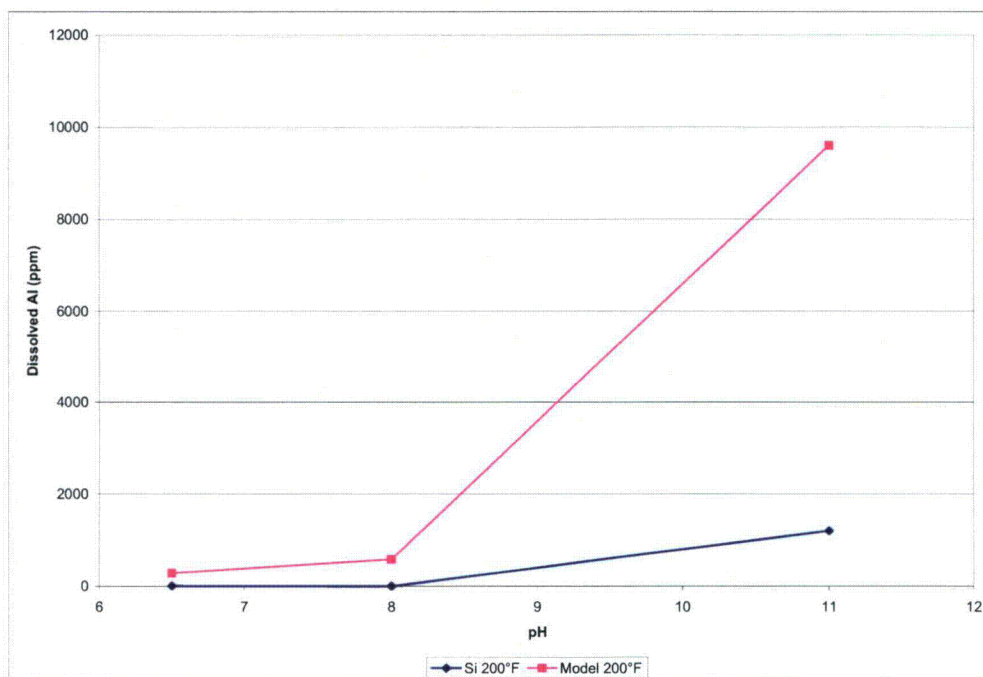
buffering agent. The aluminum release was reduced from 56.6 ppm for the no silicon case to 0.6 ppm for the 75 ppm silicon sample, a factor of 94 reduction in aluminum release ( $56.6/0.6 = 94$ ).

**Figure 5-2: Aluminum Release in 75 ppm Silicon versus WCAP-16530 Model Prediction at 150°F**



**Figure 5-3: Aluminum Release in 75 ppm Silicon versus WCAP-16530 Model Prediction at 200°F**





## 5.2 TASK 2: COMPARATIVE CORROSION RATES OF ALUMINUM ALLOYS

In the scoping test for Task 2, Aluminum Alloy Corrosion Rates, coupons of aluminum alloys 3003, 5005 and 6061 were exposed to sodium hydroxide-buffered boric acid solutions. The initial solution pH was adjusted to 8.0, the boric acid concentration was 2500 ppm (as boron), and the solution temperature was maintained at 200°F for the duration of the exposure. Coupons were removed after 12 hours and at the end of the 24-hour test exposure. The coupons were evaluated for weight loss before and after removal of the deposit developed on the coupon surface during the exposure. The test solutions were analyzed for pH and dissolved aluminum. The acceptance criterion for the scoping test was that the rate of corrosion for the alloy was 25 percent or less than the rate determined for commercially pure aluminum.

The Task 2 scoping test results show that the corrosion rates of the alloys tested were only marginally less than the corrosion rate of commercially pure aluminum (Table 5-3). Based on these test results, additional testing of aluminum alloy corrosion rates is not considered warranted.

This conclusion is based on the observation that corrosion of the alloys tested was from 68 to 82 percent of the corrosion measured on Alloy 1100 coupons. These results are based on weight loss prior to de-scaling for the 12-hour specimens. The de-scaled corrosion of the alloys is 90 to 102 percent of the corrosion measured for commercially pure aluminum. Dissolved aluminum in the test solutions for the alloys range from 79.2 percent to 92.1 percent of that measured for the Alloy 1100 control. Given that none of the alloys tested is the only type of aluminum present at any of the participating plants, the net reduction in aluminum precipitate generation that would result from including alloy-specific corrosion rates in the chemical model would be low.

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

Coupon	Exposure Time (hours)	Corrosion ( $\mu\text{m}$ )		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	

### 5.3 TASK 3: PHOSPHATE INHIBITION OF ALUMINUM CORROSION

In the scoping test for Task 3, Phosphate Inhibition, coupons of commercially pure aluminum (Alloy 1100) were exposed to a trisodium phosphate-buffered boric acid solution. The initial solution pH was adjusted to 8.0, the boric acid concentration was 2500 ppm (as boron), and the solution temperature was maintained at 200°F for the duration of the exposure. Coupons were removed after 12 hours and at the end of the 24-hour test exposure. The coupons were evaluated for weight loss before and after removal of the deposit developed on the coupon surface during the exposure. The test solutions were analyzed for pH and dissolved aluminum. The acceptance criterion for the scoping test was that the rate of corrosion in the presence of phosphate was 25 percent or less than the rate determined without phosphate present.

The results of the Task 3 scoping test confirm that phosphate inhibits corrosion of aluminum (Table 5-4). As shown in Table 5-4, aluminum corrosion is reduced by a factor of 2.8 in the presence of phosphate under the conditions evaluated in the scoping test, and aluminum release is reduced by a factor of 3.6.

**Table 5-4: Summary of Corrosion Results for Phosphate Inhibition Scoping Test**

Coupon	12-Hour Descaled Corrosion ( $\mu\text{m}$ )	Corrosion Reduction Factor (w/ respect to no phosphate)	Percentage of Corrosion without Phosphate	Aluminum Release (ppm)	Al Release Reduction Factor (w/ respect to no phosphate)
1100 Control-1	5.92	NA	NA	202	NA
1100 Phosphate-1	2.14	2.8	36	56.6	3.6

### 5.3.1 Task 3.1 Results

Under Task 3.1, the degree of phosphate inhibition obtained was determined over a range of pH values at temperatures of 150 and 200°F. In all cases, pH was adjusted with trisodium phosphate and the solutions contained 2500 ppm boron, added as boric acid. The results of these tests, summarized in Table 5-5, show that phosphate inhibits aluminum corrosion over the range of temperatures and pH values evaluated. Figures 5-4 and 5-5 show the aluminum release measured phosphate-buffered solutions relative to that predicted by the WCAP-16530-NP chemical model for sodium hydroxide-buffered solutions.

Based on the corrosion and aluminum release measured in Task 3.1, a phosphate-inhibited release rate equation may be obtained using the methodology presented in WCAP-16530-NP. This equation was developed using a multivariate regression analysis to determine the constants by fitting the aluminum release data in Table 5-5 to the functional form shown below. This equation is valid over a pH range of 4.5 to 9.0 and at temperatures below 200°F. Extension of the results to temperatures below 150°F is justified by the fact that corrosion rates are lower and more predictable at more moderate temperatures. The original WCAP-16530-NP aluminum release equation must be used outside these conditions.

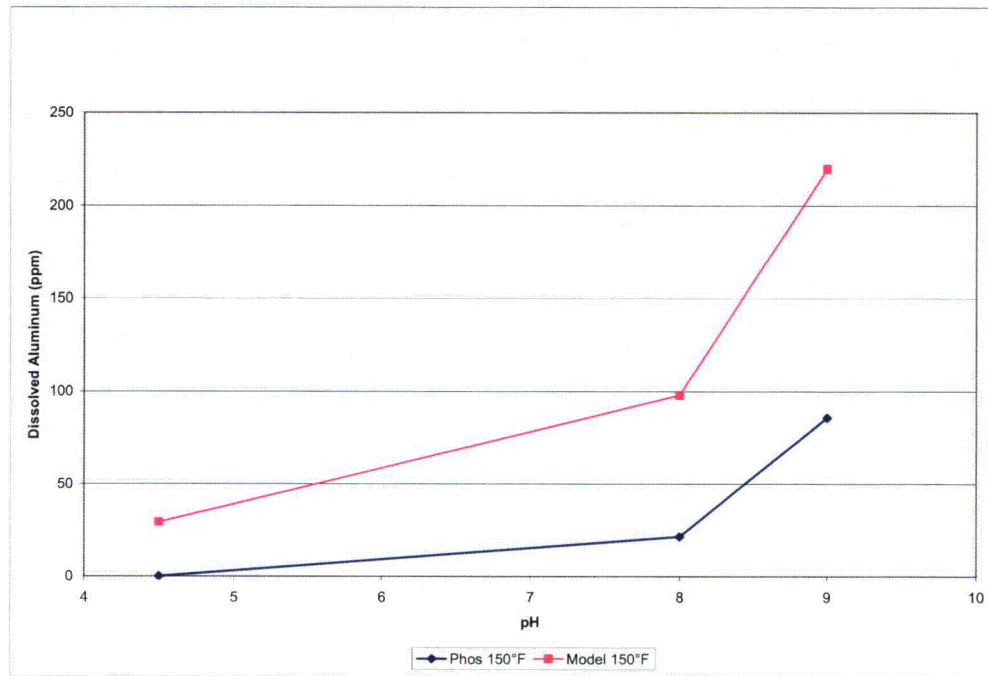
$$\text{Log}_{10}(\text{RR}) = -9.08291 + 1.086785 * (1000/T) - 0.02243 * (\text{pH})^2 + 2.798738 * (\text{pH} * T/1000)$$

Where RR is the aluminum release rate in mg/m<sup>2</sup>/min, pH is corrected to 25°C and T is the temperature in Kelvin.

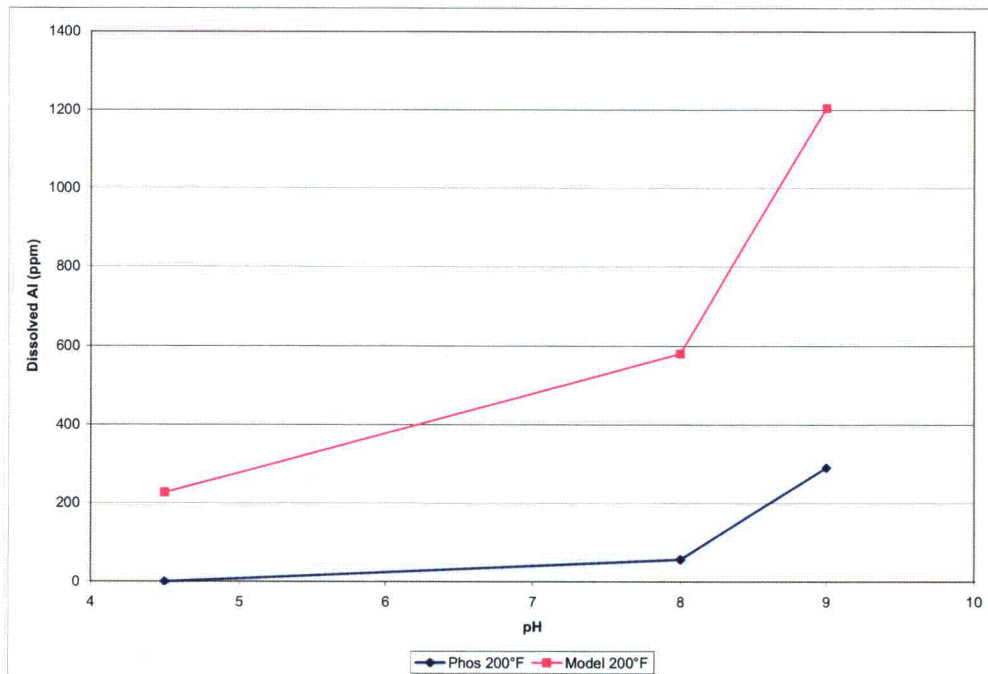
**Table 5-5: Aluminum Corrosion and Aluminum Release in TSP Determined in Task 3-1**

pH	12-Hour Descaled Corrosion (μm)		Dissolved Aluminum (ppm)		Aluminum Release (mg/m <sup>2</sup> /min)	
	150°F	200°F	150°F	200°F	150°F	200°F
4.5	1.12	1.08	0.11	0	0.13	0.27
8.0	1.29	2.14	21.5	56.6	0.79	2.45
9.0	2.61	6.53	85.9	291	4.08	15.67

**Figure 5-4: Aluminum Release in Trisodium Phosphate versus WCAP-16530 Model Prediction at 150°F**



**Figure 5-5: Aluminum Release in Trisodium Phosphate versus WCAP-16530 Model Prediction at 200°F**



## 5.4 TASK 4: SOLUBILITY OF ALUMINUM AND CALCIUM PRECIPITATES

Under this task, the solubility of the three key chemical precipitates was determined as a function of temperature. The precipitates included sodium aluminum silicate, aluminum oxyhydroxide and calcium phosphate. For each precipitate, a scoping test was performed in which incremental additions were made until a visually observable precipitate was formed. Based on the results of the short term scoping test, long-term solubility testing was performed. The scoping tests were performed at 200°F in a 2500 ppm boric acid solution. The pH was adjusted to 8.0 using either sodium hydroxide, trisodium phosphate or sodium tetraborate for the aluminum precipitates and trisodium phosphate for the calcium precipitate.

### 5.4.1 Task 4.1 Results: Solubility of Sodium Aluminum Silicate

In the scoping test for sodium aluminum silicate solubility, aluminum and silicon were incrementally added in a stoichiometric ratio (approximately 3 parts silicon for 1 part aluminum). The scoping test for sodium aluminum silicate showed that no precipitation occurs at 20 ppm aluminum and 60 ppm silicon over the 10 minute observation period. A precipitate immediately formed at 40 ppm aluminum/119 ppm silicon. Based on this result, additional short term testing was performed at 140°F and 80°F. These tests showed that at the lower temperatures no precipitates formed at 40 ppm aluminum/119 ppm silicon, but a precipitate formed immediately at 60 ppm aluminum/178 ppm silicon at both temperatures. A final short-term test was performed for sodium aluminum silicate precipitation at 200°F using trisodium phosphate buffering rather than sodium hydroxide. This test showed no precipitate formation at 79 ppm aluminum/236 ppm silicon, and immediate precipitate formation at 99 ppm aluminum/294 ppm silicon.

Based on the short-term solubility test results, long-term tests were performed in which solutions were prepared with aluminum and silicon at concentrations that did not form precipitates in the short-term tests. These solutions were observed daily for indication of precipitate formation. Precipitates were observed in all of the sodium hydroxide buffered solutions, with a time to onset of precipitate formation from 1 hour to six days. Based on these observations, sodium aluminum silicate should continue to be treated as insoluble in WCAP-16530-NP model calculations. This solubility limit is applicable to all buffering agents other than trisodium phosphate. This includes sodium hydroxide, sodium tetraborate and the alternative buffering agents identified in WCAP - 16596.

Long-term observation of a trisodium phosphate-buffered solutions containing 79 ppm aluminum and 236 ppm silicon showed precipitate formation within 24 hours. Solutions containing 10, 20, 30, 40 and 50 ppm aluminum, with corresponding concentrations of silicon were then prepared for additional long-term observation. No precipitates were observed to form in trisodium phosphate-buffered solutions containing up to 40 ppm aluminum during a 30-day observation period.

Sensitivity testing was performed on trisodium phosphate buffered solutions containing 30 and 40 ppm aluminum to determine whether perturbations to temperature or pH would cause precipitate formation. This testing showed that perturbations to the system temperature from 200°F to 80°F and back to 200°F over a four-day period did not cause precipitate formation. Likewise,

adjustment of the pH downward from 8.0 to 7.0 and upward from 8.0 to 9.0 did not cause precipitate formation.

Based on these results, the solubility limit of sodium aluminum silicate in trisodium phosphate-buffered solutions at 140 to 200°F is 40 ppm aluminum and 119 ppm silicon. Thus, under these conditions, sodium aluminum silicate will not precipitate until the aluminum concentration is above 40 ppm.

#### **5.4.2 Task 4.2 Results: Solubility of Aluminum Oxyhydroxide**

Based on the results of the long-term solubility test for sodium aluminum silicate and limited initial short-term tests for aluminum oxyhydroxide precipitation, the test methodology for determination of the short-term solubility threshold for aluminum oxyhydroxide was revised. In the scoping test, solutions of varying concentration of aluminum were prepared and maintained at the specified test temperature (140 or 200°F).

Solutions containing 24, 50, 98 and 150 ppm aluminum were prepared for long-term observation at 200°F, and solutions containing 10, 20, 30, 40 and 50 ppm aluminum were prepared for long-term observation at 140°F. At 200°F, no precipitates were observed to form in solutions containing up to 98 ppm aluminum during a 30-day observation period. At 140°F, no precipitates were observed to form in solutions containing up to 40 ppm aluminum during a 30-day observation period.

Sensitivity testing was performed on solutions containing 40 and 98 ppm aluminum to determine whether perturbations to temperature or pH would cause precipitate formation. This testing showed that perturbations to the system temperature from 200°F to 80°F and back to 200°F over a four-day period did not cause precipitate formation. Likewise, adjustment of the pH downward from 8.0 to 7.0 and upward from 8.0 to 9.0 did not cause precipitate formation.

Based on these results, the solubility limit of aluminum oxyhydroxide solutions at 140°F to 200°F is 40 ppm aluminum and at 200°F or above is 98 ppm aluminum. Thus, under these conditions, aluminum oxyhydroxide will not precipitate until the aluminum concentration is above the respective solubility limits (i.e., 40 or 98 ppm). This solubility limit is applicable to all buffering agents currently in use, as well as the alternative buffering agents identified in WCAP-16596.

#### **5.4.3 Task 4.3 Results: Solubility of Calcium Phosphate**

As with the initial scoping test for sodium aluminum silicate, incremental additions of calcium were made to a 2500 ppm boron solution buffered to pH 8.0 with trisodium phosphate. In tests performed at both 140°F and 200°F, a precipitate formed upon the first addition of calcium to the solutions. Based on these results, calcium phosphate should continue to be treated as insoluble in WCAP-16530-NP model calculations.

## 5.5 REFERENCES

- 5.5-1 FAI/07-48, Revision 0, "Evaluation of Additional Inputs to the WCAP 16530-NP Chemical Model," May 2007.
- 5.5-2 LTR-CDME-07-41, Rev. 0, "PWROG PA-SEE-0354 Additional Inputs to the WCAP 16530-NP Chemical Model Interim Report 1," March 2007.
- 5.5-3 LTR-CDME-07-97, Rev. 1, "WCAP 16785-P Aluminum Release Equations," May 2007.

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

The following recommendations are made based on the results of the testing presented in Section 5:

1. For plants with predicted silicon concentrations in excess of the 75 ppm threshold, the aluminum release rate equation below may be used once the silicon concentration reaches a specified threshold value. As noted in Section 5.1, this equation is valid over a pH range of 6.55 to 11.0 and at temperatures below 200°F. Outside of these conditions, the original WCAP-16530-NP aluminum release equation should continue to be used. As also noted in Section 5.1, and consistent with the original WCAP-16530-NP chemical model, the validity of the equation is independent of the buffering agent used.

$$\text{Log}_{10}(\text{RR}) = 51.15271 - 12.8577 * (1000/T) + 0.260448 * (\text{pH})^2 - 11.3727 * (\text{pH} * T/1000)$$

To account for conservatism in the quantity of silicon predicted to be released by the WCAP-16530-NP chemical model, consideration may be given to use of a silicon threshold higher than the 75 ppm value determined in the Task 1 testing.

Based on the results of Task 1 testing, limited silicate inhibition may be credited at dissolved silicon values from 50 to 75 ppm. The results suggest a factor of 2.0 reduction in aluminum release may be credited at moderate temperatures (below 200°F) and pH (7.0 to 9.0).

2. Based on the results of the evaluation of the corrosion rates of aluminum alloys tested under Task 2, relative to the corrosion rate of commercially pure aluminum (Alloy 1100), there is no benefit to the development and implementation of alloy-specific aluminum release rate equations.

This conclusion is based on the observation that corrosion of the alloys tested was from 68 to 82 percent of the corrosion measured on Alloy 1100 coupons and dissolved aluminum in the test solutions for the alloys range from 79.2 percent to 92.1 percent of that measured for the Alloy 1100 control. Given that none of the alloys tested is the only type of aluminum present at any of the participating plants, the net reduction in aluminum

precipitate generation that would result from including alloy-specific corrosion rates in the chemical model would be low.

As an example of the effect on precipitate generation if the preliminary corrosion rates of specific alloys were used, consider a TSP plant with 10,000 ft<sup>2</sup> total aluminum metal, 10 percent of which is submerged, 5,000 ft<sup>2</sup> exposed concrete and 1,500 ft<sup>3</sup> NUKON insulation. Using the current model with the aluminum corrosion rate based on Alloy 1100 data results in a predicted aluminum release of 15.8 kilograms, and a total precipitate generation of 202.2 kilograms. If 50 percent of the submerged aluminum is positively identified as Alloy 3003 and the Alloy 3003 corrosion rate is used for this fraction of the aluminum, the predicted aluminum release is reduced to 14.1 kilograms and the total precipitate generation is reduced to 186.1 kilograms. This is a net reduction in precipitate generation of only 8 percent.

Although the results of the Task 2 scoping test did not support performance of additional parametric testing, the results for specific alloys may be used to calculate reduced aluminum release under moderate temperature and pH conditions (temperature less than 200°F and pH from 7.0 to 9.0).

3. For plants that use trisodium phosphate buffering, the aluminum release rate equation below may be used once the temperature is below 200°F. As noted in Section 5.3, this equation is valid over a pH range of 4.5 to 9.0 and a temperature range of 150 to 200°F.

$$\text{Log}_{10}(\text{RR}) = -9.08291 + 1.086785 * (1000/T) - 0.02243 * (\text{pH})^2 + 2.798738 * (\text{pH} * T/1000)$$

4. The effects of silicate inhibition (item 1) and phosphate inhibition (item 3) are applicable to both submerged and non-submerged aluminum metal. Both silicate and phosphate form conversion coatings (i.e., protective aluminum silicate or aluminum phosphate) that impart corrosion resistance. Both spray and bath applications of such coatings are common industrial practices for preparation of metal components (see Reference 6.1-1). In these applications, the spray duration is typically one hour or less, so inhibition of non-submerged aluminum metal corrosion is applicable as long as the sprays have been on for one hour.
5. Sodium aluminum silicate should continue to be treated as insoluble in sodium hydroxide, sodium tetraborate and sodium metaborate buffered solutions.
6. The solubility limit of sodium aluminum silicate in trisodium phosphate-buffered solutions is 40 ppm aluminum, with a corresponding silicon concentration of 119 ppm. This limit is valid at temperatures above 140°F. To implement this limit in WCAP-16530-NP chemical model calculations, the aluminum concentration may be reduced by 40 ppm and the silicon concentration may be reduced by 119 ppm prior to calculation of the quantity of sodium aluminum silicate generated.
7. The solubility limit of aluminum oxyhydroxide is 40 ppm aluminum. This limit is valid at temperatures from 140°F to 200°F. Above 200°F, the solubility limit is 98 ppm



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aluminum. To implement this limit in WCAP-16530-NP chemical model calculations, the aluminum concentration may be reduced by 40 ppm prior to calculation of the quantity of aluminum oxyhydroxide generated. This solubility limit is applicable in all currently used buffering agents as well as the alternative buffering agents identified in WCAP-16596.

8. Calcium phosphate should continue to be treated as insoluble in trisodium phosphate buffered solutions.

## **6.1 REFERENCES**

- 6.1-1 Davis, J. R. (editor), Surface Engineering for Corrosion and Wear Resistance, Woodhead Publishing, 2001.

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## **Appendix A: Test Results**

## **TASK 1: SILICATE INHIBITION OF ALUMINUM CORROSION**

### **Scoping Test: Determination of Silicate Inhibition Threshold at pH of 8.0**

- 1.4 liters of stock 2500 ppm boron test solution was prepared by adding 20.1152 grams of boric acid to about 1200 ml of deionized water. The final volume was adjusted to 1.4 liters. Based on the mass of boric acid used, the actual boron concentration was 2512 ppm.
- The initial mass and dimensions of 10 Aluminum Alloy 1100 coupons were measured. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	7.1230	50.9	19.0	2.9	9.6
2	7.1628	50.9	19.1	2.9	9.6
3	7.1931	51.0	19.1	2.9	9.6
4	7.1500	51.0	19.1	2.9	9.6
5	7.1531	50.9	19.1	2.9	9.6
6	7.1493	51.0	19.1	2.9	9.6
7	7.2150	51.0	19.2	2.9	9.6
8	7.1253	50.9	19.1	2.9	9.6
9	7.1214	50.9	19.2	2.9	9.6
10	7.1559	50.9	19.2	2.9	9.6

- 200 ml of stock boron solution was transferred to an Erlenmeyer flask. Sufficient 40% sodium silicate solution was added to achieve the desired silicon concentration. The pH was then adjusted to 8.0 using sodium hydroxide. The table below shows details of each sodium silicate solution.

Solution ID	Mass of 40% Na <sub>4</sub> O <sub>4</sub> Si [g]	pH After Addition of 40% Na <sub>4</sub> O <sub>4</sub> Si	pH After NaOH Adjustment	Final Volume [ml]	Silicon Concentration [ppm]
0 ppm Si	0	4.55	8.10	201	0
50 ppm Si	0.1642	6.42	8.02	201	49.9
75 ppm Si	0.2595	6.67	7.99	201	78.8
100 ppm Si	0.3389	6.81	8.01	201	102.9
125 ppm Si	0.4279	6.88	7.99	201	130.0

- Each solution was placed into an oven at 93°C. This temperature was maintained throughout the duration of the test.
- 2 of the aforementioned aluminum coupons were placed in each silicate solution. Coupons 1 and 2 were placed in the solution containing 0 ppm Si. Coupons 3 and 4 were

placed in the solution containing 50 ppm Si. Coupons 5 and 6 were placed in the solution containing 75 ppm Si. Coupons 7 and 8 were placed in the solution containing 100 ppm Si. Finally, coupons 9 and 10 were placed in the solution containing 125 ppm Si.

6. After 12 hours, the odd numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
0 ppm Si	1	7.0950	7.0859	Yes
50 ppm Si	3	7.1815	7.1770	No
75 ppm Si	5	7.1508	7.1423	No
100 ppm Si	7	7.2126	7.2069	No
125 ppm Si	9	7.1194	7.1143	No

Pictures of these coupons were taken both before descaling. They are shown in Figure 1-1.

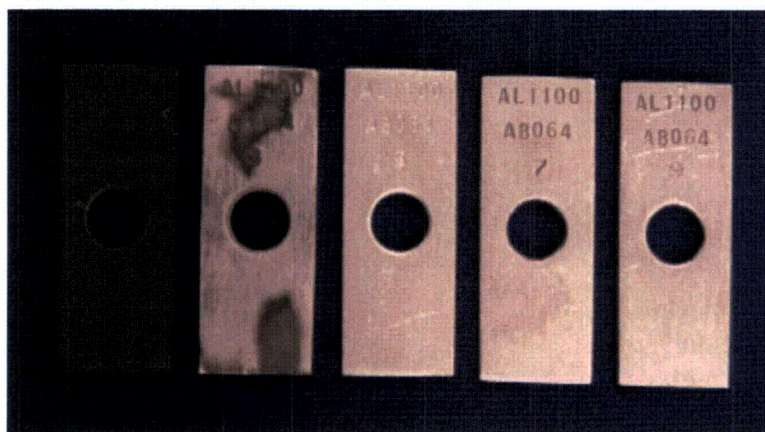


Figure 1-1: Task 1 scoping test - scaled aluminum coupons after 12 hours.

7. After 24 hours, the even numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass	Precipitates
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			[g]	Present?
0 ppm Si	2	7.1368	7.1146	Yes
50 ppm Si	4	7.1458	7.1299	No
75 ppm Si	6	7.1492	7.1438	No
100 ppm Si	8	7.1250	7.1195	No
125 ppm Si	10	7.1546	7.1496	No

Pictures of these coupons were taken before descaling. They are shown in Figure 1-2.

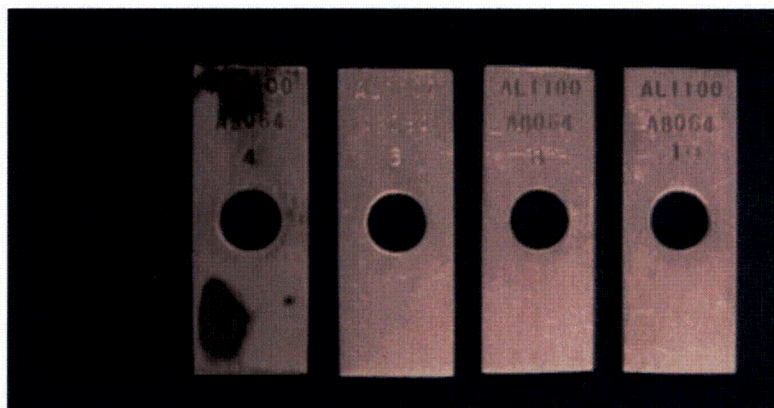


Figure 1-2: Task 1 scoping test – scaled aluminum coupons after 24 hours

8. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured for each silicate solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
0 ppm Si	7.97	201.60	Yes
50 ppm Si	8.03	116.24	No
75 ppm Si	8.02	1.64	No
100 ppm Si	8.05	0.25	No
125 ppm Si	8.04	0.32	No

A picture of the solutions after they had cooled was also taken and can be seen in Figure 1-3.





Figure 1-3: Task 1 scoping test - sodium silicate solutions after 24 hours of testing

9. In order to verify the boron concentration in the stock 2500 ppm boron solution, a titration was performed on 50 ml of the stock solution using 1.00 M sodium hydroxide. It can be seen from the resulting titration curve in Figure 1-4 that the equivalence point is reached after 11.2 ml of 1.00 M NaOH is added. This corresponds to a boron concentration of 2421 ppm.

Task 1: Titration of 50 mL of Stock Boron Solution

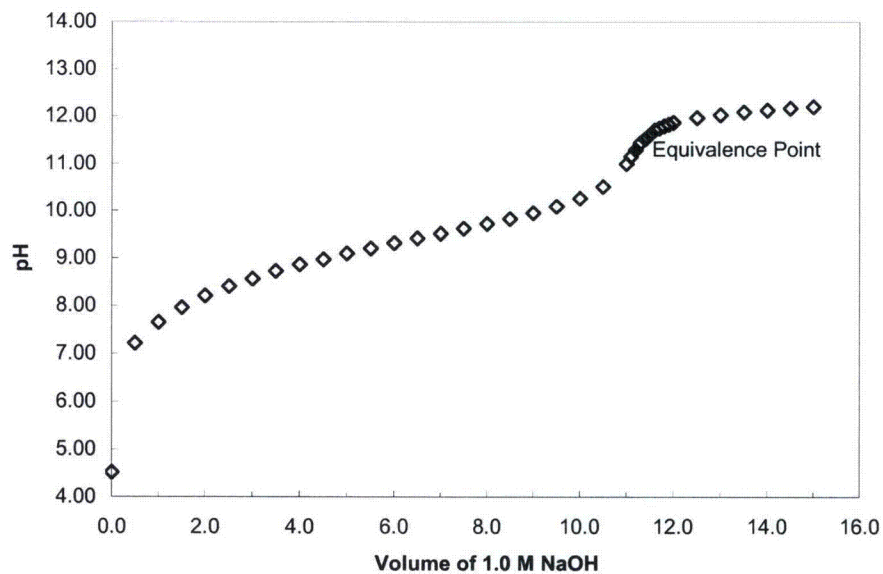


Figure 1-4: Task 1 scoping test - titration curve of stock 2500 ppm boron solution

**Parametric Testing 1.1: Determination of Silicate Inhibition as a Function of pH at a Temperature of 65.6°C**

1. The initial masses and dimensions of 6 Aluminum Alloy 1100 coupons were measured and recorded. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	6.9071	50.7	18.7	2.7	9.6
2	6.8505	50.7	18.7	2.7	9.6
3	7.0444	50.9	18.9	2.8	9.6
4	6.9847	50.9	18.9	2.7	9.6
5	7.1623	50.7	18.7	2.8	9.6
6	7.0269	50.8	18.8	2.8	9.6

2. The following steps were performed for pH values of 6.0, 8.0, and 11.0:
  - a. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5717 g of boric acid to 200 ml of deionized water.
  - b. 0.3071 g of 40% sodium silicate solution was added to achieve the threshold silicon concentration of 75 ppm as determined by the scoping test. The solution was adjusted to the desired pH by addition of sodium hydroxide. The final volume was then adjusted to 250 ml. At this time the pH was measured and recorded. The table below shows details of each solution.

Solution ID	Mass of 40% $\text{Na}_4\text{O}_4\text{Si}$ [g]	Silicon Concentration [ppm]	Mass of $\text{H}_3\text{BO}_3$ [g]	Boron Concentration [ppm]	pH After NaOH Adjustment
pH 6.0	0.3146	76.8	3.5883	2509	6.55*
pH 8.0	0.3136	76.6	3.5775	2502	8.08
pH 11.0	0.3248	79.3	3.5988	2517	11.10

\* - no NaOH added because pH after addition of sodium silicate solution was already above 6.0.

- c. The solution was transferred to an Erlenmeyer flask.
- d. The solution was then heated to 65.6°C. This temperature was maintained for the duration of the test.
- e. Two alloy 1100 coupons were inserted into the test solution.
- f. After 12 hours, one coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 6.0	1	6.9066	6.9013	No
pH 8.0	3	7.0440	7.0389	No
pH 11.0	5	6.9549	6.9084	Yes

Pictures of these coupons were taken before descaling. They are shown in Figure 1-5.

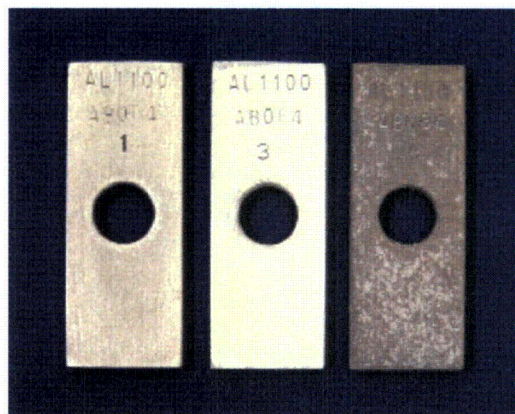


Figure 1-5: Parametric testing 1.1 at 65.6°C – scaled aluminum coupons after 12 hours.

- g. After 24 hours, the second coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 6.0	2	6.8485	6.8459	No
pH 8.0	4	6.9841	6.9817	No
pH 11.0	6	6.9151	6.8450	Yes

Pictures of these coupons were taken before descaling. They are shown in Figure 1-6.



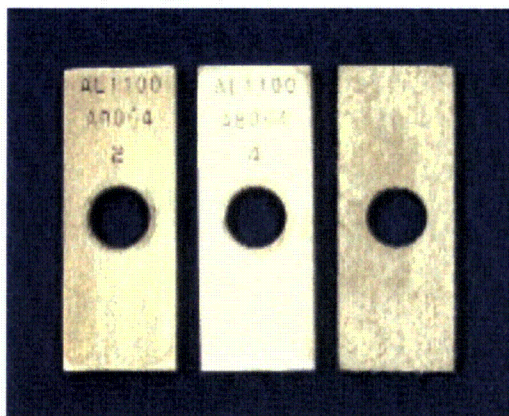


Figure 1-6: Parametric testing 1.1 at 65.6°C – scaled aluminum coupons after 24 hours.

- h. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured and recorded for each solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
pH 6.0	6.62	9.00	No
pH 8.0	8.38	0.62	No
pH 11.0	10.92	1414.08	Yes

A picture of the solutions after they had cooled was also taken and can be seen in Figure 1-7.

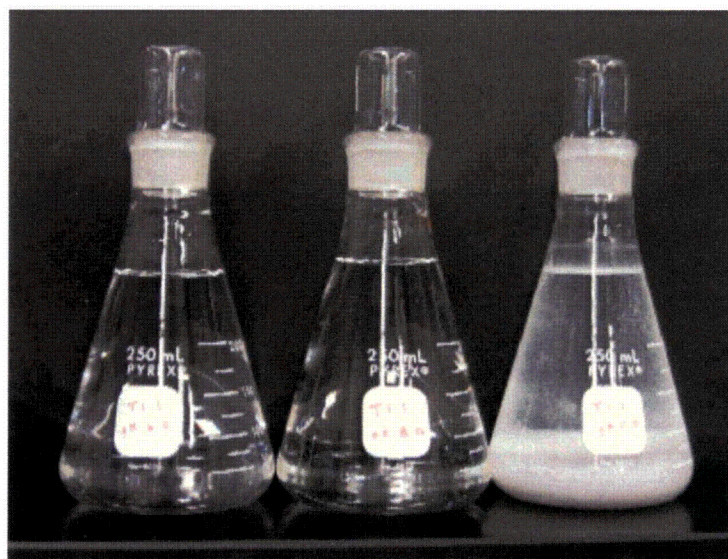


Figure 1-7: Parametric testing 1.1 at 65.6°C - sodium silicate solutions after 24 hours.

**Parametric Testing 1.1: Determination of Silicate Inhibition as a Function of pH at a Temperature of 93°C**

1. The initial masses and dimensions of 4 Aluminum Alloy 1100 coupons were measured and recorded. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	6.8293	50.7	18.7	2.7	9.6
2	7.0428	50.8	18.8	2.8	9.6
3	6.8857	50.9	18.8	2.7	9.6
4	6.9234	50.9	18.8	2.7	9.6

2. The following steps were performed for pH values of 6.0 and 11.0:
  - a. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5717 g of boric acid to 200 ml of deionized water.
  - b. 0.3071 g of 40% sodium silicate solution was added to achieve the threshold silicon concentration of 75 ppm as determined by the scoping test. The solution was adjusted to the desired pH by addition of sodium hydroxide. The final volume was then adjusted to 250 ml. At this time the pH was measured and recorded. The table below shows details of each solution.

Solution ID	Mass of 40% $\text{Na}_2\text{O}_4\text{Si}$ [g]	Silicon Concentration [ppm]	Mass of $\text{H}_3\text{BO}_3$ [g]	Boron Concentration [ppm]	pH After NaOH Adjustment
pH 6.0	0.2889	70.5	3.5628	2492	6.57*
pH 11.0	0.3014	73.6	3.5684	2496	11.20

\* - no NaOH added because pH after addition of sodium silicate solution was already above 6.0.

- c. The solution was transferred to an Erlenmeyer flask.
- d. The solution was then heated to 93°C. This temperature was maintained for the duration of the test.
- e. Two alloy 1100 coupons were inserted into the test solution.
- f. After 12 hours, one coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 6.0	1	6.8292	6.8207	No
pH 11.0	4	6.4974	6.4458	Yes

Pictures of these coupons were taken before descaling; they are shown in Figure 1-8.

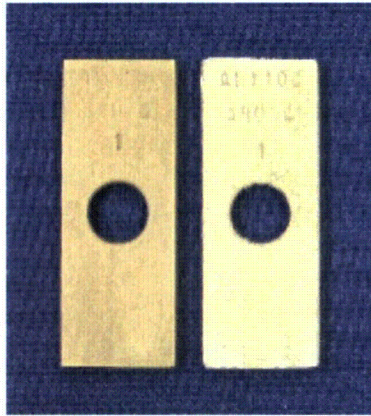


Figure 1-8: Parametric testing 1.1 at 93°C – scaled aluminum coupons after 12 hours.

- g. After 24 hours, the second coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 6.0	2	7.0410	7.0320	No
pH 11.0	3	6.1809	6.0801	Yes

Pictures of these coupons were taken before descaling; they are shown in Figure 1-9.



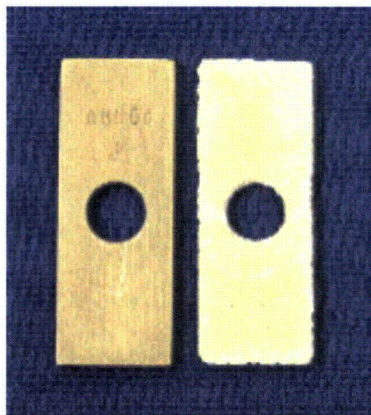


Figure 1-9: Parametric testing 1.1 at 93°C – scaled aluminum coupons after 24 hours.

- h. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured and recorded for each solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
pH 6.0	6.53	6.44	No
pH 11.0	10.81	1200.60	Yes

A picture of the solutions after they had cooled was also taken and can be seen in Figure 1-10.

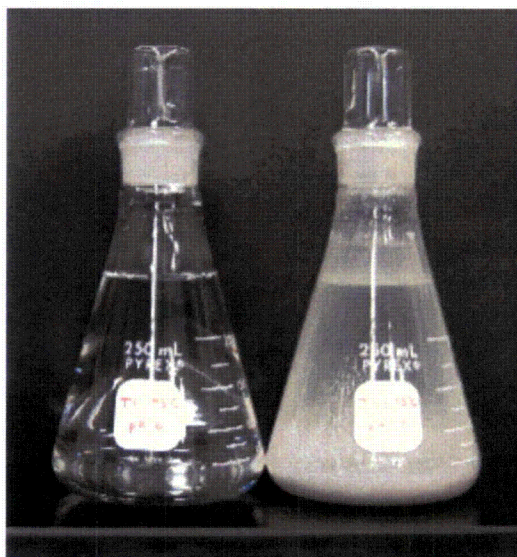


Figure 1-10: Parametric testing 1.1 at 93°C - sodium silicate solutions after 24 hours.

### **Parametric Test 1.2: Determination of Effect of Phosphate on Silicate Inhibition**

1. 1.4 liters of stock 2500 ppm boron test solution was prepared by adding 20.0435 grams of boric acid to about 1200 ml of deionized water. The final volume was adjusted to 1.4 liters. Based on the mass of boric acid used, the actual boron concentration was 2503 ppm.
2. The initial mass and dimensions of 10 Aluminum Alloy 1100 coupons were measured. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	7.0440	50.6	19.0	2.8	9.6
2	6.9949	50.8	19.0	2.8	9.6
3	6.8758	50.8	19.0	2.7	9.6
4	6.7434	50.7	19.0	2.7	9.6
5	7.1346	50.7	19.0	2.9	9.6
6	7.1268	50.8	19.0	2.9	9.5
7	7.1983	50.9	19.1	2.9	9.6
8	7.0960	50.4	19.0	2.9	9.6
9	7.0840	50.9	19.1	2.8	9.6
10	7.1105	50.9	19.1	2.8	9.6

3. 200 ml of stock boron solution was transferred to an Erlenmeyer flask. Sufficient 40% sodium silicate solution was added to achieve the desired silicon concentration. The pH was then adjusted to 8.0 using trisodium phosphate. The table below shows details of each sodium silicate solution.

Solution ID	Mass of 40% Na <sub>4</sub> O <sub>4</sub> Si [g]	pH After TSP Adjustment	Final Volume [ml]	Silicon Concentration [ppm]
0 ppm Si	0	8.00	201	0
50 ppm Si	0.1634	8.00	201	49.9
75 ppm Si	0.2560	8.02	201	78.1
100 ppm Si	0.3110	8.01	201	94.9
125 ppm Si	0.4031	8.01	201	123.0

4. Each solution was placed into an oven at 93°C. This temperature was maintained throughout the duration of the test.
5. 2 of the aforementioned aluminum coupons were placed in each silicate solution. Coupons 1 and 2 were placed in the solution containing 0 ppm Si. Coupons 3 and 4 were placed in the solution containing 50 ppm Si. Coupons 5 and 6 were placed in the solution

containing 75 ppm Si. Coupons 7 and 8 were placed in the solution containing 100 ppm Si. Finally, coupons 9 and 10 were placed in the solution containing 125 ppm Si.

6. After 12 hours, the odd numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
0 ppm Si	1	7.0381	7.0266	No
50 ppm Si	3	6.8627	6.8434	No
75 ppm Si	5	7.1312	7.1285	No
100 ppm Si	7	7.1956	7.1907	No
125 ppm Si	9	7.0831	7.0780	No

Pictures of these coupons were taken before descaling. They are shown in Figure 1-11.

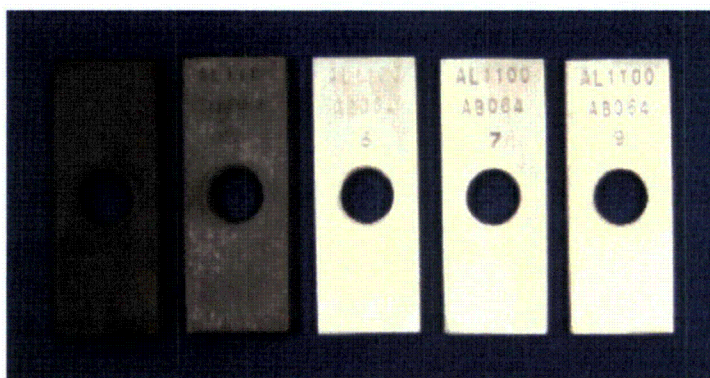


Figure 1-11: Parametric testing 1.2 – scaled aluminum coupons after 12 hours

7. After 24 hours, the even numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.



Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
0 ppm Si	2	6.9346	6.9183	No
50 ppm Si	4	7.0713	7.0577	No
75 ppm Si	6	7.1251	7.1233	No
100 ppm Si	8	7.0925	7.0912	No
125 ppm Si	10	7.1101	7.1060	No

Pictures of these coupons were taken before descaling. They are shown in Figure 12.

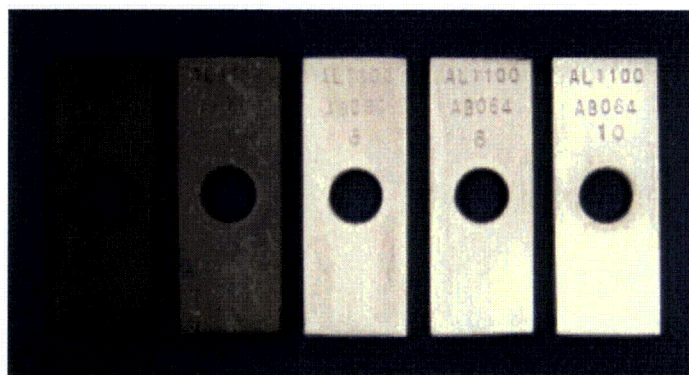


Figure 12: Parametric testing 1.2 – scaled aluminum coupons after 24 hours

8. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured for each silicate solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
0 ppm Si	7.98	56.6	No
50 ppm Si	8.00	NA	No
75 ppm Si	8.04	0.61	No
100 ppm Si	8.02	0.36	No
125 ppm Si	8.03	0.03	No

A picture of the solutions after they had cooled was taken and can be seen in Figure 13.

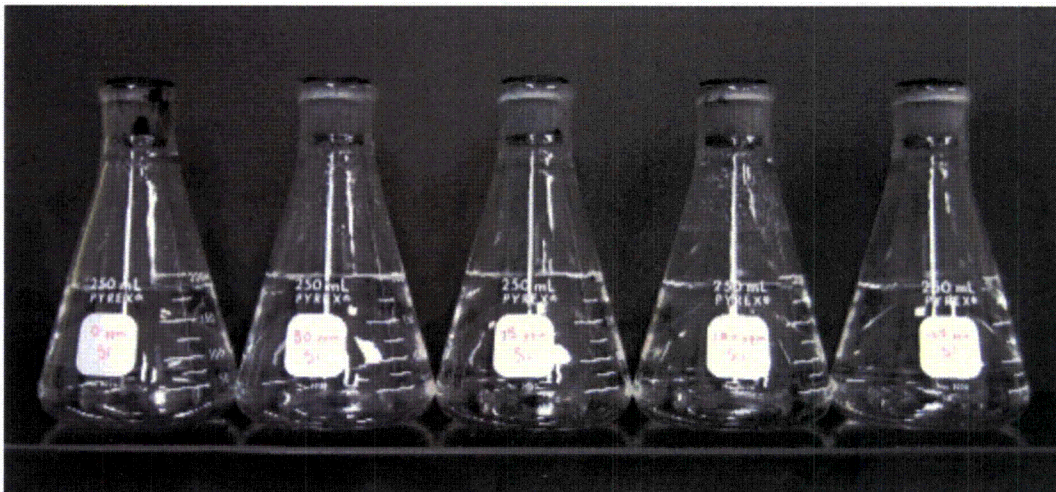


Figure 13: Parametric testing 1.2 - sodium silicate solutions after 24 hours.



## **TASK 2: CORROSION RATES OF VARIOUS ALUMINUM ALLOYS**

### **Scoping Test: Determination of Corrosion Rates at pH of 8.0**

1. 1 liter of stock 2500 ppm boron test solution was prepared by adding 14.2803 grams of boric acid to about 900 ml of deionized water. The pH was adjusted to 8.02 using sodium hydroxide, and then the final volume was adjusted to 1.0 liters. Based on the mass of boric acid used, the actual boron concentration was 2497 ppm.
2. The initial masses and dimensions of Aluminum Alloys 3003, 5005, and 6061 coupons were measured. These masses and dimensions are shown in the table below.

Coupon Number	Coupon Type	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	AL3003	7.4988	51.0	19.0	3.0	9.5
2	AL3003	7.5585	50.9	19.0	3.0	9.5
1	AL5005	3.6613	51.1	19.1	1.4	9.5
2	AL5005	3.6729	51.1	19.2	1.4	9.4
1	AL6061	7.4635	51.1	19.1	3.0	9.5
2	AL6061	7.4751	50.8	19.0	3.0	9.5

3. For each set of corrosion coupons, 225 ml of stock boron solution was transferred to an Erlenmeyer flask. Each solution was then placed into an oven at 93°C. This temperature was maintained throughout the duration of the test.
4. After the solutions had reached the target temperature of 93°C, 2 of the aforementioned aluminum coupons were placed in each Erlenmeyer flask.
5. After 12 hours, the odd numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then again rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.

Coupon Number	Coupon Type	Mass [g]	Descaled Mass [g]	Precipitates Present?
1	AL3003	7.4794	7.4646	Yes
1	AL5005	3.6395	3.6255	Yes
1	AL6061	7.4415	7.4284	Yes

Pictures of these coupons were taken before descaling. They are shown in Figure 2-1.

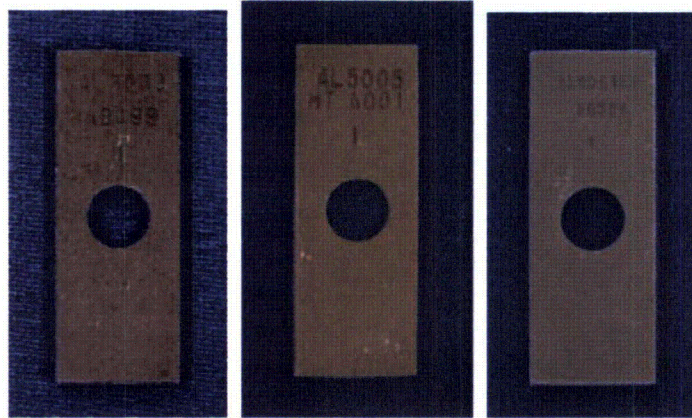


Figure 2-1: Task 2 scoping test – scaled AL3003, AL5005, AL6061 coupons after 12 hours.

6. After 24 hours, the even numbered coupons were removed from their respective solutions. These coupons were rinsed with deionized water and acetone. The mass of each coupon was taken and recorded. Using a wire brush, the coupons were then descaled. They were then rinsed with deionized water and acetone. Their descaled masses were then taken and recorded as well. The following table summarizes these results.

Coupon Number	Coupon Type	Mass [g]	Descaled Mass [g]	Precipitates Present?
2	AL3003	7.5385	7.5226	Yes
2	AL5005	3.6466	3.6312	Yes
2	AL6061	7.4508	7.4364	Yes

Pictures of these coupons were taken before descaling. They are shown in Figure 2-2.

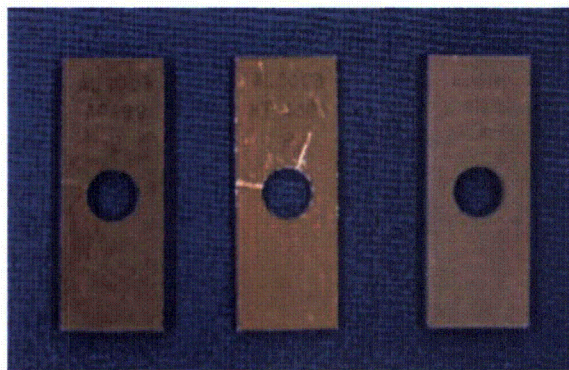


Figure 2-2: Task 2 scoping test – scaled AL3003, AL5005, AL6061 coupons after 24 hours.

7. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured for each solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
AL3003	8.13	159.68	Yes
AL5005	8.09	185.60	Yes
AL6061	8.08	181.80	Yes

A picture of the solutions after they had cooled was taken and can be seen in Figure 2-3.

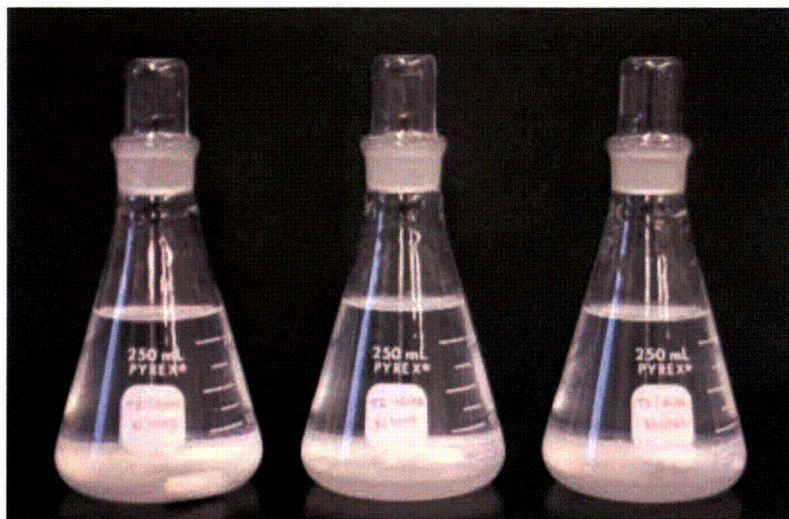


Figure 2-3: Task 2 scoping test - boron solutions after 24 hours.

### **TASK 3: PHOSPHATE INHIBITION OF ALUMINUM CORROSION**

#### **Scoping Test: Determination of Phosphate Inhibition at 93°C and pH of 8.0**

1. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5886 grams of boric acid to about 200 ml of deionized water. The pH was adjusted to 8.01 using trisodium phosphate, and then the final volume was adjusted to 250 ml. Based on the mass of boric acid used, the actual boron concentration was 2510 ppm.
2. The initial masses and dimensions of two Aluminum Alloy 1100 coupons were measured. These masses and dimensions are shown in the table below.

Coupon Number	Coupon Type	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	AL1100	7.0232	50.8	18.9	2.8	9.6
2	AL1100	7.0098	50.9	18.9	2.8	9.6

3. The boron solution was transferred to an Erlenmeyer flask. The solution was then placed into an oven at 93°C. This temperature was maintained throughout the duration of the test.
4. After the solution had reached the target temperature of 93°C, the aforementioned aluminum coupons were placed into the Erlenmeyer flask.
5. After 12 hours, the odd numbered coupon was removed from the solution. This coupon was rinsed with deionized water and acetone. The mass of the coupon was taken and recorded. Using a wire brush, the coupon was then descaled. It was then again rinsed with deionized water and acetone. The descaled mass were then taken and recorded as well. The following table summarizes these results.

Coupon Number	Coupon Type	Mass [g]	Descaled Mass [g]	Precipitates Present?
1	AL1100	7.0204	7.0096	No

6. After 24 hours, the even numbered coupon was removed from the solution. This coupon was rinsed with deionized water and acetone. The mass of the coupon was taken and recorded. Using a wire brush, the coupon was then descaled. It was then rinsed with deionized water and acetone. The descaled mass was then taken and recorded as well. The following table summarizes these results.

Coupon Number	Coupon Type	Mass [g]	Descaled Mass [g]	Precipitates Present?
2	AL1100	7.0057	6.9902	No



Pictures of the 12 and 24 hour coupons were taken before descaling. They are shown in Figure 3-1.

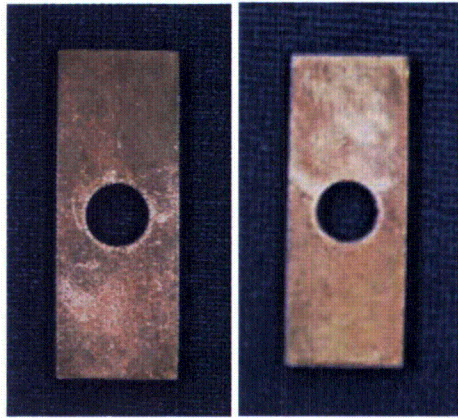


Figure 3-1: Task 3 scoping test – scaled aluminum coupon after 12 and 24 hours.

7. The solution was allowed to cool. Then, the pH and aluminum concentration was measured for the solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
AL1100	8.02	56.60	No

A picture of the solution after it had cooled was also taken and can be seen in Figure 3-2.



Figure 3-2: Task 3 scoping test - boron solution after 24 hours.

**Parametric Testing 3.1: Determination of Corrosion Rates as a Function of pH at a Temperature of 65.6°C**

1. The initial masses and dimensions of 6 Aluminum Alloy 1100 coupons were measured and recorded. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	7.1769	50.7	18.6	2.8	9.6
2	7.1628	50.8	18.8	2.8	9.6
3	7.1147	50.8	18.9	2.8	9.6
4	7.1407	50.7	18.9	2.8	9.6
5	7.0962	50.6	18.8	2.8	9.6
6	7.0706	50.6	18.5	2.8	9.6

2. The following steps were performed for pH values of 4.5, 8.0, and 9.0:
  - a. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5717 g of boric acid to 200 ml of deionized water.
  - b. The solution was adjusted to the desired pH by addition of trisodium phosphate. The final volume was then adjusted to 250 ml. At this time the pH was measured and recorded. The table below shows details of each solution.

Solution ID	Mass of H <sub>3</sub> BO <sub>3</sub> [g]	Boron Concentration [ppm]	pH of Solution
pH 4.5	3.5803	2504	4.65
pH 8.0	3.5802	2504	8.04
pH 9.0	3.5765	2501	8.95

- c. The solution was transferred to an Erlenmeyer flask.
- d. The solution was then heated to 65.6°C. This temperature was maintained for the duration of the test.
- e. Two alloy 1100 coupons were inserted into the test solution.
- f. After 12 hours, one coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 4.5	1	7.1766	7.1696	No
pH 8.0	3	7.1144	7.1064	No
pH 9.0	5	7.0905	7.0794	No

Pictures of these coupons were taken before descaling. They are shown in Figure 3-3.

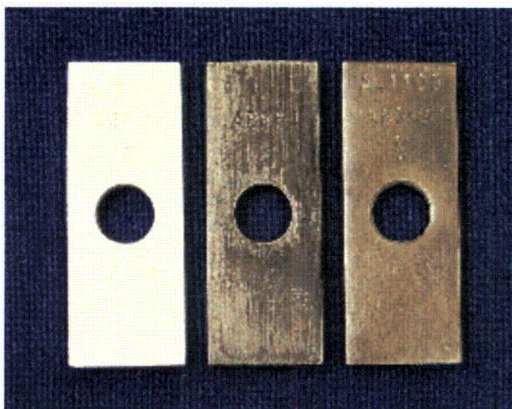


Figure 3-3: Parametric testing 3.1 at 65.6°C – scaled aluminum coupons after 12 hours.

- g. After 24 hours, the second coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 4.5	2	7.1622	7.1546	No
pH 8.0	4	7.1390	7.1328	No
pH 9.0	6	7.0646	7.0550	No

Pictures of these coupons were taken before descaling. They are shown in Figure 3-4.



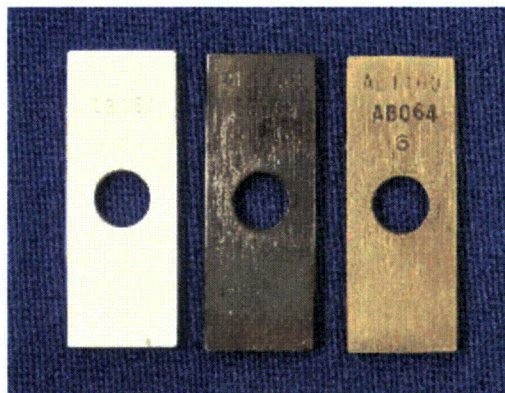


Figure 3-4: Parametric testing 3.1 at 65.6°C – scaled aluminum coupons after 24 hours.

- h. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured and recorded for each solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
pH 4.5	5.28	0.11	No
pH 8.0	8.27	21.48	No
pH 9.0	9.01	85.90	No

A picture of the solutions after they had cooled was taken and can be seen in Figure 3-5.

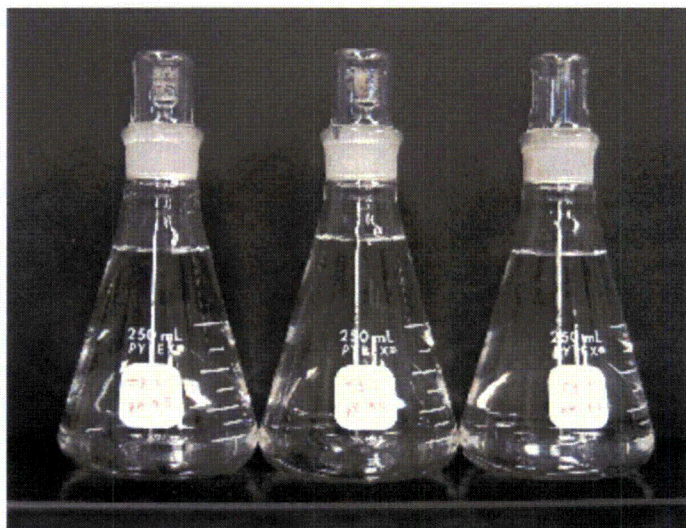


Figure 3-5: Parametric testing 3.1 at 65.6°C - boron solutions after 24 hours.



**Parametric Testing 3.1: Determination of Corrosion Rates as a Function of pH at a Temperature of 93°C**

1. The initial masses and dimensions of 4 Aluminum Alloy 1100 coupons were measured and recorded. These masses and dimensions are shown in the table below.

Coupon Number	Mass [g]	Length [mm]	Width [mm]	Thickness [mm]	Hole Diameter [mm]
1	7.1101	50.7	18.6	2.8	9.6
2	6.7903	50.7	18.7	2.7	9.6
3	6.9761	50.8	18.8	2.8	9.6
4	6.9702	50.8	18.9	2.7	9.6

2. The following steps were performed for pH values of 4.5 and 9.0:
  - a. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5717 g of boric acid to 200 ml of deionized water.
  - b. The solution was adjusted to the desired pH by addition of trisodium phosphate. The final volume was then adjusted to 250 ml. At this time the pH was measured and recorded. The table below shows details of each solution.

Solution ID	Mass of H <sub>3</sub> BO <sub>3</sub> [g]	Boron Concentration [ppm]	pH of Solution
pH 4.5	3.5838	2506	4.81
pH 8.0	3.5893	2510	8.99

- c. The solution was transferred to an Erlenmeyer flask.
- d. The solution was then heated to 93°C. This temperature was maintained for the duration of the test.
- e. Two alloy 1100 coupons were inserted into the test solution.
- f. After 12 hours, one coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 4.5	1	7.1094	7.1031	No
pH 9.0	3	6.9489	6.9348	No

Pictures of these coupons were taken before descaling. They are shown in Figure 3-6.

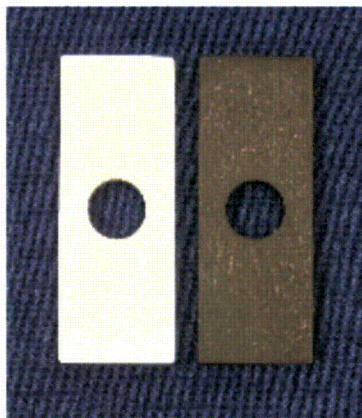


Figure 3-6: Parametric testing 3.1 at 93°C – scaled aluminum coupons after 12 hours.

- g. After 24 hours, the second coupon was removed and then rinsed with deionized water and acetone. The mass was measured and recorded. The coupon was then descaled and rinsed with deionized water and acetone once again. The mass was measured and recorded. The following table summarizes these results.

Solution ID	Coupon Number	Mass [g]	Descaled Mass [g]	Precipitates Present?
pH 4.5	2	6.7891	6.7824	No
pH 9.0	4	6.9460	6.9341	No

Pictures of these coupons were taken before descaling. They are shown in Figure 3-7.

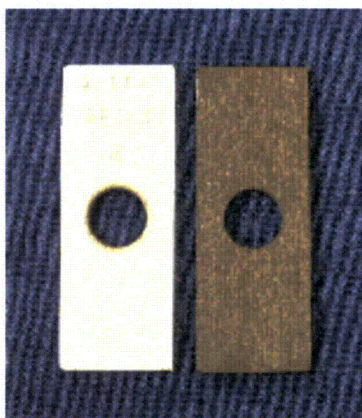


Figure 3-7: Parametric testing 3.1 at 93°C – scaled aluminum coupons after 24 hours.

- h. The solutions were allowed to cool. Then, the pH and aluminum concentration was measured and recorded for each solution. Those results can be seen in the following table.

Solution ID	pH	Aluminum Concentration (ppm)	Precipitates Present
pH 4.5	5.06	<0.01	No
pH 9.0	8.97	291.00	Yes

A picture of the solutions after they had cooled was also taken and can be seen in Figure 3-8.

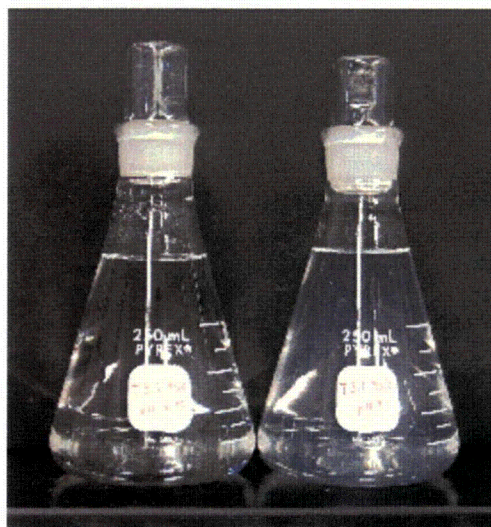


Figure 3-8: Parametric testing 3.1 at 93°C - boron solutions after 24 hours.

## **TASK 4: SOLUBILITY OF ALUMINUM AND CALCIUM PRECIPITATES**

### **Scoping Test: Solubility of Sodium Aluminum Silicate**

1. 100 ml of concentrated aluminum solution was prepared by adding 14.0216 g of aluminum nitrate nonahydrate to 90 ml of water. The final volume was adjusted to 100 mL. This solution contained 10.08 mg/ml aluminum and had a pH of 2.49.
2. 100 ml of concentrated silicon solution was prepared by adding 49.1388 g of 40% sodium silicate solution to 50 ml of deionized water. The final volume was adjusted to 100 ml. This solution contained 30.00 mg/ml silicon and had a pH of 11.46.
3. 250 ml of boron test solution was prepared by adding 3.5715 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide, and then the final volume was adjusted to 250 ml. The pH of the final solution was measured and recorded.
4. The boron solution was heated to 93°C, with stirring.
5. The temperature was maintained at 93±3°C. Concentrated aluminum solution and concentrated silicate solution was added in 0.5 ml increments until a precipitate was noted. 10 minutes was allowed for precipitate formation between additions. The volume of aluminum and silicon solutions added was recorded. The pH of the solution was also measured and recorded.
6. The concentration of sodium aluminum at the point of precipitate formation was determined.
7. Steps 3-6 above were repeated at 26.7°C and 60°C. These steps were also repeated at 93°C using trisodium phosphate to adjust the pH in place of sodium hydroxide in step 3. The results of these scoping tests are shown in the following table:

Temperature [°C]	H <sub>3</sub> BO <sub>3</sub> Used [g]	pH Adjuster	Initial pH	Final pH	Volume of Al and Si Solution at POP [ml]	Concentration of Al at POP [ppm]
93.0	3.6052	NaOH	8.16	7.78	1.0	40.0
60.0	3.5913	NaOH	8.05	7.92	1.5	59.8
26.7	3.5833	NaOH	8.07	8.03	1.5	59.8
93.0	3.5691	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	8.08	7.58	2.5	98.8

In the cases in which sodium hydroxide was used as the pH adjuster, the volumes of solution reported are those at which the first signs of precipitate formation occur. At these addition volumes, the solutions appeared to be slightly cloudy yet no distinct precipitate particles could be seen. At the next 0.5 ml increment, however, precipitate began to coalesce as fluffy particles. In the case in which trisodium phosphate was used as the pH adjuster, the precipitate particles seemed to be more crystalline in nature.

### Long Term Solubility Test: Sodium Aluminum Silicate

1. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5674 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide. The final volume was then adjusted to 250 ml. At this time, the pH of the final solution was measured and recorded.
2. The boron solution was heated to 93°C.
3. 2.0 ml of concentrated aluminum solution and 2.0 ml of concentrated silicon solution were added as determined by the scoping test. No precipitates were present at this time. The pH was measured and recorded.
4. The solution was maintained at a temperature of 93°C for one week. The solution was observed daily for precipitate formation. Deionized water was slowly added as necessary in order to maintain the solution volume.
5. This test was repeated at a temperature of 93°C using sodium hydroxide as the pH buffer. 0.5 ml of concentrated aluminum solution and 0.5 ml of concentrated silicon solution were added in this test. The results of this testing can be seen in the following table.

Temperature [°C]	H <sub>3</sub> BO <sub>3</sub> Used [g]	pH Adjuster	Volume of Al and Si Solutions Added [ml]	pH	Time of First Observed Precipitation
93.0	3.5674	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	2.0	8.02	~1 hr
93.0	3.5811	NaOH	0.5	8.09	6 days

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**Scoping Test: Sensitivity Test For NAS in TSP**

1. 1000 mL of boron test solution was prepared by adding 14.3098 g of boric acid to 900 mL of deionized water. The pH was adjusted to 8.0 using TSP, and then the final volume was adjusted to 1000 mL.
2. The boron solution was heated to 93°C, with stirring.
3. 4 ml of concentrated aluminum solution containing 10.06 mg/ml aluminum (from aluminum nitrate) was added to the heated solution. This corresponds to an aluminum concentration of 40.2 ppm. Additionally, 4 ml of concentrated silicon solution containing 30.00 mg/ml silicon was added to the heated solution.
4. It was visually verified that no precipitates were present.
5. The temperature was maintained at 93°C for 72 hours as the solution was allowed to "age".
6. Nitric acid was added to one 250 ml aliquot of this solution to decrease the pH by 1.02. No precipitates were formed from this change in pH.
7. Sodium hydroxide was added to another 250 ml aliquot of solution to increase the pH by 1.02. No precipitates were formed from this change in pH.
8. A third aliquot of 250 ml was cooled to 60°C and held for 24 hours. After this time no precipitates were present. This solution was then cooled to 25°C and held for 24 hours. After this time no precipitates were present. The solution was then reheated to 60°C and held for 24 hours. After this time no precipitates were present. The solution was then reheated to 93°C and held for 24 hours. At this time no precipitates were present.

### **Scoping Test: Solubility of Aluminum Oxyhydroxide**

1. 200 ml of concentrated aluminum solution was prepared by adding 3.5910 g of sodium aluminate (52.8%  $\text{Al}_2\text{O}_3$ ) to 180 ml of water. The final volume was adjusted to 200 ml. This solution contained 5.02 mg/ml aluminum.
2. 250 ml of boron test solution was prepared by adding 3.5760 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide, and then the final volume was adjusted to 250 ml. The pH of the final solution was measured and recorded.
3. The boron solution was heated to 93°C, with stirring.
4. The temperature was maintained at 93±3°C. Concentrated aluminum solution was added in 1.0 ml increments until a precipitate was noted. 10 minutes was allowed for precipitate formation between additions. The volume of aluminum solution added was recorded. The pH of the solution was also measured and recorded.
5. The concentration of aluminum at the point of precipitate formation was determined.
6. Steps 3-5 above were repeated at 26.7°C and 60°C. These steps were also repeated at 93°C using trisodium phosphate to adjust the pH in place of sodium hydroxide in step 3. The results of these scoping tests are shown in the following table:

Temperature [°C]	H <sub>3</sub> BO <sub>3</sub> Used [g]	pH Adjuster	Initial pH	Final pH	Volume of Al Solution at POP [mL]	Concentration of Al at POP [ppm]
93.0	3.5760	NaOH	8.09	8.13	18.0	337.2
60.0	3.5840	NaOH	8.04	8.14	5.0	98.4
26.7	3.5768	NaOH	8.02	8.04	1.0	20.0
93.0	3.5771	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	8.00	8.23	32.0	570

**Long Term Solubility Test: Aluminum Oxyhydroxide**

1. 250 ml of 2500 ppm boron test solution was prepared by adding 3.5820 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide. The final volume was then adjusted to 250 ml. At this time, the pH of the final solution was measured and recorded.
2. The boron solution was heated to 93°C.
3. 17.0 ml of concentrated aluminum solution were added as determined by the scoping test. No precipitates were present at this time. The pH was measured and recorded.
4. The solution was maintained at a temperature of 93°C for one week. The solution was observed daily for precipitate formation. Deionized water was slowly added as necessary in order to maintain the solution volume.

Temperature [°C]	H <sub>3</sub> BO <sub>3</sub> Used [g]	pH Adjuster	Volume of Al Solution Added [ml]	pH	Time of First Observed Precipitation
93.0	3.5820	NaOH	17.0	8.08	~1 hr



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**Scoping Test: Solubility of Aluminum Oxyhydroxide (Part 2)**

1. 250 ml of boron test solution was prepared by adding 3.5754 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide, and then the final volume was adjusted to 250 ml.
2. The boron solution was heated to 93°C, with stirring.
3. Based on the aluminum analysis from task 5, an aluminum test concentration of 250 ppm was decided upon. 13 ml of concentrated aluminum solution containing 5.0172 mg/ml aluminum (from sodium aluminate) was added to the heated solution. This corresponds to an aluminum concentration of 248.0 ppm.
4. It was visually verified that no precipitates were present.
5. The temperature was maintained at 93°C throughout the duration of the test.
6. Observations were made after 1, 2, 3, and 18 hours. No precipitates were present at 1, 2, or 3 hours. At 18 hours, precipitates were present.

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**Scoping Test: Solubility of Aluminum Oxyhydroxide (Part 3)**

9. 250 ml of boron test solution was prepared by adding 3.5742 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using sodium hydroxide, and then the final volume was adjusted to 250 ml.
10. The boron solution was heated to 93°C, with stirring.
11. 13 ml of concentrated aluminum solution containing 5.0172 mg/ml aluminum (from sodium aluminate) was added to the heated solution. This corresponds to an aluminum concentration of 248.0 ppm.
12. It was visually verified that no precipitates were present.
13. The temperature was maintained at 93°C throughout the duration of the test.
14. To investigate the solubility with the presence of additional nucleation sites, small stainless steel particles were added to the solution. These additional nucleation sites did not initiate precipitate formation.
15. A pipette was used to extract precipitates from the solution in the previous scoping test. These precipitates were then added to the test solution in another attempt to initiate precipitate formation. These precipitates went into solution in a matter of seconds.

**Modified Scoping / Long Term Solubility Testing:**

The following steps were performed for each set of experimental conditions:

1. A sufficient quantity of boron test solution was prepared. The pH of the solution was adjusted to 8.0 using the appropriate buffer.
2. The boron solution was heated to the desired test temperature.
3. The following steps were performed for the desired aluminum concentrations:
  - a. 250 ml of the boron solution were measured out and poured into an Erlenmeyer flask.
  - b. The amount of concentrated aluminum solution required to obtain the desired concentration of aluminum was added to the boron solution. The same amount of concentrated silicon solution was also added if testing for sodium aluminum silicate was being performed. (If NAS was being tested for, the Al solution was made using aluminum nitrate nonahydrate and contained 10.08 mg/ml Al. If AlOOH was being tested for, the Al solution was made using sodium aluminate and contained 5.02 mg/ml Al.) No precipitates were present at this time.
  - c. The solution was maintained at the test temperature for 30 days. The solution was observed daily for precipitate formation. Deionized water was slowly added as necessary in order to maintain the solution volume.

A summary of test parameters and results can be seen in the following table:

Precipitate	Temperature [°C]	Boron Concentration [ppm]	pH Adjuster	pH	Volume of Al Solution [mL]	Volume of Si Solution [mL]	Concentration of Al [ppm]	Date Started	Date of First Observed Precipitate
NAS	93	2499	TSP	7.98	0.25	0.25	10.1	3-23-07	DNP
NAS	93	2499	TSP	7.98	0.50	0.50	20.1	3-23-07	DNP
NAS	93	2499	TSP	7.98	0.75	0.75	30.1	3-23-07	DNP
NAS	93	2499	TSP	7.98	1.00	1.00	40.2	3-23-07	DNP
AlOOH	93	2498	NaOH	8.04	1.2	NA	24.0	3-22-07	DNP
AlOOH	93	2498	NaOH	8.04	2.5	NA	50.0	3-22-07	DNP
AlOOH	93	2498	NaOH	8.04	5.0	NA	98.4	3-22-07	DNP
AlOOH	93	2498	NaOH	8.04	7.7	NA	149.9	3-22-07	3-23-07
AlOOH	60	2498	NaOH	8.00	0.5	NA	10.0	3-27-07	DNP
AlOOH	60	2498	NaOH	8.00	1.0	NA	20.0	3-27-07	DNP
AlOOH	60	2498	NaOH	8.00	1.5	NA	29.9	3-27-07	DNP
AlOOH	60	2498	NaOH	8.00	2.0	NA	39.8	3-27-07	DNP
AlOOH	60	2498	NaOH	8.00	2.5	NA	49.7	3-27-07	4-23-07

DNP means the solution did not form any precipitates in the allotted time period of 30 days.

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**Scoping Test: Sensitivity Test For AlOOH in NaOH**

1. 1000 mL of boron test solution was prepared by adding 14.3020 g of boric acid to 900 mL of deionized water. The pH was adjusted to 8.0 using NaOH, and then the final volume was adjusted to 1000 mL.
2. The boron solution was heated to 93°C, with stirring.
3. 8 ml of concentrated aluminum solution containing 5.06 mg/ml aluminum (from sodium aluminate) was added to the heated solution. This corresponds to an aluminum concentration of 40.5 ppm.
4. It was visually verified that no precipitates were present.
5. The temperature was maintained at 93°C for 72 hours as the solution was allowed to "age".
6. Nitric acid was added to one 250 ml aliquot of this solution to decrease the pH by 1.05. No precipitates were formed from this change in pH.
7. Sodium hydroxide was added to another 250 ml aliquot of solution to increase the pH by 1.03. No precipitates were formed from this change in pH.
8. A third aliquot of 250 ml was cooled to 60°C and held for 24 hours. After this time no precipitates were present. This solution was then cooled to 25°C and held for 24 hours. After this time no precipitates were present. The solution was then reheated to 60°C and held for 24 hours. After this time no precipitates were present. The solution was then reheated to 93°C and held for 24 hours. After this time period, no precipitates were present.

### Scoping Test: Solubility of Calcium Phosphate

1. 100 ml of concentrated calcium solution was prepared by adding 4.4022 g of calcium acetate to 90 mL of water. The final volume was adjusted to 100 ml. This solution contained 11.16 mg/ml calcium.
2. 250 ml of boron test solution was prepared by adding 3.5918 g of boric acid to 200 ml of deionized water. The pH was adjusted to 8.0 using trisodium phosphate, and then the final volume was adjusted to 250 ml. The pH of the final solution was measured and recorded.
3. The boron solution was heated to  $93^{\circ}\text{C}$ , with stirring.
4. The temperature was maintained at  $93 \pm 3^{\circ}\text{C}$ . Concentrated calcium solution was added in 0.5 ml increments until a precipitate was noted. 10 minutes was allowed for precipitate formation between additions. The volume of calcium solution added was recorded. The pH of the solution was also measured and recorded.
5. The concentration of calcium at the point of precipitate formation was determined.

Temperature [ $^{\circ}\text{C}$ ]	$\text{H}_3\text{BO}_3$ Used [g]	pH Adjuster	Initial pH	Final pH	Volume of Ca Solution at POP [ml]	Concentration of Ca at POP [ppm]
93.0	3.5918	$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	8.04	8.04	0.5	22.3