Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

We put science to work.™

Savannah River
National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

A U.S. DEPARTMENT OF ENERGY NATIONAL LABORATORY • SAVANNAH RIVER SITE • AIKEN, SC

Equilibrium Studies of Oxalate and Aluminum Containing Solutions

M. S. Hay
W. D. King
T. B. Peters
D. H. Jones

November 2015

SRNL-STI-2015-00507, Rev. 0

SRNL.DOE.GOV

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2015-00507
Revision 0

Keywords: *Supernate Analysis, Solubility*

Retention: *Permanent*

Equilibrium Studies of Oxalate and Aluminum Containing Solutions

M. S. Hay
W. D. King
T. B. Peters
D. H. Jones

November 2015

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory ™
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

M. S. Hay, Advanced Characterization and Processing Date

W. D. King, Advanced Characterization and Processing Date

T. B. Peters, Advanced Characterization and Processing Date

D. H. Jones, Advanced Characterization and Processing Date

TECHNICAL REVIEW:

D. J. McCabe, Hanford Mission Programs Date

APPROVAL:

F. M. Pennebaker, Manager Date
Advanced Characterization and Processing

D. E. Dooley, Manager Date
Environmental & Chemical Process Technology Research Programs

R. T. McNew, Manager Date
SRR Flowsheet Development & Facility Integration

EXECUTIVE SUMMARY

The Savannah River National Laboratory (SRNL) was tasked to develop data on the solubility and conditions leading to precipitation of sodium oxalate, sodium nitrate, Bayerite (a polymorph of gibbsite, $Al(OH)_3$), and sodium aluminosilicate solids recently found in the Modular Caustic Side Solvent Extraction Unit (MCU). The data generated will be used to improve the OLI Systems thermodynamic database for these compounds allowing better prediction of solids formation by the modeling software in the future.

A set of thirty-four simple salt solutions were developed containing various concentrations of sodium hydroxide and sodium nitrate dissolved in water. The simple salt solutions were mixed with sodium oxalate or gibbsite solids to determine the solubility of these solids. Kinetics tests of simple salt solutions in contact with either sodium oxalate or gibbsite solids determined that the sodium oxalate reached equilibrium within a few days while the gibbsite solids required nine weeks or more to reach equilibrium.

The simple solution sodium oxalate test results indicate that sodium oxalate solubility is mostly governed by the total sodium concentration of the salt solution. There appears to be an additional smaller effect on the sodium oxalate solubility based on the amount of hydroxide present in the solution. The two different test methods used showed reasonably good agreement. The presence of dissolved aluminum in the solution produced little effect on the sodium oxalate solubility in these simple solutions.

The gibbsite solubility in the simple solutions appears to be governed primarily by the hydroxide concentration in the solution with an additional smaller effect from the total sodium in solution. The smaller sodium effect on the gibbsite solubility increases in magnitude as the hydroxide concentration increases. The data showed significant differences in the final equilibrated aluminum concentration depending on the test method employed. The presence of dissolved sodium oxalate in these solutions had little effect on the solubility of gibbsite.

The sodium and hydroxide concentrations have opposite effects on the solubility of sodium oxalate and gibbsite solids. Adding a strong NaOH solution to a salt solution saturated in sodium oxalate and gibbsite solids will likely precipitate sodium oxalate while increasing the solubility of the gibbsite. Diluting the same solution with water will increase the solubility of sodium oxalate while likely causing the precipitation of gibbsite solids.

Filtered samples of the simple solutions saturated in sodium oxalate or gibbsite at 25 °C were found to be stable to precipitation if maintained at a temperature near 25 °C. However, solutions with >6 M sodium nitrate concentrations in an 8 M total sodium concentration formed crystalline sodium nitrate solids after several days from both the sodium oxalate and gibbsite test solutions.

The complex simulant solutions (containing 7-10 components) showed oxalate concentrations within the range expected based on comparison with the simple solutions results for solutions with similar sodium molarity. The aluminum concentrations in the equilibrated complex simulant solutions appears significantly lower than expected based on comparison with the simple solutions tests with similar hydroxide concentrations. No measureable difference in oxalate or aluminum concentrations was observed between solutions with and without calcium and silicon. Nearly all of the silicon appears to have been removed from the equilibrated complex simulant solutions. However, the concentration of silicon in the initial complex simulant solutions appears to have been too low to produce a measureable effect on oxalate or aluminum concentrations. Contact of the 6.5 M complex simulant solutions with MCU solvent does not appear to cause precipitation of solids from the solution.

Most of the OLI predictions for the oxalate concentrations in the sodium oxalate tests were much lower than the measured concentrations. For solutions with 5 M sodium or higher, the OLI predictions were 5-10X lower than the measured concentrations. The OLI modeling predictions for the aluminum concentrations in the gibbsite tests were generally ~20-30% lower or higher than the measured concentrations depending on the test method. Interestingly, the OLI predictions match reasonably well with the average aluminum concentration from the two test methods.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Analytical Development
DI	De-ionized
HTL	High to Low Concentration Tests
IC	Ion chromatography
ICP-ES	Inductively Coupled Plasma Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
LTH	Low to High Concentration Tests
MCU	Modular Caustic Side Solvent Extraction Unit
NAS	Sodium aluminosilicate
NGS	Next Generation Solvent
%RSD	Percent Relative Standard Deviation
PSAL	Process Science Analytical Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
TTQAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
XRD	X-ray Diffraction

1.0 Introduction

The Modular Caustic Side Solvent Extraction Unit (MCU) at the Savannah River Site (SRS) experienced processing issues in April 2014 resulting from the formation of solids in processing equipment. Analysis of solids collected from MCU indicated the presence of sodium oxalate, sodium nitrate, Bayerite, and sodium aluminosilicate (NAS).[1] A Technical Task Request (TTR) was issued to the Savannah River National Laboratory (SRNL) to develop data on the solubility of these compounds and examine solution conditions that can lead to precipitation of solids.[2] This data will also be used to improve the OLI Systems thermodynamic database for these compounds allowing better prediction of solids formation by the modeling software in the future. A Task Technical and Quality Assurance Plan (TTQAP) was generated to define the scope of work.[3]

As proposed in the TTQAP, the program consisted of five parts:

- Conduct a literature review of research relevant to the solubility and tendency for precipitation of sodium oxalate, gibbsite/bayerite, and sodium aluminosilicates to aid in experimental design.
- Develop an experimental design for basic solubility studies using simple salt solutions composed of sodium oxalate, sodium nitrate, sodium hydroxide and sodium aluminate. The data can be used to verify/improve the predictive ability of the OLI Systems, Inc. thermodynamic database.
- Develop an experimental design for solubility/precipitation studies using more complex salt solutions based on information generated in the previous tasks. The objective of these tests will be to generate better solubility information on simulant solutions relevant to MCU processing and verify/improve the predictive ability of the OLI Systems, Inc. thermodynamic database.
- Conduct tests with radioactive waste solutions to verify that the information learned from simulant tests applies to real waste material.
- Conduct tests with simulants or radioactive waste solutions to determine if the Next Generation Solvent (NGS) flowsheet will contribute to precipitation issues in the MCU.

The first three parts and the last part of the program have been completed. The testing with radioactive waste solutions has been deferred for later evaluation.

2.0 Experimental

An experimental design was developed for the simple solution testing that covered the range of sodium molarity from 1 to 8 M. Using whole number values (plus a few fractional values for solutions with half hydroxide and half nitrate) for the molarity of sodium hydroxide and sodium nitrate, forty-eight possible solutions were formulated. For the sodium oxalate solubility tests using these simple solutions, the number of solutions was pared down to thirty-four based on preliminary OLI modeling that indicated the solubility of oxalate in a number of the solutions would be well below detection limits by ion chromatography (IC). The number of solutions for testing aluminum solubility was also pared down to thirty-four solutions for consistency. The gibbsite form of aluminum trihydroxide ($Al(OH)_3$) was used as the aluminum source for the tests. Tables 2-1 and 2-2 show the compositions of the thirty-four simple solutions used in the sodium oxalate and gibbsite solubility tests respectively. The Test ID provides the nominal total sodium concentration (the first number in the ID), the sodium hydroxide concentration (the second number in the ID), and the sodium nitrate concentration (the last number in the ID).

Prior to starting the simple solution solubility tests, a few solutions from the test matrix were chosen to determine the kinetics of dissolution for both sodium oxalate solids and gibbsite solids. The tests were run at 25 °C in a shaker oven (250-300 rpm) with samples obtained periodically until analytical results indicated the solutions had reached equilibrium. In each of these tests the simple solution was prepared by adding the required mass of $NaNO_3$ solids and 50 wt% NaOH solutions to the bottle followed by addition of deionized (DI) water to the volume calibration mark made on the bottle. Sufficient sodium oxalate or gibbsite solids were added equal to approximately three times the predicted OLI solubility in the particular solution. The OLI 40 °C predictions were used as the basis for the sodium oxalate solids mass to add to the solution since it had been observed with recent calculations modeling actual SRS waste solutions that the 40 °C predictions were much closer to measured oxalate concentrations than the 25 °C predictions. The solutions were checked daily to ensure excess solids were always present in the bottle. Periodically the solutions were sampled by obtaining ~10 mL of solution and pushing it through a 0.45 µm syringe filter into a labeled bottle to send for analysis at the Process Science Analytical Laboratory (PSAL). Oxalate and nitrate anion concentrations were determined by IC while sodium and aluminum concentrations were determined by inductively coupled plasma-emission spectroscopy (ICP-ES). Free hydroxide concentrations were not measured. Figures 2-1 and 2-2 show the results of the kinetic tests. The sodium oxalate containing solutions appear to reach equilibrium within a couple of days at 25 °C while the gibbsite containing solutions took 8-9 weeks to reach equilibrium at 25 °C. In the graph in Figure 2-1, the oxalate concentration appears to increase slightly in the last two data points at 7 and 12 days. These variations in the oxalate concentration were interpreted as being within the expected experimental/analytical error of ~10%. In Figure 2-2, the data points seem to indicate that the 5-25-25-AL solution did not reach equilibrium at nine weeks. That may be the case, however, the fact that the next to last data point at fifty-six days appears to be somewhat low enforces the impression that the concentration continues to rise. In any case the aluminum concentration appears to be very close to equilibrium at nine weeks for all three solutions tested. Based on the results of the kinetics tests, all solubility tests using sodium oxalate solids were continued for a minimum of four days while those tests using gibbsite solids were run for a minimum of nine weeks.

The simple solutions in Tables 2-1 and 2-2 were prepared in the same manner as described above for the kinetics tests. The simple solution solubility tests were conducted using two methods. In the first test method, after adding the sodium oxalate (or gibbsite) solids to the bottles, one set of the bottles were placed in a shaker oven (250-300 rpm) set at 25 °C and allowed to reach equilibrium. The solutions were visually monitored daily to ensure excess sodium oxalate (or gibbsite) solids still remained in the bottle and additional solids added if necessary. At the end of the test, the solutions were filtered and sampled for analysis. Some difficulty was encountered in getting all of the added sodium nitrate solids to dissolve in the three 8 M sodium solutions for the simple solution sodium oxalate tests and the 8-1-7-AL solution of the simple solution gibbsite tests. Eventually, all of the sodium nitrate solids visually appeared to go into solution.

For the second test method, sodium oxalate (or gibbsite) solids were added to the bottles containing filtered solutions from the first test method and the bottles placed in a shaker oven (250-300 rpm) set at 60 °C and allowed to reach equilibrium. The solutions were sampled at 60 °C and then the oven temperature was reduced to 40 °C and allowed to reach equilibrium again. After sampling at 40 °C, the oven temperature was finally reduced to 25 °C, allowed to reach equilibrium, and sampled once again. The first test method provides solubility data coming from a zero concentration up to a higher equilibrium concentration. The second test method provides solubility data coming from a higher concentration down to a lower concentration and additionally, solubility data at higher temperatures. Due to the longer length of time required to reach equilibrium for the gibbsite solids tests, those solutions were only equilibrated at 40 °C before reducing the oven temperature to 25 °C.

With both test methods, sampled solutions were pressed through a 0.45 µm syringe filter into a labeled bottle to send for analysis at the PSAL. For samples obtained at elevated temperatures, the syringe and filter were preheated to the sampling temperature prior to filtration. Samples from the first method for both the sodium oxalate and gibbsite tests were not diluted prior to sending for analysis. The samples from the second method were diluted by 3-7X prior to sending for analysis at PSAL. The samples from the second method oxalate tests were diluted 3X with DI water. The samples from the second method gibbsite tests were diluted 7X with 5 M nitric acid for ICP-ES analysis and undiluted for IC analysis. A filtered aliquot of each 25 °C solution, generated using the first test method, was set aside at room temperature and visually monitored for signs of solids precipitation for one month.

A small subset of the simple solutions from the previous testing described above was used in tests to determine the solubility of sodium oxalate in a simple solution already saturated in aluminum and to test the solubility of gibbsite solids in a solution already saturated in oxalate. These tests were conducted in a shaker oven (250-300 rpm) set at 25 °C and allowed to reach equilibrium over a nine week period. At the end of that time, samples of the solutions were pressed through a 0.45 µm syringe filter into a labeled bottle to send for analysis at the PSAL.

A series of complex simulant solution tests were conducted to provide solubility data in solution compositions more relevant to the MCU process. A spreadsheet of salt batch compositions was provided via email by the customer to use in developing the complex simulant solutions. For each component in the simulant, a concentration value half way between the average and the maximum concentration present in salt batches 1-8 was chosen. A series of three solutions at three different total sodium concentrations (5.5 M, 6.5 M. and 7.5 M) were developed for testing. As with the simple solution compositions, the sodium hydroxide and sodium nitrate concentrations were varied in the three solutions of a given total sodium molarity. Table 2-3 shows the nine solution compositions before addition of oxalate or gibbsite solids. A duplicate set of solutions were prepared without the metals (Ca, Ti, Si) present to be able to see the effect of these metals on the oxalate/aluminum solubility. The titanium was added as a 14.8 wt% monosodium titanate (MST) slurry in 0.01 M NaOH. The complex simulant solutions were prepared by adding the required mass of each chemical (except the Ca, Ti, and Si compounds) to a bottle followed by addition of deionized (DI) water to the volume calibration mark made on the bottle. Each solution was divided into two bottles and the three metal compounds were added to one of the bottles from each set providing solutions with and without the metal compounds. After being agitated overnight in a shaker oven (250-300 rpm) set at 25 °C, the initial solutions were passed through a 0.45 µm filter and sent for analysis by ICP-ES and IC. Excess amounts of sodium oxalate and gibbsite solids were added to each bottle and the bottles placed in a shaker oven (250-300 rpm) set at 25 °C for nine weeks. At the end of the nine week test, small portions of each solution were passed through a 0.45 µm filter and sent undiluted for analysis by ICP-ES and IC.

A series of tests were conducted using two of the complex simulant solutions after saturation with sodium oxalate and gibbsite solids. These solutions were contacted with freshly prepared MCU blend solvent to determine if the contact induced precipitation of saturated salt solutions. After equilibration with sodium oxalate solids and gibbsite solids as described in the previous paragraph, 40 mL of the filtered complex simulant solutions 6.5 M Sodium #2 and #3 (see Table 2-3) were mixed with 10 mL of freshly prepared "blend solvent". The composition of the blend solvent was designed to mimic the solvent material used at MCU during the changeover from the old solvent formulation in late 2013.[4] The initial composition of the blend solvent is detailed in Table 2-4.

A small tissue homogenizer, set to its second lowest setting was used to thoroughly mix the complex simulant solution and solvent mixture for 120 seconds. Care was taken to keep the tip of the homogenizer at the phase boundary at the start of the mixing, but as the time progressed, was swept through the height of the solution. This ensures the maximum amount of mixing energy was imparted into the mixture. As a result, the two phases were thoroughly mixed, resulting in a single cloudy dispersion. The mixtures did not immediately separate. Additionally, 10 mL control samples of each of the two complex simulant solutions (without solvent) were mixed in the same fashion using the tissue homogenizer. These controls were performed to ensure that mixing alone did not trigger solids precipitation. All four solutions were placed in tightly capped bottles and placed in a shaker oven set to 25 °C and 60 rpm. Each of the four samples was visually observed once/day over a one week time period (excepting weekends) to look for evidence of precipitation.

A model was developed using the OLI Systems Inc., Environmental Simulation Program (ESP), version 9.1.5. For modeling the simple solution solubility tests, the chemistry model employed the chemical species listed in the left hand column of Table 2-5. Modeling the complex simulant solubility tests used the chemical species listed in right hand column of Table 2-5. All of the models used the MSE framework. All of the chemical species used in the model were contained in the MSEPUB databank. In addition to the liquid phase, solid and vapor phases were also included in the chemistry model. The process model contained a single Mix block to combine the salt solution stream and the sodium oxalate (or gibbsite) solids stream. The Mix block used the isothermal calculation option. Modeling runs were conducted at 25 °C, 40 °C and 60 °C as necessary to duplicate expected experimental conditions. Modeling runs for each of the solutions listed in Table 2-1 through 2-3 were made prior to starting experiments. The predicted concentrations of oxalate (or aluminum) provided a basis for estimating how much solid sodium oxalate (or gibbsite) to add to the solution.

Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Manual E7, Procedure 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2. Data are recorded in the electronic laboratory notebook system as notebook/experiment number Y7081-00081-02.

Table 2-1. Simple Solution Compositions for Sodium Oxalate Solubility Tests

Test No.	Test ID	Target Na (M)	Target NaOH (M)	Target $NaNO_3$ (M)	OLI 25 °C Predicted Oxalate (M)
1	1-0-1-OX	1	0	1	0.079
2	1-1-0-OX	1	1	0	0.068
3	1-05-05-OX	1	0.5	0.5	0.074
4	2-0-2-OX	2	0	2	0.028
5	2-2-0-OX	2	2	0	0.015
6	2-1-1-OX	2	1	1	0.021
7	3-0-3-OX	3	0	3	0.013
8	3-3-0-OX	3	3	0	0.0036
9	3-1-2-OX	3	1	2	0.0085
10	3-2-1-OX	3	2	1	0.0056
11	4-0-4-OX	4	0	4	0.0064
12	4-4-0-OX	4	4	0	0.0009
13	4-1-3-OX	4	1	3	0.0041
14	4-2-2-OX	4	2	2	0.0025
15	5-0-5-OX	5	0	5	0.0036
16	5-1-4-OX	5	1	4	0.0021
17	5-4-1-OX	5	4	1	0.0004
18	5-2-3-OX	5	2	3	0.0013
19	5-3-2-OX	5	3	2	0.0008
20	5-25-25-OX	5	2.5	2.5	0.0010
21	6-0-6-OX	6	0	6	0.0021
22	6-1-5-OX	6	1	5	0.0012
23	6-5-1-OX	6	5	1	0.0001
24	6-4-2-OX	6	4	2	0.0002
25	6-2-4-OX	6	2	4	0.0007
26	6-3-3-OX	6	3	3	0.0004
27	7-0-7-OX	7	0	7	0.0012
28	7-1-6-OX	7	1	6	0.0007
29	7-2-5-OX	7	2	5	0.0004
30	7-3-4-OX	7	3	4	0.0002
31	7-4-3-OX	7	4	3	0.0001
32	8-0-8-OX	8	0	8	0.0008
33	8-1-7-OX	8	1	7	0.0004
34	8-2-6-OX	8	2	6	0.0002

Table 2-2. Simple Solution Compositions for Gibbsite Solubility Tests

Test No.	Test ID	Target Na (M)	Target NaOH (M)	Target $NaNO_3$ (M)	OLI 25 °C Predicted Aluminum (M)
1	1-0-1-AL	1	0	1	1.43E-08
2	1-1-0-AL	1	1	0	0.065
3	1-05-05-AL	1	0.5	0.5	0.036
4	2-0-2-AL	2	0	2	1.31E-08
5	2-2-0-AL	2	2	0	0.140
6	2-1-1-AL	2	1	1	0.077
7	3-3-0-AL	3	3	0	0.244
8	3-1-2-AL	3	1	2	0.082
9	3-2-1-AL	3	2	1	0.165
10	3-15-15-AL	3	1.5	1.5	0.124
11	4-4-0-AL	4	4	0	0.393
12	4-1-3-AL	4	1	3	0.082
13	4-3-1-AL	4	3	1	0.283
14	4-2-2-AL	4	2	2	0.178
15	5-5-0-AL	5	5	0	0.602
16	5-1-4-AL	5	1	4	0.076
17	5-4-1-AL	5	4	1	0.448
18	5-2-3-AL	5	2	3	0.179
19	5-3-2-AL	5	3	2	0.305
20	5-25-25-AL	5	2.5	2.5	0.240
21	6-6-0-AL	6	6	0	0.889
22	6-1-5-AL	6	1	5	0.067
23	6-5-1-AL	6	5	1	0.676
24	6-4-2-AL	6	4	2	0.481
25	6-2-4-AL	6	2	4	0.171
26	6-3-3-AL	6	3	3	0.310
27	7-1-6-AL	7	1	6	0.056
28	7-2-5-AL	7	2	5	0.155
29	7-5-2-AL	7	5	2	0.721
30	7-3-4-AL	7	3	4	0.301
31	7-4-3-AL	7	4	3	0.491
32	8-1-7-AL	8	1	7	0.045
33	8-7-1-AL	8	7	1	1.37
34	8-3-5-AL	8	3	5	0.278

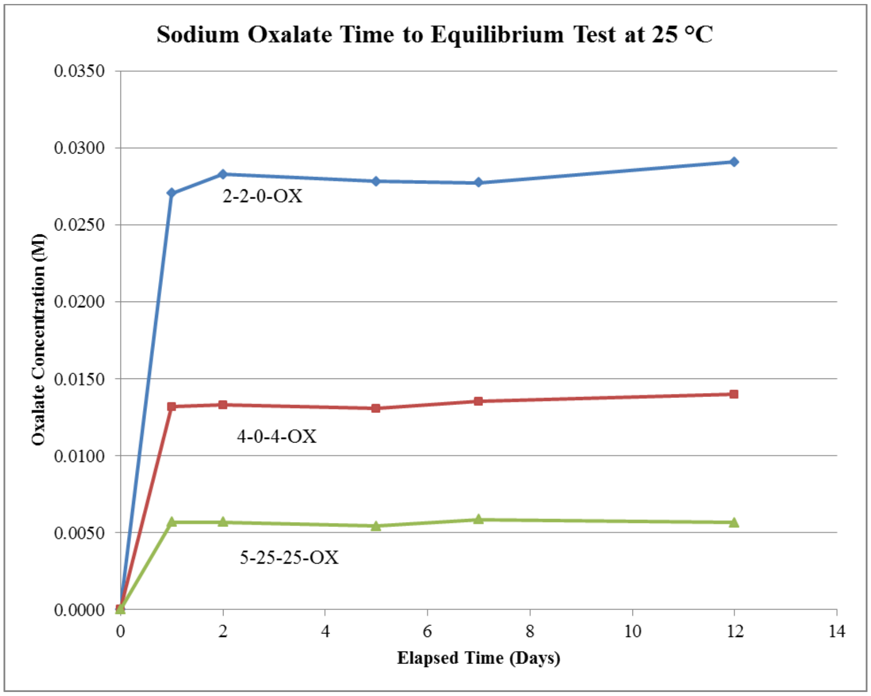

Figure 2-1. Sodium Oxalate Kinetics Test Results

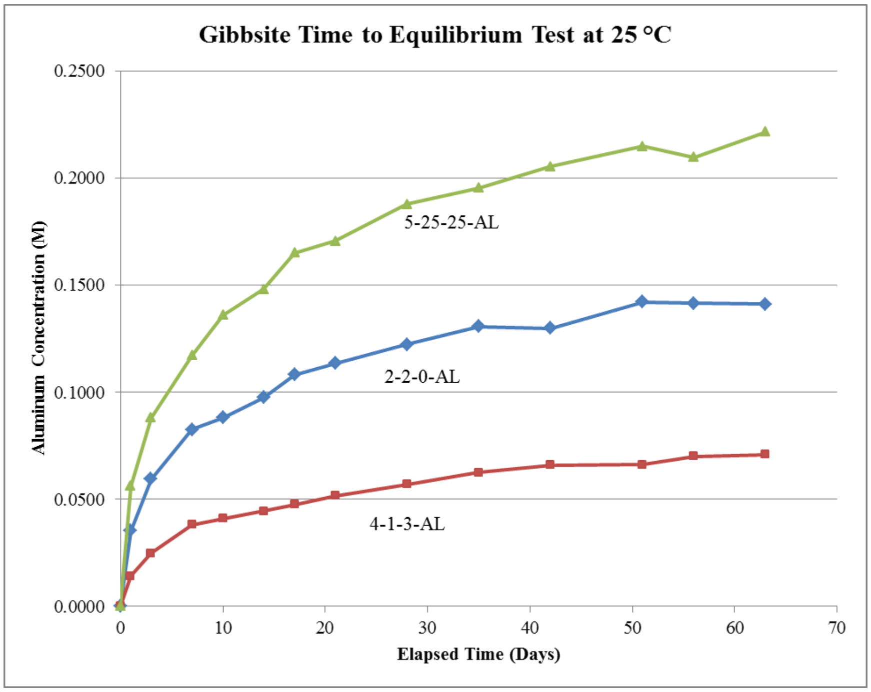

Figure 2-2. Gibbsite Kinetics Tests Results

Table 2-3. Complex Simulant Solution Compositions for Oxalate Solubility Tests

Compound	5.5 M Sodium #1 (M)	5.5 M Sodium #2 (M)	5.5 M Sodium #3 (M)	6.5 M Sodium #1 (M)	6.5 M Sodium #2 (M)	6.5 M Sodium #3 (M)
NaOH	2.0	3.0	1.0	2.5	3.0	2.0
$NaNO_3$	2.0	1.0	3.0	2.5	2.0	3.0
$NaNO_2$	0.750	0.750	0.750	0.750	0.750	0.750
Na_2SO_4	0.110	0.110	0.110	0.110	0.110	0.110
$Na_3PO_4.12H_2O$	0.003	0.003	0.003	0.003	0.003	0.003
Na_2CO_3	0.250	0.250	0.250	0.250	0.250	0.250
NaCl	0.002	0.002	0.002	0.002	0.002	0.002
$Ca(NO_3)_2.4H_2O$	0.00005	0.00005	0.00005	0.00005	0.00005	0.00005
$Na_2Ti_2O_5$	0.00005	0.00005	0.00005	0.00005	0.00005	0.00005
$Na_2SiO_3 \cdot 9H_2O$	0.005	0.005	0.005	0.005	0.005	0.005
Na, Total	5.49	5.49	5.49	6.49	6.49	6.49

Compound	7.5 M Sodium #1 (M)	7.5 M Sodium #2 (M)	7.5 M Sodium #3 (M)
NaOH	3.0	4.0	2.0
$NaNO_3$	3.0	2.0	4.0
$NaNO_2$	0.750	0.750	0.750
Na_2SO_4	0.110	0.110	0.110
$Na_3PO_4.12H_2O$	0.003	0.003	0.003
Na_2CO_3	0.250	0.250	0.250
NaCl	0.002	0.002	0.002
$Ca(NO_3)_2.4H_2O$	0.00005	0.00005	0.00005
$Na_2Ti_2O_5$	0.00005	0.00005	0.00005
$Na_2SiO_3 \cdot 9H_2O$	0.005	0.005	0.005
Na, Total	7.49	7.49	7.49

* Duplicate test solutions were prepared. One of each solution with and without the Ca, Ti, and Si.

Table 2-4. MCU Blend Solvent Composition

Component	Concentration (M)
MaxCalix	0.0465
BOBCalixC6	0.0035
TOA	0.0015
Modifier	0.5
TiDG	0.003
Isopar™ L	balance

Table 2-5. Chemical Species Input List for OLI Modeling of Solubility Tests

Input Compound	Simple Solution Model Species	Complex Simulant Solution Model Species
H_2O	X	X
NaOH	X	X
$NaNO_3$	X	X
$NaNO_2$		X
Na_2SO_4		X
Na_3PO_4		X
Na_2CO_3		X
NaCl		X
$Ca(NO_3)_2.4H_2O$		X
Na_2TiO_3		X
$Na_2SiO_3{\cdot}9H_2O$		X
$Na_2C_2O_4$	X	X
$Al(OH)_3$ (Gibbsite)	X	X

3.0 Results and Discussion

3.1 Literature Review

There is an abundance of papers examining aluminum solution chemistry in the chemical literature. Much of this literature relates to the Bayer process, an important industrial process for producing aluminum from bauxite ore.[5,6] Although relevant in a general sense, much of the work relating to the Bayer process centers on higher temperatures and concentrations than observed in SRS tank waste salt solutions. The precipitation of oxalate from Bayer process liquors is a confounding process that can limit the aluminum production rate and therefore also much studied.[7,8,9] However, again finding data directly relevant to SRS tank waste chemistry proves challenging. Significant effort has been expended to model the solubility of aluminum solutions of the Bayer process in the hopes of increasing efficiency.[10,11,12] The plethora of modeling attempts found in the literature indicates the difficulty in satisfactorily modeling aluminum solubility and precipitation.

Gibbsite is the most common form of aluminum trihydroxide found in nature.[13] The bayerite form of aluminum trihydroxide is much less common but can form under certain conditions. Typically, bayerite converts to gibbsite in strongly caustic solutions over time. Gibbsite will convert to boehmite (AlOOH) at high temperatures in caustic solutions.[14] The solubility of gibbsite is known to increase with increasing caustic concentrations and with increasing solution ionic strength.

Most SRS tank waste samples of precipitated aluminum solids show the presence of crystalline forms of gibbsite or boehmite and occasionally bayerite. The solubility of aluminum in SRS waste tank solutions appears to be governed mostly by gibbsite. Boehmite has very low solubility and doesn't contribute appreciably to the aluminum concentration at temperatures below about 40 °C. Sodium aluminate ($Na_2O.Al_2O_3.3H_2O$) has very high solubility in caustic solution and therefore is unlikely to be the solubility limiting species based on the typical aluminum concentrations observed in SRS tank waste salt solutions with aluminum containing solids.

3.2 Simple Solution Oxalate Solubility Tests from Low to High (LTH) Concentration Results

As described in the experimental section, the kinetics of the sodium oxalate and gibbsite dissolutions was determined prior to beginning the simple solution tests. The results of the kinetic tests showed the sodium oxalate reached an equilibrium concentration in the simple solutions within a few days. The gibbsite required a significantly longer period of at least nine weeks to reach equilibrium in the simple solutions. All sodium oxalate tests were allowed to run for at least five days while the gibbsite tests were limited to nine weeks to minimize the test time.

The simple solution sodium oxalate LTH solubility tests were conducted in solutions containing varying amounts of sodium nitrate and sodium hydroxide. Excess sodium oxalate solids were added to each of the solutions that were then agitated at 25 °C for five days to equilibrate. Table 3-1 shows the results of the simple solution LTH sodium oxalate tests. The measured sodium and nitrate values show close agreement with the targeted values for each solution with typically less than 10% difference. The measured oxalate decreases as the sodium molarity increases going down the table. The densities were measured on the final equilibrated solution after filtration.

As can be seen in Table 3-1, the OLI predicted oxalate concentration shows good agreement with the measured concentrations for the 1 M sodium solutions. However, the percent difference between the predicted and measured oxalate values increases significantly as the sodium concentration of the solutions increase. Most of the OLI predictions for the solutions with 5 M sodium or higher were nearly an order of magnitude lower than the measured concentrations. Although not listed in the Table 3-1, the OLI density predictions for each of the solutions were within 2% of the measured values.

Figures 3-1 and 3-2 show the data from Table 3-1 graphically. The graphs show that the oxalate concentration decreases with increasing sodium concentration. Additionally, for any given nominal sodium concentration shown on the graph (see Figure 3-2), the highest oxalate concentration was found in the solution with the lowest hydroxide concentration. For example, with the three points at the 1 M sodium line on the graph, the highest point (highest oxalate concentration) was the 1-0-1-OX solution containing no sodium hydroxide, the next point down represents the 1-05-05-OX containing 0.5 M sodium hydroxide, and the lowest point represents the 1-1-0-OX solution containing 1 M sodium hydroxide. This general trend is seen throughout the data for the simple solution sodium oxalate tests. Figure 3-2 shows the oxalate concentration as a function of the nominal (or targeted) sodium concentration but with the data in Table 3-1 divided up by nominal (or targeted) sodium hydroxide concentration. These graphs indicate the oxalate solubility is mostly governed by the total sodium concentration with a small additional effect from the amount of hydroxide present in the solution.

3.3 Simple Solution Solubility Gibbsite Tests from Low to High (LTH) Concentration Results

The simple solution gibbsite LTH solubility tests also used varying amounts of sodium nitrate and sodium hydroxide as the solution components. Excess gibbsite solids (aluminum trihydroxide) were added to each of the solutions that were then agitated at 25 °C for nine weeks to equilibrate. Table 3-2 shows the results of the simple solution gibbsite tests. As with the oxalate solution tests, the measured sodium and nitrate values show good agreement with the targeted values for each solution with typically less than a 10% difference. The densities were measured on the final equilibrated solution after filtration.

The OLI modeling predictions for the aluminum concentration in the solutions generally predicts a concentration ~20-30% higher (range of -4 to +55%) than the measured concentrations. The data doesn’t appear to show any trends of poorer predictions relative to higher sodium concentrations or other variables. Figure 3-3 shows the data in Table 3-2 graphically with the aluminum concentration plotted as a function of the nominal (or targeted) free hydroxide concentration. The graph clearly indicates that the aluminum concentration increases with increasing hydroxide concentration. For the gibbsite tests, the nominal free hydroxide indicated in the graph reflects the initial concentration of sodium hydroxide in the solutions, however, the dissolution of the gibbsite solids will consume a mole of sodium hydroxide per mole of gibbsite dissolved lowering the actual free hydroxide concentration in solution.

Figure 3-4 shows the data grouped by the nominal hydroxide concentration with the aluminum concentration plotted as a function of the nominal (or targeted) sodium concentration. The graph illustrates that the aluminum concentration increases with increasing hydroxide concentration and with increasing sodium concentration for a given hydroxide concentration. At low hydroxide concentrations the sodium concentration appears to have little effect on the aluminum concentration as seen in the points on the graph related to the 1 M NaOH. Above 1 M hydroxide the sodium begins to have a larger effect on the gibbsite solubility. At 4 M and 5 M sodium hydroxide the additional sodium has a substantial effect on the aluminum concentration. Based on the data from the tests, the gibbsite solubility appears to be governed primarily by the hydroxide concentration in the solution with an additional effect from the total sodium in solution, which increases in magnitude as the hydroxide concentration increases.

3.4 Simple Solution Stability Tests Results

All of the simple solution sodium oxalate and gibbsite equilibrated LTH test solutions were monitored for stability for one month at ambient laboratory temperature (~20 -25 °C). The solutions were filtered prior to the start of the stability tests so no seed crystals were present in the solutions. Of the sixty-four solutions, only three of the oxalate solutions and one of the aluminum solutions showed the formation of a precipitate. A precipitate formed in all three of the equilibrated sodium oxalate solutions containing 8 M sodium and one of the equilibrated gibbsite solutions containing 8 M sodium. In the three oxalate solutions, several very large crystals started to form within a few days. Analysis of several of these crystals by x-ray diffraction (XRD) and from dissolution of a small portion of the crystal followed by ICPE-ES and IC analysis showed them to be quite pure sodium nitrate. Figure 3-5 shows a photograph of one of the bottles containing an approximately one-half inch long sodium nitrate crystal. Figure 3-6 contains the XRD of the crystals from solution 8-2-6-OX (8 M Na, 2 M NaOH, 6 M $NaNO_3$). The aluminum solution 8-1-7-AL contained crystalline solids that formed within ~7 days after the completion of the solubility test. These solids were not analyzed but were likely sodium nitrate crystals also. These results indicate that most of these simple solutions equilibrated with sodium oxalate or gibbsite solids are stable to precipitation at ~25 °C. However, oxalate and aluminum solutions with >6 M sodium nitrate concentrations in an 8 M total sodium concentration may precipitate sodium nitrate solids. As noted in the experimental section, some difficulty was encountered during solution preparation in getting all of the added sodium nitrate solids to dissolve in these four solutions.

3.5 Simple Solution Oxalate Solubility Tests from High to Low (HTL) Concentration Results

In these tests, the solutions were equilibrated first at a higher temperature and then re-equilibrated at a lower temperature to examine the solubility that results when coming from a higher concentration down to a lower concentration. This also allowed the collection of solubility data for oxalate in these solutions at higher temperatures. For the simple solution oxalate HTL tests, the solutions were first equilibrated at 60 °C, followed by 40 °C, and finally 25 °C.

Table 3-3 shows the oxalate concentrations at 60°C and 40 °C for each of the thirty-four oxalate test solutions along with the OLI predicted concentrations at those temperatures. As seen with the results of the LTH 25 °C tests discussed in section 3.2, the oxalate concentrations from the 60 °C and 40 °C tests generally decrease with increasing sodium. The oxalate concentration drops about 30% going from 60 °C down to 40 °C. The differences between the OLI predicted concentrations and the measured concentrations are also similar in magnitude to the LTH 25 °C tests.

Table 3-4 contains the composition of the solutions after dropping the temperature from 40 °C to 25 °C and allowing the solutions to re-equilibrate at the new lower temperature. The oxalate concentrations dropped another ~20% over the 15 °C temperature change. The sodium and nitrate ion concentrations agree reasonably well with the nominal concentrations with differences of generally less than ~15%. However, the nitrate values appear to be consistently low and the sodium values consistently high. The densities were measured on the final equilibrated solution after filtration. Table 3-5 shows the measured oxalate concentrations from the LTH 25 °C tests compared with the HTL 25 °C tests. The oxalate concentrations from the two test methods show reasonable agreement; however, all of the HTL 25 °C oxalate concentrations are lower than the LTH concentrations. That may be an actual difference due to the differing test method or possibly an analytical bias that mirrors the low nitrate ion results measured using the same IC method. Table 3-6 shows the results of a repeat simple solution sodium oxalate solubility test using a small subset of the solutions. The new tests were conducted simultaneously using splits of the same initial sodium hydroxide/sodium nitrate solutions. The HTL samples were equilibrated at 60 °C in a shaker oven and then moved to a 25 °C oven along with the LTH samples. All of the final equilibrated samples were analyzed together as a group in PSAL. The oxalate concentrations from the HTL and LTH show very close agreement indicating that the same concentration can be obtained using the two test methods for the simple solution tests. Figure 3-7 shows the HTL 25 °C oxalate concentration as a function of the nominal (or targeted) sodium concentration with the data divided up by nominal sodium hydroxide concentration. As with the LTH 25 °C oxalate test data in Figure 3-2, this graph also indicates the oxalate solubility is mostly governed by the total sodium concentration with a small additional effect from the amount of hydroxide present in the solution.

3.6 Simple Solution Gibbsite Solubility Tests from High to Low (HTL) Concentration Results

The simple solutions for the gibbsite HTL tests were equilibrated at 40 °C first and then re-equilibrated at 25 °C. Table 3-7 shows the aluminum concentration data collected for the HTL 40 °C solutions along with the OLI predicted aluminum concentration at 40 °C. The agreement between the measured and predicted aluminum concentrations at 40 °C is reasonably good, much better than the comparison at 25 °C. Table 3-8 contains the solution compositions after re-equilibration at 25 °C. The sodium and nitrate ion concentrations agree reasonably well with the nominal concentrations with differences of generally less than ~10%. The densities were measured on the final equilibrated solution after filtration. The OLI predicted aluminum concentrations are generally lower than measured concentrations at 25 °C.

Table 3-9 provides a comparison of the LTH and HTL 25 °C measured aluminum concentrations. The data shows significant differences in the final equilibrated aluminum concentration depending on the test method. The aluminum concentrations obtained from the HTL method show ~50-250% higher aluminum concentrations than the LTH method. The majority of the differences appear to be in the 50-100% range. These solutions contained excess gibbsite solids so seed crystals were present to promote precipitation as the solution was brought down from a higher aluminum concentration at 40 °C to 25 °C. The large offset between the final aluminum concentrations of the two test methods can’t easily be explained away by analytical bias/error. The OLI predictions for the 25 °C gibbsite solubility are generally 20-30% lower than the measured HTL aluminum concentrations. Interestingly, the average aluminum concentration from the two test methods matches reasonably well with the OLI predicted concentrations as shown in Table 3-10.

Figure 3-8 and 3-9 show the LTH and HTL 25 °C data grouped by sodium hydroxide concentration and the aluminum concentration plotted as a function of the nominal (or targeted) sodium concentration. The graphs both illustrates that the aluminum concentration increases with increasing hydroxide concentration and with increasing sodium concentration for a given hydroxide concentration. The equations for the “lines of best fit” show that the slope of the line generally increases with increasing sodium hydroxide concentration. The exception is the line for the 1 M NaOH of the LTH test that remains relatively flat as the sodium concentration increases. For any given hydroxide concentration the aluminum concentration in solution increases slightly with increasing sodium concentration. Both the LTH and the HTL data show the same trends indicating that the gibbsite solubility appears to be governed primarily by the hydroxide concentration with an additional smaller effect from the total sodium in solution. The smaller sodium concentration effect increases in magnitude as the hydroxide concentration increases. However, the LTH test produced lower aluminum concentrations and slightly lower slopes to the lines of best fit.

3.7 Simple Solution Solubility Tests with both Sodium Oxalate and Gibbsite Results

A small subset of ten of the simple solutions from the previous testing already equilibrated with either oxalate or aluminum were used to determine the effect of oxalate or aluminum on the solubility of each other. Five of the solutions were already saturated at 25 °C with sodium oxalate and five with gibbsite. Gibbsite solids were added to the solutions already saturated with sodium oxalate and sodium oxalate solids were added to the solutions already saturated with aluminum.

Table 3-11 shows the equilibrated composition of the ten solutions after nine weeks at 25 °C. The "Original $C_2O_4^{2-}$" and "Original Al" columns indicate the measured concentrations of these species in the original solution at the beginning of the test. The results in the table indicate the oxalate concentration remained essentially unchanged in the solution originally saturated in sodium oxalate after equilibration with gibbsite solids. The small differences in the values can likely be attributed to experimental/analytical error. From these results, the presence of dissolved aluminum in the solution appears to have no effect on the sodium oxalate solubility.

The aluminum concentration varied slightly in the solutions depending on the presence of oxalate in the original solution; however, the effect is small and likely within experimental/analytical error. In the solution already saturated in aluminum, the aluminum concentration went up ~10-20% even though no additional gibbsite was added. The fact that the aluminum concentration in the solution saturated in oxalate is slightly lower than the Original Al concentrations by 15-25% may also just be due to experimental/analytical error. The results of the test seem to indicate that the presence of oxalate in the solution has very little effect on the gibbsite solubility.

3.8 Complex Simulant Solution Solubility Tests with both Sodium Oxalate and Gibbsite Results

The results of the analysis of the eighteen complex simulant solutions before the addition of sodium oxalate and gibbsite solids are shown in Table 3-12. The analytical results indicate the sodium and anion concentrations closely match the targeted concentrations. The sodium and anion concentrations of the solutions without metals in the top half of the table also match well with the concentrations measured in the solutions with metals in the lower half of the table (sample ID's ending in –MT). These solutions should show good agreement since the two sets of solutions were splits of the same "no metal" containing solutions. Metals (Ca, Si, Ti) were then added to the nine solutions in the bottom half of the table. The densities were measured on the final equilibrated solution after filtration.

The silicon concentration for the nine solutions in the bottom half of Table 3-12 (designated as "-MT") show slightly higher concentrations than the 5.0E-03 M targeted. The nine solutions in the top half of the table should contain no silicon, but a small silicon impurity must be present in the chemicals used for the solution preparation. The measured silicon concentration in these "no metals" solutions was deemed insignificant being approximately two orders of magnitude lower than the concentration in the solutions with metals ("-MT" solutions). The calcium concentration appears similar in all eighteen solutions and close to the target concentration of 5.0E-05 M. In fact, the calcium concentration seems to track the nitrate concentration indicating the calcium may be an impurity in the sodium nitrate reagent used in the solution preparation. Titanium was not detected in any of the solutions. Clearly none of the MST slurry used as the titanium source dissolved into the salt solutions during solution preparation. Because of the very low concentrations of titanium and presence of calcium in all the solutions, only the effect of silicon on the solubility of sodium oxalate and gibbsite can be evaluated in the tests.

Table 3-13 provides the composition of the eighteen complex simulant solutions after equilibration for nine weeks at 25 °C with sodium oxalate and gibbsite solids. The sodium and nitrate concentrations are consistent with the concentrations measured in the initial solutions. The densities were measured on the final equilibrated solution after filtration. The oxalate concentrations appear to be what would be expected based on the solubilities measured in the simple solution tests for solutions with similar sodium concentrations. For example, from Table 3-1 the oxalate concentrations measured in the 5 M sodium simple solutions ranged from 0.0058 M to 0.010 M. The six ~5 M complex simulant solutions (three without metals and three with metals) show oxalate concentrations mostly within that same range. The same comparison of the ~6 M and ~7 M complex simulant solutions with the simple solutions of the same approximate sodium concentration show oxalate concentrations within the same ranges. The small differences in oxalate concentrations between the solutions without metals and the solutions with metal likely fall within the experimental/analytical error.

The measured aluminum concentrations for the equilibrated complex simulant solutions in Table 3-13 can also be compared to the simple solution results for solutions with comparable hydroxide concentrations. From Table 3-2, the aluminum concentration from solutions containing 2 M hydroxide range from 0.116 M to 0.161 M. For the complex simulant solutions in Table 3-13 with 2 M hydroxide (solutions with the middle number 2 in the Test ID), the aluminum ranges from 0.077 M to 0.094 M. A similar comparison between the 3 M and 4 M hydroxide solutions shows significantly lower aluminum concentrations in the complex simulant solutions than expected based on the simple solution results. The reason for the lower aluminum concentrations in the complex simulant is not readily apparent. The concentration of all the metals (Ca, Si, Ti) combined is insufficient to account for the difference. Although the complex simulant solutions with metals in the lower half of the table appear slightly lower than those without metals, the differences are within expected analytical error (<10%).

Although not shown in the table, no titanium was detected in any of the final solutions, similar to what was observed in the initial solutions. No calcium was detected in any of the final solutions after equilibration either, however; because of different dilution factor during analysis, the detection limit was higher than the measured concentrations in the initial solutions so nothing can be inferred from the results. Nearly all of the silicon appears to have precipitated from the equilibrated complex simulant solutions, but this did not produce a measurable effect on the equilibrated aluminum concentration because the initial concentration of silicon in the complex simulant solution was too low (~0.005-9 M).

Table 3-14 compares the measured aluminum and oxalate concentrations in the equilibrated complex simulant solutions with the OLI predicted concentrations at 25 °C. The comparison shows significantly lower measured aluminum concentrations than predicted by the OLI software. Conversely, the measured oxalate concentrations were significantly higher than predicted by OLI.

3.9 Complex Simulant Solution Solubility Tests with Next Generation Solvent (NGS)

These tests were conducted using two of the complex simulant solutions after saturation with sodium oxalate and gibbsite solids to determine if contact with MCU blend solvent induced precipitation of saturated salt solutions. Each day all four samples, two salt solution/solvent mixtures and two control samples containing just salt solution, were removed from the shaker oven and visually examined. It was noted after one day that the two salt solution/solvent mixtures had clarified with the two layers cleanly separated. No solids precipitation was observed in any of the four samples over the one week test period. The contact with MCU solvent does not appear to cause precipitation from 6.5 M sodium salt solutions saturated in oxalate and aluminum.

Table 3-1. Results of Simple Solution Sodium Oxalate Solubility Tests from Low to High Concentration at 25 °C

Test ID	Measured Na (M)	Measured NO_3^- (M)	Measured $C_2O_4^{2-}$ (M)	Measured Density (g/mL)	OLI 25 °C Predicted $C_2O_4^{2-}$ (M)	% Difference Predicted vs Measured
1-0-1-OX	0.959	0.876	0.083	1.06	0.079	-4.8
1-1-0-OX	0.940	<0.002	0.074	1.05	0.068	-7.5
1-05-05-OX	0.966	0.416	0.079	1.06	0.074	-6.4
2-0-2-OX	1.79	1.82	0.038	1.11	0.028	-27
2-2-0-OX	1.78	<0.002	0.032	1.08	0.015	-53
2-1-1-OX	1.79	0.887	0.029	1.10	0.021	-27
3-0-3-OX	2.73	2.90	0.022	1.16	0.013	-44
3-3-0-OX	2.76	<0.002	0.016	1.12	0.0036	-78
3-1-2-OX	2.76	1.84	0.019	1.15	0.0085	-56
3-2-1-OX	2.73	0.890	0.018	1.13	0.0056	-69
4-0-4-OX	3.81	3.73	0.014	1.22	0.0064	-55
4-4-0-OX	3.63	<0.002	0.010	1.15	0.0009	-91
4-1-3-OX	3.73	2.92	0.013	1.20	0.0041	-68
4-2-2-OX	3.78	1.90	0.011	1.18	0.0025	-77
5-0-5-OX	4.70	4.95	0.010	1.26	0.0036	-64
5-1-4-OX	4.94	3.95	0.0083	1.25	0.0021	-75
5-4-1-OX	4.74	0.890	0.0058	1.20	0.0004	-93
5-2-3-OX	4.94	2.92	0.0073	1.23	0.0013	-82
5-3-2-OX	4.72	1.82	0.0064	1.22	0.0008	-87
5-25-25-OX	4.83	2.31	0.0067	1.23	0.0010	-85
6-0-6-OX	5.81	5.81	0.0068	1.32	0.0021	-69
6-1-5-OX	5.94	5.03	0.0057	1.30	0.0012	-79
6-5-1-OX	5.70	0.890	0.0033	1.23	0.0001	-96
6-4-2-OX	5.61	1.92	0.0038	1.24	0.0002	-94
6-2-4-OX	5.50	3.84	0.0053	1.28	0.0007	-87
6-3-3-OX	5.89	2.87	0.0043	1.26	0.0004	-91
7-0-7-OX	6.94	6.97	0.0050	1.36	0.0012	-76
7-1-6-OX	6.96	5.98	0.0040	1.35	0.0007	-82
7-2-5-OX	7.07	4.87	0.0032	1.33	0.0004	-88
7-3-4-OX	6.89	3.35	0.0028	1.31	0.0002	-93
7-4-3-OX	6.72	2.77	0.0023	1.30	0.0001	-95
8-0-8-OX	8.13	7.69	0.0040	1.39	0.0008	-80
8-1-7-OX	8.03	6.58	0.0030	1.38	0.0004	-87
8-2-6-OX	8.16	5.79	0.0022	1.37	0.0002	-90

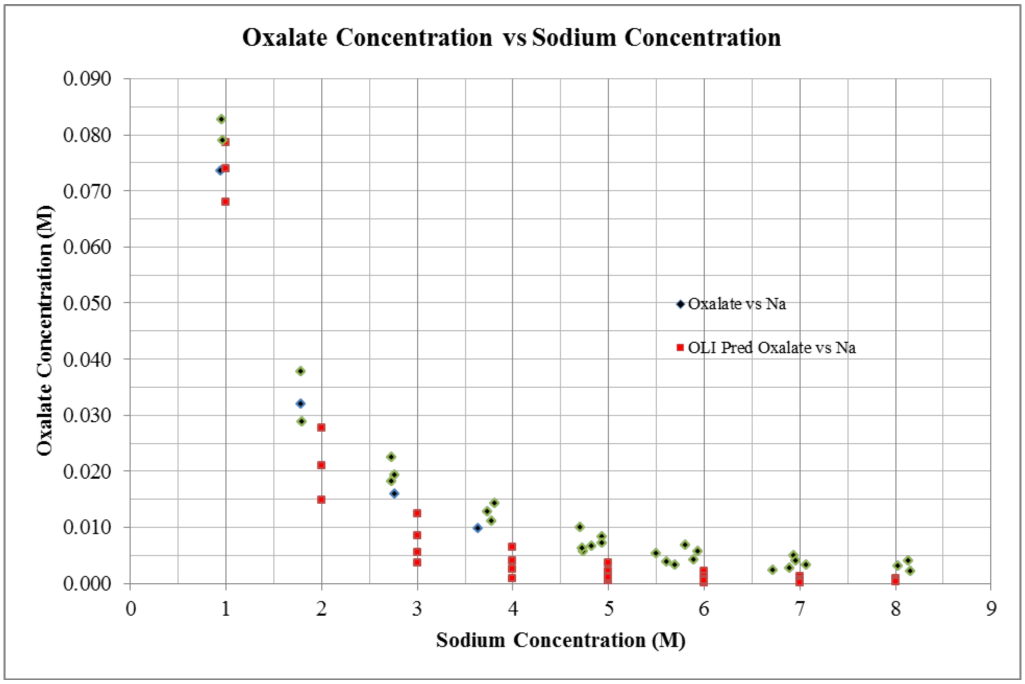

Figure 3-1. Simple Solution Oxalate Solubility LTH Test at 25 °C - Oxalate Concentration vs. Sodium Concentration

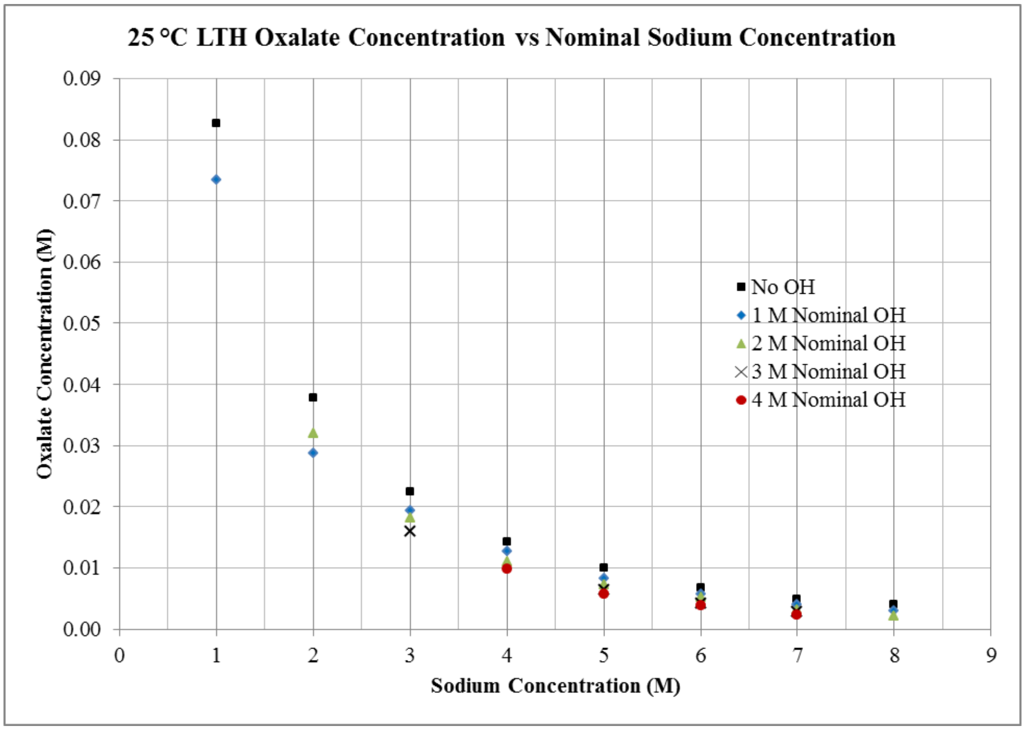

Figure 3-2. Simple Solution Oxalate Solubility LTH Test at 25 °C - Oxalate Concentration vs. Nominal Sodium Concentration

Table 3-2. Results of Simple Solution Gibbsite Solubility Tests from Low to High Concentration at 25 °C

Test ID	Measured Na (M)	Measured NO_3^- (M)	Measured Al (M)	Measured Density (g/mL)	OLI 25 °C Predicted Al (M)	% Difference Predicted vs Measured
1-0-1-AL	0.935	0.823	<3.7E-05	1.05	1.43E-08	-
1-1-0-AL	0.948	<0.002	0.057	1.04	0.065	14
1-05-05-AL	0.981	0.397	0.027	1.05	0.036	33
2-0-2-AL	1.98	1.87	<3.7E-05	1.11	1.31E-08	-
2-2-0-AL	1.95	<0.002	0.116	1.08	0.140	20
2-1-1-AL	1.94	0.847	0.054	1.09	0.077	43
3-3-0-AL	2.88	<0.002	0.213	1.12	0.244	14
3-1-2-AL	3.02	1.95	0.061	1.15	0.082	35
3-2-1-AL	2.88	0.871	0.139	1.13	0.165	18
3-15-15-AL	3.26	1.46	0.090	1.14	0.124	38
4-4-0-AL	4.03	<0.002	0.337	1.16	0.393	16
4-1-3-AL	4.21	3.02	0.061	1.20	0.082	33
4-3-1-AL	4.11	0.905	0.237	1.17	0.283	19
4-2-2-AL	4.37	1.85	0.143	1.19	0.178	24
5-5-0-AL	5.05	<0.002	0.476	1.18	0.602	26
5-1-4-AL	5.15	3.52	0.054	1.25	0.076	41
5-4-1-AL	5.00	0.914	0.348	1.20	0.448	29
5-2-3-AL	5.39	2.74	0.151	1.23	0.179	19
5-3-2-AL	5.42	1.71	0.232	1.22	0.305	31
5-25-25-AL	5.44	2.53	0.205	1.23	0.240	17
6-6-0-AL	5.85	0.003	0.680	1.23	0.889	31
6-1-5-AL	6.07	4.60	0.051	1.29	0.067	32
6-5-1-AL	6.02	0.934	0.439	1.24	0.676	54
6-4-2-AL	6.20	1.92	0.426	1.26	0.481	13
6-2-4-AL	6.44	3.82	0.161	1.29	0.171	5.9
6-3-3-AL	6.44	3.14	0.274	1.27	0.310	13
7-1-6-AL	7.48	6.52	0.052	1.35	0.056	8.3
7-2-5-AL	7.44	5.32	0.161	1.33	0.155	-3.6
7-5-2-AL	7.20	1.94	0.628	1.29	0.721	15
7-3-4-AL	7.55	4.26	0.313	1.32	0.301	-4.0
7-4-3-AL	7.57	3.03	0.469	1.30	0.491	4.7
8-1-7-AL	8.33	6.35	0.050	1.38	0.045	-10
8-7-1-AL	8.11	0.893	1.08	1.31	1.37	27
8-3-5-AL	8.63	5.23	0.319	1.37	0.278	-13

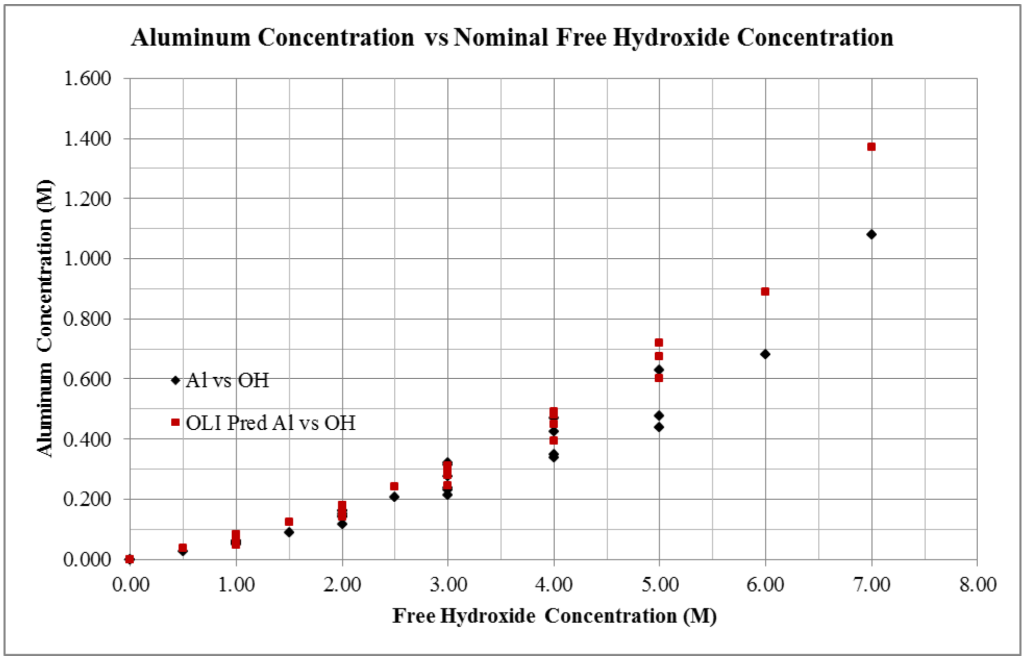

Figure 3-3. **Simple Solution Gibbsite Solubility LTH Test at 25 °C - Aluminum Concentration vs. Nominal Free Hydroxide Concentration**

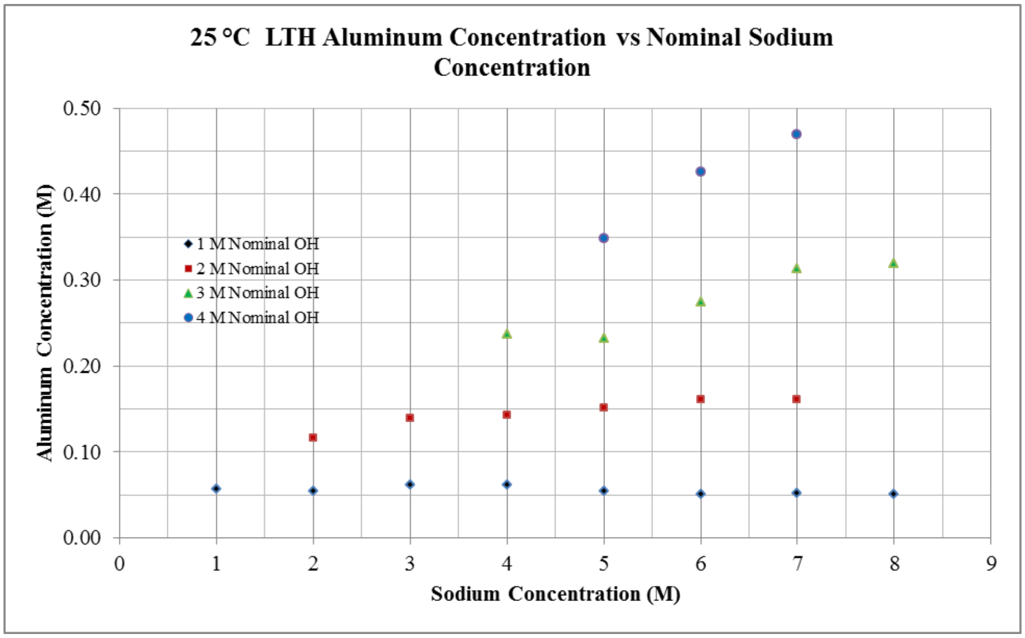

Figure 3-4. **Simple Solution Gibbsite Solubility LTH Test at 25 °C - Aluminum Concentration vs. Nominal Sodium Concentration**

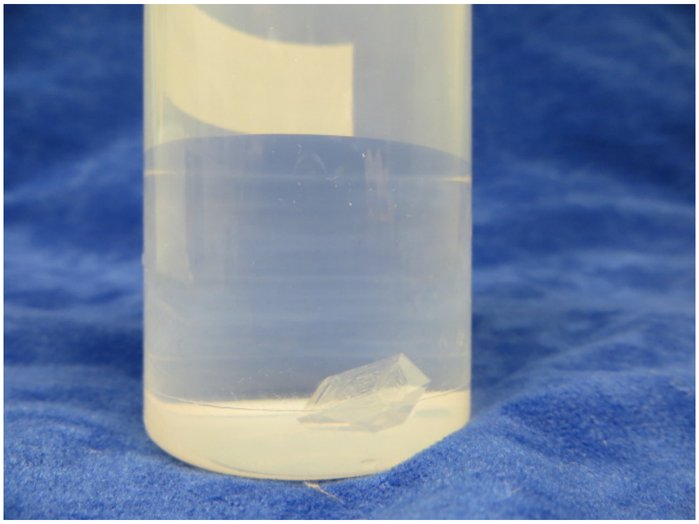

Figure 3-5. Photograph of Sodium Nitrate Crystal in an Oxalate Solution

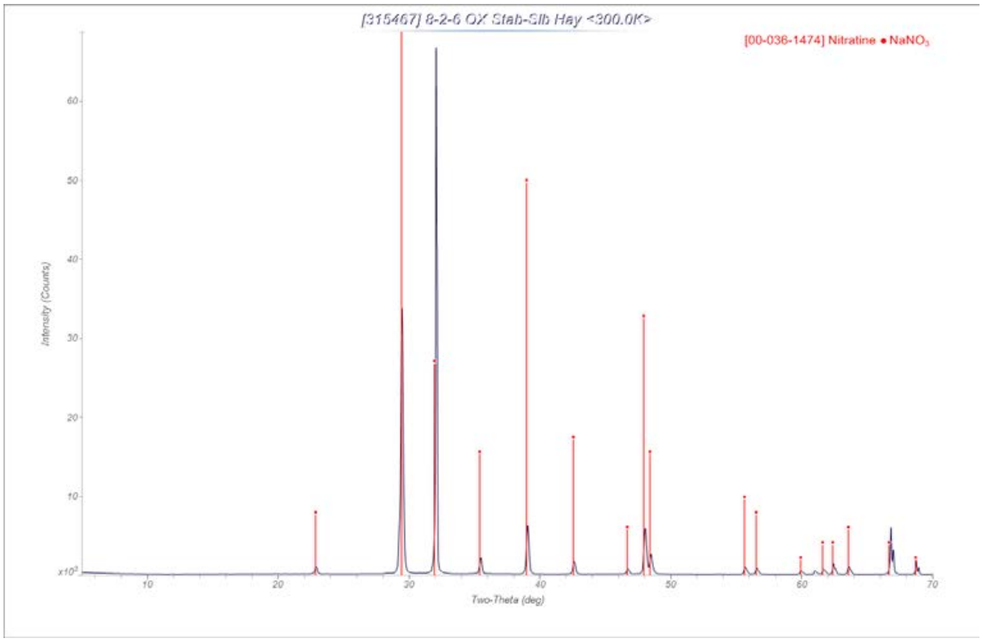

Figure 3-6. XRD of Sodium Nitrate Crystals from Solution 8-2-6-OX

Table 3-3. Simple Solution Sodium Oxalate Solubility Tests from High to Low Concentrations – 60 °C and 40 °C Results

Test ID	Measured 60 °C $C_2O_4^{2-}$ (M)	OLI 60 °C Predicted $C_2O_4^{2-}$ (M)	% Difference Predicted vs Measured	Measured 40 °C $C_2O_4^{2-}$ (M)	OLI 40 °C Predicted $C_2O_4^{2-}$ (M)	% Difference Predicted vs Measured
1-0-1-OX	0.121	0.126	4.3	0.082	0.099	20
1-1-0-OX	0.126	0.115	-8.5	0.092	0.087	-4.8
1-05-05-OX	0.105	0.122	16	0.061	0.094	54
2-0-2-OX	0.048	0.063	30	0.033	0.041	24
2-2-0-OX	0.054	0.040	-26	0.035	0.023	-34
2-1-1-OX	0.046	0.051	11	0.030	0.032	5.9
3-0-3-OX	0.028	0.044	59	0.018	0.022	24
3-3-0-OX	0.027	0.016	-42	0.019	0.0070	-64
3-1-2-OX	0.032	0.032	0.6	0.021	0.016	-27
3-2-1-OX	0.029	0.023	-21	0.021	0.011	-50
4-0-4-OX	0.021	0.036	71	0.014	0.014	-2.0
4-4-0-OX	0.017	0.0068	-61	0.0091	0.0022	-76
4-1-3-OX	0.019	0.025	27	0.012	0.0091	-21
4-2-2-OX	0.019	0.016	-15	0.012	0.0058	-52
5-0-5-OX	0.014	0.034	149	0.010	0.010	2.2
5-1-4-OX	0.013	0.021	66	0.0076	0.0060	-21
5-4-1-OX	0.010	0.0051	-51	0.0060	0.0013	-78
5-2-3-OX	0.011	0.013	16	0.0072	0.0036	-50
5-3-2-OX	0.010	0.0082	-17	0.0063	0.0022	-65
5-25-25-OX	0.012	0.010	-11	0.0065	0.0028	-57
6-0-6-OX	0.015	0.035	128	0.0067	0.0073	9.4
6-1-5-OX	0.0058	0.020	241	0.0054	0.0042	-22
6-5-1-OX	0.0055	0.0025	-55	0.0034	0.0005	-86
6-4-2-OX	0.0060	0.0042	-30	0.0042	0.0008	-81
6-2-4-OX	0.0071	0.012	65	0.0054	0.0024	-55
6-3-3-OX	0.0050	0.0070	40	0.0044	0.0014	-68
7-0-7-OX	0.011	0.037	243	0.0049	0.0056	14
7-1-6-OX	0.0060	0.020	230	0.0040	0.0031	-23
7-2-5-OX	0.0048	0.011	131	0.0037	0.0017	-54
7-3-4-OX	0.0044	0.0063	44	0.0032	0.0010	-70
7-4-3-OX	0.0035	0.0037	3.2	0.0028	0.0005	-81
8-0-8-OX	0.0073	0.041	456	0.0038	0.0044	16
8-1-7-OX	0.0049	0.021	333	0.0037	0.0023	-37
8-2-6-OX	0.0034	0.011	223	0.0027	0.0012	-56

Table 3-4. Simple Solution Sodium Oxalate Solubility Tests from High to Low Concentrations – 25 °C Results

Test ID	Measured Na (M)	Measured NO_3^- (M)	Measured $C_2O_4^{2-}$ (M)	Measured Density (g/mL)	OLI 25 °C Predicted $C_2O_4^{2-}$ (M)	% Difference Predicted vs Measured
1-0-1-OX	1.22	0.834	0.064	1.06	0.079	23
1-1-0-OX	1.17	<0.005	0.072	1.05	0.068	-5.5
1-05-05-OX	1.27	0.479	0.076	1.06	0.074	-3.4
2-0-2-OX	2.21	1.84	0.027	1.11	0.028	3.3
2-2-0-OX	2.20	<0.005	0.030	1.08	0.015	-51
2-1-1-OX	2.23	0.896	0.024	1.10	0.021	-12
3-0-3-OX	3.38	2.87	0.015	1.16	0.013	-17
3-3-0-OX	3.40	<0.005	0.016	1.12	0.0036	-77
3-1-2-OX	3.39	1.73	0.017	1.15	0.0085	-49
3-2-1-OX	3.40	0.849	0.018	1.13	0.0056	-69
4-0-4-OX	4.25	3.98	0.012	1.22	0.0064	-49
4-4-0-OX	4.16	<0.005	0.0072	1.15	0.0009	-88
4-1-3-OX	4.33	2.67	0.010	1.20	0.0041	-60
4-2-2-OX	4.11	1.72	0.0093	1.18	0.0025	-73
5-0-5-OX	5.25	4.50	0.0074	1.27	0.0036	-51
5-1-4-OX	5.37	3.63	0.0064	1.25	0.0021	-67
5-4-1-OX	5.32	0.837	0.0043	1.20	0.0004	-91
5-2-3-OX	5.32	2.72	0.0059	1.24	0.0013	-78
5-3-2-OX	5.23	1.70	0.0048	1.22	0.0008	-83
5-25-25-OX	5.33	2.42	0.0049	1.23	0.0010	-80
6-0-6-OX	6.43	5.46	0.0052	1.32	0.0021	-60
6-1-5-OX	6.41	4.42	0.0043	1.30	0.0012	-72
6-5-1-OX	6.35	0.764	0.0023	1.23	0.0001	-94
6-4-2-OX	6.28	1.67	0.0029	1.25	0.0002	-92
6-2-4-OX	6.32	3.84	0.0037	1.28	0.0007	-81
6-3-3-OX	6.31	2.63	0.0032	1.27	0.0004	-87
7-0-7-OX	7.50	6.11	0.0031	1.37	0.0012	-61
7-1-6-OX	7.51	6.54	0.0038	1.35	0.0007	-81
7-2-5-OX	7.36	5.13	0.0024	1.33	0.0004	-83
7-3-4-OX	7.29	3.67	0.0024	1.31	0.0002	-91
7-4-3-OX	7.22	2.54	0.0019	1.30	0.0001	-94
8-0-8-OX	7.82	7.95	0.0029	1.39	0.0008	-73
8-1-7-OX	7.95	7.07	0.0023	1.38	0.0004	-83
8-2-6-OX	8.12	5.21	0.0019	1.38	0.0002	-89

Table 3-5. Comparison of Simple Solution Sodium Oxalate Solubility Tests – LTH and HTL Solubilities at 25 °C Results

Test ID	LTH $C_2O_4^{2-}$ (M)	HTL $C_2O_4^{2-}$ (M)	Average $C_2O_4^{2-}$ (M)	%RSD
1-0-1-OX	0.083	0.064	0.073	18
1-1-0-OX	0.074	0.072	0.073	1.5
1-05-05-OX	0.079	0.076	0.078	2.3
2-0-2-OX	0.038	0.027	0.032	24
2-2-0-OX	0.032	0.030	0.031	4.0
2-1-1-OX	0.029	0.024	0.026	13
3-0-3-OX	0.022	0.015	0.019	28
3-3-0-OX	0.016	0.016	0.016	0.3
3-1-2-OX	0.019	0.017	0.018	11
3-2-1-OX	0.018	0.018	0.018	0.7
4-0-4-OX	0.014	0.012	0.013	10
4-4-0-OX	0.010	0.0072	0.0085	22
4-1-3-OX	0.013	0.010	0.011	16
4-2-2-OX	0.011	0.0093	0.010	12
5-0-5-OX	0.010	0.0074	0.0087	22
5-1-4-OX	0.0083	0.0064	0.0074	19
5-4-1-OX	0.0058	0.0043	0.0050	21
5-2-3-OX	0.0073	0.0059	0.0066	15
5-3-2-OX	0.0064	0.0048	0.0056	20
5-25-25-OX	0.0067	0.0049	0.0058	22
6-0-6-OX	0.0068	0.0052	0.0060	18
6-1-5-OX	0.0057	0.0043	0.0050	19
6-5-1-OX	0.0033	0.0023	0.0028	23
6-4-2-OX	0.0038	0.0029	0.0033	20
6-2-4-OX	0.0053	0.0037	0.0045	25
6-3-3-OX	0.0043	0.0032	0.0037	21
7-0-7-OX	0.0050	0.0031	0.0040	32
7-1-6-OX	0.0040	0.0038	0.0039	4.1
7-2-5-OX	0.0032	0.0024	0.0028	21
7-3-4-OX	0.0028	0.0024	0.0026	12
7-4-3-OX	0.0023	0.0019	0.0021	13
8-0-8-OX	0.0040	0.0029	0.0035	22
8-1-7-OX	0.0030	0.0023	0.0027	18
8-2-6-OX	0.0022	0.0019	0.0021	10

Table 3-6. Repeat of Simple Solution Sodium Oxalate Solubility Tests – LTH and HTL Solubilities at 25 °C Results

Test ID	Original LHT $C_2O_4^{2-}$ (M)	Original HLT $C_2O_4^{2-}$ (M)	New Test LHT $C_2O_4^{2-}$ (M)	New Test HLT $C_2O_4^{2-}$ (M)	Average $C_2O_4^{2-}$ (M)	%RSD
1-1-0-OX	0.074	0.072	0.072	0.072	0.073	1.2
1-05-05-OX	0.079	0.076	0.076	0.078	0.077	1.8
2-2-0-OX	0.032	0.030	0.029	0.038	0.032	12
2-1-1-OX	0.029	0.024	0.031	0.031	0.029	11
3-3-0-OX	0.016	0.016	0.016	0.016	0.016	1.1
3-2-1-OX	0.018	0.018	0.018	0.016	0.018	4.2
4-4-0-OX	0.010	0.0070	0.0077	0.0077	0.0081	16
4-1-3-OX	0.013	0.010	0.012	0.012	0.012	11
5-5-0-OX	-	-	0.0043	0.0045	0.0044	2.7
5-3-2-OX	0.0060	0.0050	0.0063	0.0059	0.0058	9.8

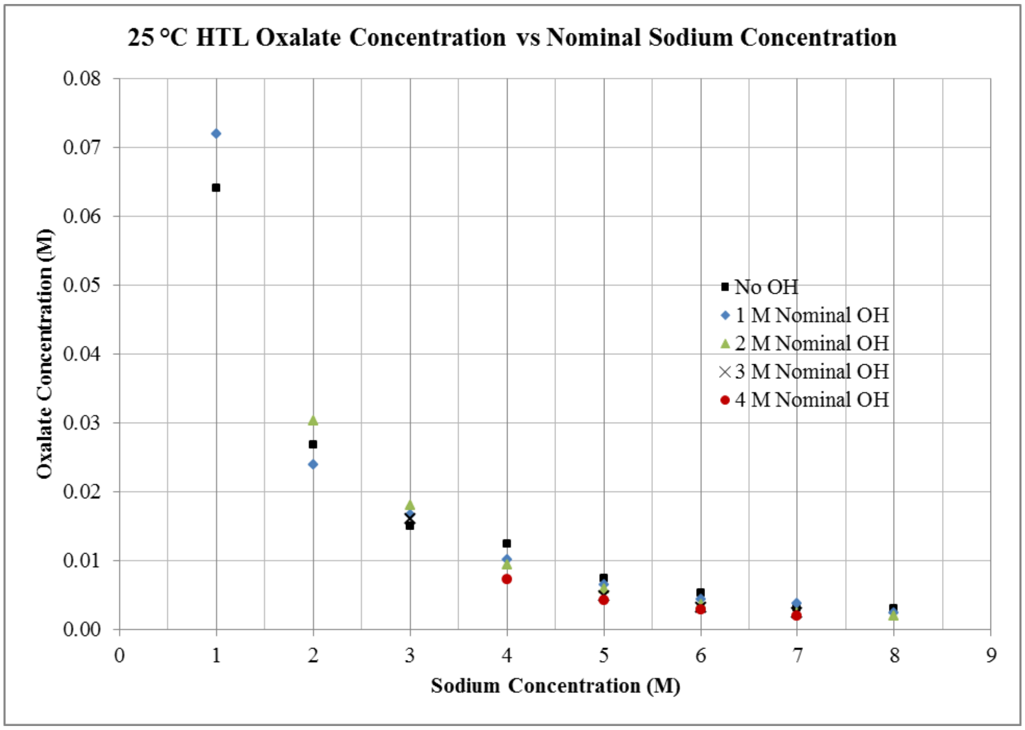

Figure 3-7. Simple Solution Oxalate Solubility HTL Test at 25 °C - Oxalate Concentration vs. Nominal Sodium Concentration

Table 3-7. Simple Solution Gibbsite Solubility Tests from High to Low Concentrations – 40 °C Results

Test ID	Measured 40 °C Al (M)	OLI 40 °C Predicted Al (M)	% Difference Predicted vs Measured
1-0-1-AL	<2.8E-05	3.56E-08	-
1-1-0-AL	0.123	0.100	-19
1-05-05-AL	0.065	0.053	-18
2-0-2-AL	<2.6E-05	3.37E-08	-
2-2-0-AL	0.249	0.219	-12
2-1-1-AL	0.130	0.116	-11
3-3-0-AL	0.379	0.382	0.8
3-1-2-AL	0.138	0.130	-5.9
3-2-1-AL	0.292	0.258	-11
3-15-15-AL	0.217	0.195	-10
4-4-0-AL	0.569	0.605	6.2
4-1-3-AL	0.152	0.142	-6.1
4-3-1-AL	0.453	0.449	-0.8
4-2-2-AL	0.328	0.294	-10
5-5-0-AL	0.773	0.901	17
5-1-4-AL	0.156	0.153	-2.2
5-4-1-AL	0.635	0.706	11
5-2-3-AL	0.334	0.326	-2.3
5-3-2-AL	0.525	0.513	-2.3
5-25-25-AL	0.440	0.418	-4.9
6-6-0-AL	1.14	1.28	12
6-1-5-AL	0.183	0.162	-12
6-5-1-AL	0.912	1.04	14
6-4-2-AL	0.694	0.802	16
6-2-4-AL	0.379	0.355	-6.2
6-3-3-AL	0.510	0.572	12
7-1-6-AL	0.189	0.169	-11
7-2-5-AL	0.376	0.382	1.6
7-5-2-AL	1.00	1.17	17
7-3-4-AL	0.562	0.627	12
7-4-3-AL	0.789	0.893	13
8-1-7-AL	0.178	0.174	-2.3
8-7-1-AL	1.69	1.96	15
8-3-5-AL	0.606	0.678	12

Table 3-8. Simple Solution Gibbsite Solubility Tests from High to Low Concentrations – 25 °C Results

Test ID	Measured Na (M)	Measured NO_3^- (M)	Measured Al (M)	Measured Density (g/mL)	OLI 25 °C Predicted Al (M)	% Difference Predicted vs Measured
1-0-1-AL	1.00	1.05	<2.6E-04	1.06	1.43E-08	-
1-1-0-AL	0.943	<0.002	0.092	1.04	0.065	-30
1-05-05-AL	0.961	0.498	0.046	1.05	0.036	-22
2-0-2-AL	1.89	2.10	<2.5E-04	1.11	1.31E-08	-
2-2-0-AL	1.88	0.002	0.210	1.09	0.140	-34
2-1-1-AL	1.90	1.05	0.103	1.10	0.077	-26
3-3-0-AL	2.87	<0.002	0.353	1.13	0.244	-31
3-1-2-AL	3.00	2.11	0.106	1.16	0.082	-22
3-2-1-AL	2.90	1.03	0.226	1.14	0.165	-27
3-15-15-AL	2.87	1.59	0.173	1.16	0.124	-28
4-4-0-AL	3.53	<0.002	0.509	1.17	0.393	-23
4-1-3-AL	3.59	3.14	0.117	1.21	0.082	-30
4-3-1-AL	3.62	1.03	0.404	1.18	0.283	-30
4-2-2-AL	3.66	2.10	0.263	1.20	0.178	-32
5-5-0-AL	4.41	<0.002	0.725	1.21	0.602	-17
5-1-4-AL	4.56	4.19	0.125	1.26	0.076	-39
5-4-1-AL	4.45	0.982	0.567	1.22	0.448	-21
5-2-3-AL	4.92	3.10	0.289	1.24	0.179	-38
5-3-2-AL	4.85	2.05	0.473	1.23	0.305	-36
5-25-25-AL	5.59	2.61	0.379	1.24	0.240	-37
6-6-0-AL	5.53	<0.002	1.02	1.24	0.889	-13
6-1-5-AL	6.48	5.06	0.135	1.30	0.067	-50
6-5-1-AL	5.65	0.982	0.848	1.26	0.676	-20
6-4-2-AL	5.57	2.03	0.643	1.27	0.481	-25
6-2-4-AL	6.03	4.29	0.321	1.31	0.171	-47
6-3-3-AL	5.73	3.11	0.502	1.29	0.310	-38
7-1-6-AL	6.74	6.40	0.162	1.36	0.056	-65
7-2-5-AL	6.57	5.21	0.347	1.35	0.155	-55
7-5-2-AL	6.29	1.98	0.955	1.30	0.721	-25
7-3-4-AL	6.56	4.13	0.532	1.34	0.301	-44
7-4-3-AL	6.35	3.03	0.725	1.32	0.491	-32
8-1-7-AL	7.10	6.64	0.179	1.38	0.045	-75
8-7-1-AL	7.04	0.955	1.62	1.33	1.37	-15
8-3-5-AL	7.40	5.13	0.561	1.38	0.278	-50

Table 3-9. Comparison of Simple Solution Gibbsite Solubility Tests – LTH and HTL Solubilities at 25 °C Results

Test ID	LTH Al (M)	HTL Al (M)	Average Al (M)	%RSD
1-0-1-AL	<3.7E-05	<2.6E-04	-	-
1-1-0-AL	0.057	0.092	0.075	34
1-05-05-AL	0.027	0.046	0.037	37
2-0-2-AL	<3.7E-05	<2.5E-04	-	-
2-2-0-AL	0.116	0.210	0.163	41
2-1-1-AL	0.054	0.103	0.079	45
3-3-0-AL	0.213	0.353	0.283	35
3-1-2-AL	0.061	0.106	0.084	38
3-2-1-AL	0.139	0.226	0.183	34
3-15-15-AL	0.090	0.173	0.131	45
4-4-0-AL	0.337	0.509	0.423	29
4-1-3-AL	0.061	0.117	0.089	44
4-3-1-AL	0.237	0.404	0.321	37
4-2-2-AL	0.143	0.263	0.203	42
5-5-0-AL	0.476	0.725	0.601	29
5-1-4-AL	0.054	0.125	0.090	56
5-4-1-AL	0.348	0.567	0.458	34
5-2-3-AL	0.151	0.289	0.220	44
5-3-2-AL	0.232	0.473	0.353	48
5-25-25-AL	0.205	0.379	0.292	42
6-6-0-AL	0.680	1.02	0.851	28
6-1-5-AL	0.051	0.135	0.093	64
6-5-1-AL	0.439	0.848	0.644	45
6-4-2-AL	0.426	0.643	0.535	29
6-2-4-AL	0.161	0.321	0.241	47
6-3-3-AL	0.274	0.502	0.388	41
7-1-6-AL	0.052	0.162	0.107	73
7-2-5-AL	0.161	0.347	0.254	52
7-5-2-AL	0.628	0.955	0.792	29
7-3-4-AL	0.313	0.532	0.423	37
7-4-3-AL	0.469	0.725	0.597	30
8-1-7-AL	0.050	0.179	0.115	79
8-7-1-AL	1.08	1.62	1.35	29
8-3-5-AL	0.319	0.561	0.440	39

Table 3-10. Comparison of Simple Solution Gibbsite Solubility Tests – Average LTH and HTL Solubilities at 25 °C Results versus OLI Predicted Solubility

Test ID	Two Method Average Al (M)	OLI 25 °C Predicted Al (M)	% Difference Predicted vs Measured
1-0-1-AL	-	1.43E-08	-
1-1-0-AL	0.075	0.065	-13
1-05-05-AL	0.037	0.036	-2
2-0-2-AL	-	1.31E-08	-
2-2-0-AL	0.163	0.140	-14
2-1-1-AL	0.079	0.077	-2
3-3-0-AL	0.283	0.244	-14
3-1-2-AL	0.084	0.082	-2
3-2-1-AL	0.183	0.165	-10
3-15-15-AL	0.131	0.124	-6
4-4-0-AL	0.423	0.393	-7
4-1-3-AL	0.089	0.082	-9
4-3-1-AL	0.321	0.283	-12
4-2-2-AL	0.203	0.178	-13
5-5-0-AL	0.601	0.602	0
5-1-4-AL	0.090	0.076	-15
5-4-1-AL	0.458	0.448	-2
5-2-3-AL	0.220	0.179	-18
5-3-2-AL	0.353	0.305	-14
5-25-25-AL	0.292	0.240	-18
6-6-0-AL	0.851	0.889	4
6-1-5-AL	0.093	0.067	-28
6-5-1-AL	0.644	0.676	5
6-4-2-AL	0.535	0.481	-10
6-2-4-AL	0.241	0.171	-29
6-3-3-AL	0.388	0.310	-20
7-1-6-AL	0.107	0.056	-47
7-2-5-AL	0.254	0.155	-39
7-5-2-AL	0.792	0.721	-9
7-3-4-AL	0.423	0.301	-29
7-4-3-AL	0.597	0.491	-18
8-1-7-AL	0.115	0.045	-61
8-7-1-AL	1.35	1.37	2
8-3-5-AL	0.440	0.278	-37

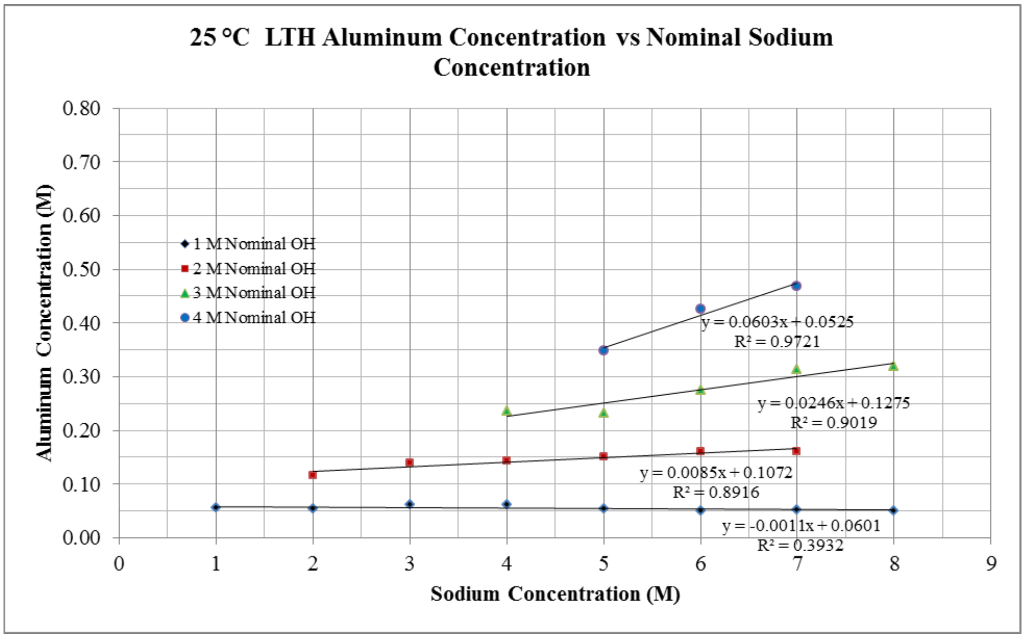

Figure 3-8. Simple Solution Gibbsite Solubility LTH Test at 25 °C - Aluminum Concentration vs. Nominal Sodium Concentration

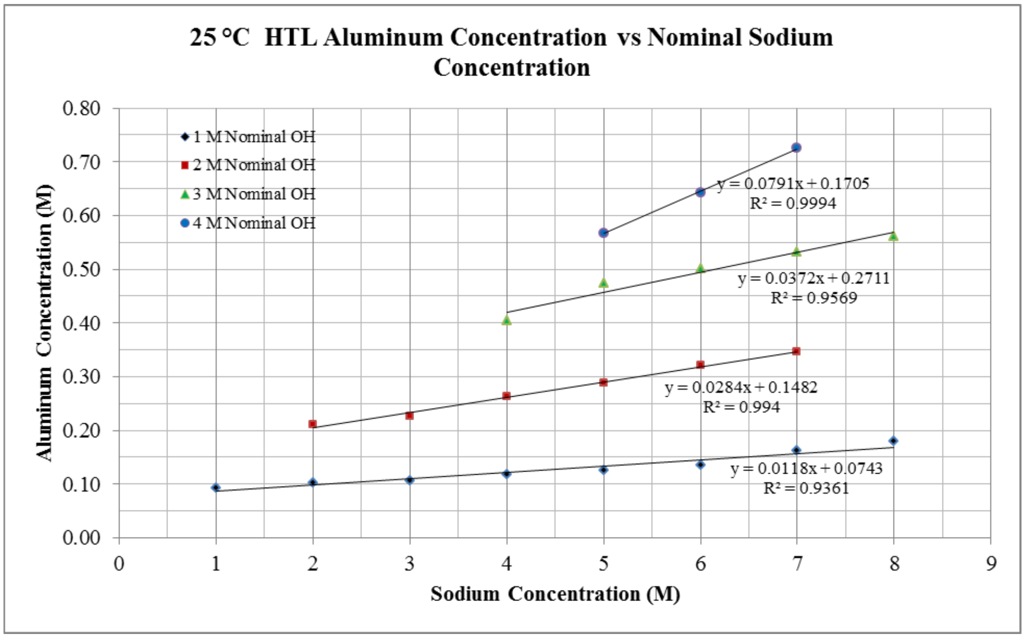

Figure 3-9. Simple Solution Gibbsite Solubility HTL Test at 25 °C - Aluminum Concentration vs. Nominal Sodium Concentration

Table 3-11. Results of Simple Solution Solubility Tests Containing both Oxalate and Aluminum at 25 °C Results

Test ID	Original Al (M)	Measured Al (M)	Measured Na (M)	Measured NO_3^- (M)	Measured $C_2O_4^{2-}$ (M)	Original $C_2O_4^{2-}$ (M)
2-1-1-OX	-	0.046	2.14	0.931	0.033	0.029
3-2-1-OX	-	0.106	3.13	0.914	0.018	0.018
4-2-2-OX	-	0.109	4.16	2.29	0.011	0.011
5-3-2-OX	-	0.196	5.24	1.92	0.004	0.006
6-3-3-OX	-	0.223	6.24	2.90	0.005	0.004
2-1-1-AL	0.054	0.067	2.05	0.916	0.030	-
3-2-1-AL	0.139	0.146	3.10	0.919	0.017	-
4-2-2-AL	0.143	0.157	4.26	1.94	0.011	-
5-3-2-AL	0.232	0.279	5.11	1.94	0.005	-
6-3-3-AL	0.274	0.302	6.61	2.98	0.004	-

Table 3-12. Composition of the Initial Complex Simulant Solutions with and without Metals before Addition of Sodium Oxalate and Gibbsite Solids

Test ID	Ca (M)	Na (M)	Si (M)	Ti (M)	NO_2^- (M)	NO_3^- (M)	SO_4^{2-} (M)	Density (g/mL)
5-2-2	4.1E-05	4.33	5.8E-05	<2.1E-06	0.850	1.98	0.111	1.21
5-3-1	2.9E-05	3.85	4.7E-05	<2.1E-06	0.841	0.96	0.113	1.18
5-1-3	4.6E-05	4.59	6.5E-05	<2.1E-06	0.850	3.03	0.107	1.25
6-25-25	4.2E-05	5.15	6.2E-05	<2.1E-06	0.859	2.52	0.023	1.25
6-3-2	3.9E-05	4.96	5.7E-05	<2.1E-06	0.852	2.02	0.110	1.23
6-2-3	4.9E-05	5.50	7.1E-05	<2.1E-06	0.869	3.11	0.116	1.27
7-3-3	4.8E-05	5.55	6.8E-05	<2.1E-06	0.861	3.08	0.125	1.28
7-4-2	4.2E-05	4.83	6.4E-05	<2.1E-06	0.852	2.00	0.112	1.25
7-2-4	5.4E-05	6.15	8.0E-05	<2.1E-06	0.850	4.08	0.112	1.31
5-2-2-MT	5.1E-05	4.17	6.9E-03	<2.1E-06	0.854	1.98	0.125	1.21
5-3-1-MT	2.6E-05	3.75	6.6E-03	<2.1E-06	0.839	0.96	0.116	1.18
5-1-3-MT	5.9E-05	4.72	8.1E-03	<2.1E-06	0.861	3.13	0.119	1.25
6-25-25-MT	6.1E-05	4.59	9.1E-03	<2.1E-06	0.850	2.50	0.121	1.25
6-3-2-MT	5.3E-05	4.57	8.5E-03	<2.1E-06	0.861	2.03	0.128	1.23
6-2-3-MT	6.1E-05	4.92	7.1E-03	<2.1E-06	0.863	3.35	0.104	1.26
7-3-3-MT	6.9E-05	5.79	7.7E-03	<2.1E-06	0.872	3.11	0.117	1.28
7-4-2-MT	5.6E-05	5.15	8.1E-03	<2.1E-06	0.852	2.00	0.115	1.25
7-2-4-MT	5.9E-05	6.00	8.8E-03	<2.1E-06	0.843	4.06	0.123	1.31

Table 3-13. Results of the Complex Simulant Solutions Solubility Tests Equilibrated with Sodium Oxalate and Gibbsite Solids

Test ID	Na (M)	NO_3^- (M)	$C_2O_4^{2-}$ (M)	Al (M)	Si (M)	Density (g/mL)
5-2-2	4.74	2.23	0.009	0.086	<3.6E-04	1.21
5-3-1	4.33	0.932	0.011	0.131	<3.6E-04	1.18
5-1-3	5.44	3.08	0.009	0.038	<3.6E-04	1.25
6-25-25	5.63	2.48	0.007	0.114	<3.6E-04	1.25
6-3-2	5.42	2.08	0.007	0.140	<3.6E-04	1.24
6-2-3	6.00	3.06	0.006	0.090	<3.6E-04	1.27
7-3-3	6.42	3.00	0.005	0.151	<3.6E-04	1.29
7-4-2	5.85	1.87	0.005	0.199	<3.6E-04	1.25
7-2-4	6.94	3.89	0.005	0.094	<3.6E-04	1.31
5-2-2-MT	4.74	1.95	0.010	0.077	<3.6E-04	1.21
5-3-1-MT	4.20	0.923	0.007	0.124	6.36E-04	1.18
5-1-3-MT	5.44	2.81	0.007	0.030	<3.6E-04	1.25
6-25-25-MT	5.61	2.61	0.007	0.109	<3.6E-04	1.25
6-3-2-MT	5.33	2.05	0.005	0.135	<3.6E-04	1.24
6-2-3-MT	5.98	3.24	0.006	0.084	<3.6E-04	1.27
7-3-3-MT	6.46	3.05	0.005	0.149	<3.6E-04	1.29
7-4-2-MT	5.74	1.77	0.006	0.197	6.65E-04	1.25
7-2-4-MT	6.85	4.00	0.005	0.087	<3.6E-04	1.31

Table 3-14. Results of the Equilibrated Complex Simulant Solutions Solubility Tests Compared with OLI Predictions at 25 °C

Test ID	Measured Al (M)	OLI Al (M)	% Difference Predicted vs Measured	Measured $C_2O_4^{2-}$ (M)	OLI $C_2O_4^{2-}$ (M)	% Difference Predicted vs Measured
5-2-2	0.086	0.166	92	0.009	0.0010	-89
5-3-1	0.131	0.294	124	0.011	0.0007	-94
5-1-3	0.038	0.067	77	0.009	0.0017	-81
6-25-25	0.114	0.221	94	0.007	0.0004	-94
6-3-2	0.140	0.296	111	0.007	0.0003	-96
6-2-3	0.090	0.157	75	0.006	0.0006	-90
7-3-3	0.151	0.285	88	0.005	0.0002	-96
7-4-2	0.199	0.480	142	0.005	0.0001	-98
7-2-4	0.094	0.142	51	0.005	0.0003	-93

4.0 Conclusions

Kinetics tests of simple salt solutions in contact with either sodium oxalate or gibbsite solids determined that the sodium oxalate reached equilibrium within a few days while the gibbsite solids required nine weeks or more to reach equilibrium.

The results of the simple solution sodium oxalate tests indicate that sodium oxalate solubility is mostly governed by the total sodium concentration of the salt solution. There appears to be an additional smaller effect on the sodium oxalate solubility based on the amount of hydroxide present in the solution. The oxalate concentrations generated from both the HTL and LTH test methods show reasonably good agreement. The measured oxalate concentrations at 60 °C dropped ~30% going from 60 °C to 40 °C and another ~20% going from 40 °C to 25 °C.

Based on the data from the simple solution gibbsite tests, the gibbsite solubility appears to be governed primarily by the hydroxide concentration in the solution with an additional smaller effect from the total sodium in solution. The smaller sodium effect on the gibbsite solubility increases in magnitude as the hydroxide concentration increases. The data show significant differences in the final equilibrated aluminum concentration depending on the test method. The aluminum concentrations obtained from the HTL method show ~50-250% higher aluminum concentrations than the LTH method with the majority of the differences in the 50-100% range. This difference in gibbsite solubility based on the test method should be investigated further to determine if the deviation is real or due to experimental design and/or analytical errors.

Interestingly, the effect of the sodium and the hydroxide concentration on the solubility of sodium oxalate is opposite to the effects of these species on the solubility of gibbsite. Therefore, adding a strong NaOH solution to a salt solution saturated in sodium oxalate and gibbsite will likely precipitate sodium oxalate while increasing the solubility of the gibbsite. Diluting the same solution with water will increase the solubility of sodium oxalate while likely causing the precipitation of gibbsite solids.

The presence of dissolved aluminum in the solution appears to have little effect on the sodium oxalate solubility in these simple solutions. Also, the presence of oxalate in the solution had little effect on the solubility of gibbsite.

Filtered samples of the simple solutions saturated in sodium oxalate or gibbsite at 25 °C were found to be stable to precipitation if maintained at a temperature near 25 °C. However, filtered solutions of both the oxalate and aluminum solutions with >6 M sodium nitrate concentrations in an 8 M total sodium concentration formed sodium nitrate solids after several days. During makeup of these four solutions, some difficulty was encountered in getting all of the added sodium nitrate solids to dissolve completely.

The complex simulant solutions after equilibration with sodium oxalate and gibbsite solids showed oxalate concentrations within the range expected based on comparison with the simple solutions results for solutions with similar sodium molarity. No measureable difference in oxalate concentrations was observed between solutions with and without calcium and silicon (no titanium in any of the solutions). The aluminum concentrations in the equilibrated complex simulant solutions appear significantly lower than expect based on comparison with the simple solution results for solutions of similar hydroxide concentration. The reason for the lower aluminum concentrations in the complex simulant is unknown but can’t be attributed to the presence of calcium and silicon in the solutions. No measureable difference in aluminum concentrations was observed between solutions with and without calcium and silicon (no titanium in any of the solutions). Nearly all of the silicon appears to have precipitated from the equilibrated complex simulant solutions, but this did not produce a measurable effect on the equilibrated aluminum concentration because the initial concentration of silicon in the complex simulant solution was too low (~0.005-9 M). Contact of the 6.5 M complex simulant solutions, saturated with sodium oxalate and gibbsite, with MCU solvent does not appear to cause precipitation of solids from the solution.

Most of the OLI predictions for the oxalate concentrations in the simple solution sodium oxalate tests at 25 °C were much lower than the measured 25 °C oxalate concentrations. For solutions with 5 M sodium or higher, the OLI predictions were 5-10X lower than the measured concentrations. The differences between the measured and OLI predicted 60 °C and 40 °C oxalate concentrations were low by about the same magnitude as the 25 °C data. The data generated from the simple solution sodium oxalate tests should be suitable for developing a new thermodynamic database for OLI that will provide more accurate oxalate concentration predictions for SRS salt solutions.

The OLI modeling predictions for the aluminum concentration in the 25 °C simple solution gibbsite tests generally predicts a concentration ~20-30% lower than the measured concentrations for the LTH tests and ~20-30% higher than the aluminum concentrations measured in the HTL tests. The OLI predictions match reasonably well with the average aluminum concentration from the two test methods.

The OLI modeling predictions for the complex simulant solution tests showed the same trends observed for the simple solutions tests. The aluminum predictions were significantly higher and the oxalate predictions significantly lower than the measured concentrations.

5.0 Acknowledgements

The contributions of Whitney Riley for providing analytical services and Holly Hall for facilitating many aspects of the program are appreciated and acknowledged.

6.0 References

1. Peters, T. B., *Initial Analysis of Solids from the Extraction, Scrub Contactors and Tank 49H Variable Depth Samples*, SRNL-L3100-2014-00121, Rev. 0, June 13, 2014.

2. Fellinger, T. L., *Research & Development Studies for Addressing Solids Precipitation at Modular Caustic Side Solvent Extraction Unit*, X-TTR-H-00048, Rev. 0, August 19, 2014.

3. Hay, M. S., King, W. D., Peters, T. B., *Task Technical and Quality Assurance Plan for Equilibrium Studies of Oxalate Solutions*, SRNL-RP-2014-00881, Rev. 0, September 2014.

4. Peters, T. B., Fondeur, F. F., Taylor-Pashow, K. M., *Results from the Salt Disposition Project (SDP) Next Generation Solvent (NGS) Demonstration Plan*, SRNL-STI-2014-00101, Rev. 0, April 2014.

5. Gontijo, G. S., Brandao de Araujo, A. C., Prasad, S., Vasconcelos, L. G. S., Alves, J. J. N., Brito, R. P., *Improving the Bayer Process Productivity – An Industrial Case Study*, Minerals Engineering, 22 (2009), 1130-1136.

6. Watling, H., Loh, J., Gatter, H., *Gibbsite Crystallization Inhibition 1. Effects of Sodium Gluconate on Nucleation, Agglomeration and Growth*, Hydrometallurgy, 55 (2000), 275-288.

7. Farquharson, G. J., Kildea, J. D., *Method of Controlling Oxalate Precipitation in the Bayer Process Liquor*, U. S. Patent, US 6,293,973, September 25, 2001.

8. Power, G., Loh, J. S. C., Wajon, J. E., Busetti, F., Joll, C., *A Review of the Determination of Organic Compounds in Bayer Process Liquids*, Analytica Chimica Acta, 689 (2011), 8-21.

9. Lowe, J., Ogden, M., McKinnon, A., Parkinson, G., *Crystal Growth of Sodium Oxalate from Aqueous Solutions*, Journal of Crystal Growth, 237-239 (2002), 408-413.

10. Nortier, P., Chagnon, P., Lewis, A. E., *Modeling the Solubility in Bayer Liquors: A Critical Review and New Models*, Chemical Engineering Science, 66 (2011), 2596-2605.

11. Konigsberger, E., Eriksson, G., May, P. M., Hefter, G., *Comprehensive Model of Synthetic Bayer Liquors. Part 1. Overview*, Ind. Eng. Chem. Res., 44 (2005), 5805-5814.

12. Li, X., Li, Y., Zhou, Q., Liu, G., Peng, Z., *Thermodynamic Model for Equilibrium Solubility of Gibbsite in Concentrated NaOH Solutions* , Ind. Eng. Chem. Res., 44 (2005), 5805-5814.

13. Wefers, K., Misra, C., *Oxides and Hydroxides of Aluminum*, Alcoa Technical Paper No. 19, Alcoa Laboratories, 1987.

14. Gong, X., Nie, Z., Qian, M., Lui, J., Pederson, L. A., Hobbs, D. T., McDuffie, N. G., *Gibbsite to Boehmite Transformations in Strongly Caustic and Nitrate Environments*, WSRC-MS-2002-00850, Rev. 0, November 2002.

Distribution:

A. P. Fellinger. 773-42A
T. B. Brown, 773-A
M. E, Stone, 999-W
S. D. Fink, 773-A
C. C. Herman, 773-A
E. N. Hoffman, 999-W
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
Records Administration (EDWS)
E. A. Brass, 241-121H
C. K. Chiu, 704-30S
E. J. Freed, 704-S
A. G. Garrison, 241-121H
B. A. Gifford, 704-56H
V. Jain, 766-H
R. T. McNew, 766-H
M. A. Rios-Armstrong, 766-H
A. R. Shafer, 766-H
C. Sudduth, 707-7E
J. R Vitali, 704-30S
A. W. Wiggins, 241-168H