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Chemical Equilibrium of Aluminate in Hanford Tank Waste Originating from Tanks 241-AN-105 and 241-AP-108

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Acronyms and Abbreviations

AN-105	tank 241-AN-105
AP-108	tank 241-AP-108
ATL	Advanced Technologies and Laboratories International, Inc.
CL	centrifuged liquid
CS	centrifuged solid
DI	deionized
DL	drainable liquid
EDS	energy dispersive X-ray spectroscopy
IC	ion chromatography
ICET	Institute for Clean Energy Technology
ICP	inductively coupled plasma
IS	ionic strength
NIST	National Institute of Scientific Standards
OH	free hydroxide
PFA	perfluoroalkoxy
PLM	polarized light microscopy
PMP	polymethylpentene
PNNL	Pacific Northwest National Laboratory
RCRA	Resource Conservation and Recovery Act
RPD	reported percent difference
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
TIC/TOC	total inorganic carbon/total organic carbon
WRPS	Washington River Protection Solutions LLC
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray diffraction

Units

°C	degrees Celsius
g	gram(s)
hr	hour(s)
in.	inch
kg	kilogram
µL	microliter
µm	micrometer(s)
M	molal (moles per kg H_2O)
mL	milliliter(s)
M	Molar (moles per liter solution)
rpm	revolutions per minute
wt%	weight percent
σ	standard deviation
ρ	density in g/mL

1. INTRODUCTION

The Hanford Nuclear Reservation was the largest producer of plutonium in the United States during World War II and the Cold War. Between 1943 and 1990, Hanford produced 54.5 metric tons of plutonium or 60% of the total plutonium produced in the United States (DOE/RL-97-1047, *History of the Plutonium Production Facilities at the Hanford Site Historic District, 1943-1990*). The signing of the Tri-Party agreement in May 1989 moved the Hanford site from the production era into the clean-up era with a promise made by the Department of Energy to have the site cleaned in 30 years.

During plutonium process operations, 245 million gallons of waste material was produced; following waste reduction operations, 54 million gallons of waste material was stored in 177 underground tanks (DOE/RL-97-1047). The tank waste is made up of many constituents including aluminum that originated mainly from aluminum nitrate nonahydrate in the reduction-oxidation, or REDOX, process as a salting agent and from aluminum cladding that covered the uranium metal fuel rods.

The aluminum within the tank waste is of great interest as it has complex solution dynamics and exists in many solid phases within the waste. Aluminum hydroxide is amphoteric, making it readily soluble in both acid and caustic. In the tank farms aluminum exists as the aluminate ion in the liquid phase, as the waste is held basic with excess hydroxide to inhibit corrosion of the carbon steel tanks. Aluminum can exist as many different solid phases within the tank waste. Some of the most common forms include gibbsite, boehmite, cancrinite, and various aluminosilicates. Also, the removal *or addition* of water to a saturated aluminate solution can promote the formation of aluminum solids. The solid component of tank waste is generally in the form of either a saltcake or sludge, which is generally considered soluble or insoluble, respectively. The solid aluminum species are generally found in the sludge component of the waste.

One mission of the Tank Operations Contractor is to transfer the tank waste to the Waste Treatment and Immobilization Plant (WTP) for vitrification. In most cases, the supernate is separated from the solids component of the waste, leaving behind either a saltcake or sludge. Solid aluminum species exist in both matrixes; however, the methods used to mobilize the sludge and saltcake are quite different. Sludges are typically slurried with water or a basic solution and pumped from the tanks. The saltcakes are dissolved into water or a caustic solution and pumped from the tanks.

In both cases, many uncertainties exist regarding the fate of aluminum within the liquid and solid components of tank waste during waste retrieval and transport operations. Currently, the fate of aluminum in the liquid/solids system is estimated using computer models before the process is conducted in the tank. The current model is a Pitzer correlation that predicts the ultimate equilibrium value at some caustic loading and some electrolyte loading. Studies of saturated aluminum systems ("Solubility and Reaction Rates of Aluminum Solid Phases under Geothermal Conditions," [Bénézeth et al., 2000]) indicate that the precipitation kinetics of aluminum is slow;

therefore, the models implemented into the process engineering may not accurately predict precipitation of aluminum in the retrieval scenario.

Many caustic leaching studies using real tank waste have been conducted, but little work has been conducted to verify that the equivalent thermodynamic equilibrium is present when equilibrium is approached either from the dissolution of aluminum solids or from the precipitation of aluminum solids in a tank waste matrix. G. S. Barney, in ARH-ST-133, *Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford*, published aluminum solubility curves at multiple caustic loadings for simulated tank waste saturated with $NaNO_3$, $NaNO_2$, Na_2SO_4, and Na_2CO_3 and compared them with the pure-component solubility data from the literature. D. L. Herting and associates have also studied aluminum solubility in caustic solutions with many of the same electrolytes found in tank waste. They quantified the effect that ionic strength (IS) has on the solubility of aluminum in these solutions approaching equilibrium from below the saturation point, (Internal letter 65453-85-098, “Gibbsite Solubility”). Personnel at the Pacific Northwest National Laboratory (PNNL) have conducted several experiments to quantify thermodynamic equilibrium of aluminum in different supernatant liquid simulants under WTP operating conditions: NaOH = 5 molal, Temperature = 85 °C and 40 °C ("Boehmite Dissolution Model Based on Simulant Data" [Russell et al, 2010]; PNNL-18597, Rev. 1, *PEP Support: Laboratory Scale Leaching and Permeate Stability Tests*; "Bench-Scale Testing of the Continuous Sludge Leaching Process" [Edwards et al, 2010]; "Boehmite Dissolution Studies Supporting High Level Waste Pretreatment – 9383” [Peterson et al, 2009]; PNNL-18013, *Development and Characterization of Gibbsite Component Simulant*; PNNL-18876, *Laboratory Tests on Post Filtration Precipitation in the WTP Pretreatment Process*; PNNL-18597, Rev. 0, *PEP Support: Laboratory Scale Leaching and Permeate Stability Tests*; PNNL-18176, *Development and Characterization of Boehmite Component Simulant*). The supernatant liquids were formulated with a varied matrix to encompass the feed composition envelopes that will be delivered to WTP from the Tank Operations Contractor.

The purposes of the study described in this document follow.

- Determine or estimate the thermodynamic equilibrium of gibbsite in contact with two real tank waste supernatant liquids through both dissolution of gibbsite (bottom-up approach) and precipitation of aluminum-bearing solids (top-down approach).
- Determine or estimate the thermodynamic equilibrium of a mixture of gibbsite and real tank waste saltcake in contact with real tank waste supernatant liquid through both dissolution of gibbsite and precipitation of aluminum-bearing solids.
- Characterize the solids present after equilibrium and precipitation of aluminum-bearing solids.

2. METHOD

2.1. Brief Overview

The equilibrium concentration of aluminum in two different supernatant liquids at a temperature of 40 °C was determined for two supernatant liquids originating from Hanford tank 241-AP-108

(AP-108) and tank 241-AN-105 (AN-105). Four experiments were conducted on each of the two supernatant liquids, as outlined below.

- Experiments 5AN-1 and 8AP-1: Determine the equilibrium concentration of aluminum in tank waste supernatant liquid at 40 °C through the precipitation of aluminum-bearing solids from a solution first saturated with aluminum at 85 °C (top-down approach).
- Experiments 5AN-2 and 8AP-2: Determine the equilibrium concentration of aluminum in tank waste supernatant liquid through dissolution of gibbsite at 40 °C (bottom-up approach).
- Experiments 5AN-3 and 8AP-3: Determine the equilibrium concentration of aluminum in tank waste supernatant liquid at 40 °C in contact with tank waste solids through the precipitation of aluminum-bearing solids from a solution first saturated with aluminum and soluble tank waste solids at 85 °C (top-down approach; same as above but with the addition of tank waste solids).
- Experiment 5AN-4 and 8AP-4: Determine the equilibrium concentration of aluminum in tank waste supernatant liquid in contact with tank waste solids through the dissolution of gibbsite at 40 °C (bottom-up approach; same as above but with the addition of tank waste solids).

2.2. Selection of Tank Samples

The goal of the sample selection process was to choose samples that displayed enhanced solubility compared to models that were used in the WTP feed vector models. Several of these samples were chosen because historical aluminate and hydroxide analytical data show that the aluminate concentrations in the supernatant liquids are relatively high compared to calculated results using a simple model. The data also indicate that the aluminate concentrations fall within past experimental results of Barney (ARH-ST-133), as shown in Figure 1. The AN-105 and AP-108 results are above the model-predicted solid line, but below the experimental-data dashed line (Barney Curve).

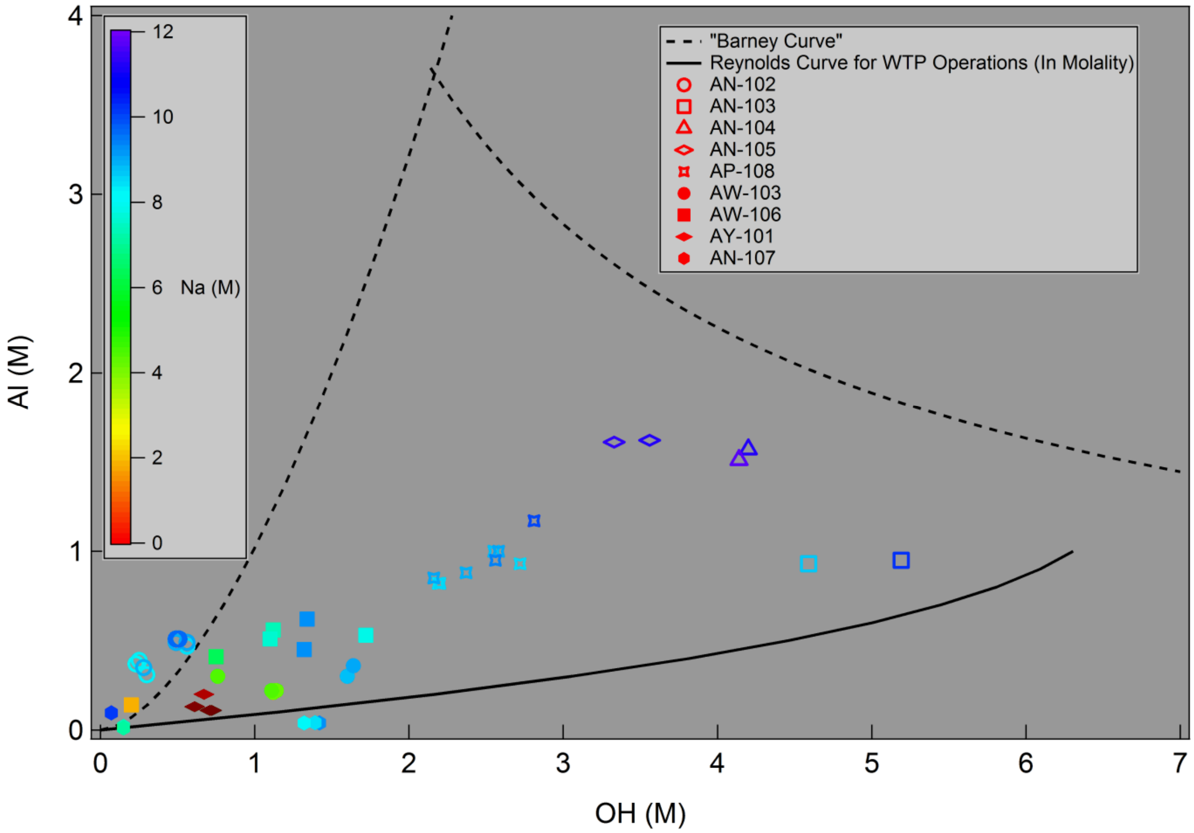

Figure 1. Analytical Data from Many Tanks Plotted with a Simple Solubility Model (Solid Line) and Barney's Experimental Results (Dashed Line)

Archived supernatant liquid and saltcake samples originating from tanks AN-105 and AP-108 were chosen for use in these experiments. The following tables contain selected data from the hot cell database describing the sampling event for each of the samples and the amount of sample. A supernatant liquid composite was formed for each tank. No saltcake composite was required because the available samples were adequate.

Table 1. Tank 241-AN-105 Archived Samples

Date	Jar/ Vial #	Tank #	Core #	Net Wt (g)	Matrix	Laboratory #	Sample #
28-Jul-96	10751	AN-105	153	44.0	DL	S96T003996	S13R000147
28-Jul-96	10753	AN-105	153	43.8	DL	S96T003998	S13R000148
28-Jul-96	10754	AN-105	153	46.8	DL	S96T003999	S13R000149
09-Aug-96	10874	AN-105	153	54.3	DL	S96T004307	S13R000150
16-Aug-96	10875	AN-105	153	52.8	DL	S96T004416	S13R000151
16-Aug-96	10877	AN-105	153	48.6	DL	S96T004418	S13R000152
16-Aug-96	11098	AN-105	153	51.1	DL	S96T004332	S13R000153
19-Aug-96	11100	AN-105	153	40.8	DL	S96T004431	S13R000154
19-Aug-96	11101	AN-105	153	47.7	DL	S96T004432	S13R000155
07-Feb-02	19316	AN-105	153	65.4	DL	S96T004414	S13R000156
28-Jul-96	10748	AN-105	153	53.7	DL	S96T003994	S13R000157
28-Jul-96	10750	AN-105	153	49.9	DL	S96T003995	S13R000158
28-Jul-96	10752	AN-105	153	26.4	DL	S96T003997	S13R000159
09-Aug-96	10872	AN-105	153	14.2	DL	S96T004306	S13R000160
26-Jul-96	11120	AN-105	152	62.2	Salt	S96T004255	S13R000214

DL = drainable liquid

Table 2. Tank 241-AP-108 Archived Samples

Date	Jar/ Vial #	Tank #	Core #	Net Wt (g)	Matrix	Laboratory #	APD Laboratory #
24-Mar-08	20031	AP-108	330	69.7	CS	S08T002364	S13R000083
18-Mar-08	20257	AP-108	330	63.7	DL	S08T002108	S13R000161
14-Feb-08	20484	AP-108	330	243.1	DL	S08T002330	S13R000162
18-Mar-08	20494	AP-108	330	90.2	DL	S08T002332	S13R000163
24-Mar-08	20390	AP-108	330	12.7	CL	S08T002353	S13R000164
25-Mar-08	20418	AP-108	330	23.4	CL	S08T002355	S13R000165
24-Mar-08	20419	AP-108	330	11.7	CL	S08T002354	S13R000166

CL = centrifuged liquid
CS = centrifuged solid
DL = drainable liquid

Samples from other tanks were considered, but due to limited sample being available in the hot cell sample archives, the samples from AP-108 and AN-105 were ultimately chosen. Also, the chosen samples prominently displayed the enhanced solubility behavior.

2.3. Description of Experiment Matrix

Experiments X-1 and X-2 (where X = 5AN or 8AP) used a mixture of supernatant liquid and reagent-grade gibbsite. The mixtures were made up of roughly 20 wt% Almatis C33 gibbsite and 80 wt% supernatant liquid. Experiments X-3 and X-4 were made up of roughly 10 wt% Almatis C33 gibbsite, 10 wt% tank waste solids, and 80 wt% supernatant liquid. Table 3 tabulates the exact weights and weight percent of solids and supernatant liquids for each of the eight experiments. The solids loading fraction (grams of dry solids per gram of supernatant liquid) is calculated using values of 71.3 wt% solids for the AN-105 saltcake and 72.6 wt% solids for the AP-108 saltcake. For example, the solids loading fraction for Experiment 5AN-3 is calculated as: ((16.49 g saltcake)(0.713 g solids/g saltcake) + 11.50 g gibbsite) / 91.95 g supernate = 0.25 g solids / g supernate.

Table 3. Experimental Slurry Composition

Experiment	Supernate (g)	Saltcake (g)	Gibbsite (g)	Solids Loading Fraction
Exp. 5AN-1	97.26	0.00	24.23	0.25
Exp. 5AN-2	84.64	0.00	21.52	0.25
Exp. 5AN-3	91.95	16.49	11.50	0.25
Exp. 5AN-4	91.24	16.57	11.56	0.26
Exp. 8AP-1	95.02	0.00	23.18	0.24
Exp. 8AP-2	103.39	0.00	24.01	0.23
Exp. 8AP-3	88.12	15.44	11.13	0.25
Exp. 8AP-4	90.66	16.09	11.62	0.26

2.4. Description of Sampling Process

Experiments X-1 and X-3 of each experimental set were similar in that the solids were first leached in the supernatant liquid at 85 °C for 4 – 6 hr, at which point the slurry was sampled; then the solution was cooled to 40 °C. The slurry remained at 40 °C for about 60 days, and the solution was sampled intermittently to determine when the aluminum in the sample was at equilibrium. The aluminum was considered at equilibrium when the aluminum concentration of three consecutive samples formed a horizontal asymptote as a function of time within experimental error. Both the solids and supernatant liquid were sampled during the collection of the final sample.

The equilibrium of aluminum in a 40 °C supernatant solution was approached from below the equilibrium point in Experiments X-2 and X-4. In both experiments, solids were added to the supernatant solution and the slurry temperature adjusted to 40 °C and continuously stirred using a stirring hotplate. The slurry was intermittently sampled for about 45 days and assumed to be at equilibrium at the end of the 45-day period. The first seven samples were of supernatant solution only, and the solids and supernatant solution were both sampled at the end of the experiment. The sampling diagrams are contained in Appendix 1. The diagrams illustrate a general timeline, the sample matrix, and the analysis conducted. Also, the samples are identified by a laboratory number and an experiment label.

2.5. Experimental Apparatus Description

The experiments were carried out in a custom fabricated reactor made from a 250-mL polymethylpentene (PMP) jar. (Three of these reactors in the hot cell are shown in Figure 2. A sample port made of a ½ in. perfluoroalkoxy (PFA) fitting, and a ½ in. PFA rod was installed on the lid of the jar for ease of sampling. An 18 in. long, 1/8th in. outside diameter PFA tube with glass wool in the outer end was attached to the lid through a PFA fitting to act as a refluxer. The refluxer was installed to decrease vapor losses and ensure the contents of the reactor did not pressurize upon heating of the solution.

The reactors were heated and stirred by means of a hot plate/stirrer. They were encased in an aluminum block to provide even heat distribution and to moderate temperature cycling. The temperature of the aluminum block was regulated to ±1 °C by the hot plate temperature controller and checked regularly with a National Institute of Standards and Technology (NIST) traceable thermometer. The hot plate thermocouple was also verified against a NIST traceable digital thermometer. A 3 in. long by 3/8 in. diameter Teflon™[1] coated stir bar was used to stir the slurry. A stirring rate of 200 rpm was maintained to ensure the slurry was well mixed.

Figure 2. Reactors in Hot Cell

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[1] Teflon is a trademark of I. E. du Pont de Nemours and Company, Wilmington, Delaware.

2.6. Sampling

Supernatant liquid was sampled from the reactors at temperature using a long disposable PFA pipette, and the slurry was delivered into a 5-mL syringe filter to remove the solids. The filtered solution was delivered from the syringe filter into a 5-mL polycarbonate test tube. Using a volumetric pipette, three 1-mL aliquots of sample were then delivered to a 20-mL polypropylene sample jar containing equal amounts of 5 M NaOH to stabilize the solution and to inhibit solids precipitation. In the case of the samples collected in this experiment, about 3 mL of sample was added to 3 mL of 5 M NaOH. A calibrated 1000-μL Eppendorf Reference™[2] volumetric pipette was used to deliver 1-mL aliquots of NaOH and sample to the sample jar. The volumetric pipette was calibrated during each sampling event using the 3 aliquots of 5 M NaOH solution. In addition, blanks containing six 1-mL aliquots of NaOH were delivered as samples for analysis. The calibration results can be found in Appendix 2.

A general description of the sampling procedure is as follows. Please refer to the test plan, LAB-PLN-12-00011, *Dissolution and Precipitation of Aluminum-Bearing Compounds in Hanford Tank Waste,* for a complete description of the sampling procedure.

1. Three 1-mL aliquots of 5 M NaOH were added to a pre-weighed plastic sample vial. After addition of each aliquot, the sample vial and contents were weighed.
2. About 5 mL of the hot slurry was drawn from the sample jar using a long pipette and transferred quickly to a syringe filter with the plunger removed.
3. The plunger was inserted and the solution pushed through the filter into a 5-mL polycarbonate test tube to remove any undissolved solids. If the filter clogged, the plunger was removed and the unfiltered contents were transferred to a new syringe filter assembly. This process was repeated until about 4 or 5 mL of solution was in the test tube.
4. Finally, three 1-mL aliquots of sample were transferred from the test tube to the sample vial containing the 5 M NaOH. After each aliquot of sample was delivered to the sample vial, the weight of the vial was captured.

The sample and NaOH were delivered to the sample vial as 1-mL aliquots to determine the density of the sample and define the quality attributes of the method, respectively. By collecting three aliquots of sample, the precision of the density measurement could be defined. Also, the accuracy of the aliquot volume delivered to the sample vial could be inferred through the use of the 5 M NaOH as a standard, assuming the sample and NaOH physical characteristics were similar. Finally, monitoring the mass of each aliquot of 5 M NaOH delivered to the sample vial provided a real time indication of the integrity of the volumetric pipette.

2.7. Description of Analytical Protocol

Each saltcake and supernatant liquid sample was analyzed for the chemical and physical constituents listed in Table 4. For each sample taken prior to aluminum equilibrium, only select analyses were conducted to reduce costs and save work resources. The analyses conducted for these samples were inductively coupled plasma (ICP) spectroscopy (aluminum only), free

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[2] Eppendorf Reference is a trademark of Eppendorf AG, Hamburg, Germany.

hydroxide (OH), density, and thermogravimetric analysis (TGA) for weight percent water. A full analysis was conducted on the last sample in each experiment. In some cases, the last sample in the experiment may have incurred severe evaporative losses, and for that reason the full analysis was conducted on an intermediate sample. Each saltcake sample analyzed by ICP first underwent acid digestion with nitric acid and peroxide solution to dissolve the solids. (The term "saltcake" in this context may refer to the original saltcake composite samples or the test samples containing undissolved gibbsite.)

Table 4. Analysis Techniques Conducted by Advanced Technologies and Laboratories International, Inc.

Method	Analytes
ICP	Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Eu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, S, Sb, Se, Si, Sr, Th, Ti, Tl, U, V, Y, Zn, Zr
IC	NO_3^-, NO_2^-, SO_4^{2-}, PO_4^{3-}, Cl^-, F^-, Br^-, $HCOO^-$, $C_2H_3O_3^-$, $C_2H_2O_2^-$, $C_2O_4^{2-}$
TIC/TOC	CO_3^{2-}
OH	OH^-
TGA	wt% H_2O
Density	Density

IC = ion chromatography
TIC/TOC = total inorganic carbon/total organic carbon

Selected solids analyses were performed by the Washington River Protection Solutions LLC (WRPS) Special Analytical Group using x-ray diffraction (XRD), polarized light microscopy (PLM), and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDS).

2.8. Interpretation of Analytical Data and Spreadsheet Development

A spreadsheet was developed to analyze and interpret the analytical data. A series of calculations was carried out in Microsoft™[3] Excel to perform the following analysis.

- Determine the weight percent water in the saltcake samples.
- Calculate the concentration of several chemical species from the laboratory analytical data.
- Determine the concentration of solids as oxides and hydroxides.
- Construct plots of aluminum and hydroxide concentration versus time to determine the aluminum and hydroxide equilibrium concentrations.
- Perform a statistical evaluation to determine the agreement between the mean aluminum and hydroxide equilibrium concentrations of two different experiments.
- Calculate the quality statistics of the volumetric pipette.

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[3] Microsoft is a trademark of Microsoft Corporation, Redmond, Washington.

A detailed explanation of the equations used in the spreadsheet to calculate the observations found in the results section of this document is supplied in the spreadsheet verification document, SVF-2881, Rev. 0, "Gibbsite Dissolution 2013." The next few sections are a brief overview of the methodology used for the calculations. Also, all exceptions to the standard methodology are described.

2.8.1. Saltcake Weight Percent Water

The weight percent water was determined as the percentage of water loss during the drying of the saltcake. Three samples of saltcake were dried on a hot plate at about 105 °C until the mass became stable. The difference in wet weight and the first dry point of a series of dry points of equal mass were recorded and used in the calculation.

2.8.2. Chemical Concentration in Supernatant Liquids

The supernatant liquid samples, diluted in 5 M NaOH in 1:1 ratio by volume, were delivered to Advanced Technologies and Laboratories International, Inc., (ATL) for analysis. Upon receipt of the data, the concentration for all species in solution other than sodium and hydroxide were dilution corrected. The dilution correction was determined from the mass of the sample and the mass of the NaOH used to stabilize the sample. For the sodium and hydroxide concentrations, an additional correction was applied to account for the NaOH used to stabilize the sample. The corrected results were then quality checked by performing a mass balance and charge balance.

2.8.3. Chemical Concentration in Slurry Solids

The chemical speciation of the solids was also determined for each of the eight experiments. The samples given to ATL for analysis were a mixture of supernatant liquid, gibbsite, and/or saltcake solids. At the conclusion of the experiment, a sample of the mixture was poured into a sample vial and set aside for up to 7 days. The excess supernatant liquid was then decanted off the top of the solids, being careful to avoid discarding any of the solids. The sample was then submitted to ATL for analysis.

Knowing the weight percent water in the solids sample and in the corresponding supernatant liquid, the fraction of supernatant liquid in the solids sample submitted to ATL could be calculated. Unfortunately, the weight percent water reported by ATL for the solids sample was nearly equal to that of the supernatant liquid, indicating an error in analysis. Most of the supernatant liquid was decanted from the mixture; therefore, the weight percent water of the saltcake solids sample should have been significantly lower than the weight percent water of the supernatant liquid.

An alternative approach was then carried out to determine the solids composition. Essentially, the fractions of supernatant liquid and solids were iterated until the error of the mass balance of analyte concentrations and the ratio of positive and negative analytes was minimized. The constraining bounds were the total mass of the analytes in a given gram of sample and the charge balance of the analytes in the sample. In a perfect system, the sum of the analyte concentrations should equal 1 million µg/g of sample, and the ratio of the positive and negative charges should be one.

The equations used in this calculation are further explained in SVF-2881, Rev. 0. Also, analytical error is propagated through the set of equations considering that nearly every analytical result is involved in this calculation. Therefore, some skepticism should be cast on the solid-phase results given for trace species, and error exists for the major species. However, the results present an indication of the major species present in the solids.

2.8.4. Equilibrium Plots

For each experiment, the aluminum and hydroxide concentrations were plotted versus time to determine the point at which the aluminate in solution was at equilibrium at 40 °C. Also the sodium results were determined in this section, but only points where data existed. The mean and standard deviation with a greater than 99% confidence for aluminate, hydroxide, sodium, density, and weight percent water were also determined from the series of samples that were determined to be at equilibrium.

2.8.5. Mean Aluminum and Hydroxide Statistical Analysis

A statistical analysis of the mean aluminum and hydroxide concentration was also performed to test the agreement of the means from two different experiments. This process was conducted for each combination of experiments from an experimental set. The process involved first testing if the variance of the mean from two different experiments was equal and then conducting the proper t-test to test the agreement of the means. In Excel, a t-test assuming equal variances and a t-test assuming unequal variances is available. The correct test must be chosen depending on the results of the F-test. In all cases, the two-tailed t-test was used for the comparison, and the alpha parameter was compared to the two-sided P statistic to draw a conclusion from the t-test results.

2.8.6. Volumetric Pipette Quality Statistics

As part of the experimental process, three 1-mL aliquots of 5 M NaOH solution were delivered to the sample vials to stabilize the aluminum and hydroxide in the samples. The aliquots of NaOH were used as a measure to assess the quality of the volumetric pipette performance. It was assumed that the physical and chemical characteristics of the NaOH solution would be representative of the sample, and the quality of the sample aliquots was assumed to be equal to the NaOH aliquots.

The calculation was rather straightforward. First, the volume of each aliquot was calculated using the reported density of a 5 M NaOH solution found in the 57th edition of the CRC Handbook of Chemistry and Physics (1976). Next, the mean volume of the three aliquots was calculated, and the reported percent difference (RPD) from the device set point volume of 1 mL was calculated from the resulting mean. Results are reported in Appendix 2.

3. TANK 241-AN-105 RESULTS

3.1. Experiment 5AN-1: Supernatant Liquid Plus Gibbsite, Top-Down

Figure 3 is a time series plot of liquid-phase aluminate and free hydroxide concentrations in a slurry composed of supernatant liquid originating from tank AN-105, with added gibbsite, approaching thermodynamic equilibrium from above the aluminate saturation point. The gibbsite was first leached into the supernatant liquid at 85 °C for 4 hr and then mixed at 40 °C for about 90 days. A careful examination of the figure shows a trend ending at day 21, followed by three pairs of data from day 62 to 93. Originally, data for the experiment was to be taken on days 25, 35, and 45, but the laboratory experienced a power outage resulting in a loss of heat to the system. It was decided to let the experiment proceed for approximately 41 additional days before acquiring additional samples. The average weight percent water for each series of samples dropped from 48.8% ± 0.31% (3σ) to 46.1% ± 0.35% (3σ), indicating that evaporation occurred during the 41-day period, resulting in two different solution conditions for thermodynamic equilibrium of aluminate. The data also indicate that for each case, the solution was at equilibrium.

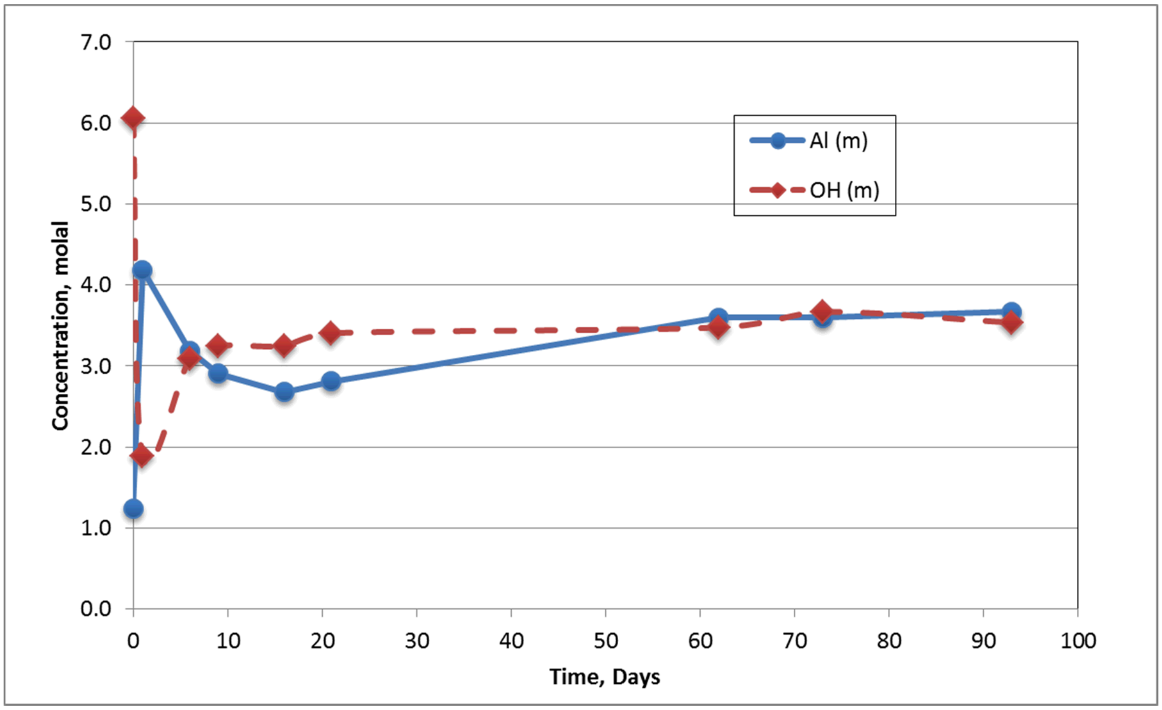

Figure 3. Experiment 5AN-1, Leach at 85 °C, Equilibrate at 40 °C

For the first case, consider the three data pairs from days 9 – 21. This case represents the supernatant liquid as received from the archived sample storage (and presumably from the tank farms). Both the aluminum and free hydroxide trends suggest an equilibrium state, but some doubt exists because there are only three data points. The equilibrium point of aluminate was 2.8 ± 0.35 molal (3σ) with 3.3 ± 0.27 molal (3σ) free hydroxide, and an IS represented as the sodium concentration of 15.5 ± 0.87 molal (3σ). The data in Table 5 are reported as the average values for analytical data collected on days 9, 16, and 21.

Table 5. Experiment 5AN-1, Average Equilibrium Concentrations and Properties for Case 1

At Equilibrium Days 9,16,21	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)[*]	ρ (g/mL)	Wt% H_2O
Average	2.8	3.3	15.5	1.45	48.8
Standard Deviation (3σ)	0.35	0.27	0.87	0.013	0.38

*Data only available for days 10 and 20.

For the second case, water was evaporated from the system and the concentration of aluminum in solution increased from an average value of 2.8 ± 0.35 molal (3σ) to 3.6 ± 0.12 molal (3σ). The hydroxide also had a modest increase from 3.3 ± 0.22 molal (3σ) to 3.6 ± 0.29 (3σ). If the increase in aluminum concentration were due to gibbsite dissolution, the hydroxide concentration would decrease proportionately. An increase in both aluminum and hydroxide may be explained by a loss of water. The IS also increases, resulting in enhanced solubility of aluminum. Averaged analytical data for the solutions collected on days 62, 73, and 93 are tabulated in Table 6.

Table 6. Experiment 5AN-1, Average Equilibrium Concentrations and Properties for Case 2

At Equilibrium Days 62,73,93	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	3.6	3.6	17.3	1.52	46.1
Standard Deviation (3σ)	0.12	0.29	1.17	0.107	1.29

*Data only available for days 73 and 93.

3.2. Experiment 5AN-2: Supernatant Liquid Plus Gibbsite, Bottom-Up

In Experiment 5AN-2, supernatant liquid from tank AN-105 with added gibbsite was mixed at 40 °C for about 45 days, and periodic samples were taken over the length of the experiment. Figure 4 demonstrates that the slurry was first undersaturated with aluminum and approached equilibrium from below the saturation point in about 15-20 days. The slurry was considered saturated with aluminum at day 12, and the analytical data for days 12-45 were used for calculation purposes.

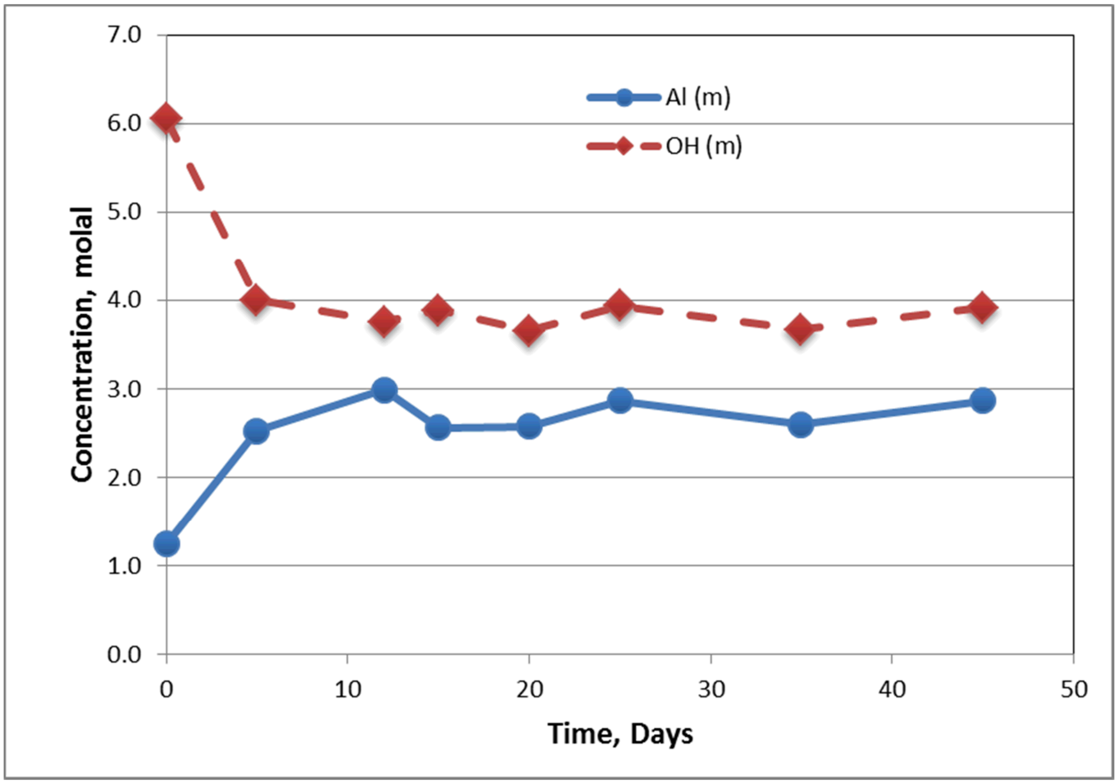

Figure 4. Experiment 5AN-2, No Leach, Equilibrate at 40 °C

Table 7 contains the average concentration of aluminum and hydroxide in thermodynamic equilibrium. The concentrations are 2.7 ± 0.56 molal (3σ) and 3.8 ± 0.38 molal (3σ), respectively. As expected, the concentrations compare well to the results of Case One for Experiment 5AN-1. The aluminum concentrations are nearly identical with a difference that falls within the standard deviation of the two values. The hydroxide concentrations differ slightly with only the tails of the standard deviation of each average intersecting.

The change in moles of aluminum and hydroxide from initial concentrations to the equilibrium concentrations should be equal, assuming the reaction of gibbsite ($Al(OH)_3$) to aluminate ($Al(OH)_4^-$) is the only sink for hydroxide. This was not observed in this experiment, however. The hydroxide concentration decreased 2.26 molal while the aluminate increased only about 1.5 molal in concentration. This observation suggests that another sink for hydroxide exists in the supernatant liquid and gibbsite system.

Table 7. Experiment 5AN-2, Average Equilibrium Concentrations and Properties

At Equilibrium Days 18AP-45	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	2.7	3.8	15.6	1.45	48.66
Standard Deviation (3σ)	0.56	0.38	--	0.05	2.48

*Data only available for day 45.

3.3. Experiment 5AN-3: Supernatant Liquid, Saltcake and Gibbsite, Top-Down

Figure 5 shows the results for an experiment where AN-105 supernatant liquid, AN-105 saltcake, and gibbsite were mixed, leached at 85 °C for 4 hr, and then mixed for about 58 additional days at 40 °C for equilibrium. An inspection of the figure shows some curious results. The aluminate concentration increased during the leach (point 2) to a concentration of about 3.7 molal and then increased further to an average concentration of 4.2 ± 0.31 molal (3σ) when the temperature was dropped to 40 °C. Also note that the aluminate data point for day 16 was omitted as it appeared erroneous and did not trend with the other data in the time series. The example shown in Figure 3 (Experiment 5AN-1) is more representative of the expected behavior of this system. In a normal situation, the aluminate concentration would have dropped after the leach (point 2). The maximum aluminate concentration of 4.2 molal was observed during the leach and then fell to an average concentration of 2.8 ± 0.35 molal (3σ) after the temperature was decreased to 40 °C. The difference between the two systems was the presence of the saltcake in Experiment 5AN-3.

One potential reason for the unusually high Al concentration in this experiment is that *all* of the added gibbsite dissolved during the leach process, leaving no seed crystals to initiate gibbsite precipitation after the leach process, thereby leaving the system in a supersaturated condition. Solid phase analysis of the residual solids from this experiment showed the absence of gibbsite crystals (see Section 3.7). Gibbsite crystals were present in the residual solids from all other experiments.

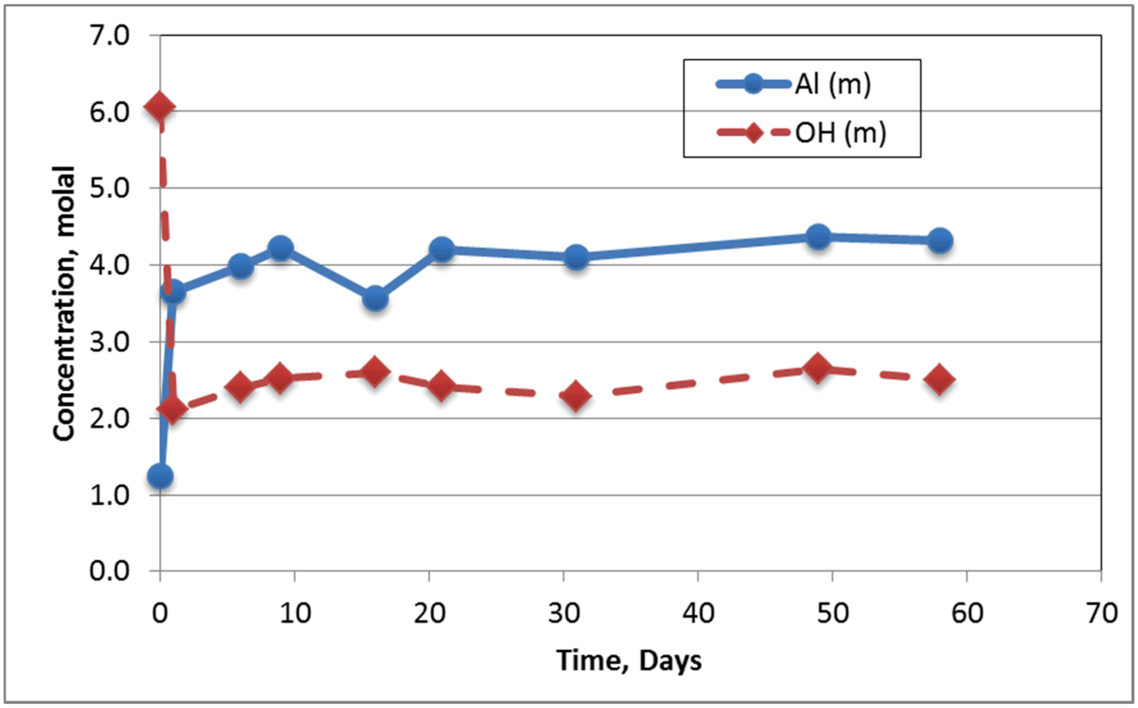

Figure 5. Experiment 5AN-3, Leach at 85 °C, Equilibrate at 40 °C

The behavior of the hydroxide is also interesting. The hydroxide concentration was lowest during the leach with a concentration of 2.11 molal and then increased to an average concentration of 2.5

± 0.39 molal (3σ) when the temperature was dropped to 40 °C for the 58 day period. These results are normally expected if the aluminate concentration falls due to the loss of a hydroxide from aluminate during the precipitation of gibbsite. But in this case, the aluminate concentration increased. These results suggest that some other species was undergoing a transition and freeing hydroxide during the cooling period, or that a significant amount of water was lost from the system.

Table 8 is a tabulation of the aluminate, free hydroxide, and sodium concentrations in the liquid phase for days 9-58 of Experiment 5AN-3. It also contains the average density and weight percent water. Notice that the sodium concentration is quite high at 16.5 ± 0.98 molal (3σ); however, this value is lower than the initial sodium concentration of 17.5 molal, suggesting that some sodium may have precipitated.

The density and weight percent water values of 1.53 ± 0.08 g/ml (3σ) and 44.9 ± 3.06% (3σ), respectively, are also consistent with elevated aluminate concentrations. The earlier experiments with aluminate concentrations nearer to 2.8 molal had a density around 1.45 g/mL and weight percent water around 47%.

Table 8. Experiment 5AN-3, Average Equilibrium Concentrations and Properties

At Equilibrium Days 9-58[a]	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)[b]	ρ (g/mL)	Wt% H_2O
Average	4.2	2.5	16.5	1.53	44.9
Standard Deviation(3σ)	0.31	0.39	0.98	0.08	3.35

[a] The aluminate data from day 16 was omitted from the average.

[b] Data only available for days 31 and 58.

3.4. Experiment 5AN-4: Supernatant Liquid, Saltcake, and Gibbsite, Bottom-Up

In Experiment 5AN-4, supernatant liquid from AN-105, saltcake from AN-105, and gibbsite were mixed and given 47 days to attain thermodynamic equilibrium at 40 °C. The results of this experiment, shown in Figure 6, are more indicative of an expected outcome. The aluminate concentration increased from an initial concentration of 1.24 molal on day 0 to the final average concentration of 2.6 ± 0.46 molal (3σ).

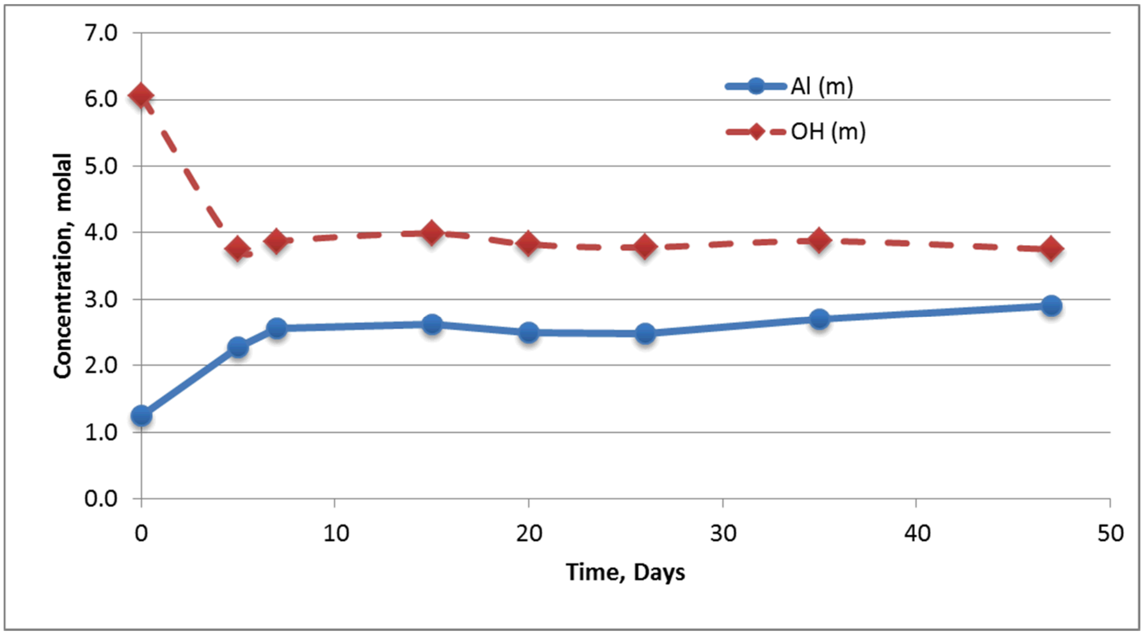

Figure 6. Experiment 5AN-4, No Leach, Equilibrate at 40 °C

Table 9 shows the equilibrium concentrations of aluminate, hydroxide, and sodium along with the equilibrium density and weight percent water. The results of this experiment compare well with those of Experiment 5AN-2. The equilibrium concentrations of aluminate and hydroxide for Experiment 5AN-4 were 2.6 ± 0.51 molal (3σ) and 3.8 ± 0.28 molal (3σ), respectively, and the equilibrium concentrations of aluminate and hydroxide for Experiment 5AN-2 were 2.7 ± 0.56 molal (3σ) and 3.8 ± 0.38 molal (3σ), respectively. This result demonstrates that for temperatures up to 40 °C, the saltcake component likely does not play a role in the solubility of aluminum in supernatant liquid.

Table 9. Experiment 5AN-3, Average Equilibrium Concentrations and Properties

At Equilibrium Days 15-47	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	2.6	3.8	16.31	1.49	47.7
Standard Deviation (3σ)	0.51	0.28	--	0.08	1.92

*Data only available for day 47.

3.5. Statistical Analysis of Mean Aluminum Equilibrium of Tank 241-AN-105 Experiments

A statistical analysis of the mean aluminum and hydroxide concentrations was conducted to determine if the calculated means agree within some statistical significance. Table 10 and Table 11 illustrate the results.

Table 10. Mean Concentrations for Tank 241-AN-105 Experiment Set

Experiment	Exp. 5AN-1		Exp. 5AN-2		Exp. 5AN-3		Exp. 5AN-4	
	Al	OH	Al	OH	Al	OH	Al	OH
Concentration (moles/kg H_2O)	2.91	3.25	2.99	3.76	4.21	2.52	2.63	3.99
	2.68	3.25	2.56	3.89		2.59	2.50	3.83
	2.81	3.41	2.58	3.65	4.20	2.41	2.48	3.78
	--	--	2.87	3.94	4.10	2.28	2.70	3.88
	--	--	2.60	3.67	4.37	2.64	2.90	3.75
	--	--	2.86	3.92	4.31	2.50	--	--
Mean Concentration (moles/kg H_2O)	2.8	3.3	2.7	3.8	4.2	2.5	2.6	3.8
Standard Deviation (3σ)	0.35	0.27	0.56	0.38	0.31	0.39	0.51	0.28

A manual inspection of the mean aluminum concentration of Experiments 5AN-1, -2, and -4 demonstrate that the values are similar. In fact, the statistical analysis demonstrates that the mean aluminum concentrations for the three experiments agree with a confidence greater than 99%. In other words, both experiments in which equilibrium at 40 °C was approached from below the aluminum equilibrium point agree (Experiments 5AN-2 and -4). Also, the experiment where equilibrium was approached from above the aluminum equilibrium point, but included no saltcake, had mean aluminum concentrations that agreed with Experiments 5AN-2 and -4 within a 99% confidence interval.

The outlier was Experiment 5AN-3. In that experiment, the slurry approached aluminum equilibrium from above the equilibrium point by first leaching the gibbsite and saltcake at about 85 °C. In this case, the aluminum concentration was nearly double the concentration of the other experiments.

Table 11. F-test and t-test Results for Tank 241-AN-105 Experiments

Al	F-test	t-test	α	Confidence
Exp. 5AN-1 vs. 5AN-2	Equal Variance	Equal Means	0.01	>99%
Exp. 5AN-1 vs. 5AN-3	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-1 vs. 5AN-4	Equal Variance	Equal Means	0.01	>99%
Exp. 5AN-2 vs. 5AN-3	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-2 vs. 5AN-4	Equal Variance	Equal Means	0.01	>99%
Exp. 5AN-3 vs. 5AN-4	Equal Variance	Unequal Means	0.99	-
OH	**F-test**	**t-test**	**α**	**Confidence**
Exp. 5AN-1 vs. 5AN-2	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-1 vs. 5AN-3	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-1 vs. 5AN-4	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-2 vs. 5AN-3	Equal Variance	Unequal Means	0.99	-
Exp. 5AN-2 vs. 5AN-4	Equal Variance	Equal Means	0.01	>99%
Exp. 5AN-3 vs. 5AN-4	Equal Variance	Unequal Means	0.99	-

The hydroxide concentrations at equilibrium between the four experiments did not show much agreement. In fact, only Experiments 5AN-2 and 5AN-4 showed agreement. In both cases, equilibrium was approached from below the aluminum saturation point, but Experiment 5AN-4 had saltcake present, and Experiment 5AN-2 did not have saltcake present.

The results of these tests suggest that heating the solutions above the saturation point affects the equilibrium behavior of the aluminum-hydroxide system. The data also suggest that the heating of these solutions above the aluminum saturation point with the saltcake component present may be responsible for the enhanced solubility observed in Experiment 5AN-3. This effect may be a kinetic artifact, however. Slow precipitation kinetics is the simplest explanation, but this effect will still be problematic for process operations.

3.6. Supernatant Liquid Analysis of Tank 241-AN-105 Experiments

The supernatant liquid where the aluminate and hydroxide were considered in equilibrium was also examined for other chemical constituents.

Table 12 illustrates the concentration of the other chemical species. Also included in Table 12 are the analyses of the supernatant liquid before any gibbsite was added (Original Supernate) and the supernatant liquid immediately following the leach step at 85 ºC (Leach). One item to note is that the reported values in this table for Al, OH, Na, density, and %H_2O may differ from the results of the previous sections as the Table 12 values are just a single measurement for the final point in the series of data that was averaged and reported in the previous sections.

The results presented in Table 12 were generally expected considering the experiments. The equilibrium density at 40 °C for the experiments conducted with just supernatant liquid and gibbsite did not change much from the supernatant values (5AN-1 and 5AN-2 Last). There was a modest increase in the aluminum concentration from 1.24 molal to a range of 2.74 – 2.86 molal. The leach of the supernatant liquid and gibbsite system at 85 °C did result in an increase in density likely due to the large increase in aluminum concentration from 1.24 to 4.18 molal. An interesting detail to note is the general decrease in all cations and anions and agreement for the 40 °C equilibrium results of the supernatant liquid and gibbsite systems.

The systems with supernatant liquid, gibbsite, and saltcake displayed a slightly different behavior than the supernatant liquid and gibbsite systems. The density of the sample increased due the addition of soluble species found in the saltcake. Generally, chrome, phosphorous, and bromide differed from the supernatant and gibbsite systems.

Table 12. Supernatant Liquid Chemical Analysis of Tank 241-AN-105 Experiments

(concentrations in molality except as noted)

Analyte	**5AN Original Supernate**	**5AN-1 Leach**	**5AN-1 Final**	**5AN-2 Final**	**5AN-3 Leach**	**5AN-3 Final**	**5AN-4 Final**
	S13R000027	**S13R000034**	**S13R000038**	**S13R000053**	**S13R000059**	**Average S13R000064, S13R000066**	**S13R000079**
Density (g/mL)	1.45	1.49	1.45	1.45	1.53	1.56	1.52
% H_2O	45.4	46.9	48.7	47.1	47.9	45.0	47.1
Aluminum	1.24	4.18	2.74	2.86	3.64	4.21	2.90
Boron	0.38	0.32	0.34	0.35	0.29	0.31	0.31
Chromium	0.006	0.005	0.005	0.006	0.006	0.015	0.018
Potassium	0.30	0.25	0.28	0.28	0.26	0.28	0.29
Sodium	17.48	13.73	15.66	15.56	14.85	16.51	16.30
Phosphorus	0.018	0.013	0.013	0.015	0.021	0.023	0.023
Sulfur	0.054	0.046	0.048	0.051	0.053	0.052	0.051
Silicon	0.014	0.010	0.011	0.012	0.009	0.011	0.010
Fluoride	0.015	0.011	0.011	0.011	0.026	0.016	0.018
Glycolate	0.017	0.013	0.015	0.013	0.014	0.014	0.015
Acetate	0.049	0.036	0.036	0.040	0.039	0.040	0.043
Formate	0.064	0.051	0.048	0.056	0.052	0.053	0.053
Chloride	0.510	0.426	0.429	0.467	0.412	0.445	0.448
Nitrite	4.58	3.88	3.86	4.17	3.72	4.08	4.29
Sulfate	0.019	0.017	0.023	0.018	0.026	0.018	0.017
Oxalate	0.015	--	--	--	0.003	--	0.004
Bromide	--	0.016	0.025	0.017	0.015	0.024	0.024
Nitrate	4.08	3.40	3.45	3.97	3.87	3.95	3.96
Phosphate	0.017	--	0.013	--	--	0.025	0.021
TIC as CO3	0.33	0.30	0.35	0.34	0.27	0.24	0.28
TOC	0.34	0.28	0.30	0.31	0.21	0.31	0.32
OH	6.06	1.89	3.41	3.92	2.11	2.39	3.75

NOTE: Concentrations lower than 0.01 m not shown: Ag, As, Ba, Be, Bi, Ca, Cd, Co, Cu, Eu, Fe, La, Li, Mg, Mn, Mo, Nd, Ni, Pb, Sb, Se, Sr, Th, Ti, Tl, U, V, Yt, Zn, Zr.

3.7. Solid Phase Characterization of Tank 241-AN-105 Samples

Solid phase characterization consisted of analysis of solids samples by x-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS), and polarized light microscopy (PLM). Emphasis was placed on the identification of gibbsite and other Al-containing phases. The XRD results were previously published as WRPS-1304176, “Gibbsite Dissolution in Archived Supernatant X-Ray Diffractometry (XRD) Results,” which is attached as Appendix 3.

3.7.1. Original Saltcake (Sample S13R000019)

The untreated AN-105 saltcake sample was described as avocado green fine-grained solids. The sample contained little or no gibbsite. Gibbsite was not detected by any of the three characterization methods. Aluminum was detected in several different minor to trace phases. Solid phases that were detected include:

- Major: thermonatrite, $Na_2CO_3 \cdot H_2O$, identified by XRD, SEM/EDS and PLM **(**Figure 7)
- Major: sodium nitrate, $NaNO_3$, identified by XRD only (possibly an artifact)
- Minor: kogarkoite, Na_3FSO_4, identified by XRD and SEM/XRD (Figure 8)
- Minor: natroxalate, $Na_2C_2O_4$, identified by XRD only (very difficult to distinguish from $Na_2CO_3 \cdot H_2O$ by SEM/EDS or PLM)
- Trace: natrophosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$, identified by XRD only (possibly an artifact)
- Trace: cancrinite, $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$, identified by XRD and SEM/EDS (although the SEM/EDS phase contained little or no Ca; see Figure 9)

Other trace phases identified by SEM/EDS include:

- Na-Al-Cr-rich phase, Figure 10
- Agglomerate containing Na-Al-Fe-U
- Na-Al-Ca-Cr-rich phase (“garnetoid”)

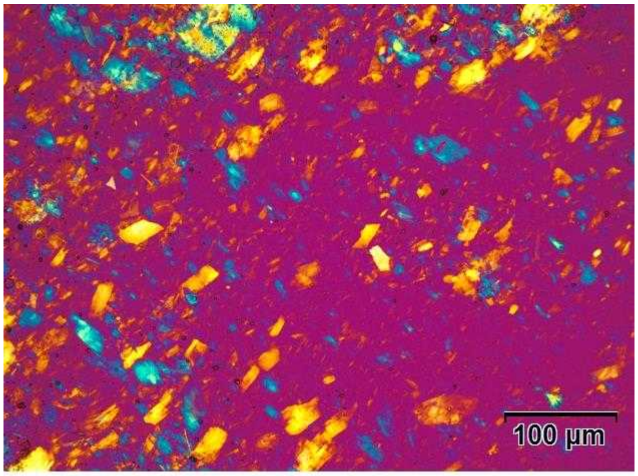

Figure 7. AN-105 Untreated Saltcake

(Mainly $Na_2CO_3 \bullet H_2O$; crossed polars with Red I compensator)

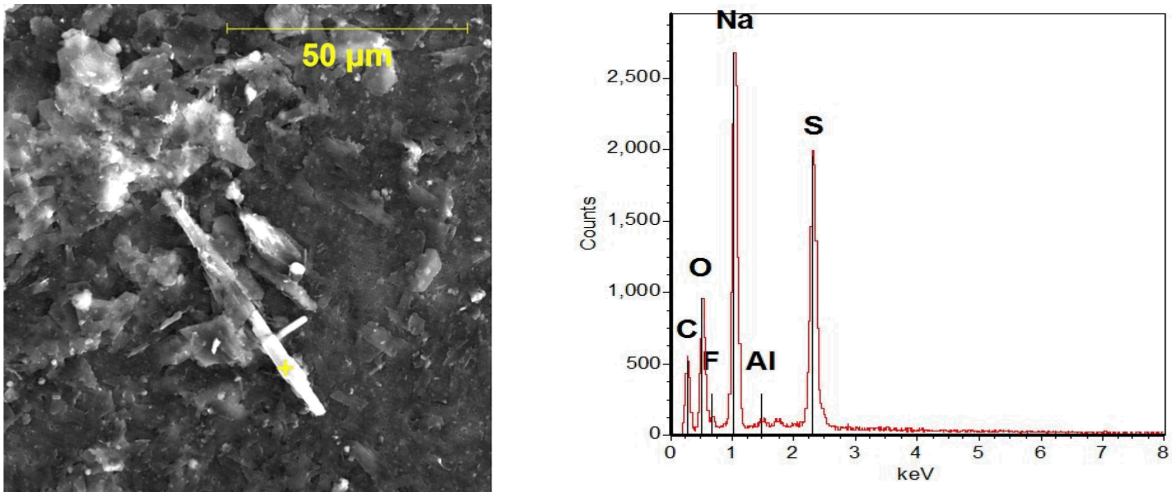

Figure 8. AN-105 Saltcake, Kogarkoite Needle

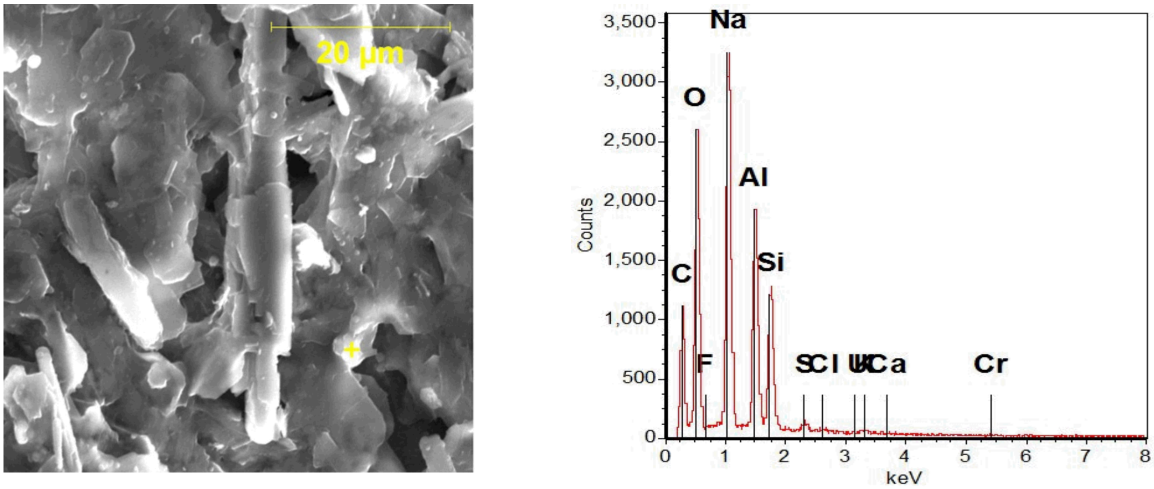

Figure 9. AN-105 Saltcake, Cancrinite Particle (without Ca)

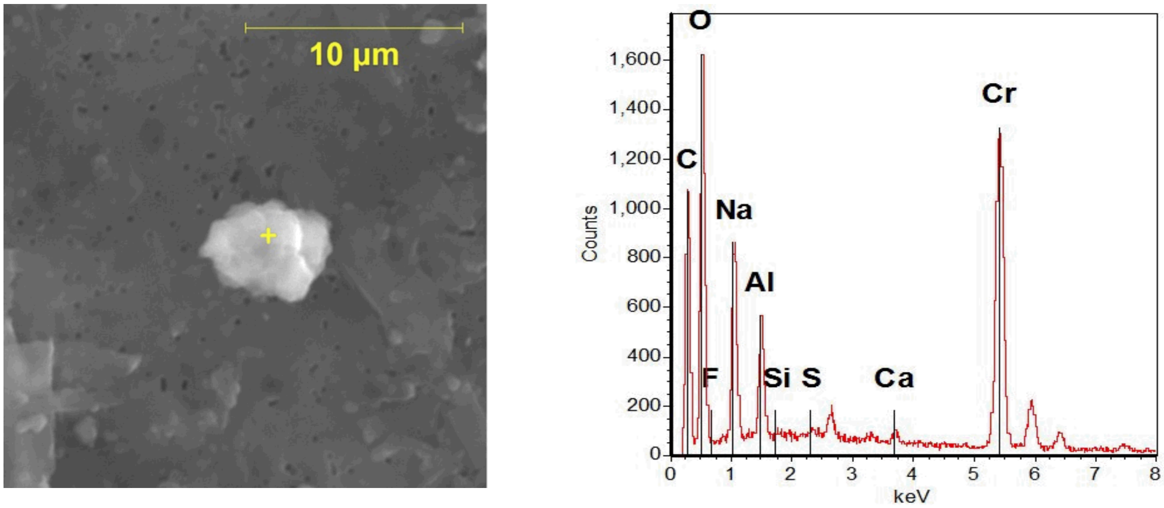

Figure 10. AN-105 Saltcake, Na-Al-Cr-Rich Phase

3.7.2. Test 5AN-1 (Sample S13R000042)

Test 5AN-1 was a mixture of AN-105 supernatant liquid plus reagent gibbsite leached at 85 ºC and equilibrated at 40 ºC. Sample S13R000042 was described as light brown solids. The solids phases identified include:

- Major: gibbsite, $Al(OH)_3$, identified as the dominant solid phase by all three methods. Figure 11 shows a PLM comparison between reagent gibbsite (left) and test 5AN-1 residual solids (right). The residual solids are composed of approximately 98% gibbsite and 2% unidentified blue/yellow needles. Figure 12 shows an SEM photograph and EDS spectrum of the sample. No other Al-containing phases were identified.
- Major: sodium nitrate, identified by XRD and PLM (Figure 13)
- Minor: sodium nitrite, identified by XRD only (possibly an artifact)
- Trace: thermonatrite, identified by XRD and possibly by PLM (the tiny blue/yellow needles in Figure 11, right).

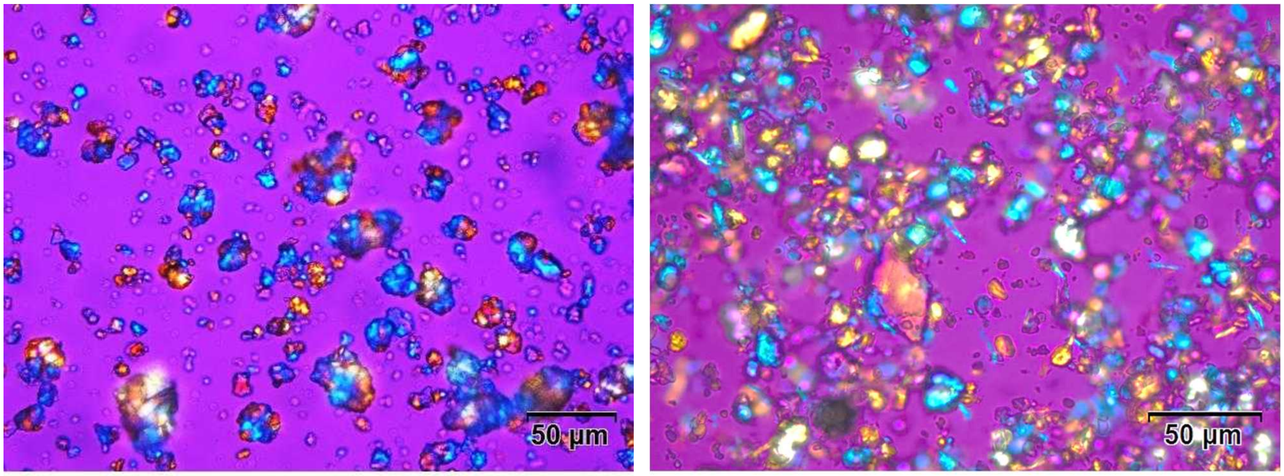

Figure 11. Left: Reagent Gibbsite, Almatis C33. Right: Experiment 5AN-1 Residual Solids

(Both photos are crossed polars with Red I compensator)

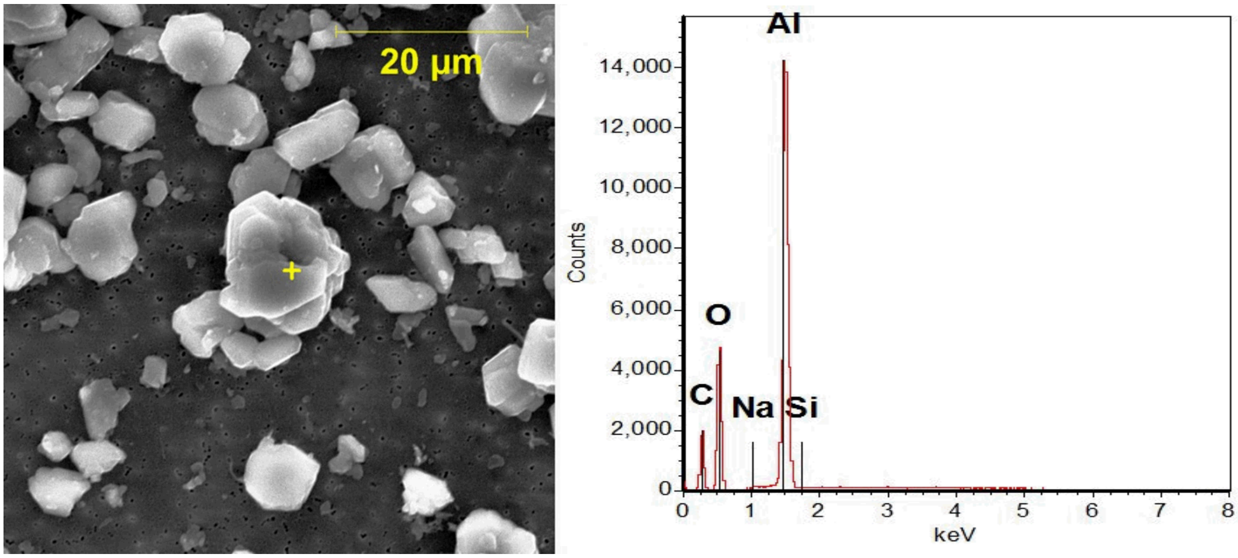

Figure 12. Experiment 5AN-1 Residual Solids, Typical Gibbsite Particle

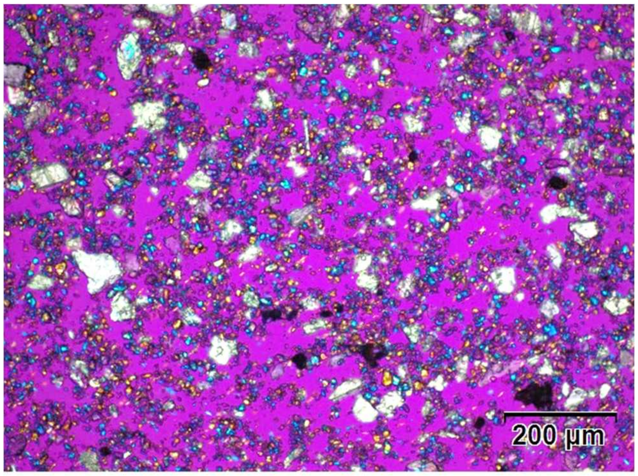

Figure 13. Experiment 5AN-1 Residual Solids, Low Magnification Sample Overview

(Mixture of gibbsite and $NaNO_3$; crossed polars with Red I compensator)

3.7.3. Test 5AN-2 (Sample S13R000054)

Test 5AN-2 was a mixture of AN-105 supernatant liquid plus reagent gibbsite, not leached, equilibrated at 40 ºC. Sample S13R000054 was described as egg-white solids with white crystallites. The solids phases identified include:

- Major: gibbsite, identified as the dominant solid phase by all three methods. No other Al-containing phases were identified.

- Major: thermonatrite, identified by XRD only
- Minor: sodium nitrate, identified by XRD and PLM (Figure 14)

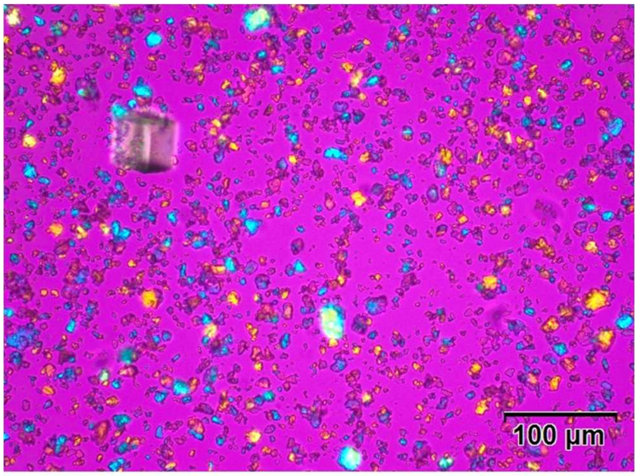

Figure 14. Experiment 5AN-2 Residual Solids

(Nearly 100% gibbsite, trace of $NaNO_3$ – large crystal in upper left)
(Crossed polars with Red I compensator)

3.7.4. Test 5AN-3 (Sample S13R000067)

Test 5AN-3 was a mixture of AN-105 supernatant liquid plus reagent gibbsite plus AN-105 saltcake, leached at 85 °C, and equilibrated at 40 °C. Sample S13R000067 was described as light-colored solids. Gibbsite was not detected by XRD or PLM, though a few particles of gibbsite were identified by SEM/EDS. The relative absence of gibbsite is consistent with the unusually high concentration of aluminum in the liquid phase for this experiment.

The solids phases identified include:

- Major: sodium nitrate, identified by XRD only
- Major: thermonatrite, identified by PLM as the dominant phase in the sample (Figure 15), by XRD as a minor phase, and by SEM/EDS (without indication of relative amount)
- Minor: sodium nitrite, identified by XRD only (possibly an artifact)
- Trace: kogarkoite, identified by XRD only
- Trace: natrophosphate, identified by XRD only
- Trace: cancrinite, identified by XRD and by SEM/EDS (with and without Ca)

Additional trace phases identified by SEM/EDS only include:

- Na-Al-Ca-Cr-rich phase (“garnetoid”), Figure 16.
- Al-Ca phase (with little Na, Cr, or Si)
- Al-Ca-Si phase

- Na-Al-U phase
- Fe-Cr-Al-Ni phase
- Sn-rich phase

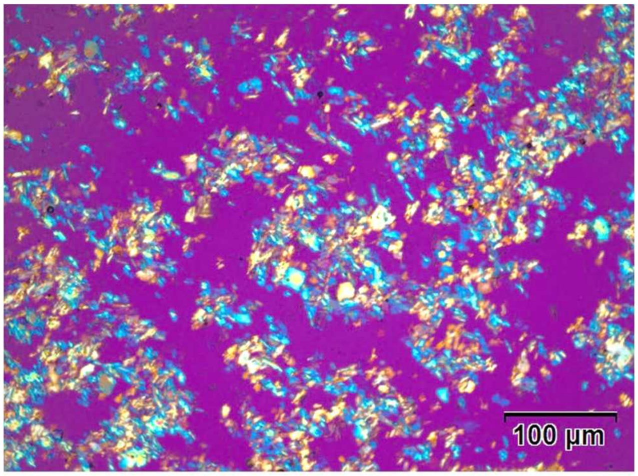

Figure 15. Experiment 5AN-3 Residual Solids

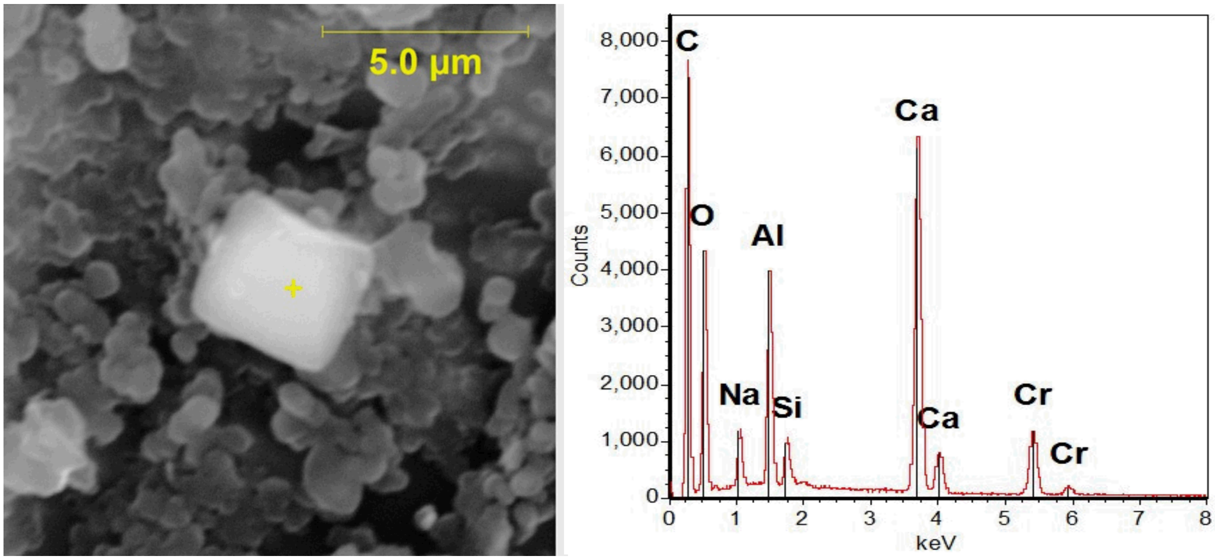

Figure 16. Experiment 5AN-3, "Garnetoid" Crystal

(Nearly 100% $Na_2CO_3 \cdot H_2O$; crossed polars with Red I compensator)

3.7.5. Test 5AN-4 (Sample S13R000082)

Test 5AN-4 was a mixture of AN-105 supernatant liquid plus reagent gibbsite plus AN-105 saltcake, not leached, equilibrated at 40 ºC. Sample S13R000082 was described as light-colored solids. Gibbsite was the dominant phase, as determined by XRD, SEM/EDS, and PLM.

The solids phases identified include:

- Major: gibbsite, identified by all three methods (Figure 17)
- Major: sodium nitrate, identified by XRD only (possibly an artifact)
- Major: sodium nitrite, identified by XRD only (possibly an artifact)
- Minor: thermonatrite, identified by XRD, identified as major phase by PLM (Figure 17), not identified by SEM/EDS
- Minor: natrophosphate, identified by XRD and PLM (Figure 17)

Additional trace phases identified by SEM/EDS only include:

- Several "garnetoid" crystals (e.g., Figure 18, Figure 19)
- Cancrinite (no Ca)
- Al-Ca-Si phase
- Na-Al-U phase

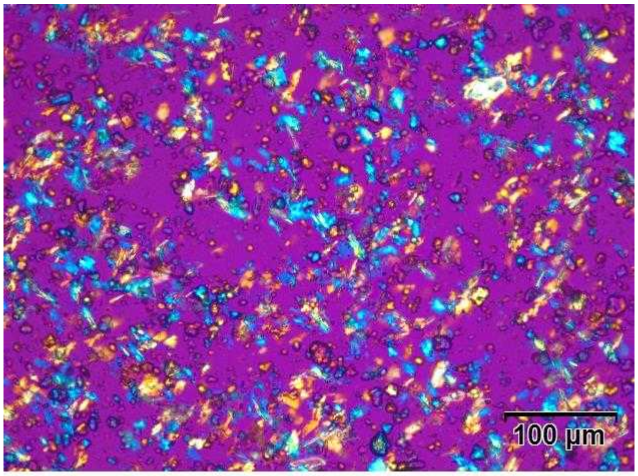

Figure 17. Experiment 5AN-4 Residual Solids

(Mixture of $Na_2CO_3 \cdot H_2O$ and undissolved gibbsite, trace of $Na_7FPO_4 \cdot 19H_2O$;
Crossed polars with Red I compensator)

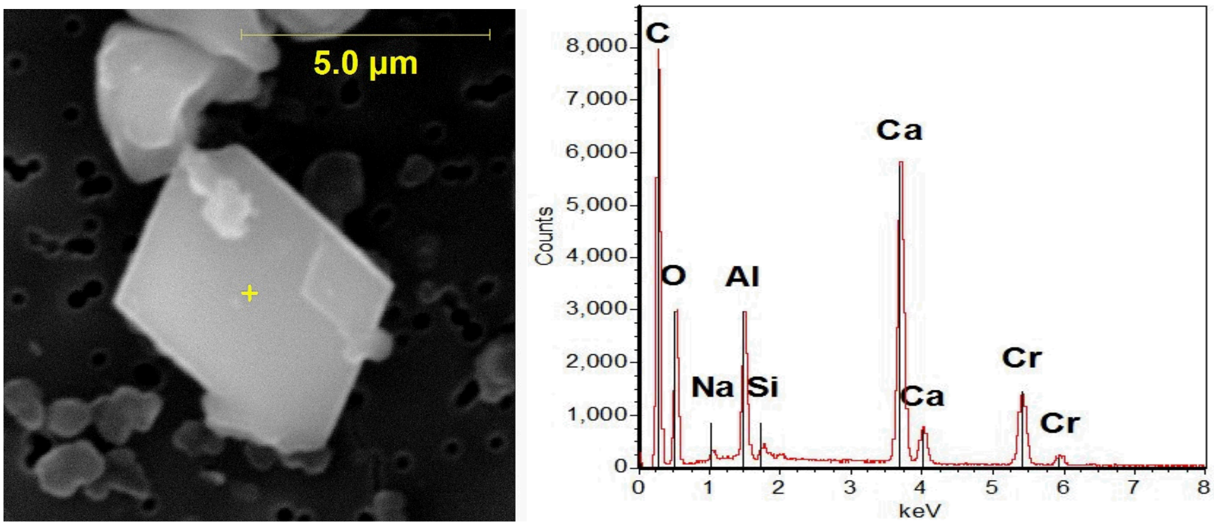

Figure 18. Experiment 5AN-4, "Garnetoid" Plate Crytal

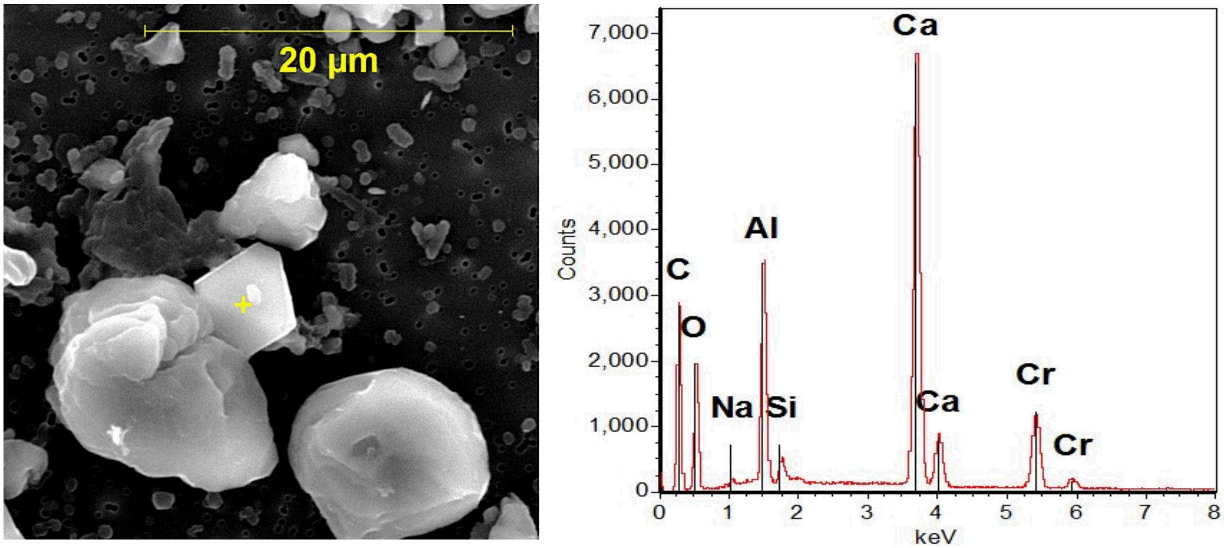

Figure 19. Experiment 5AN-4, “Garnetoid” Octahedral Crystal

4. TANK 241-AP-108 RESULTS

4.1. Experiment 8AP-1: Supernatant Liquid plus Gibbsite, Top-Down

The data represented in Figure 20 illustrate a time series to equilibrium solubility in a slurry containing supernatant liquid from tank AP-108 and about 25 wt% added gibbsite. In this experiment, the slurry was first heated to about 85 °C for about 4 hr, and then the temperature was lowered to 40 °C. Aluminate equilibrium was approached from above the saturation point at 40 °C. The data shows that the solid gibbsite was leached into the solution at 85 °C with a final concentration of about 2.7 molal. When the temperature was dropped to 40 °C, the aluminum concentration also fell to an average concentration of 1.6 ± 0.05 molal (see Table 15). This is the average of the samples taken on days 7, 14, 18, and 31. The data point for day 21 was dismissed as it did not trend well with the other data. Also, aliquots 2 and 3 for the sample taken on day 21 crystalized during the sampling process due to errors with equipment in the hot cell. Near the end of the time series, the sample seemed to crystalize rather quickly once taken off the heat, making it difficult to filter. Therefore, these data were omitted from the results.

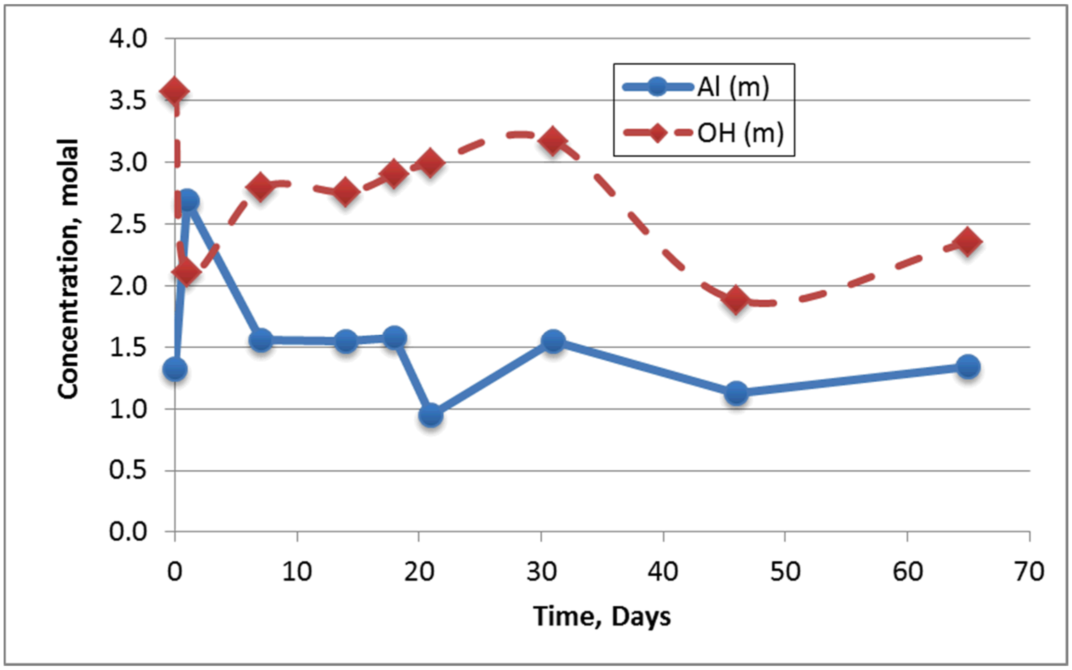

Figure 20. Experiment 8AP-1, Leach at 85 °C, Equilibrate at 40 °C

Table 13. Experiment 8AP-1, Average Equilibrium Concentrations and Properties

At Equilibrium Days 7-18, 31	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	1.6	2.9	14.4	1.41	51.4
Standard Deviation (3σ)	0.05	0.56		0.06	2.47

*Data only available for day 18.

4.2. Experiment 8AP-2: Supernatant Liquid Plus Gibbsite, Bottom-Up

For this experiment, supernatant liquid from tank AP-108 was mixed with excess gibbsite and allowed to come to equilibrium at 40 °C. However, the experiment suffered from a vapor leak in the reactor, making the data suspect. The existing data are not sufficient to assign an equilibrium solubility value.

4.3. Experiment 8AP-3: Supernatant Liquid, Saltcake, and Gibbsite, Top-Down

This experiment was conducted by mixing AP-108 supernatant liquid and AP-108 saltcake with added gibbsite, heating the resulting slurry for 4 hr at 85 °C to saturate the solution with aluminum and then maintaining the solution at 40 °C for about 60 days for aluminum and hydroxide equilibrium. The results of the experiment are displayed as a time series in Figure 21, and they show that aluminum reached equilibrium on day 5, but the hydroxide never seemed to reach equilibrium.

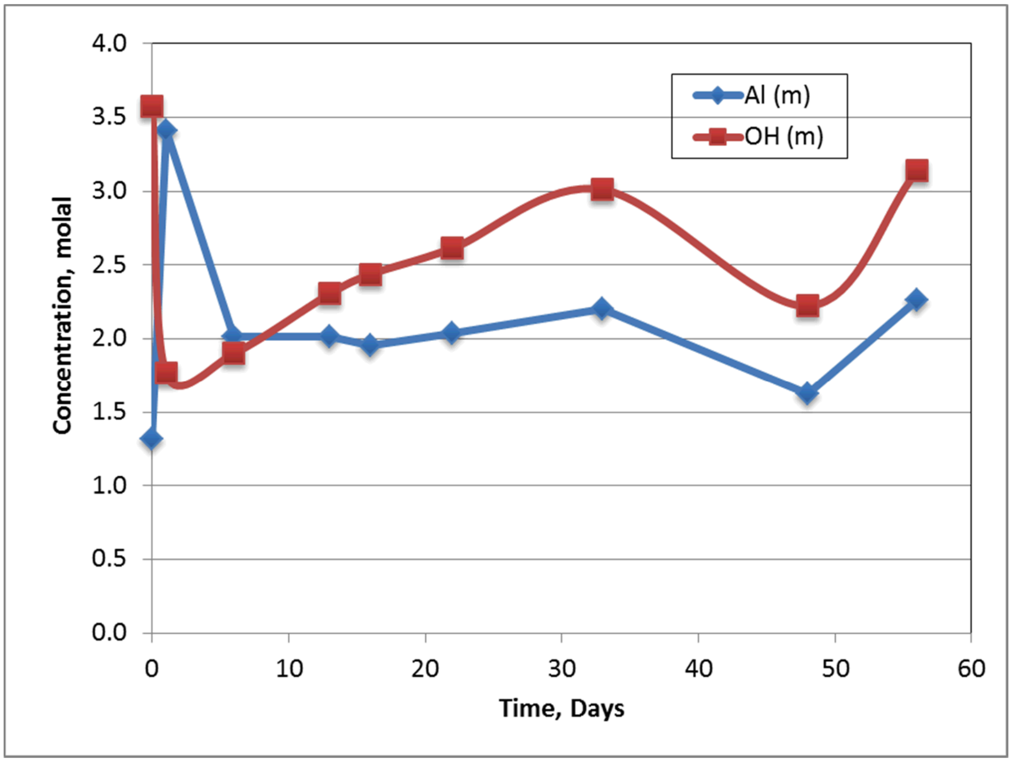

Figure 21. Experiment 8AP-3, Leach at 85 °C, Equilibrate at 40 °C

The aluminum was constant for days 5 through 22 and then rose slightly on day 33. Days 5 through 22 were considered to be at equilibrium. On days 33 and 56, the aluminum was elevated, seeming to suggest that some water loss from the reactor had occurred. The sample density for those two sets of points increased to about 1.51 g/mL vice 1.44 ± 0.06 g/mL for the other points, which also suggests some evaporation. The hydroxide continued to increase in concentration over the length of the experiment. For convenience, the reported hydroxide value displayed in

Table 14 was calculated using the same points used to determine the equilibrium concentration of aluminum. This value should be used with some caution as it is obvious that the hydroxide was never at equilibrium during this experiment. The aluminum and hydroxide data for day 48 were omitted because they did not fit the trend of the time series. Table 14 contains average values for aluminate, hydroxide, density, and weight percent water that were determined by averaging the values from days 5-22. A single value for sodium was available for this period; therefore, no error was reported for sodium.

Table 14. Experiment 8AP-3, Average Equilibrium Concentrations and Properties

At Equilibrium Days 5-22	$Al(OH)_4^-$ (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	2.0	2.3	15.9	1.44	50.5
Standard Deviation (3σ)	0.10	0.91	--	0.06	10.9

*Used closest available data point from day 22.

4.4. Experiment 8AP-4: Supernatant Liquid, Saltcake, and Gibbsite, Bottom-Up

The time series plot of the dissolution of gibbsite in AP-108 supernatant liquid solution with AP-108 saltcake solids and added gibbsite is displayed in Figure 22. The plot demonstrates that the aluminum concentration increased from an initial concentration of about 1.32 molal to an equilibrium concentration of 1.6 ± 0.20 molal by day 6. The equilibrium concentration (see Table 17) is calculated as the average of days 6-31. The final data point taken on day 49 was omitted due to the upward trend in concentration of aluminum and hydroxide, which is evidence of loss of water from the system. The sample density and weight percent water for the sample taken on day 49 increased and dropped, respectively, from the equilibrium values tabulated in Table 15. These results provide additional credence that the analytical results from day 49 were compromised from loss of water from the system.

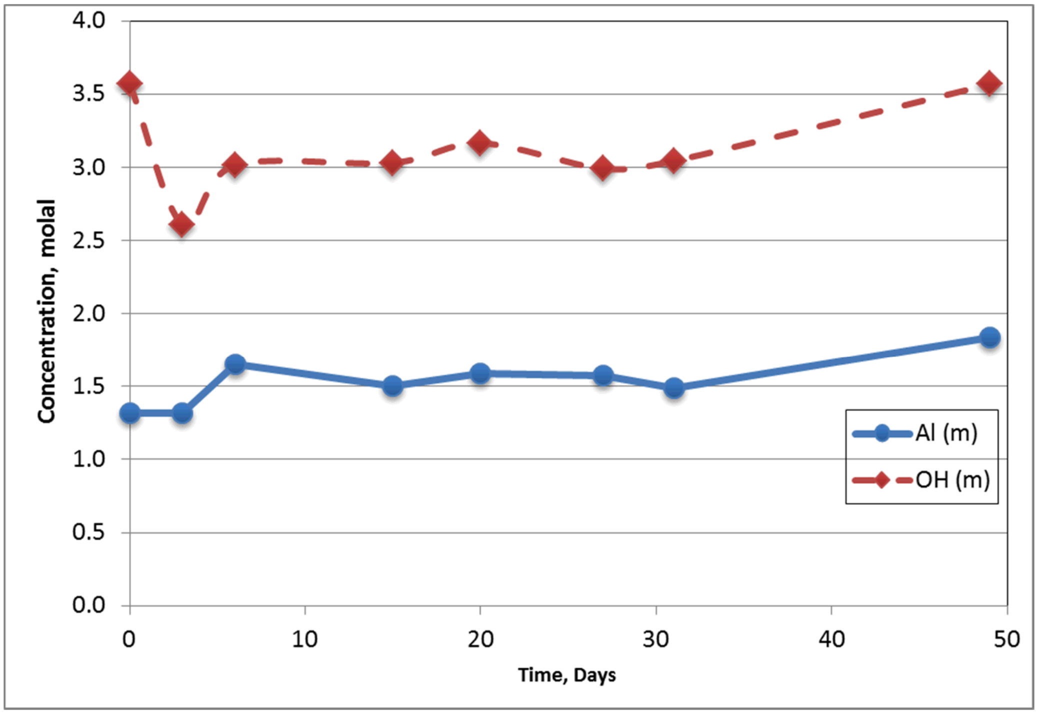

Figure 22. Experiment 8AP-4, No Leach, Equilibrate at 40 °C

Table 15. Experiment 8AP-4, Average Equilibrium Concentrations and Properties

At Equilibrium Days 6-31	$Al(OH)_4$- (m)	OH^- (m)	Na^+(m)*	ρ (g/mL)	Wt% H_2O
Average	1.6	3.0	12.8	1.43	49.9
Standard Deviation(3σ)	0.20	0.20	--	0.08	4.3

*Used closest available data point from day 31.

4.5. Statistical Analysis of Mean Aluminum Equilibrium of Tank 241-AP-108 Experiments

Table 16 contains tabulated data of the aluminum and hydroxide concentration values used to calculate the mean concentration and standard deviation for the AP-108 experiments considered at equilibrium. An F-test and t-test were conducted using the results in Table 16 to determine the agreement of the equilibrium values between each of the four AP-108 experiments.

For the experiments where the gibbsite was first leached at 85 °C and then allowed to come to equilibrium at 40 °C (Experiments 8AP-1 and 8AP-3) with the only difference being that Experiment 8AP-3 contained saltcake, both the aluminum and hydroxide equilibrium concentrations were statistically different. The results of Experiment 8AP-1 and Experiment 8AP-4 showed good agreement with both the aluminum and hydroxide equilibrium concentrations proving statistically the same. Experiment 8AP-4 did have saltcake added to the system, but was not heated prior to aluminum reaching equilibrium at 40 °C. The results suggest that when gibbsite is leached at 85 °C in the presence of saltcake, the equilibrium concentration of aluminum is elevated as compared to an unheated system containing saltcake or a supernatant liquid system containing only gibbsite.

Table 16. Mean Concentrations for Tank 241-AP-108 Experiments

Experiment	Exp. 8AP-1		Exp. 8AP-3		Exp. 8AP-4	
	Al	OH	Al	OH	Al	OH
Concentration (moles/kg H_2O)	1.55	2.79	2.02	1.90	1.65	3.02
	1.55	2.76	2.02	2.31	1.50	3.03
	1.58	2.90	1.96	2.44	1.59	3.16
	--	2.99	2.04	2.62	1.58	2.99
	1.55	3.17	--	--	1.49	3.04
Mean Concentration (moles/kg H_2O)	1.56	2.92	2.01	2.32	1.56	3.05
Standard Deviation (3σ)	0.06	0.50	0.10	0.91	0.20	0.20

Table 17. F-test and t-test Results for Tank 241-AP-108 Experiments

Al	F-test	t-test	α	Confidence
Exp. 8AP-1 vs. Exp. 8AP-3	Equal Variance	Unequal Means	0.99	-
Exp. 8AP-1 vs. Exp. 8AP-4	Equal Variance	Equal Means	0.01	>99%
Exp. 8AP-3 vs. Exp. 8AP-4	Equal Variance	Unequal Means	0.99	-
OH	**F-test**	**t-test**	**α**	**Confidence**
Exp. 8AP-1 vs. Exp. 8AP-3	Equal Variance	Unequal Means	0.99	-
Exp. 8AP-1 vs. Exp. 8AP-4	Equal Variance	Equal Means	0.01	>99%
Exp. 8AP-3 vs. Exp. 8AP-4	Unequal Variance	Equal Means	0.01	>99%

4.6. Supernatant Liquid Analysis of Tank 241-AP-108 Experiments

The supernatant liquid where the aluminate and hydroxide were considered at equilibrium was also examined for other chemical constituents. Table 18 illustrates the concentration of the other chemical species. One item to note is that the reported values in this table may differ from the results of the previous sections; these values are just a single measurement for the final point in the series of data that was averaged and reported in the previous sections.

The results presented in Table 18 were generally to be expected considering the experiments. For most of the analytes, the concentration is more-or-less constant across all of the samples in the table. The notable exceptions, of course, are Al and OH. The Al concentration was higher in all of the test samples than in the original supernatant liquid due to dissolution of the excess gibbsite that was added in all of the tests. The OH concentration was correspondingly lower in all of the test samples than in the original supernatant liquid for the same reason.

The lack of significant increase in other analytes indicates that the AP-108 saltcake contained little, if any, soluble salts.

Table 18. Supernatant Liquid Chemical Analysis of Tank 241-AP-108 Experiments

(concentrations in molality except as noted)

Analyte	8AP Original Supernate	8AP-1 Leach	8AP-1 Final	8AP-3 Leach	8AP-3 Final	8AP-4 Final
	S13R000091	S13R000098	S13R000105	S13R000123	Average S13R000128, S13R000130	S13R000141
Density (g/mL)	1.411	1.45	1.49	1.50	1.49	1.46
% H_2O	47.3	47.9	49.3	42.3	44.9	51.2
Aluminum	1.32	2.69	1.57	3.41	2.24	1.49
Boron	0.02	--	--	0.00	0.01	0.00
Chromium	0.022	0.020	0.022	0.027	0.027	0.022
Potassium	0.43	0.39	0.43	0.49	0.51	0.41
Sodium	14.70	12.45	14.29	17.15	15.36	12.78
Phosphorus	0.021	0.017	--	0.053	0.045	0.042
Sulfur	0.050	0.045	--	0.064	0.043	0.038
Silicon	0.024	0.012	--	0.015	0.013	0.011
Fluoride	0.023	0.018	0.017	0.031	0.013	0.015
Glycolate	0.017	0.015	0.019	0.021	0.025	0.016
Acetate	0.041	0.034	0.040	0.043	0.050	0.034
Formate	0.094	0.076	0.080	0.084	0.090	0.075
Chloride	0.279	0.247	0.249	0.273	0.324	0.243
Nitrite	3.33	2.90	3.07	3.46	3.87	2.91
Sulfate	0.043	0.040	0.039	0.051	0.090	0.026
Oxalate	0.004	0.003	0.012	0.012	0.004	--
Bromide	0.012	--	0.020	0.021	0.018	0.009
Nitrate	5.08	4.78	4.65	5.13	5.20	4.59
Phosphate	0.025	--	0.021	0.039	0.039	0.041
TIC as CO_3	0.76	0.75	0.57	0.82	0.39	0.42
TOC	0.36	0.33	0.38	0.39	0.38	0.35
OH	3.57	2.10	2.89	1.77	3.08	3.04

NOTE: Concentrations lower than 0.01 m not shown: Ag, As, Ba, Be, Bi, Ca, Cd, Co, Cu, Eu, Fe, La, Li, Mg, Mn, Nd, Ni, Pb, Sb, Se, Sr, Th, Ti, Tl, U, V, Yt, Zn, Zr

4.7. Solid Phase Characterization of Tank 241-AP-108 Samples

The original AP-108 sludge sample and the residual solids from the AP-108 solubility tests were analyzed by XRD, SEM/EDS and PLM. Characterization was focused on speciation of aluminum in the solid phase. Details of the XRD results are given in Appendix 3.

4.7.1. Original Saltcake (Sample S13R000084)

The untreated AP-108 sludge sample was described as light brown fine-grained solids. The sample contained little or no gibbsite. Gibbsite was identified as a trace component by XRD and SEM/EDS. Other solid phases that were detected include:

- Major: thermonatrite, $Na_2CO_3 \cdot H_2O$, identified by XRD, SEM/EDS and PLM (Figure 23)
- Major: sodium nitrate, $NaNO_3$, identified by XRD, SEM/EDS (Figure 24) and PLM (Figure 23)
- Minor: natrophosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$, identified by XRD, SEM/EDS and PLM (Figure 23)
- Trace: cancrinite, $Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$, identified by XRD and SEM/EDS (although the SEM/EDS phase contained no Ca)

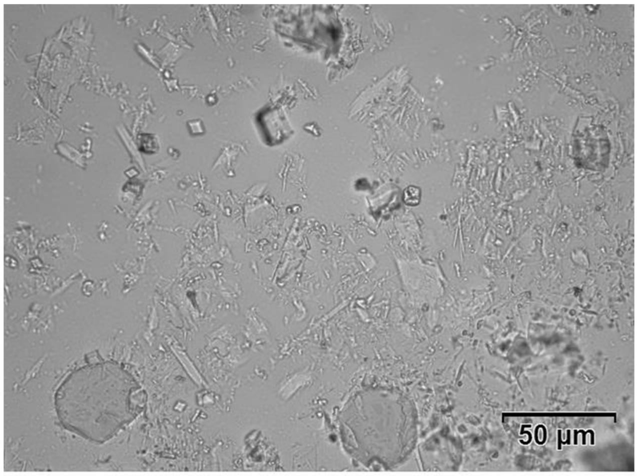

Figure 23. AP-108 Untreated Sludge

($Na_2CO_3 \bullet H_2O$, $NaNO_3$, $Na_7FPO_4 \bullet 19H_2O$, and unidentified phases; uncrossed polars)

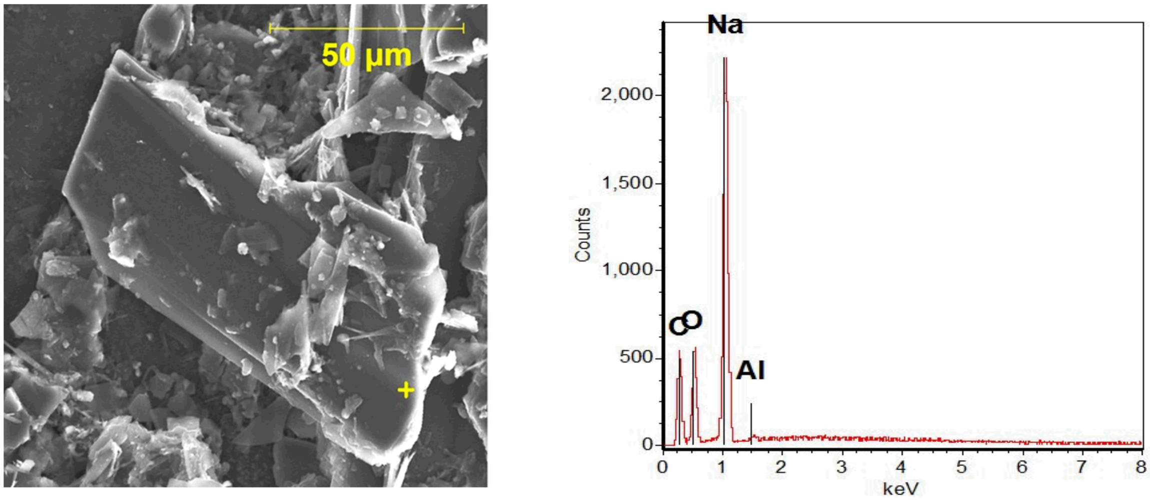

Figure 24. AP-108 Untreated Sludge, NaNO3 Crystal

Other trace phases identified by SEM/EDS include:

- Na-S-rich needles, Figure 25 (probably kogarkoite, Na_3FSO_4)
- Ca-S-rich rods, Figure 26
- Na-Al-Ca-Cr-rich crystals (“garnetoid”)
- Na-Al-Ca-rich crystals (without Cr)
- Na-Al-U-Cr-rich particle
- Na-Al-U-rich particle without Cr
- Fe-Cr-Ni-rich phase
- Fe-rich phase
- Na-Al-Fe-Cl amorphous particle
- Na-Al-rich rod-shaped crystal (possibly dawsonite, $NaAl(OH)_2CO_3$)

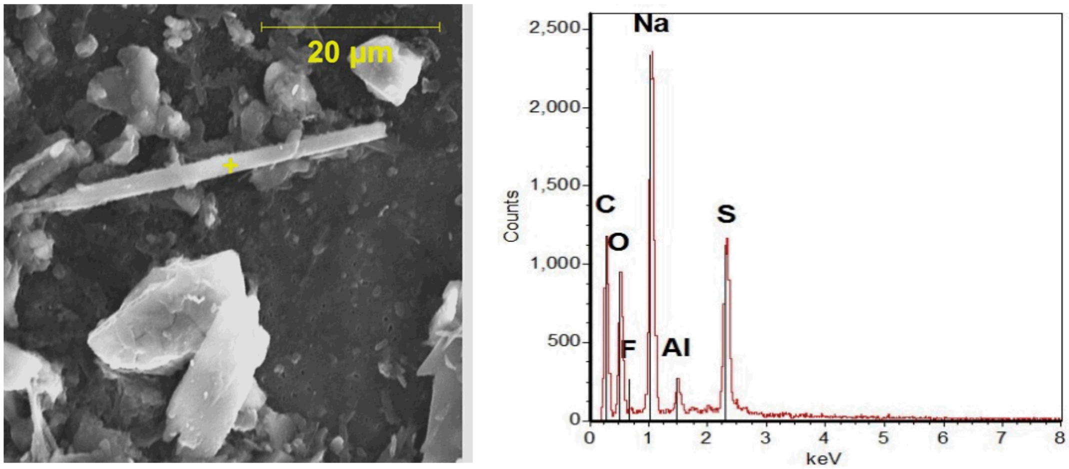

Figure 25. AP-108 Untreated Sludge, Kogarkoite Needle Crystal

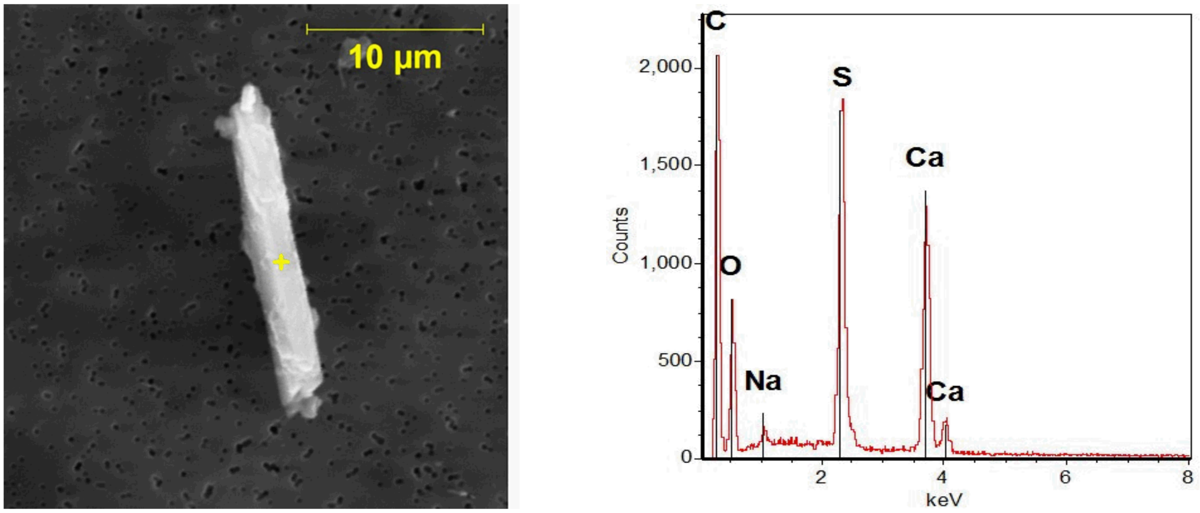

Figure 26. AP-108 Untreated Sludge, Ca-S-Rich Phase

4.7.2. Test 8AP-1 (Sample S13R000108)

Test 8AP-1 was a mixture of AP-108 supernatant liquid plus reagent gibbsite leached at 85 ºC and equilibrated at 40 ºC. Sample S13R000108 was described as light brown solids. Gibbsite was identified as the major phase by all three characterization methods. Other solid phases included:

- Major: sodium nitrate, identified by XRD and PLM (Figure 27); presence indicative of some evaporation during the equilibration period
- Minor: sodium nitrite, identified by XRD only (possibly an artifact)
- Minor: thermonatrite, identified by XRD only

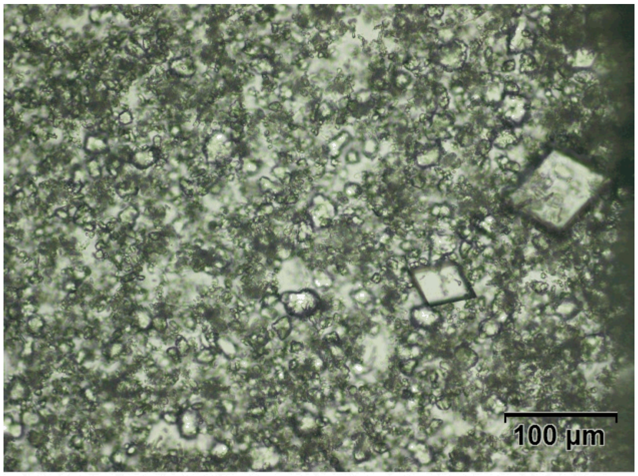

Figure 27. Experiment 8AP-1 Residual Solids

($NaNO_3$ and undissolved gibbsite; uncrossed polars)

4.7.3. Test 8AP-2 (Sample S13R000120)

Test 8AP-2 was abandoned due to equipment malfunction

4.7.4. Test 8AP-3 (Sample S13R000145)

Test 8AP-3 was a mixture of AP-108 supernatant liquid plus reagent gibbsite plus AP-108 sludge, leached at 85 ºC, and equilibrated at 40 ºC. Sample S13R000145 was described as light-colored solids. Gibbsite was identified as a major phase by XRD and SEM/EDS. Other solid phases identified include:

- Major: sodium nitrate, identified by XRD and PLM
- Major: thermonatrite, identified by XRD only
- Major: sodium nitrite, identified by XRD only (possibly an artifact)
- Trace: natrophosphate, identified by XRD only

Additional trace phases identified by SEM/EDS only include:

- Na-Al-Si-rich particle, cancrinite (without Ca)
- Al-Ca-rich crystal (Figure 28)
- Al-Fe-rich particle (Figure 29))
- Na-Al-U-rich particle (Figure 30)

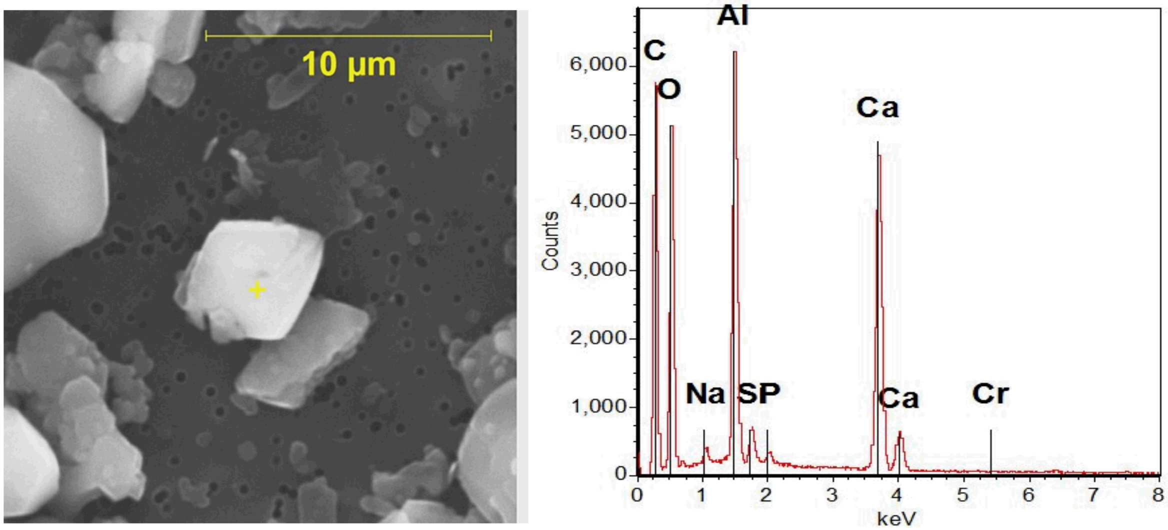

Figure 28. Experiment 8AP-3 Residual Solids, Al-Ca-Rich Crystal

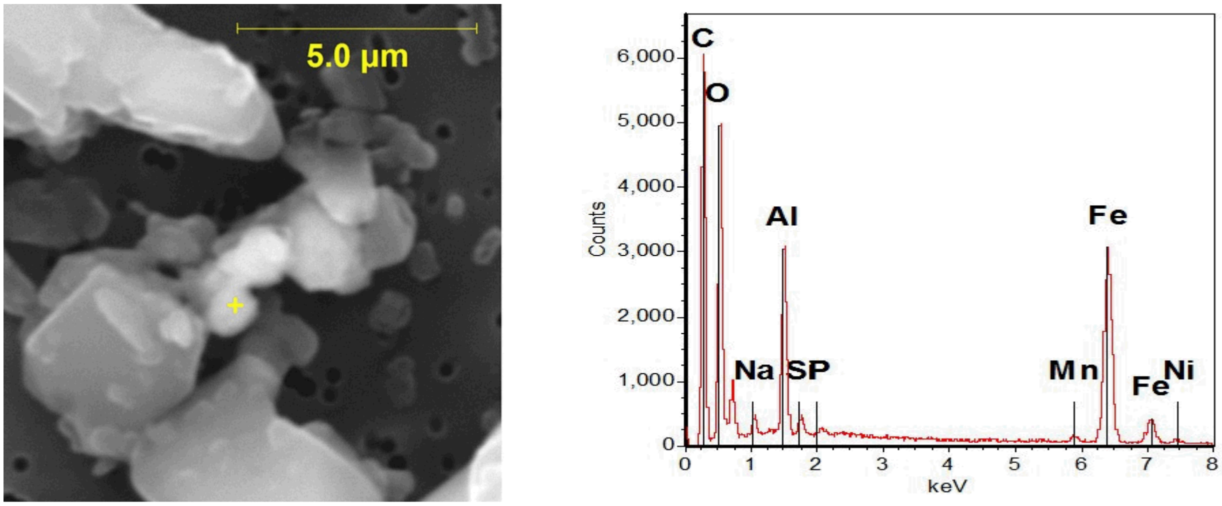

Figure 29. Experiment 8AP-3 Residual Solids, Al-Fe-Rich Phase

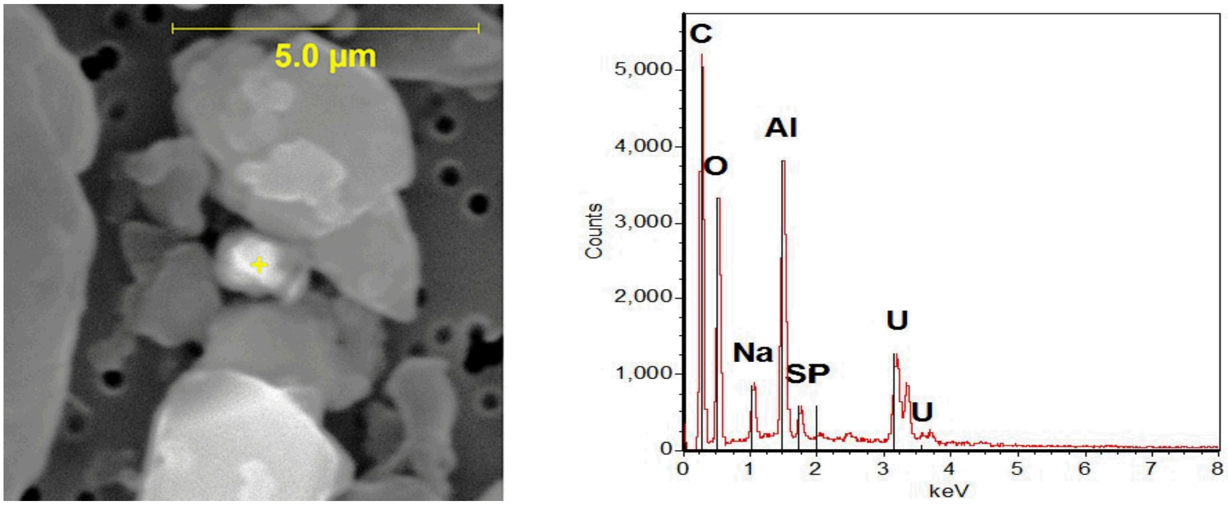

Figure 30. Experiment 8AP-3 Residual Solids, Na-Al-U-Rich Phase

4.7.5. Test 8AP-4 (Sample S13R000146)

Test 8AP-4 was a mixture of AP-108 supernatant liquid plus reagent gibbsite plus AP-108 sludge, not leached, equilibrated at 40 ºC. Sample S13R000146 was described as light brown solids. Gibbsite was identified as a major phase by all three characterization methods. Other solid phases identified include:

- Major: thermonatrite, identified by XRD and PLM (Figure 31)
- Minor: sodium nitrate, identified by XRD and PLM
- Minor: sodium nitrite, identified by XRD only (possibly an artifact)
- Trace: natrophosphate, identified by XRD and PLM (Figure 31)

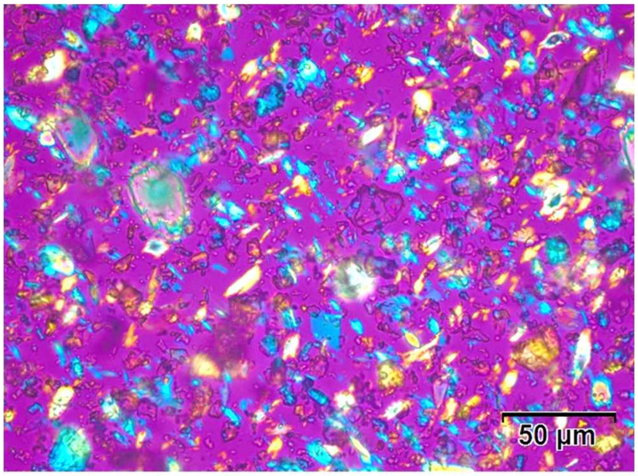

Figure 31. Experiment 8AP-4 Residual Solids

(Gibbsite, $Na_2CO_3•H_2O$, $Na_7FPO_4•19H_2O$, trace of $NaNO_3$, other unidentified phases)
(Crossed polars with Red I compensator)

Additional trace phases identified by SEM/EDS only include:

- "Garnetoid" crystals (Al-Ca-Cr-rich)
- Garnetoid-shaped crystals, but without Cr (Figure 32)
- Garnetoid-shaped crystals, but without Cr and with F (Figure 33)
- Na-Al-Si-Ca-rich agglomerate (Cancrinite *with* Ca)
- Ca-Al-P-rich agglomerate

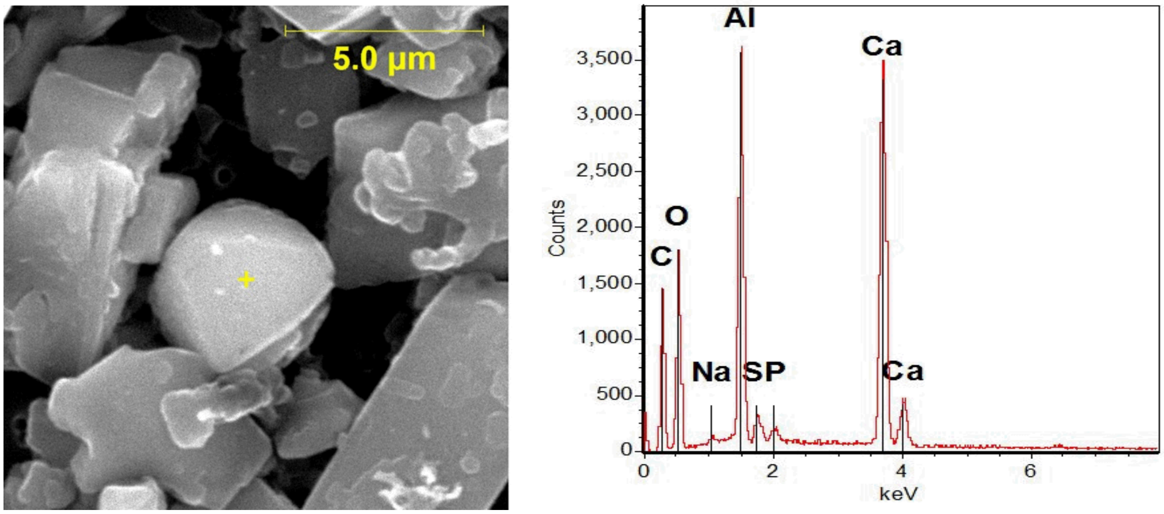

Figure 32. Experiment 8AP-4 Residual Solids, Al-Ca-Rich Crystal

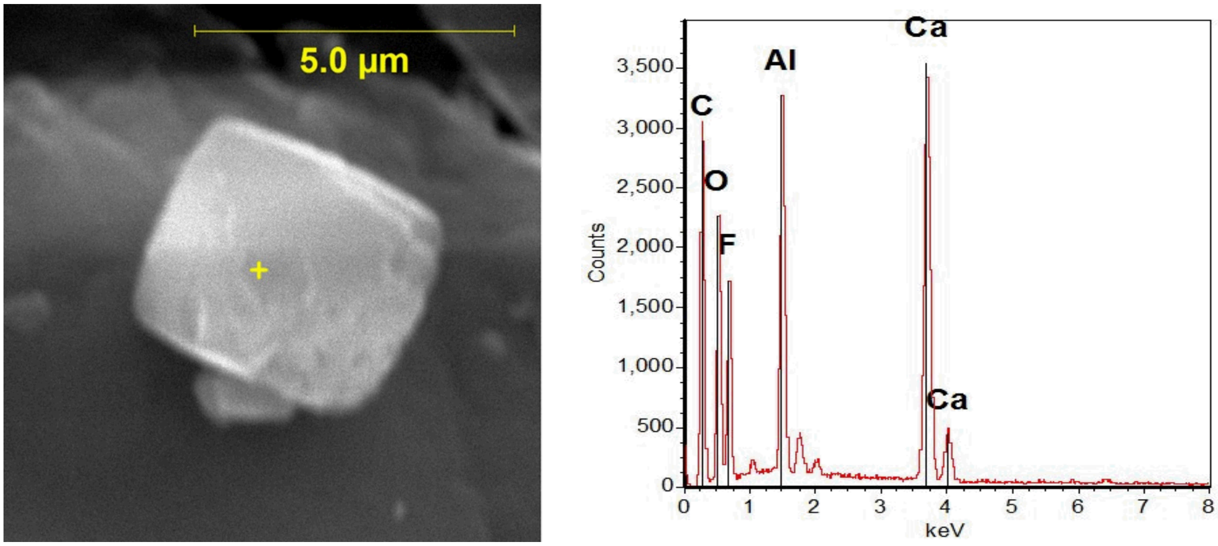

Figure 33. Experiment 8AP-4 Residual Solids, Al-Ca-F-Rich Crystal

5. SUMMARY

Table 19 shows a summary of the equilibrium concentrations of Al, OH, and Na for each of the experiments. Due to the inherent difficulty in performing these long-range experiments coupled with the intermittent power outages in the laboratory during the execution of the tests, there is some scatter in the data. Nevertheless, some general trends are apparent. For ease in visualizing the trends, the data are plotted in Figure 34 along with some relevant data from other sources.

The line in Figure 34labeled "Jenkins (WTP)" represents the computer algorithm used by the WTP to predict Al solubility at 40 °C. The points labeled ICET-1 represent unpublished data from Mississippi State University Institute for Clean Energy Technology (ICET) at nominal 3 molal OH and 40 °C. The points labeled ICET-2 represent ICET data at nominal 4.3 molal OH and 40 °C.

The most obvious trend apparent in Figure 34 is that all of the current data points (AN-105 and AP-108) fall far above the WTP and ICET data sets. The solubility of aluminum as measured in the actual tank waste supernatant liquids is far above the solubility measured in simulated tank waste. The reason for the enhanced solubility remains unclear, but the current data, even though scattered, strongly suggest that the enhanced solubility in tank waste is real.

The current data points for each tank tend to fall on a line with a slope of -1, i.e., OH concentration decreases by one unit for each unit of increase in Al. This is expected as a normal consequence of the gibbsite dissolution reaction:

$$Al(OH)_3 + NaOH \rightarrow NaAl(OH)_4$$

The points with the highest Al concentration for each tank result from the leaching experiments, i.e., the "top/down" approach to equilibrium. The enhanced solubility in those tests could be due to slow kinetics of precipitation, resulting in solutions that remain supersaturated in aluminum. However, slow kinetics cannot explain the discrepancy between the tank waste samples and the simulant samples (ICET) or the computer prediction based on literature data (Jenkins-WPT). Even the "bottom/up" data points for the actual tank waste samples fall well above the ICET and Jenkins data points, by a factor of about two in aluminum concentration.

The results suggest that the presence or absence of saltcake plays little or no role in the enhancement of aluminum solubility in tank waste. There was no discernable (statistical) difference, overall, between the solubility test run in the absence (Experiments 1 and 2) or presence (Experiments 3 and 4) of saltcake. However, due to questions about the potential lack of equilibrium in the top-down experiments (X-1 and X-3), this conclusion remains tentative.

The solubility enhancement is also not due solely to the presence of the other major sodium salts (nitrate, nitrite, carbonate). All three of these salts were included in the ICET experiments, resulting in total Na concentrations ranging from 3.5 to 11.2 molal for the experimental points plotted in Figure 34.

Table 19. Summary of Equilibrium Concentrations (molality) for All Experiments

Tank	Experiment	Al	OH	Na
AN-105 Supernate only	Exp. 1 – Top/Down	2.8	3.3	15.5
	Exp. 1 – Case 2*	3.6	3.6	17.3
	Exp. 2 – Bottom/Up	2.7	3.8	15.6
AN-105 Supernate + Saltcake	Exp. 3 – Top/Down	4.2	2.5	16.5
	Exp. 4 – Bottom/Up	2.6	3.8	16.3
AP-108 Supernate Only	Exp. 1 – Top/Down	1.6	2.9	14.4
AP-108 Supernate + Saltcake	Exp. 3 – Top/Down	2.0	2.3	15.9
	Exp. 4 – Bottom/Up	1.6	3.0	12.8

*Equilibrium established after inadvertent loss of water from reactor.

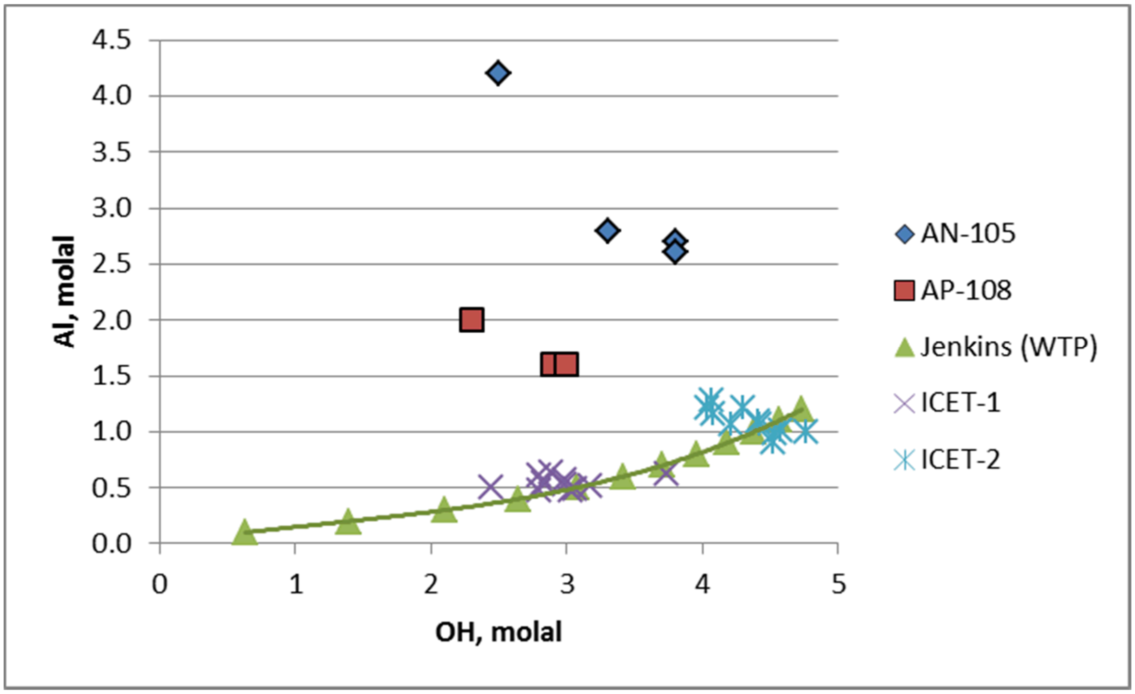

Figure 34. Comparison of Current Solubility Data with Other Relevant Data

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Appendix 1

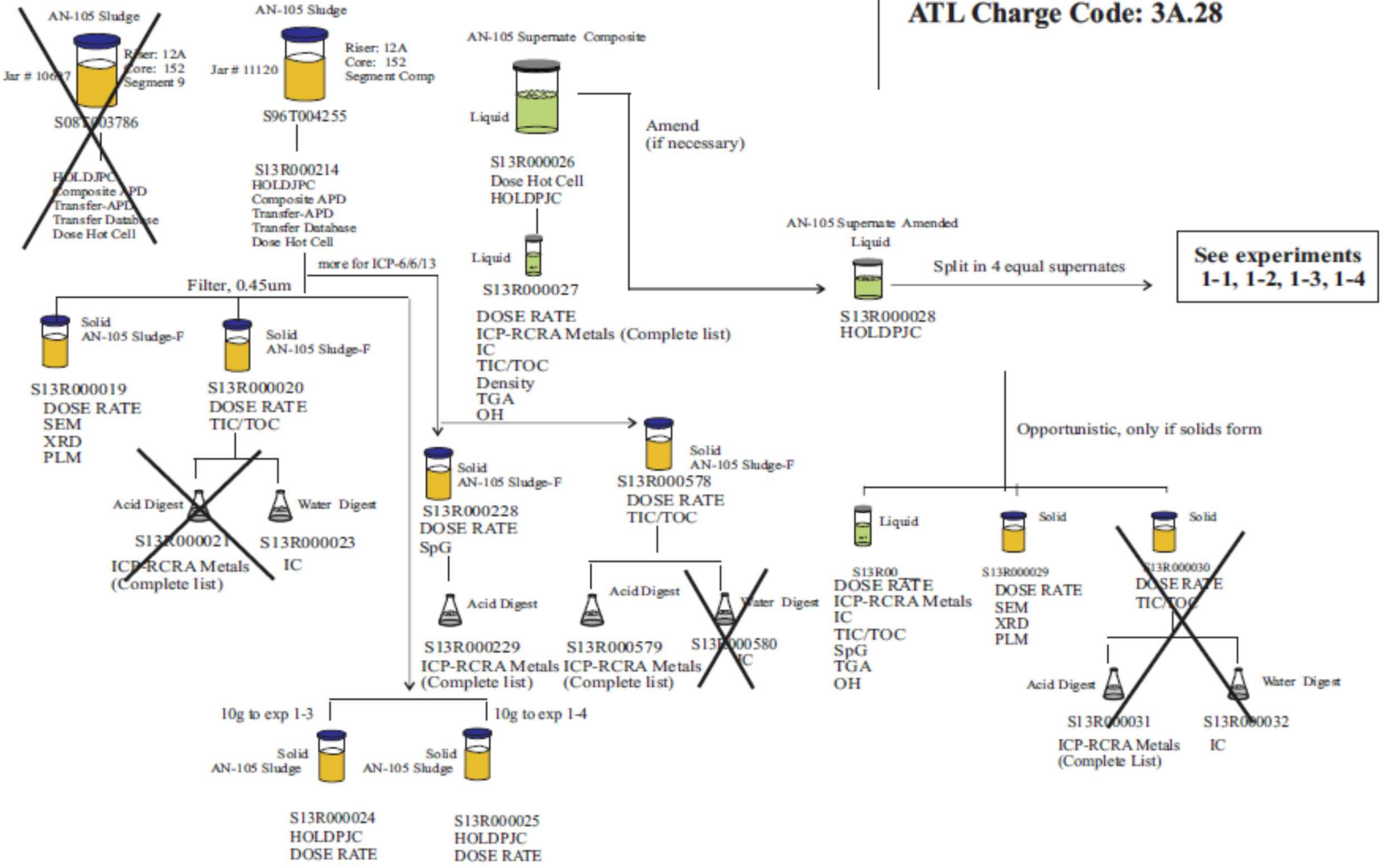
Sample Diagrams

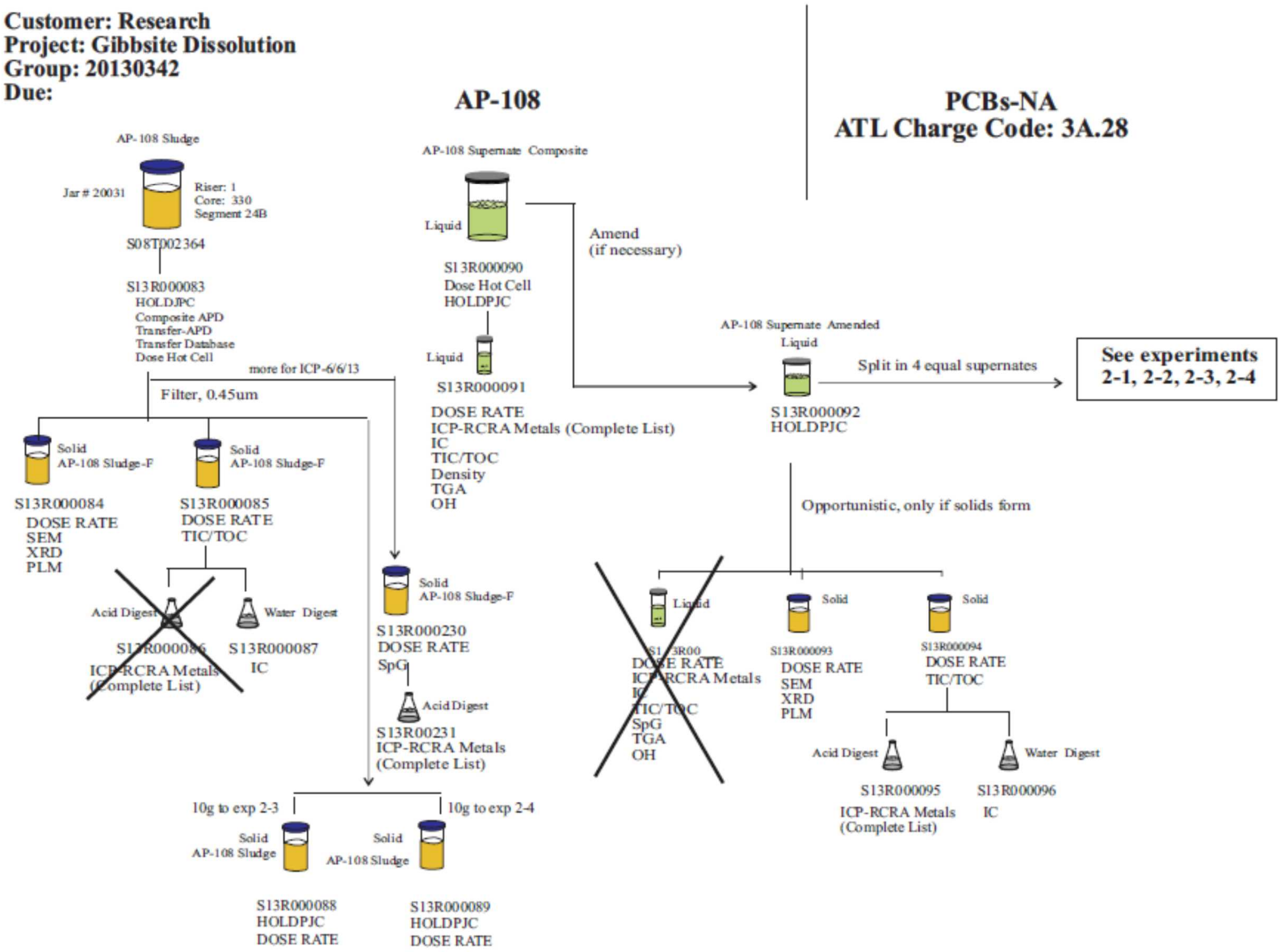
Customer: Research
Project: Gibbsite Dissolution
Group: 20130336
Due:

TSCA Regulated for PCBs
Aroclor 1254 <12ug/L liquids,
<543 ug/Kg solids.

ATL Charge Code: 3A.28

AN-105

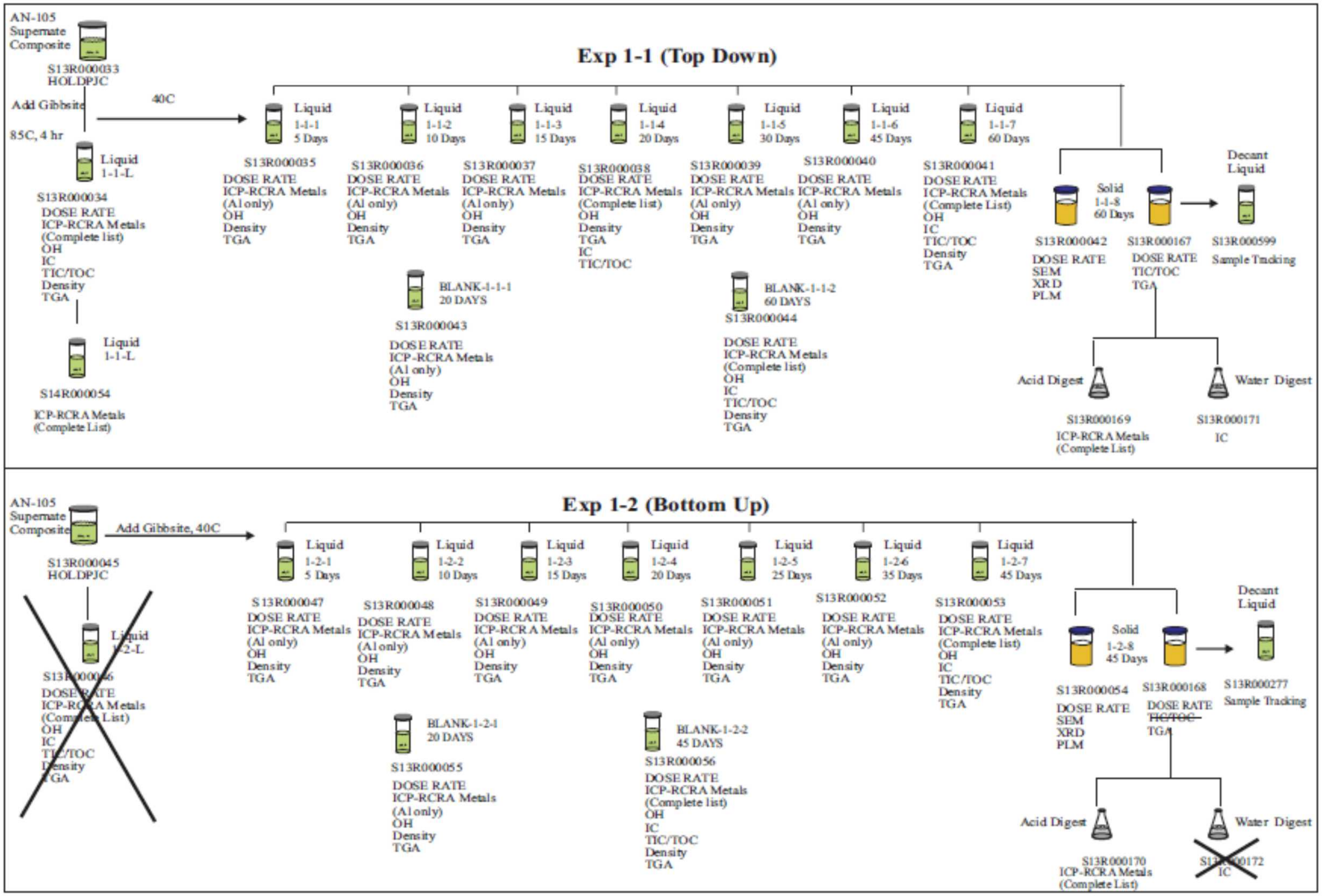



Customer: Research
Project: Gibbsite Dissolution
Group: 20130342
Due:
AP-108
PCBs-NA
ATL Charge Code: 3A.28
AP-108 Sludge
Jar # 20031
Riser: 1
Core: 330
Segment 24B
S08T002364
S13R000083
HOLDJPC
Composite APD
Transfer-APD
Transfer Database
Dose Hot Cell
more for ICP-6/6/13
Filter, 0.45um
Solid
AP-108 Sludge-F
S13R000084
DOSE RATE
SEM
XRD
PLM
Solid
AP-108 Sludge-F
S13R000085
DOSE RATE
TIC/TOC
~~Acid Digest~~
~~S13R000086~~
~~ICP-RCRA Metals (Complete List)~~
Water Digest
S13R000087
IC
Solid
AP-108 Sludge-F
S13R000230
DOSE RATE
SpG
Acid Digest
S13R00231
ICP-RCRA Metals
(Complete List)
10g to exp 2-3
Solid
AP-108 Sludge
S13R000088
HOLDPJC
DOSE RATE
10g to exp 2-4
Solid
AP-108 Sludge
S13R000089
HOLDPJC
DOSE RATE
AP-108 Supernate Composite
Liquid
S13R000090
Dose Hot Cell
HOLDPJC
Liquid
S13R000091
DOSE RATE
ICP-RCRA Metals (Complete List)
IC
TIC/TOC
Density
TGA
OH
Amend
(if necessary)
AP-108 Supernate Amended
Liquid
S13R000092
HOLDPJC
Split in 4 equal supernates
See experiments
2-1, 2-2, 2-3, 2-4
Opportunistic, only if solids form
~~Liquid~~
~~S1 3R00~~
~~DOSE RATE~~
~~ICP-RCRA Metals~~
~~IC~~
~~TIC/TOC~~
~~SpG~~
~~TGA~~
~~OH~~
Solid
S13R000093
DOSE RATE
SEM
XRD
PLM
Solid
S13R000094
DOSE RATE
TIC/TOC
Acid Digest
S13R000095
ICP-RCRA Metals
(Complete List)
Water Digest
S13R000096
IC

Customer: Research
Project: Gibbsite Dissolution
Group: 20130336
Due:

AN-105

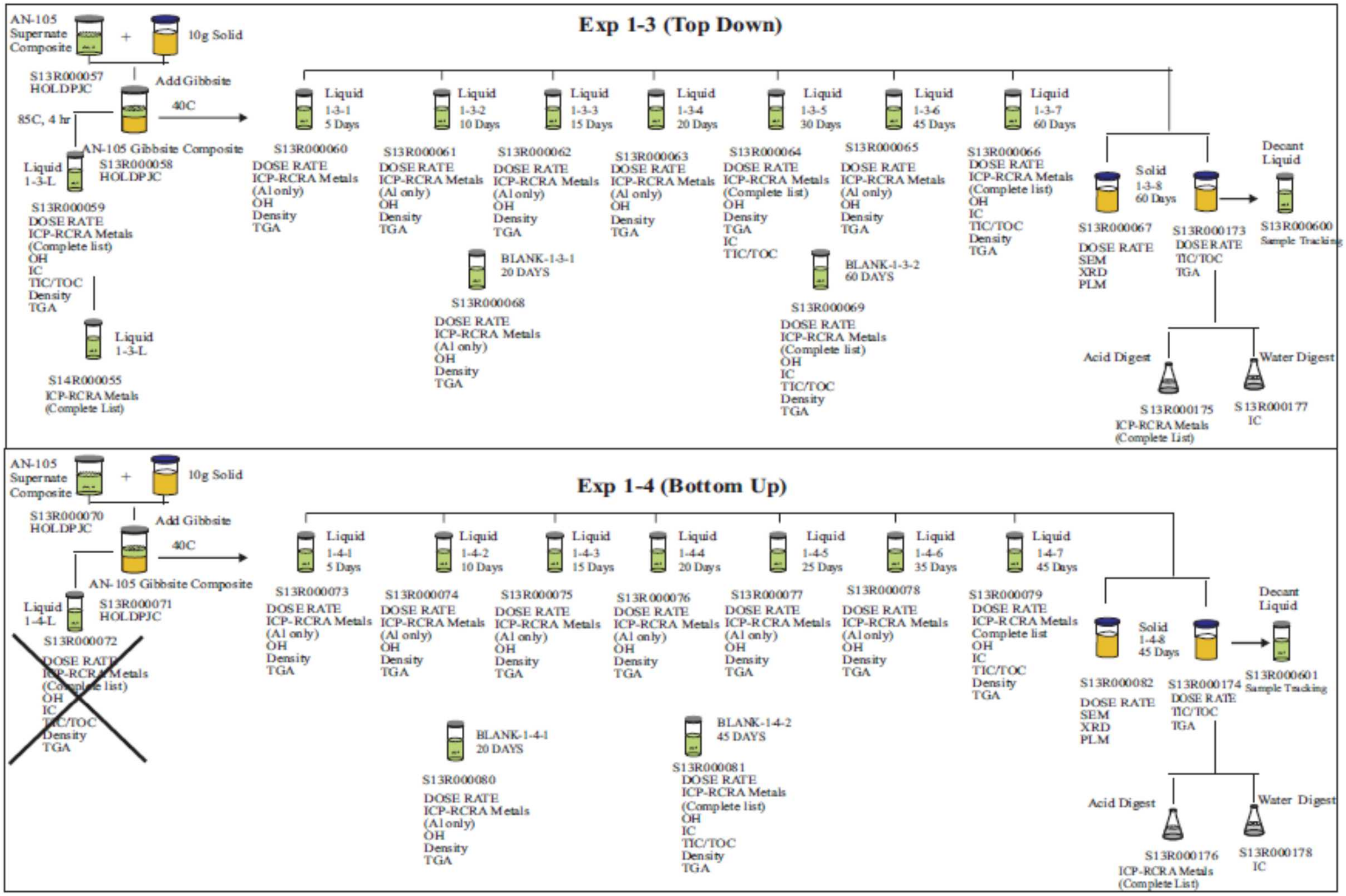
TSCA Regulated for PCBs
Aroclor 1254 <12ug/L liquids,
<543 ug/Kg solids.
ATL Charge Code: 3A.28



Customer: Research
Project: Gibbsite Dissolution
Group: 20130336
Due:

AN-105

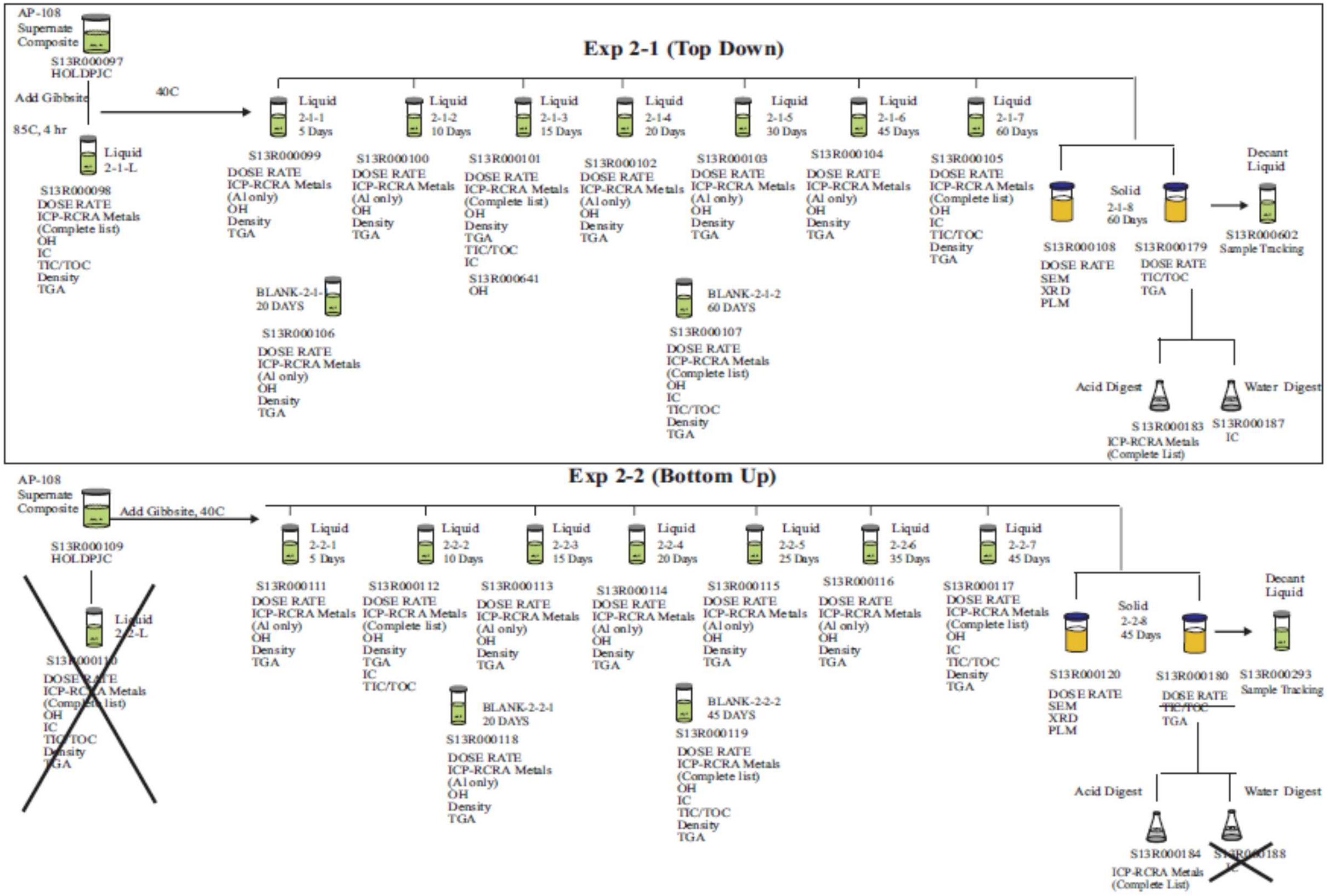
TSCA Regulated for PCBs
Aroclor 1254 <12ug/L liquids,
<543 ug/Kg solids.



Customer: Research
Project: Gibbsite Dissolution
Group: 20130342
Due:

AP-108

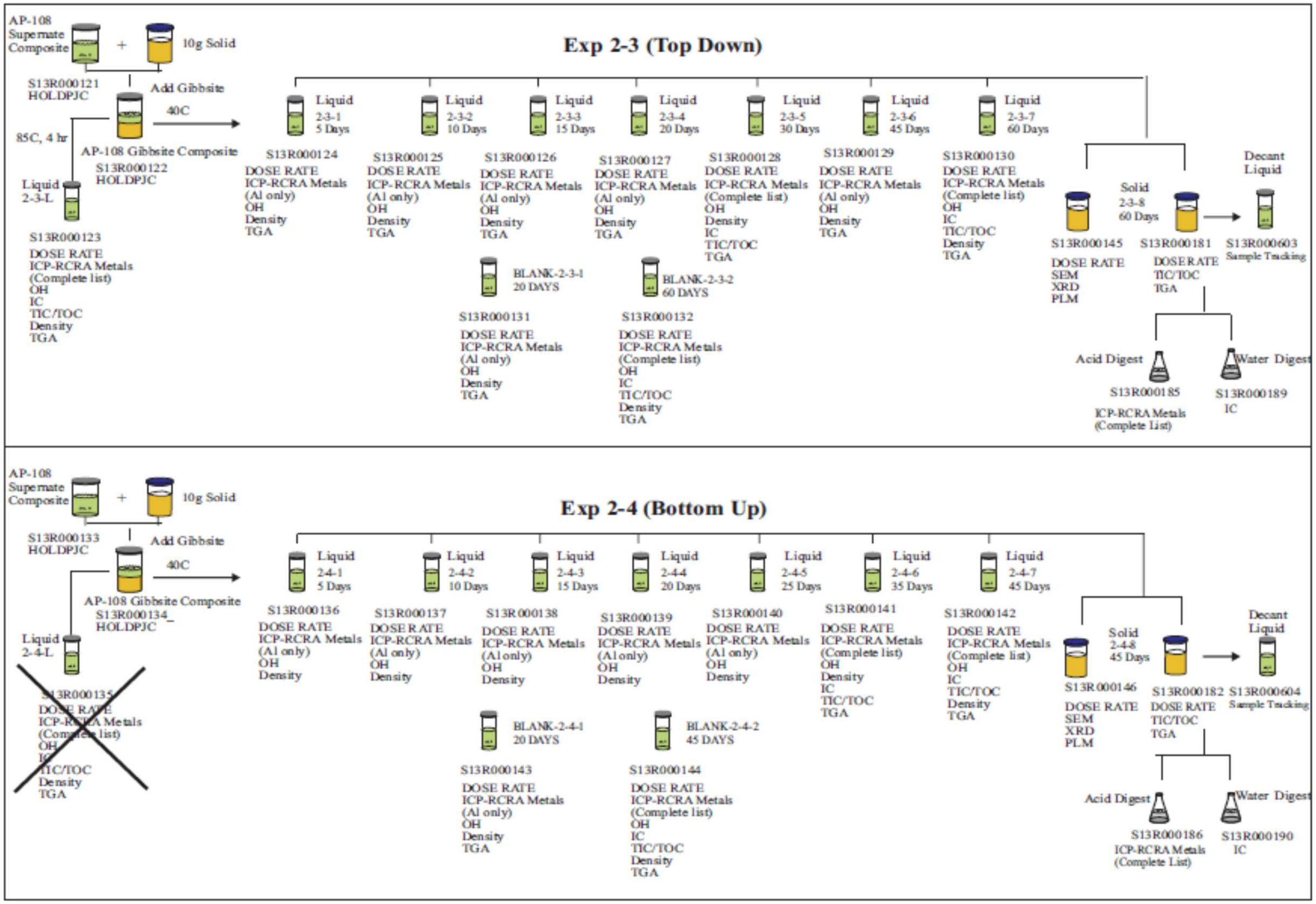
ATL Charge Code: 3A.28



Customer: Research
Project: Gibbsite Dissolution
Group: 20130342
Due:

AP-108

ATL Charge Code: 3A.28



Appendix 2

Volumetric Pipette Calibration Data

Blanks

Experiment	Lab #	Mass NaOH						Volume NaOH						Average V (mL)	StDev (3σ)	RPD
		Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 4	Aliquot 5	Aliquot 6	Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 4	Aliquot 5	Aliquot 6			
Exp. 1-1	S13R000043	1.19	1.166	1.186	1.167	1.181	1.166	1.004	0.984	1.001	0.985	0.997	0.984	0.993	0.028	-0.74%
	S13R000044	1.198	1.164	1.161	1.268	1.177	1.18	1.011	0.982	0.980	1.070	0.993	0.996	1.006	0.101	0.55%
Exp. 1-2	S13R000055	1.167	1.177	1.176	1.169	1.158	1.186	0.985	0.993	0.993	0.987	0.977	1.001	0.989	0.024	-1.07%
	S13R000056	1.181	1.17	1.17	1.173	1.169	1.168	0.997	0.988	0.988	0.990	0.987	0.986	0.989	0.012	-1.10%
Exp. 1-3	S13R000068	1.176	1.162	1.155	1.164	1.166	1.155	0.993	0.981	0.975	0.982	0.984	0.975	0.982	0.020	-1.84%
	S13R000069	1.171	1.155	1.187	1.174	1.177	1.193	0.988	0.975	1.002	0.991	0.993	1.007	0.993	0.034	-0.73%
Exp. 1-4	S13R000080	1.166	1.172	1.158	1.166	1.167	1.169	0.984	0.989	0.977	0.984	0.985	0.987	0.984	0.012	-1.56%
	S13R000081	1.183	1.176	1.172	1.183	1.145	1.193	0.998	0.993	0.989	0.998	0.966	1.007	0.992	0.042	-0.80%
Exp. 8AP-1	S13R000106	1.146	1.176	1.162	1.176	1.188	1.178	0.967	0.993	0.981	0.993	1.003	0.994	0.988	0.037	-1.17%
	S13R000107	1.194	1.141	1.172	1.175	1.17	1.168	1.008	0.963	0.989	0.992	0.988	0.986	0.988	0.043	-1.25%
Exp. 8AP-2	S13R000118	1.179	1.163	1.172	1.177	1.175	1.174	0.995	0.982	0.989	0.993	0.992	0.991	0.990	0.014	-0.97%
	S13R000119	1.153	1.183	1.1934	1.1586	1.193	1.179	0.973	0.998	1.007	0.978	1.007	0.995	0.993	0.044	-0.69%
Exp. 8AP-3	S13R000131	1.155	1.168	1.152	1.167	1.161	1.167	0.975	0.986	0.972	0.985	0.980	0.985	0.980	0.017	-1.95%
	S13R000132	1.229	1.148	1.123	1.164	1.158	1.085	1.037	0.969	0.948	0.982	0.977	0.916	0.972	0.121	-2.84%
Exp. 8AP-4	S13R000143	1.171	1.175	1.179	1.168	1.186	1.19	0.988	0.992	0.995	0.986	1.001	1.004	0.994	0.022	-0.56%
	S13R000144	1.178	1.179	1.179	1.175	1.167	1.164	0.994	0.995	0.995	0.992	0.985	0.982	0.991	0.017	-0.94%

Samples (3 pages)

Experiment	Lab #	Mass NaOH			Volume NaOH			Average V (mL)	StDev (3σ)	RPD
		Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 1	Aliquot 2	Aliquot 3			
Exp. 1-1	S13R000034	1.174	1.180	1.167	0.991	0.996	0.985	0.991	0.016	-0.94%
	S13R000035	1.172	1.175	1.137	0.989	0.992	0.960	0.980	0.053	-1.98%
	S13R000036	1.157	1.173	1.162	0.977	0.990	0.981	0.982	0.021	-1.76%
	S13R000037	1.200	1.155	1.177	1.013	0.975	0.993	0.994	0.057	-0.63%
	S13R000038	1.172	1.153	1.185	0.989	0.973	1.000	0.988	0.041	-1.25%
	S13R000039	1.191	1.156	1.186	1.005	0.976	1.001	0.994	0.048	-0.60%
	S13R000040	1.165	1.197	1.178	0.983	1.010	0.994	0.996	0.041	-0.41%
	S13R000041	1.183	1.237	1.182	0.998	1.044	0.998	1.013	0.080	1.34%
Exp. 1-2	S13R000047	1.176	1.17	1.176	0.993	0.988	0.993	0.991	0.009	-0.91%
	S13R000048	1.176	1.15	1.167	0.993	0.971	0.985	0.983	0.033	-1.73%
	S13R000049	1.163	1.164	1.149	0.982	0.982	0.970	0.978	0.021	-2.21%
	S13R000050	1.19	1.16	1.174	1.004	0.979	0.991	0.991	0.038	-0.86%
	S13R000051	1.15	1.185	1.174	0.971	1.000	0.991	0.987	0.045	-1.28%
	S13R000052	1.185	1.185	1.168	1.000	1.000	0.986	0.995	0.025	-0.46%
	S13R000053	1.187	1.185	1.173	1.002	1.000	0.990	0.997	0.019	-0.27%
Exp. 1-3	S13R000059	1.177	1.186	1.182	0.993	1.001	0.998	0.997	0.011	-0.27%
	S13R000060	1.183	1.154	1.16	0.998	0.974	0.979	0.984	0.039	-1.62%
	S13R000061	1.247	1.19	1.192	1.052	1.004	1.006	1.021	0.082	2.10%
	S13R000062	1.157	1.171	1.16	0.977	0.988	0.979	0.981	0.019	-1.87%
	S13R000063	1.163	1.166	1.155	0.982	0.984	0.975	0.980	0.014	-1.98%
	S13R000064	1.288	1.324	1.245	1.087	1.117	1.051	1.085	0.100	8.51%
	S13R000065	1.152	1.175	1.176	0.972	0.992	0.993	0.986	0.034	-1.45%
	S13R000066	1.176	1.184	1.184	0.993	0.999	0.999	0.997	0.012	-0.29%
Exp. 1-4	S13R000073	1.187	1.165	1.176	1.002	0.983	0.993	0.993	0.028	-0.74%
	S13R000074	1.165	1.18	1.17	0.983	0.996	0.988	0.989	0.019	-1.11%
	S13R000075	1.16	1.167	1.18	0.979	0.985	0.996	0.987	0.026	-1.33%
	S13R000076	1.153	1.159	1.153	0.973	0.978	0.973	0.975	0.009	-2.52%
	S13R000077	1.169	1.175	1.25	0.987	0.992	1.055	1.011	0.114	1.11%
	S13R000078	1.16	1.198	1.178	0.979	1.011	0.994	0.995	0.048	-0.52%

Samples (3 pages)

Experiment	Lab #	Mass NaOH			Volume NaOH			Average V (mL)	StDev (3σ)	RPD
		Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 1	Aliquot 2	Aliquot 3			
	S13R000079	1.174	1.138	1.162	0.991	0.960	0.981	0.977	0.046	-2.26%
Exp. 8AP-1	S13R000098	1.159	1.176	1.18	0.978	0.993	0.996	0.989	0.028	-1.11%
	S13R000099	1.172	1.174	1.177	0.989	0.991	0.993	0.991	0.006	-0.88%
	S13R000100	1.171	1.183	1.186	0.988	0.998	1.001	0.996	0.020	-0.41%
	S13R000101	1.171	1.177	1.195	0.988	0.993	1.009	0.997	0.032	-0.32%
	S13R000102	3.516	0	1.175	2.968	0.000	0.992	1.320	4.532	31.98%
	S13R000103	1.173	1.171	1.171	0.990	0.988	0.988	0.989	0.003	-1.11%
	S13R000104	1.157	1.172	1.174	0.977	0.989	0.991	0.986	0.024	-1.45%
	S13R000105	1.163	1.178	1.156	0.982	0.994	0.976	0.984	0.028	-1.62%
Exp. 8AP-2	S13R000111	1.187	1.172	1.165	1.002	0.989	0.983	0.991	0.028	-0.86%
	S13R000112	1.157	1.172	1.165	0.977	0.989	0.983	0.983	0.019	-1.70%
	S13R000113	1.174	1.177	1.183	0.991	0.993	0.998	0.994	0.012	-0.57%
	S13R000114	1.157	1.182	1.173	0.977	0.998	0.990	0.988	0.032	-1.19%
	S13R000115	1.171	1.179	1.166	0.988	0.995	0.984	0.989	0.017	-1.08%
	S13R000116	1.178	1.183	1.16	0.994	0.998	0.979	0.991	0.031	-0.94%
	S13R000117	1.169	1.16	1.168	0.987	0.979	0.986	0.984	0.012	-1.62%
Exp. 8AP-3	S13R000123	1.167	1.179	1.156	0.985	0.995	0.976	0.985	0.029	-1.48%
	S13R000124	1.182	1.158	1.191	0.998	0.977	1.005	0.993	0.043	-0.66%
	S13R000125	1.177	1.197	1.194	0.993	1.010	1.008	1.004	0.027	0.38%
	S13R000126	1.156	1.169	1.165	0.976	0.987	0.983	0.982	0.017	-1.81%
	S13R000127	1.162	1.147	1.363	0.981	0.968	1.150	1.033	0.305	3.31%
	S13R000128	1.16	1.129	1.11	0.979	0.953	0.937	0.956	0.064	-4.37%
	S13R000129	1.156	1.62	1.175	0.976	1.367	0.992	1.112	0.665	11.16%
	S13R000130	1.188	1.183	1.17	1.003	0.998	0.988	0.996	0.024	-0.38%
Exp. 8AP-4	S13R000136	1.185	1.182	1.175	1.000	0.998	0.992	0.997	0.013	-0.35%
	S13R000137	1.183	1.162	1.174	0.998	0.981	0.991	0.990	0.027	-1.00%
	S13R000138	1.174	1.182	1.172	0.991	0.998	0.989	0.993	0.013	-0.74%
	S13R000139	1.183	1.157	1.177	0.998	0.977	0.993	0.989	0.034	-1.05%
	S13R000140	1.149	1.307	1.324	0.970	1.103	1.117	1.063	0.244	6.35%

Samples (3 pages)

Experiment	Lab #	Mass NaOH			Volume NaOH			Average V (mL)	StDev (3σ)	RPD
		Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 1	Aliquot 2	Aliquot 3			
	S13R000141	1.16	1.184	1.175	0.979	0.999	0.992	0.990	0.031	-1.00%
	S13R000142	1.273	1.176	1.228	1.074	0.993	1.036	1.034	0.123	3.45%

APPENDIX 3

WRPS-1304176, "GIBBSITE DISSOLUTION IN ARCHIVED SUPERNATANT X-RAY DIFFRACTOMETRY (XRD) RESULTS"

INTEROFFICE MEMORANDUM

WRPS-1304176

Date: December 13, 2013

To: C. M. Seidel, Manager
Process Chemistry

From: J. A. Pestovich, Scientist
Special Analytical Services

Subject: GIBBSITE DISSOLUTION IN ARCHIVED SUPERNATANT X-RAY DIFFRACTOMETRY (XRD) RESULTS

Reference:

1. LAB-PLAN-09-00004, 2010, *Aluminum Solubility in Hanford Tank Waste for WTP In-Tank Separation Process*, Rev. 1, Washington River Protection Solutions LLC, Richland, Washington.
2. ATS-LT-507-103, Rev. B-0, "222-S Laboratory X-Ray Diffractometry (XRD) using the Rigaku MiniFlex II," Washington River Protection Solutions LLC, Richland, Washington.
3. HNF-N-710-1, "Rigaku MiniFlex II X-Ray Diffractometer (XRD) Maintenance and Operations (GD400212)," pp. 24-25, 27-28, 30, 222-S Laboratory, Washington River Protection Solutions LLC, Richland, Washington.

A fraction of each individual Gibbsite Dissolution Project sample was placed in the well of a quartz zero-background slide, compressed with the plane of a glass slide, fixed with collodion binder, and allowed to dry. Refer to Reference 1 for details about the origin and treatment of the samples submitted for X-ray diffraction analysis. X-ray diffraction preparation and analysis was performed in accordance with Reference 2.

Samples S13R000084 and S13R000019 were analyzed during May 2013; S13R000054 and S13R000120 during June 2013; S13R000042, S13R000108, S13R000146, and S13R000129 during September 2013; and S13R000067, S13R000082, and S13R000145 during October 2013. The samples were individually scanned at the rate of 1 degree per minute with a 2-Theta angle from 5 to 65 degrees, or slower if required. Refer to Reference 3 for test information and specifics.

Nitratine and sodium nitrite are speculated to have crystallized from the interstitial liquid when the samples were dried during sample preparation. The sample compositions reported below are relative amounts based upon all the crystalline species present in each individual sample.

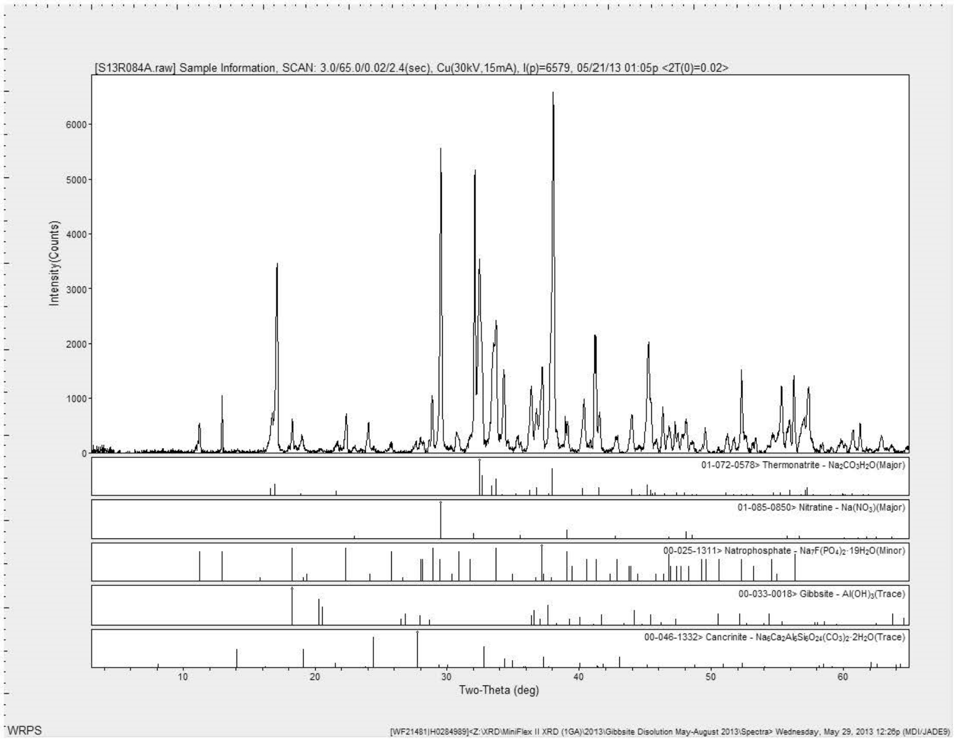
S13R000084 (AP-108 Sludge-F). Sample S13R000084 consisted of wet, whitish-tan, fine solids with a few small white particles, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous light-tan, fine solids. The major phases of the sample were identified as thermonatrite [$Na_2CO_3 \cdot H_2O$] and nitratine [$NaNO_3$]. Natrophosphate

[$Na_7F(PO_4)_2{\bullet}19H_2O$] was identified as a minor phase, and gibbsite [$Al(OH)_3$] and cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\bullet}2H_2O$] as trace phases.

Table 1. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000084.

Chemical Name	Mineral Name	Formula	Relative Amount
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3{\bullet}H_2O$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2{\cdot}19H_2O$	Minor
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Trace
NA	Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$	Trace

Figure 1. X-Ray Diffraction Pattern, Sample S13R000084.

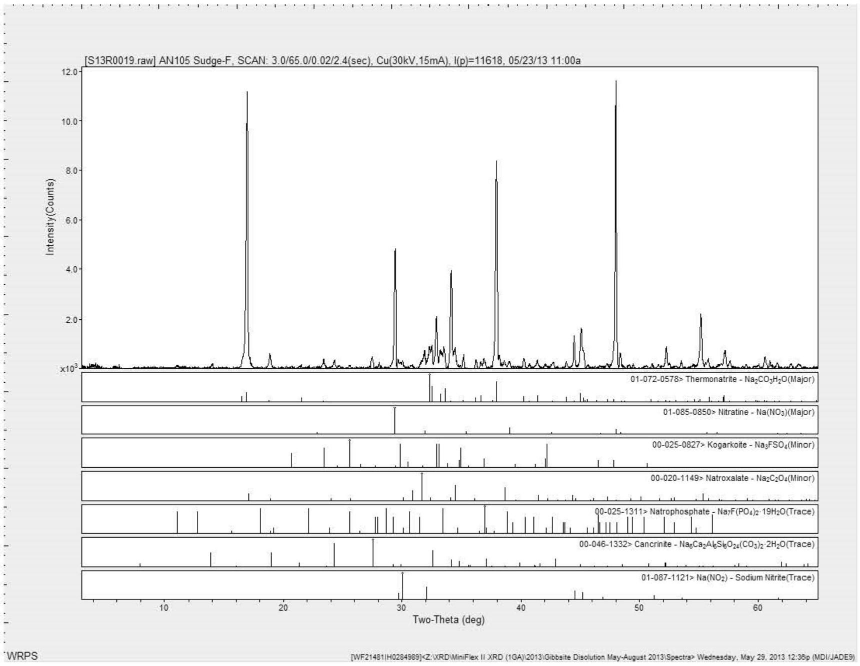


<u>S13R000019 (AN105 Sludge-F).</u> Sample S13R000019 consisted of moist, light-greenish, fine solids, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous light-greenish, fine solids. The major phases of the sample were identified as thermonatrite [$Na_2CO_3{\bullet}H_2O$] and nitratine [$NaNO_3$]. Kogarkoite [Na_3FSO_4] and natroxalate [$Na_2C_2O_4$] were identified as minor phases, and cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\bullet}2H_2O$], natrophosphate [$Na_7F(PO_4)_2{\bullet}19H_2O$], and sodium nitrite [$NaNO_2$] as trace phases.

Table 2. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000019.

Chemical Name	Mineral Name	Formula	Relative Amount
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3{\bullet}H_2O$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Fluoride Sulfate	Kogarkoite	Na_3FSO_4	Minor
Sodium Oxalate	Natroxalate	$Na_2C_2O_4$	Minor
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2{\cdot}19H_2O$	Trace
NA	Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$	Trace
Sodium Nitrite	NA	$NaNO_2$	Trace

Figure 2. X-Ray Diffraction Pattern, Sample S13R000019.

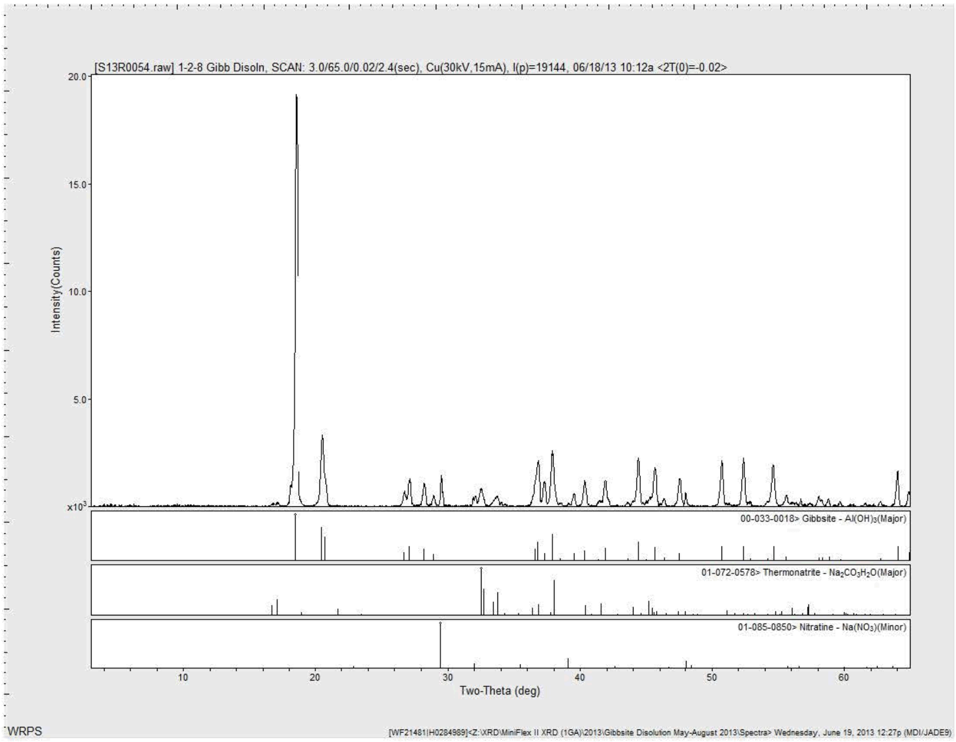


S13R000054 (1-2-8). Sample S13R000054 consisted of wet, white, fine solids with a minimal amount of yellowish liquid, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, white, fine solids. The major phases of the sample were identified as gibbsite [$Al(OH)_3$] and thermonatrite [$Na_2CO_3{\bullet}H_2O$]. Nitratine [$NaNO_3$] was identified as a minor phase.

Table 3. Major and Minor X-Ray Diffraction Phases Identification in Sample S13R000054.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3{\bullet}H_2O$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Minor

Figure 3. X-Ray Diffraction Pattern, Sample S13R000054.

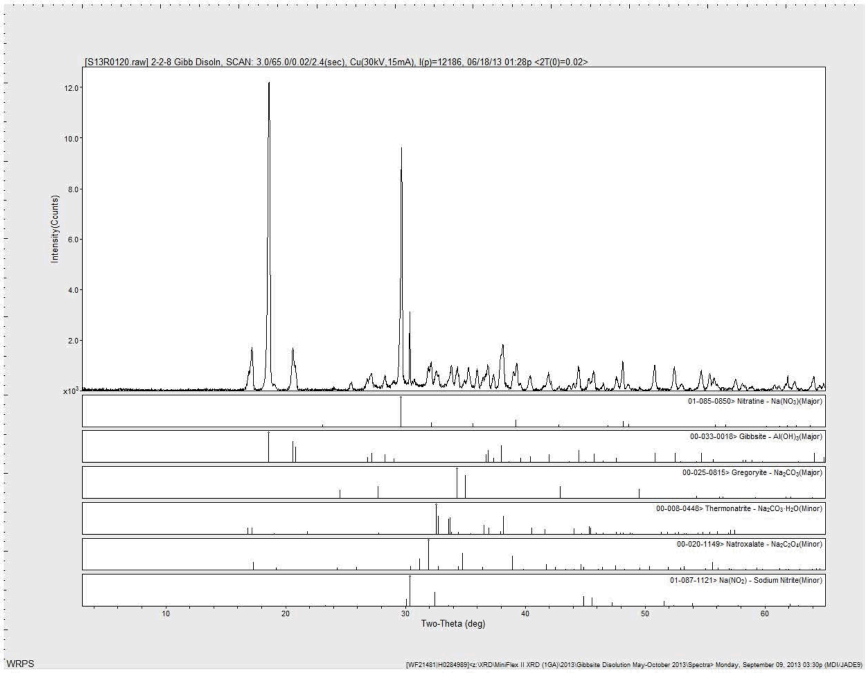


S13R000120 (2-2-8). Sample S13R000120 consisted of moist, yellowish-white, fine solids, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, yellowish-white, fine solids. The major phases of the sample were identified as nitratine [$NaNO_3$], gibbsite [$Al(OH)_3$], and gregoryite [Na_2CO_3]. Thermonatrite [$Na_2CO_3 \bullet H_2O$], natroxalate [$Na_2C_2O_4$], and sodium nitrite [$NaNO_2$] were identified as minor phases. At least one minor/trace phase potentially remains unidentified in the diffraction pattern.

Table 4. Major and Minor X-Ray Diffraction Phases Identification in Sample S13R000120.

Chemical Name	Mineral Name	Formula	Relative Amount
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Carbonate	Gregoryite	Na_2CO_3	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3 \bullet H_2O$	Minor
Sodium Oxalate	Natroxalate	$Na_2C_2O_4$	Minor
Sodium Nitrite	NA	$NaNO_2$	Minor

Figure 4. X-Ray Diffraction Pattern, Sample S13R000120.

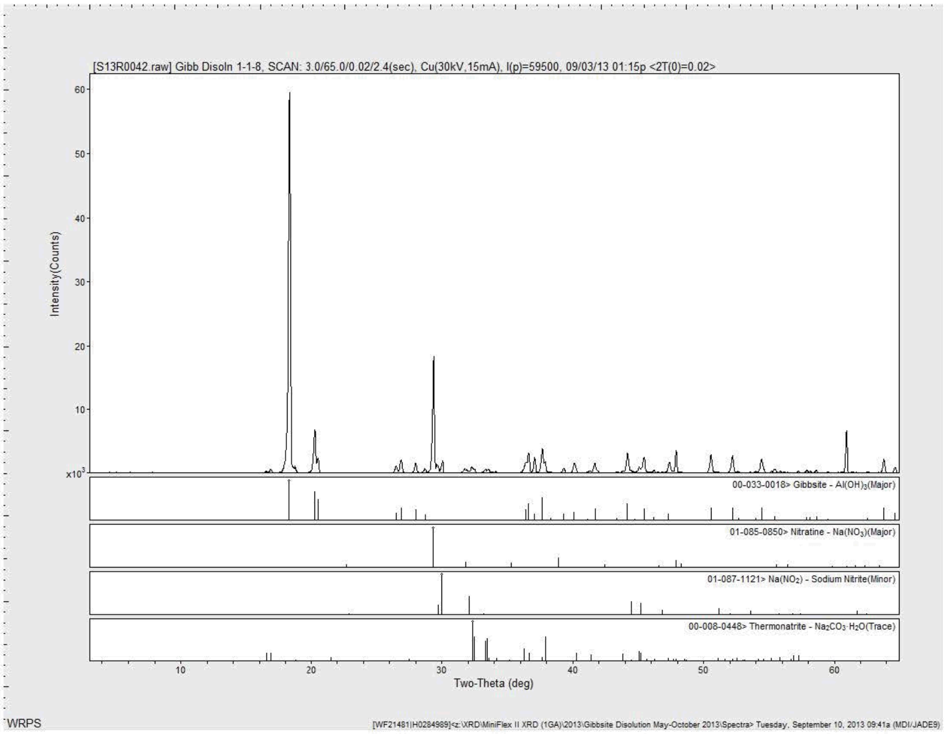


S13R000042 (1-1-8). Sample S13R000042 consisted of wet, light yellowish-white, fine solids with yellowish liquid, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, white, fine solids. The major phases of the sample were identified as gibbsite [$Al(OH)_3$] and nitratine [$NaNO_3$]. Sodium nitrite [$NaNO_2$] was identified as a minor phase and thermonatrite [$Na_2CO_3 \bullet H_2O$] as a trace phase.

Table 5. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000042.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Nitrite	NA	$NaNO_2$	Minor
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3 \bullet H_2O$	Trace

Figure 5. X-Ray Diffraction Pattern, Sample S13R000042.

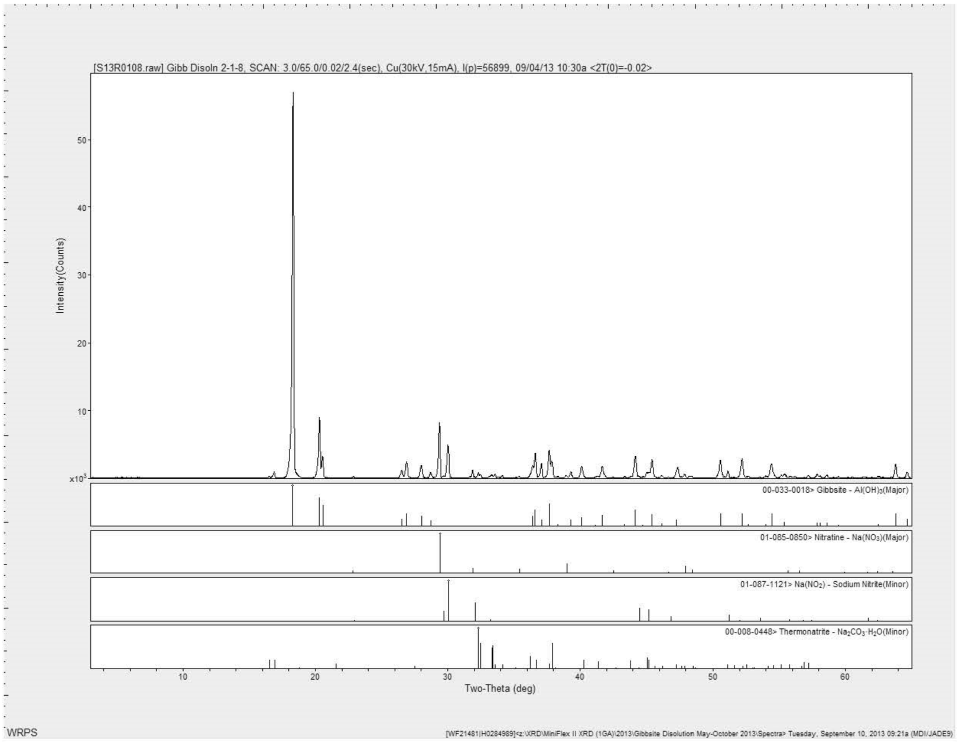


S13R000108 (2-1-8). Sample S13R000108 consisted of moist light yellowish-white fine solids, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, white, fine solids. The major phases of the sample were identified as gibbsite [$Al(OH)_3$] and nitratine [$NaNO_3$]. Sodium nitrite [$NaNO_2$] and thermonatrite [$Na_2CO_3•H_2O$] were identified as minor phases.

Table 6. Major and Minor X-Ray Diffraction Phases Identification in Sample S13R000108.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Nitrite	NA	$NaNO_2$	Minor
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3•H_2O$	Minor

Figure 6. X-Ray Diffraction Pattern, Sample S13R000108.

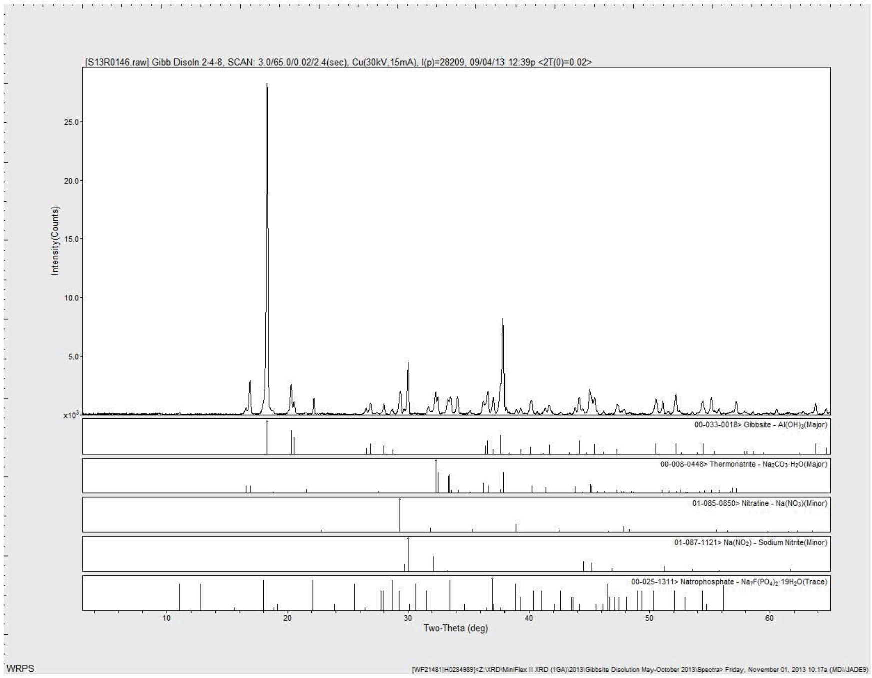


S13R000146 (2-4-8). Sample S13R000146 consisted of moist, light yellowish-white, fine solids, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, white, fine solids. The major phases of the sample were identified as gibbsite [Al(OH)$_3$] and thermonatrite [Na_2CO_3•H_2O]. Nitratine [$NaNO_3$] and sodium nitrite [$NaNO_2$] were identified as minor phases, and natrophosphate [$Na_7F(PO_4)_2$•$19H_2O$] was identified as a trace phase.

Table 7. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000146.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	Na_2CO_3•H_2O	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Minor
Sodium Nitrite	NA	$NaNO_2$	Minor
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2{\cdot}19H_2O$	Trace

Figure 7. X-Ray Diffraction Pattern, Sample S13R000146.

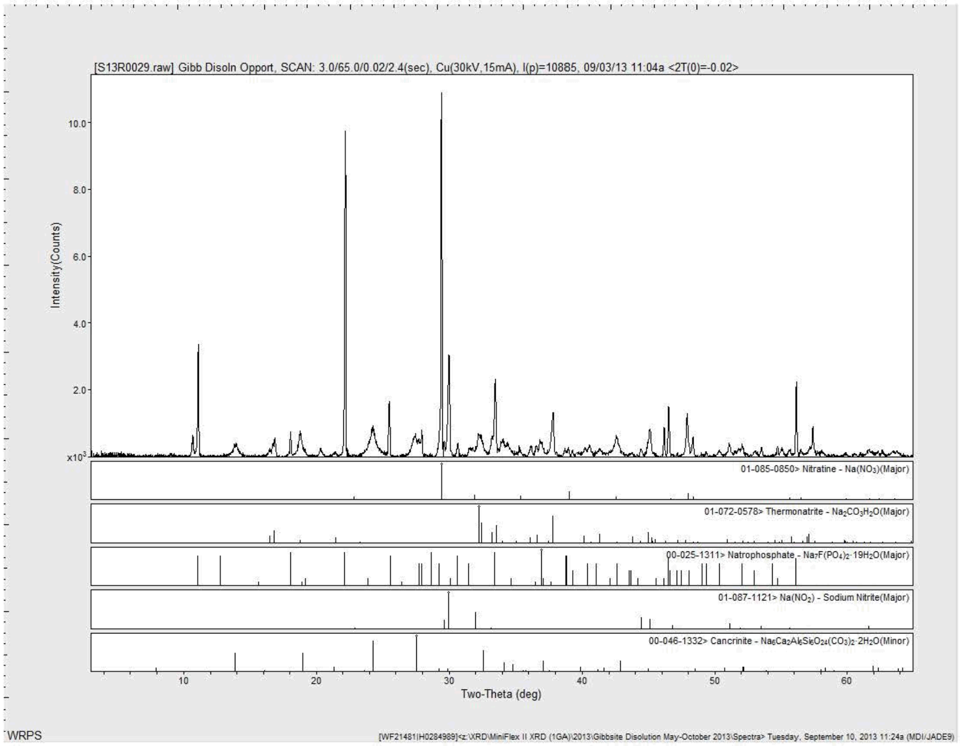


S13R000029 (Opportunistic). Sample S13R000029 consisted of moist, light yellowish-white, fine solids, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, white, fine solids. The major phases of the sample were identified as nitratine [$NaNO_3$], thermonatrite [$Na_2CO_3•H_2O$], natrophosphate [$Na_7F(PO_4)_2•19H_2O$], and sodium nitrite [$NaNO_2$]. Cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2•2H_2O$] was identified as a minor phase.

Table 8. Major and Minor X-Ray Diffraction Phases Identification in Sample S13R000029.

Chemical Name	Mineral Name	Formula	Relative Amount
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3•H_2O$	Major
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2·19H_2O$	Major
Sodium Nitrite	NA	$NaNO_2$	Major
NA	Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2·2H_2O$	Minor

Figure 8. X-Ray Diffraction Pattern, Sample S13R000029.

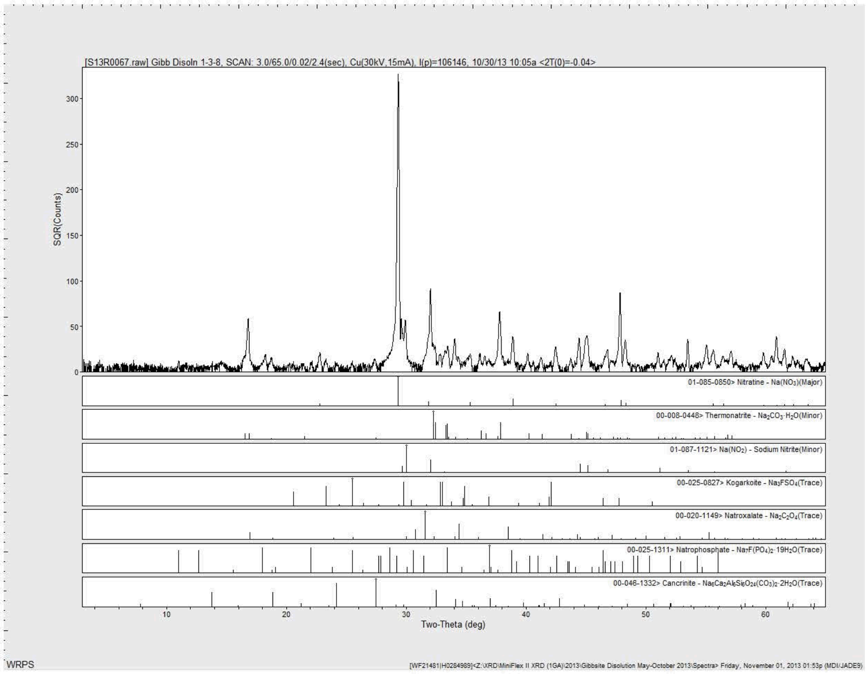


<u>S13R000067 (1-3-8).</u> Sample S13R000067 consisted of yellowish-white, fine solids with a yellowish, free liquid, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, light yellowish-white, fine solids. The major phase of the sample was identified as nitratine [$NaNO_3$]; thermonatrite [$Na_2CO_3 \bullet H_2O$] and sodium nitrite [$NaNO_2$] were identified as minor phases; and kogarkoite [Na_3FSO_4], natroxalate [$Na_2C_2O_4$], natrophosphate [$Na_7F(PO_4)_2 \bullet 19H_2O$], and cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \bullet 2H_2O$] as trace phases.

Table 9. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000067.

Chemical Name	Mineral Name	Formula	Relative Amount
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3 \bullet H_2O$	Minor
Sodium Nitrite	NA	$NaNO_2$	Minor
Sodium Fluoride Sulfate	Kogarkoite	Na_3FSO_4	Trace
Sodium Oxalate	Natroxalate	$Na_2C_2O_4$	Trace
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2 \cdot 19H_2O$	Trace
NA	Cancrinite	$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2 \cdot 2H_2O$	Trace

Figure 9. X-Ray Diffraction Pattern, Sample S13R000067.

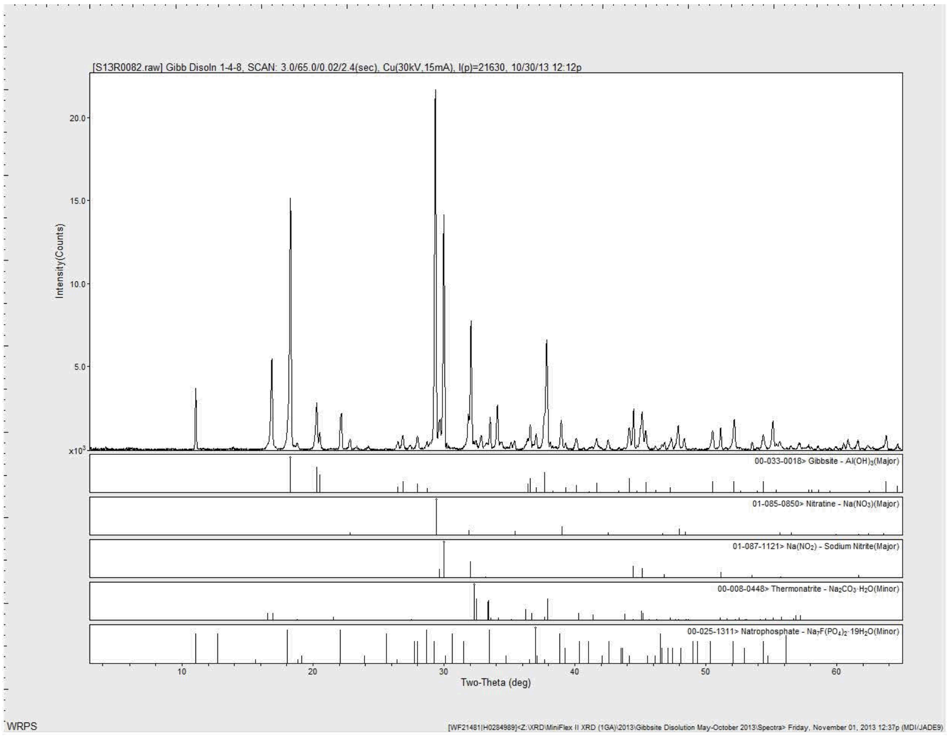


S13R000082 (1-4-8). Sample S13R000082 consisted of yellowish-white, fine solids with a yellowish, free liquid, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, light yellowish-white, fine solids. The major phases of the sample were identified as gibbsite [$Al(OH)_3$], nitratine [$NaNO_3$], and sodium nitrite [$NaNO_2$]. Thermonatrite [$Na_2CO_3 \bullet H_2O$] and natrophosphate [$Na_7F(PO_4)_2 \bullet 19H_2O$] were identified as minor phases.

Table 10. Major and Minor X-Ray Diffraction Phases Identification in Sample S13R000082.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Nitrite	NA	$NaNO_2$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3 \bullet H_2O$	Minor
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2 \cdot 19H_2O$	Minor

Figure 10. X-Ray Diffraction Pattern, Sample S13R000082.

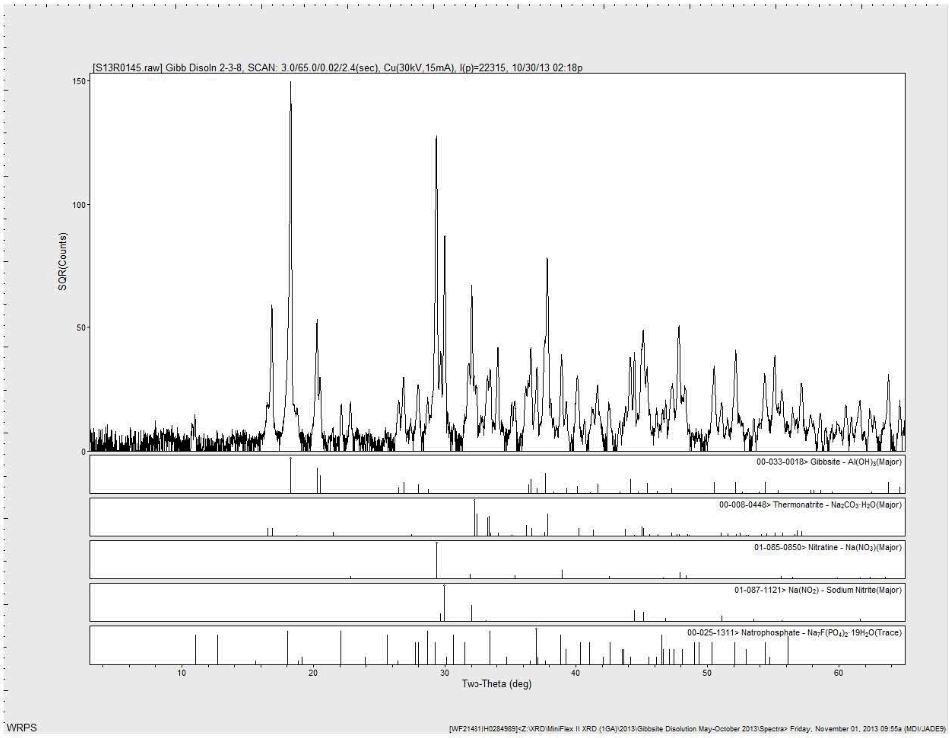


S13R000145 (2-3-8). Sample S13R000145 consisted of yellowish-white, fine solids with a yellowish, free liquid, and once mounted and dried on a quartz zero-background slide appeared to be homogeneous, light yellowish-white, fine solids. The major phases of the sample were identified as gibbsite [$Al(OH)_3$], thermonatrite [$Na_2CO_3{\bullet}H_2O$], nitratine [$NaNO_3$], and sodium nitrite [$NaNO_2$]. Natrophosphate [$Na_7F(PO_4)_2{\bullet}19H_2O$] was identified as a trace phase.

Table 11. Major, Minor, and Trace X-Ray Diffraction Phases Identification in Sample S13R000145.

Chemical Name	Mineral Name	Formula	Relative Amount
Aluminum Hydroxide	Gibbsite	$Al(OH)_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$Na_2CO_3{\bullet}H_2O$	Major
Sodium Nitrate	Nitratine	$NaNO_3$	Major
Sodium Nitrite	NA	$NaNO_2$	Major
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$Na_7F(PO_4)_2{\cdot}19H_2O$	Trace

Figure 11. X-Ray Diffraction Pattern, Sample S13R000145.



JAP/PLP

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	H. J. Huber	T6-05
	J. K. McCoskey	T6-05
	S. G. McKinney	T6-05

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UserName: Pestovich, John (h0284989)
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