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# Mixing of Process Heels, Process Solutions, and Recycle Streams: Small-Scale Simulant

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# Mixing of Process Heels, Process Solutions, and Recycle Streams: Small-Scale Simulant

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January 15, 2001

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## SUMMARY

The overall objective of this small-scale simulant mixing study was to identify the processes within the Hanford Site River Protection Project – Waste Treatment Plant (RPP-WTP) that may generate precipitates and to identify the types of precipitates formed. This information can be used to identify where mixtures of various solutions will cause precipitation of solids, potentially causing operational problems such as fouling equipment or increasing the amount of High Level Waste glass produced. Having this information will help guide protocols for flushing or draining tanks, mixing internal recycle streams, and mixing waste tank supernates. While these results do not impact the current design, understanding precipitation kinetics is essential for developing guidelines for operations, such as when tanks or vessels must be flushed. A report was

issued entitled “Milestone M4900; Simulant Mixing Analytical Results” (Kaplan et al. 2000) which contained the data generated from this task. This report contains the discussion and thermodynamic chemical speciation modeling of the raw data.

Four experiments were conducted to address the specific items identified in the test specifications (Johnson 1999). These items were derived by examining the facility design (such as tank heel volume) and operational plans (such as recycle stream fate). The four experiments were:

1. Dilution Experiment: quantify and characterize the precipitates formed by diluting simulants with 0.01 M NaOH
2. Envelope Mixing Experiment: quantify and characterize the precipitates formed by mixing simulants
3. Hydroxide-Concentration Experiment: quantify and characterize the precipitates formed by adding or partially neutralizing the free hydroxide in simulants
4. Envelope-D Leachate Mixing Experiment: quantify and characterize the precipitates formed by mixing AZ-102 caustic leachate simulant or C-106 caustic leachate simulant (both nominally 3 M NaOH) with various feed simulants.

Briefly, the simulants were made and monitored for turbidity. Once turbidity stabilized, indicating a steady state may have been reached, the simulants were filtered and used in mixing studies. The simulants were then treated by dilution, mixing, acid or base addition, or caustic leachate addition. Turbidity and temperature of the suspensions were monitored for 1 to 2 months after treatment. After this monitoring period, the suspensions were filtered and the resulting aqueous and solid phases were characterized. The aqueous phase was analyzed for total organic and inorganic carbon, free hydroxides (titration), metals (Inductively Coupled Plasma – Emission Spectroscopy; ICP-ES), $Cl^-$ and $F^-$ (Ion Specific Electrode; ISE), anions (Ion Chromatography; IC), formate, glycolate, acetate, and oxalate (Ion Exchange Chromatography; IEC), and EDTA/HEDTA (Ion Pairing Chromatography; IPC). Precipitates were analyzed by XRD to identify crystalline phases, and EDX/SEM to measure the chemical composition and morphology of amorphous solid phases.

There was no detectable increase in precipitates upon diluting simulants with 0.01 M NaOH (e.g., as may occur where wash water returns to the feed stream), or upon mixing Envelope A and B simulants with Envelope-D caustic leachates (AZ-102 and C-106; e.g., where Envelope D leachate is returned to the feed stream). However, mixing of Envelope-D caustic leachate with Envelope C did produce a precipitate. Results from tests conducted by Hassan et al. (2000) with active samples could not be compared directly to results from this study.

Experiments were conducted to simulate conditions of mixing a feed into a staging tank containing a 10 %(vol.) heel. Significant increases in turbidity were measured when AN-107 (Env. C) was mixed with AN-104 (Env. A) or AZ-101 (Env. B). A mixture of 10% AZ-101 and 90% AN-107 resulted in a 40-fold increase in turbidity with respect to the turbidity in pure AZ-101. Similarly, a mixture of 10% AN-107 and 90% AN-104 resulted in a 38-fold increase in turbidity with respect to the turbidity in pure AN-104. The dominant solids detected by X-ray Diffraction (XRD) and Scanning X-ray Microscopy (SEM) in the various mixtures that did in fact form solids were sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), dawsonite ($NaAlCO_3(OH)_2$; only in AZ-101/AN-107 mixtures), sodium hydrogen carbonate hydrate ($Na_3H(CO_3)_2 \cdot xH_2O$), and hydrous sodium carbonate ($Na_2CO_3 \cdot H_2O$; only in AN-107/AN-104 mixtures).

Small decreases in simulant pH levels often resulted in a substantial amount of precipitation, primarily as trona ($Na_3H(CO_3)_2 \cdot 2H_2O$), sodium aluminum silicate ($(Na_6(AlSiO_4)_6$, gibbsite ($Al(OH)_3$), and sodium nitrate.

AN-107 appears to be especially unstable with regard to precipitate formation. It was the only simulant that never reached full equilibrium during the 3-month monitoring period, i.e., turbidity continued to increase steadily during this period. This is likely the result of $CO_2$ gas being drawn from the air into the solution, resulting in carbonate solid phases quickly forming [$NaAl(CO_3)(OH)_2$ and $Na_3H(CO_3)_2 \cdot x$H2O]. Additionally, only small additions of other simulants or acids to AN-107 resulted in the formation of large amounts of precipitates.

The thermodynamic calculations using the software OLI did a reasonably good job predicting the XRD-detectable solids precipitated. OLI tended to predict more varied types of precipitates than were detected by XRD, but most solids (except for evaporates formed on the filters) detected by XRD were among those OLI predicted would precipitate. OLI predictions of the aqueous chemistry of pH-adjusted solutions did not agree well with experimental results. However, the experimental results were from pH-adjusted solutions that were far from equilibrium (the state predicted by OLI); thus, agreement between the two were not entirely expected. Perhaps one of the key problems in applying OLI modeling to the pretreatment waste processing system will be that the feed stream will take, based on this study, in the order of weeks to months to come to equilibrium. The various perturbations of the feed stream will likely force the feed stream out of equilibrium throughout the pretreatment process. It is recommended that the software be used as a guide, but not replace experimental determination of conditions to avoid.

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# 1. INTRODUCTION

## 1.1. *Background*

The formation of solids within the Hanford Site River Protection Project-Waste Treatment Plant (RPP-WTP) within the pretreatment vessels is undesirable for a number of reasons. Precipitation can increase the solids burden on the filtration process, settle in unstirred tanks, or block exchange sites in ion exchange resin columns. Additionally, precipitation of components otherwise targeted for low activity vitrification increases the amount of high level glass.

The test specification associated with this task identifies nine situations, or Items, in the pretreatment process where precipitation may occur (Johnson 1999). These Items can, in turn, be broadly classified into three types of stream processes: mixing, dilution, and acidification. The mixing process involves the formation of precipitates resulting from mixing the heel of Envelope C with Envelopes A or B (Item 1 in the test specification, Johnson 1999). The heel is the volume that remains in the staging tank after drainage, i.e., the portion of waste below the tank outlet. The heel has been estimated to constitute ~9% of the storage vessel's volume. Envelope C contains molar concentrations of total organic carbon (TOC) and may have the capacity to induce reductive precipitation or induce precipitation by exceeding the saturation index of salts that are not normally expected to precipitate from Envelope A or B.

Dilution of the various supernate feeds could lower the solution pH, resulting in solids precipitation. An example of mixing of streams that will result in dilution of the feed stream is where the permeate from the dewatering process of the High-Level Waste (HLW) feed is mixed with the feed stream. Another example, is where the wash water from the Low-Activity Waste (LAW) - entrained solids in mixed with the feed streams. The concern over precipitation induced by dilution is captured in Items 2, 7, and 8 in the test specification (Johnson 1999).

There are several places in the vitrification pretreatment process where acidic waste streams may be mixed with the feed (although the small volume and concentration of these streams will ensure that the feed solution never becomes acidic). The cleaning solutions from the ultrafiltration system are anticipated to be more acidic than the feed solutions. A portion of the cleaning solutions is expected to include dilute nitric acid. Mixing acidic cleaning solution with the LAW feed could lower the solution pH, resulting in the formation of precipitates and affect separation of radionuclides. The HLW melter off-gas condensate is expected to be acidic. This stream will be mixed with Envelope D. The LAW melter off-gas condensate is also expected to be acidic. This stream will be mixed with LAW feed. These process points are captured in the test specification as Items 3, 4, 5, and 6 (Johnson 1999). It should be noted that the WTP has the ability to add sodium hydroxide solutions to acidic waste solutions before mixing with the LAW solutions.

## 1.2. *Objectives*

The overall objective of this small-scale simulant mixing study was to identify the processes that generate precipitates and to identify the types of precipitates formed. Four experiments were conducted to address the specific items identified in the test specifications (Johnson 1999). The four experiments were:

1. Dilution Experiment: quantify and characterize the precipitates formed by diluting simulants with 0.01 M NaOH. Candidate LAW feed solutions may need to be diluted with 0.01 M NaOH solution prior to transfer to the RPP-WTP in order to meet pipeline transfer conditions. Candidate LAW feed solutions may need to be further diluted with 0.01 M NaOH solution after receipt at the RPP-WTP to comply with flowsheet process conditions. This set of dilution tests is intended to mimic the postulated dilution of the LAW solutions.

2. Envelope Mixing Experiment: quantify and characterize the precipitates formed by mixing simulants. Candidate LAW feed solutions will be mixed with various process solutions within the RPP-WTP. These mixing experiments are intended to address the potential range of these mixtures as identified in the RPP-WTP flowsheet.

3. Hydroxide-Concentration Experiment: quantify and characterize the precipitates formed by adding or partially neutralizing the free hydroxide in simulants with nitric acid. Candidate LAW feed solutions will be mixed with various process solutions within the RPP-WTP. These hydroxide concentration experiments mimic mixing acidic or neutral waste solutions with the LAW feed solution, to address the potential range of these mixtures as identified in the RPP-WTP flowsheet.

4. Envelope-D Leachate Mixing Experiment: quantify and characterize the precipitates formed by mixing AZ-102 caustic leachate (3 M NaOH) simulant and C-106 caustic leachate (3 M NaOH) simulant with various feed simulants. Candidate LAW feed solutions will be mixed with various process solutions within the RPP-WTP. These experiments mimic mixing the caustic leachate from pretreatment of HLW solids with the LAW feed solutions, to address the potential range of these mixtures as identified in the RPP-WTP flowsheet.

## 1.3. *Scope*

The following simulant feed solutions were used in each experiment:

AN-104 (Envelope A),
AW-101 (Envelope A),
AZ-101 (Envelope B),
AZ-102 (Envelope B), and
AN-107 (Envelope C).

Although the initial plan was to use an AN-105 simulant, AN-105 simulant was not used in these studies because its chemical composition is very similar to that of AN-104 (Herting 1997, Herting 1998). The technical basis for each simulant composition is provided in the Results section entitled “Simulant Formation.” It is anticipated that AN-102 (Envelope C) will be processed in the near future.[1] However, it was not included in this study because, at the time of this study, insufficient tank-waste characterization data was available to create a simulant recipe. The Envelope D leachate recipe used in the Envelope-D Leachate Mixing Experiment was based on 3 M NaOH leaching of AZ-102 and C-106 solids samples (Herting 1995, Brooks 1997).

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[1] The TWRS Privatization contract specifies in clause H.9 a LAW feed sequence based on metric tons of sodium in each feed envelope. Michael Johnson (now of CH2M Hill Hanford Group) provided information obtained from Russ Treat (Lockheed Martin Hanford Co.), Rudy Carreon (DOE-ORP) and Joe Cruz (DOE-ORP) concerning the LAW feed sequence. The resulting feed sequence plan follows (personal communication).

> FY2000 multi-year work plan guidance will direct the PHMC to plan on the following sequence. AZ-101 or AZ-102 (the order of these two tanks is not set) will be the first wastes treated. These two tanks will be transferred to BNFL without dilution and processed first. The pretreated LAW will be evaporated in accordance with specification 11 and stored in three (or four) of six new 250,000 gallon tanks constructed and operated by BNFL Inc. BNFL will receive AN-102 (no dilution) as the next LAW feed. After processing AN-102, BNFL will receive AN-104 as the next feed (which may possibly need dilution to 10 M Na for transfer). After processing AN-104, BNFL will receive AN-107 (no dilution) as the next feed. The sequence of AN-102 and AN-107 may be switched, depending on the difficulty of waste retrieval. AN-104 will probably remain in this sequence in order to demonstrate processing an Envelope C waste early and AN-104 needs to be emptied to receive cross-site transfer wastes.

Since the initiation of this study, additional guidance regarding the order in which the tank waste will be treated has been released (letter number 00-OPD-013 dated January 26, 2000, from R. T. French, DOE Office of River Protection, to M. P. DeLozier, President and General Manager, CH2M Hill Hanford Group, Inc.). A summary of this letter by Eric Slaathaug (CH2M Hill Hanford Group) follows.

> Tank AP-101 was designated as the first LAW feed to the WTP, followed by AZ-101, AZ-102, AN-102, AN-104, AN-107 and AP-104/SY-101. The pretreated AZ-101 and AZ-102 wastes are no longer evaporated and stored. The pretreated AZ-101 and AZ-102 waste are vitrified concurrent with pretreatment facility operations.

The experiments did not include radioactive isotopes and did not address the problem of mixing the envelopes with off-gas condensates from HLW and LAW melters. Laboratory testing of this problem was deferred until more characterization information of the two off-gas condensate streams is available.

Savannah River Technology Center (SRTC) personnel undertook these modifications to the test plan after consultation and approval by the RPP-WTP technical representative for this task.

### 1.4. *General Approach*

The experimental treatments evaluated in this study are presented in Table 1. Briefly, the simulants were made and monitored for turbidity. Once turbidity stabilized, indicating a steady state may have been reached, the simulants were filtered and used in mixing studies. The filtered simulants were treated as outlined in Table 1. Turbidity and temperature were monitored for 1 to 2 months after treatment. After this monitoring period, the suspensions were filtered and the resulting aqueous and solid phases were characterized. The aqueous phase was analyzed for total organic and inorganic carbon (TOC, TIC), free hydroxides (titration), metals by inductively coupled plasma-emission spectroscopy (ICP-ES), $Cl^-$ and $F^-$ by ion selective electrodes (ISE), anions by ion chromatography (IC), formate, glycolate, acetate, and oxalate by ion exclusion chromatography (IEC), and EDTA, HEDTA by ion pairing chromatography (IPC). Solids were analyzed by x-ray diffraction (XRD) to identify crystalline phases, and energy dispersive x-ray spectroscopy/scanning electron microscope (EDX/SEM) to measure the chemical composition and identify the morphology of amorphous solid phases. Each series of experiments included the monitoring of turbidity and temperature for the unaltered simulant to provide a baseline for solids formed.

**Table 1.** Experimental Treatment Factorial.

| **Experiment** | **Treatment** |
|---|---|
| Dilution[a] | 10, 50, 90, 100% AN-104 |
| | 10, 50, 90, 100% AW-101 |
| | 10, 50, 90, 100% AZ-101 |
| | 10, 50, 90, 100% AZ-102 |
| | 10, 50, 90, 100% AN-107 |
| Envelope Mixing | 0% AZ-101/100% AN-107, 10% AZ-101/90% AN-107, 50% AZ-101/50% AN-107, and 0% AZ-101/100% AN-107 |
| | 0% AN-107 /100% AN-104, 10% AN-107 /90% AN-104, 50% AN-107/50% AN-104, and 0% AN-107 /100% AN-104 |
| Hydroxide Conc. | pH ~10, ~11, ~13, ~14.5 AN-104 |
| | pH ~10, ~11, ~13, ~14.5 AW-101 |
| | pH ~10, ~11, ~13, ~14.5 AZ-101 |
| | pH ~10, ~11, ~13, ~14.5 AZ-102 |
| | pH ~10, ~11, ~13, ~14.5 AN-107 |
| Env. D Leachate | 0% AN-104/100% C-106 leachate, 10% AN-104/90% C-106 leachate, 50% AN-104/50% C-106 leachate, 90% AN-104/10% C-106 leachate, and 100% AN-104/0% C-106 leachate |
| | 0% AW-101/100% C-106 leachate, 10% AW-101/90% C-106 leachate, 50% AW-101/50% C-106 leachate, 90% AW-101/10% C-106 leachate, and 100% AW-101/0% C-106 leachate |
| | 0% AZ-101/100% AZ-102 leachate, 10% AZ-101/90% AZ-102 leachate, 50% AZ-101/50% AZ-102 leachate, 90% AZ-101/10% AZ-102 leachate, and 100% AZ-101/0% AZ-102 leachate |
| | 0% AZ-102/100% AZ-102 leachate, 10% AZ-102/90% AZ-102 leachate, 50% AZ-102/50% AZ-102 leachate, 90% AZ-102/10% AZ-102 leachate, and 100% AZ-102/0% AZ-102 leachate |
| | 0% AN-107/100% C-106 leachate, 10% AN-107/90% C-106 leachate, 50% AN-107/50% C-106 leachate, 90% AN-107/10% C-106 leachate, and 100% AN-107/0% C-106 leachate |

[a] Dilutions were made with 0.01-M NaOH.

# 2. EXPERIMENTAL

## 2.1. *Simulant Formulation*

1. Five simulant feed solutions, AN-104, AW-101, AZ-101, AZ-102, and AN-107, and two caustic leachate solutions (3-M NaOH), AZ-102 caustic leachate and C-106 caustic leachate simulants were prepared.
2. The solutions were permitted to come to steady state by continuous agitation over night at room temperature.
3. After one day of stirring, the turbidity and temperature of the solutions were measured.
4. The solutions were permitted to equilibrate for another 4 days. At which time, turbidity and temperature of the solutions were measured. If negligible turbidity was detected, then we proceeded to step 5. If turbidity was detected, then the solutions were filtered through a 0.45-μm filter. After the additional equilibration period, the simulant was mixed and the turbidity and temperature were measured. If negligible turbidity was detected, then we proceeded to step 5. If turbidity was detected, then the solutions were filtered. These cycles of ≥2-day equilibration periods and turbidity monitoring were continued until negligible turbidity was detected.
5. Once steady state was achieved, as defined by turbidity, the simulants were permitted to continue equilibrating for an additional 7-days. After the 7-day equilibration period, turbidity and temperature were measured and the samples were filtered.

Note: Filtration of the prepared simulant solutions and measurement of turbidity were conducted to provide a measure of whether the simulants had reached a steady state. Collection and characterization of the filtrate was not in the scope of this study. The filtration process was not designed to mimic any specific WTP process. Attempts were made to bring the simulants into steady state prior to use in the mixing studies. It is desirable for the solutions to have reached a steady state insofar that it provides a reference state. It is not known whether the solutions in the WPT will in fact exist in a steady state. pH was not used as indicator of steady state because it is very difficult to measure in high pH and high ionic strength solutions.

## 2.2. *Dilution Experiment*

1. The 5-feed simulants (AN-104, AW-101, AZ-101, AZ-102, and AN-107) created as described above were diluted with 0.01 M NaOH to make 250-mL solutions of 10, 50, 90, and 100% (vol.) simulant.
2. The mixtures were permitted to come to steady state by placing on a platform shaker.
3. Turbidity and temperature of the mixtures were measured each workday.

4. After 30 days, a system was assumed to be at steady state once turbidity remained steady for at least four consecutive readings. This equilibration period did not exceed 60 days.
5. Once steady state was achieved, as defined by turbidity, the mixtures were permitted to continue equilibrating for an additional 7 days.
6. At the end of the equilibration period, turbidity and temperature was measured and then the aqueous and solid phases of the mixtures was separated via 0.45-µm filtration. To reduce the risk of dissolving solids, solids collected on the filter were not rinsed with water to remove entrained liquids. Thus, salts formed by evaporation of the liquids may have formed, causing an experimental artifact.
7. Constituents in the aqueous phase of samples that generated large amounts of precipitates were quantified as follows: free hydroxides by strong-acid titration, anions by IC, cations by ICP-AE, and total organic carbon (TOC) by oxidation/IR.
8. For samples with a sufficient amount of solids, XRD analyses were conducted. If identification of the solids was not possible by XRD, than SEM/EDX were also conducted on the samples. Total solids were determined gravimetrically using tared 0.45-µm filters.

### 2.3. *Envelope Mixing Experiment*

1. The following simulants were combined: AZ-101 & AN-107 and AN-107 & AN-104. These combinations were selected based on the present understanding of the order in which the waste will be treated (see footnote 1). The simulants were combined to produce mixtures with the following proportions (volume percentages):

- 0% AZ-101/100% AN-107, 10% AZ-101/90% AN-107, 50% AZ-101/50% AN-107, and 0% AZ-101/100% AN-107, and
- 0% AN-107 /100% AN-104, 10% AN-107 /90% AN-104, 50% AN-107/50% AN-104, and 0% AN-107 /100% AN-104

2. – 8. These steps are identical to those in the Dilution Experiment.

### 2.4. *Hydroxide-Concentration Experiment*

1. The 5-feed simulants (AN-104, AW-101, AZ-101, AZ-102, and AN-107) created as described above were equilibrated with four different volumes of concentrated $HNO_3$ or NaOH. The $HNO_3$ amended solutions had identical volumes of simulant, 0.2 L, and varying volumes of $HNO_3$. The targeted pH was 10, 11, 13, and 14.5. Since pH is difficult to measure accurately at pH >13 and at high ionic strength, the amount of $HNO_3$ or NaOH added to each treatment was based on preliminary titration studies

using the simulant solutions. The actual pH values of the pH-adjusted simulants were calculated based on the final aqueous chemistry. The measured pH values of these solutions and the amount of $HNO_3$ added are discussed in the Results section, section 3.4.1.

2. – 8. These steps are identical to those in the Dilution Experiment.

### 2.5. *Envelope-D Leachate Mixing Experiment*

1. The 5 feed simulants (AN-104, AW-101, AZ-101, AZ-102, and AN-107) created as described above were combined with varying amounts of the AZ-102 or C-106 Caustic Leachate simulants to create 0.25 L solutions containing 0, 10, 50, 90, and 100% simulant.

2. – 8. These steps are identical to those in the Dilution Experiment.

## 3. RESULTS

These results were reported previously without supporting discussion of the data in milestone report SRT-RPP-2000-00020. To save a great deal of space, not all the quality control (QC) sample data (blanks, MS, MSD, LCS) for the analytical results were provided. This Quality Control data could be provided upon request.

### 3.1. *Simulant Formulation*

Simulants were prepared in 6-L batches to represent supernate from five Hanford waste tanks, AN-107, AW-101, AN-104, AZ-101, and AZ-102. Two additional simulants were prepared in 3-L batches to represent the solution obtained by leaching the sludge from tanks C-106 and AZ-102 with 3-M sodium hydroxide. The prepared feed was mixed, filtered, and monitored for turbidity as described in the experimental section. The feed solutions were monitored for periods ranging from 28 to 36 days depending on when a specific feed was prepared. Turbidity (in units of nephelometric turbidity units, NTU's) of the seven solutions during the equilibration period, prior to use in the mixing study, is presented in Figure 1. At the end of the stability period, each simulant was filtered through a 0.45-micron nylon filter. The final simulant feeds were therefore filtered at least twice during feed preparation. The final feed simulant was submitted for chemical characterization. The solids removed during the feed equilibration period by filtration were not submitted for analysis. Attempts were made to achieve steady state because this would be a relatively more easily defined state, as compared to some transitory state. It is not known whether actual tank waste will be in a steady state during treatment. The laboratory temperature during the monitoring period was 21.9 ± 1.3 °C. Specific details about the formulation and turbidity of each feed solution are described below.

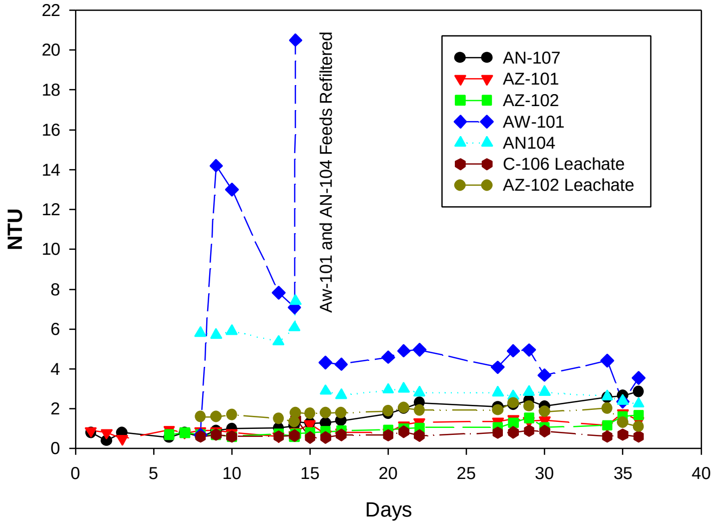

**Figure 1**. Simulant Turbidity (NTU) During Equilibration Period Prior to Mixing.

### 3.1.1. AN-107 Simulant

AN-107 simulant was based on the undiluted supernate from tank 241-AN-107 and was prepared at 8.8-M sodium. The recipe of this simulant, SRTC Envelope C Simulant, is based on Esch (1997). During the equilibrium period, the AN-107 simulant turbidity slowly increased to about 2.9 NTU. Since this increase was so small and the feed was going to be filtered at the end of the equilibrium stage, the stability period was not extended beyond 36 days. When the AN-107 feed (a brown-colored solution) was filtered, it became apparent that large, tabular crystals had formed at the bottom of the feed container despite the periodic agitation and the extremely low turbidity readings. The crystals were identified by x-ray diffraction as thermonatrite, the monohydrate of sodium carbonate ($Na_2CO_3 \cdot H_2O$) (see Figure B12 in Appendix B). Interestingly, the analyzed composition of the AN-107 simulant did show a 4% reduction in planned Na (ICP-ES) and carbonate concentrations.

The planned and as-produced composition of the AN-107 simulant feed is listed in Table 3 and Table 4. The density of the AN-107 simulant feed was 1.403 g/mL and the total solids in the simulant measured by microwave drying were 45.5 % (wt.). The produced AN-107 simulant composition was significantly lower (>20% deviation) in concentration than the planned composition for minor components Ag, Ba, Cd, Mg, Sr, Zr, and major components Al, Ca, oxalate, carbonate (based on titration), and ethylenediaminetetra-acetic acid (EDTA). The produced AN-107 simulant composition was significantly greater (>20%) in concentration than planned for the minor component Cs and major components Cl, F, $PO_4^{3-}$, TOC, $AlO_4$, free OH, N-(2-hydroxyethyl)ethylenediamine-triacetic acid (HEDTA), and iminodiacetic acid (IDA).

A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2. The larger than expected $F^-$ and $Cl^-$ anion concentrations in the AN-107 simulant may be related to interference during the ion chromatography (IC) analysis from monovalent organic anions such as formate, acetate and glycolate. The larger than expected aluminate and free hydroxide concentrations may be due to interference from organic anions during the titration analysis. Similarly, the lower than expected carbonate analysis by titration may also be related to interference from the organic anions. The TIC-carbonate concentration found in the AN-107 simulant closely matches the planned but is about 27% more than that measured by titration, supporting the assumed organic anion interference during titration analysis.

Silver was included as one of the trace metals in the AN-107 simulant, the AN-104 simulant and the AZ-102 simulants. In all three simulants the soluble silver, after the feed stability period was complete, was less than detection limits. Since none of the feeds was protected from light, photoreduction of the aqueous silver cation was the probable mechanism by which the silver target concentration was missed. Given the expected low concentration of silver in the three waste envelopes and the ease of reduction, the absence of silver from the tested solutions should not have any impact on the goal of the experiments.

**Table 2.** Some Causes Responsible for Differences Between Planned and Found Concentrations of Analytes in Simulant Feeds.

| **Analyte** | **Process/Cause** | **Affect of process on Analyte Aqueous Concentration** |
|---|---|---|
| Anions by IC | Interference during ion chromatography (IC) analysis from monovalent organic anions, such as formate, acetate, and glycolate | Increase |
| Aluminate, free hydroxide | Interference during titration with organic anions. | Increase |
| Carbonate | Interference during titration with organic anions. | Decrease |
| Ag | Photoreduction of $Ag^+$ to $Ag^0$, thereby decreasing solution Ag concentrations ($Ag^0$ would precipitate as a solid). | Decrease |
| Metals | Insufficient amount of organic complexants (e.g., HEDTA, IDA, EDTA, and gluconate) added to simulant because of analytical error in the tank characterization. | Decrease |
| EDTA, HEDTA and IDA | Ion Exclusion Chromatography (IEC) and derivatization-GCMS rely on recovery calculations to adjust final results. | Decrease or Increase |
| HEDTA and EDTA | Degradation during simulant production or during mixing study. | Decrease |
| IDA | Degradation of EDTA to form IDA | Increase |
| Free OH | Constant reopening of containers during daily turbidity measurements permitted a unusually large amount of $CO_2$ gas to be dissolved in water, thereby lowering free hydroxide concentrations. | Decrease |
| Al | Decrease in OH concentrations in solution due to removal of atmospheric $CO_2$ would result in less Al precipitation as $Al(OH)_3$. (See Free OH Process/Cause above for how OH and atmospheric $CO_2$ interact). The resulting lower solution pH would have increased solution Al concentrations. | Increase |
| Al | Al values in the Envelope A and B simulants were lower than planned because the source of Al for the simulants was a hydrated aluminum trihydroxide salt. Erroneously, the mass of the water associated with the salt was not accounted for in determining how much to include in the simulants. The salt contained 20 wt-% water; consequently, 20 wt-% less Al than needed was added to the Envelope A and B simulants. | Decrease |

The divalent metal cations that were present at less than the target concentration are generally characterized as forming insoluble carbonates and phosphates, but also stable complexes with chelating agents such as EDTA. Since the carbonate level was sufficiently high in the AN-107 simulant to generate sodium carbonate crystals (described above, see Figure B12 in Appendix B), it is not unexpected that the less soluble carbonates might also be removed during the simulant equilibration period and associated filtration. The presence of chelating agents in the AN-107 simulant should normally prevent the formation of the insoluble carbonates. However, the low level of measured EDTA might indicate that insufficient chelators were present. The AN-107 simulant also contains gluconate which also complexes metal ions. But the planned concentration of gluconate in the AN-107 simulant is not based on a measured value since a method for measuring gluconate in high ionic strength solutions similar to AN-107 has not been developed. The level of gluconate was set based upon SRTC experience with the addition of ferric nitrate to the AN-107 simulant.

Another reason that the divalent cations were less than the target concentrations can also be seen in the measured versus planned oxalate concentration. The oxalate salts of these cations are relatively insoluble and would reduce the concentration of both the cations and the oxalate anion. Therefore, the reduced level of oxalate in the AN-107 simulant could be the result of not having sufficient complexing agents for all of the divalent cations.

The measured values for three of the complexing agents differed significantly from the planned target values: EDTA less than planned, and HEDTA and IDA greater than planned (Table 3). One possible reason for the difference could be an analytical problem since both of the methods used (ion exclusion chromatography and derivatization-GCMS) rely on recovery calculations to adjust the final result. An expected low recovery would generate a high result while an expected high recovery would produce the inverse. Another possibility for the EDTA and IDA results is that decomposition of the EDTA occurred during the simulant production. IDA is included in the AN-107 simulant because it is one of the major decomposition products of the original complexing agents and is a complexing agent itself. A higher level of IDA might, therefore, be caused by EDTA decomposition.

The results for Total Organic Carbon (TOC) are slightly higher than planned. However, actual TOC levels for AN-107 supernate are three times higher, 39 g/L (Esch 1997). The planned AN-107 simulant composition did not attempt to match the measured TOC values since organic characterization has yet to identify all of the TOC in the AN-107 supernate and a portion of what has been identified is not commercially available. Scaling the measured organic compounds to the TOC result was also not attempted since this would greatly impact the charge balance. The result of attempting to match the measured TOC would require the addition of Na or some other cation beyond what has been measured.

One of the special characteristics of the supernate in AN-107 is the extremely low level of free hydroxide, less than 0.02 molar. Consequently, the level of soluble aluminum in the supernate is also extremely low. Aluminum concentration in the salt solutions with pH greater than seven can be used as an indicator of the presence of free hydroxide anion. Since the targeted aluminum concentration was not achieved, the actual free hydroxide level must be less than planned. This could be due to the reaction of $CO_2$ from the air with the free hydroxide to generate carbonate:

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O \qquad (1)$$

Contact with air during the feed stability period occurred regularly due to sampling for turbidity and more extensively during the two filtration processes. The result would be that some of the aluminate would convert back to $Al(OH)_3$ and precipitate:

$$Al(OH)_4^- \longrightarrow Al(OH)_3 + OH^- \qquad (2)$$

The form of zirconium used for the simulant recipe was zirconyl nitrate, $ZrO(NO_3)_2 \cdot xH_2O$, which is an $x$-hydrate where $x$ is from 1 to 6 water molecules. Since the level of zirconium in all of the simulants was less than 100 % of the planned concentration, the zirconyl nitrate was not adjusted for the presence of water of hydration. If $x$ was 1, the Zr level would be 93 % of the target. When $x$ is 6, the zirconium is 68 % of the target. The zirconyl nitrate used must have had 6 waters of hydration.

The impact of these variations from the planned composition on the objectives of this study is expected to be small. First, the concentrations achieved in the AN-107 simulant feed solution are within the range of concentrations observed for actual C envelope wastes. For example, the aluminum concentration in the simulant is lower than the analytical results from the actual AN-107 tank waste because of free hydroxide depletion. Hydroxide depletion is observed in the AN-107 supernate due to the impact of radiolysis in the presence of the organic complexing agents and due to $CO_2$ absorption. Samples of AN-107 supernate collected over a range of time have shown aluminum concentrations trending lower as free hydroxide has trended lower. Second, these tests will be confirmed with shielded cell and radiobench tests with active samples from the actual tanks. This is necessary due to the inability to identify all possible compounds present in the actual waste and therefore to produce a perfect simulant.

The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 3.** AN-107 Simulant Feed Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | 14 | < 2 | ICP-ES |
| Al | mg/L | 194 | 386 | 50 | ICP-ES |
| B | mg/L | 38 | 35 | 108 | ICP-ES |
| Ba | mg/L | 0.17 | 7 | 2 | ICP-ES |
| Ca | mg/L | 138 | 591 | 23 | ICP-ES |
| Cd | mg/L | <0.02 | 64 | <0.03 | ICP-ES |
| Ce | mg/L | 50.2 | 53 | 95 | ICP-ES |
| Co | mg/L | 0.39 | NM[a] | -- | ICP-ES |
| Cr | mg/L | 148 | 176 | 84 | ICP-ES |
| Cs | mg/L | 22.3 | 18.6 | 120 | AA |
| Cu | mg/L | 32 | 30 | 106 | ICP-ES |
| Fe | mg/L | 1623 | 1690 | 96 | ICP-ES |
| K | mg/L | 1921 | 1810 | 106 | AA |
| La | mg/L | 40 | 46 | 88 | ICP-ES |
| Mg | mg/L | 20 | 25 | 79 | ICP-ES |
| Mn | mg/L | 564 | 563 | 100 | ICP-ES |
| Mo | mg/L | 36 | 36 | 100 | ICP-ES |
| Na | mg/L | 188170 | 195000 | 96 | ICP-ES |
| Na | mg/L | 201400 | 195000 | 103 | AA |
| Nd | mg/L | 84.4 | 96 | 88 | ICP-ES |
| Ni | mg/L | 501 | 530 | 95 | ICP-ES |
| P | mg/L | 420 | 362 | 116 | ICP-ES |
| Pb | mg/L | 364 | 388 | 94 | ICP-ES |
| Si | mg/L | 1.4 | NM | -- | ICP-ES |
| Sn | mg/L | <0.26 | NM | -- | ICP-ES |
| Sr | mg/L | 1.3 | 6.6 | 20 | ICP-ES |
| Ti | mg/L | <0.14 | NM | -- | ICP-ES |
| Zn | mg/L | 44 | 45 | 98 | ICP-ES |
| Zr | mg/L | 45 | 70 | 64 | ICP-ES |
| Chloride | mg/L | 1330 | 1100 | 121 | IC |
| Fluoride | mg/L | 3430 | 133 | 2579 | IC |
| Formate | mg/L | 11232 | 10400 | 108 | IC |
| Nitrate | mg/L | 213930 | 230000 | 93 | IC |
| Nitrite | mg/L | 57090 | 61000 | 94 | IC |
| Oxalate | mg/L | 335 | 826 | 41 | IC |
| Phosphate | mg/L | 1500 | 1110 | 135 | IC |
| Sulfate | mg/L | 7280 | 8250 | 88 | IC |
| TIC | mg/L | 16100 | 16800 | 96 | $CO_2$ Evolution |
| TOC | mg/L | 15800 | 12450 | 127 | $CO_2$ Evolution |
| Carbonate (TIC) | mg/L | 80439 | 83940 | 96 | Calc. from TIC |
| Aluminate | Molar | 0.054 | 0.014 | 378 | Titration |
| Carbonate | Molar | 1.052 | 1.400 | 75 | Titration |
| Free OH | Molar | 0.039 | 0.020 | 197 | Titration |

[a] NM = Not Measured.

**Table 4.** AN-107 Simulant Feed Organic Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| EDTA | mg/L | 1088 | 5620 | 19 | IPC |
| HEDTA | mg/L | 3231 | 2140 | 151 | IPC |
| Glycolate | mg/L | 18864 | 18600 | 101 | IEC |
| Citrate | mg/L | 8952 | 8495 | 105 | IEC |
| Formate | mg/L | 12374 | 10400 | 119 | IEC |
| Acetate | mg/L | 964 | 1100 | 88 | IEC |
| Iminodiacetic Acid | mg/L | 8251 | 5947 | 139 | GCMS |

### 3.1.2. AW-101 Simulant

The AW-101 simulant recipe was based on chemical characterization data of the supernate from Hanford tank 241-AW-101, as diluted to a sodium concentration of 6.46 molar (Urie et al. 1999). The simulant is a high hydroxide, high aluminate, Envelope A tank. As shown in Figure 1, the turbidity of the AW-101 simulant began to increase rapidly 8-days after it was made. The feed was filtered through a 0.45-μm nylon filter and monitoring resumed. No further increase in turbidity was observed. The planned and as produced composition is presented in Table 5. The solids concentration, determined by microwave drying was 36.0 %(wt.). The density of the feed solution was 1.304 g/mL.

There was >20% deviation in concentrations between the “Found” and “Planned” concentration of the following analytes: Al, P, Pb, Cl, F, $PO_4^{3-}$, $SO_4^{2-}$, TIC, $Al(OH)_4^-$, $CO_3^{2-}$, and free hydroxide. The differences can be categorized as the results of: (1) starting reagent, (2) lack of complexing reagents, (3) absorption of carbon dioxide during filtering and turbidity monitoring and (4) solubility problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in the study contained 20 wt-% water. The same trihydroxide source was used in the other A and B Tank simulants (AN-104, AZ-101, and AZ-102). The resulting aluminum levels are still within the range expected for actual A and B envelope tanks.

The basis for the simulant feed did not report any organic species such as oxalate as present in the diluted supernate despite the diluted AW-101 supernate having a measured TOC of 1.56 grams/Liter (Urie et al. 1999). Therefore, no potential complexing agents were included in the simulant feed. Thus, lower than planned concentrations of metals such as lead might be due to the lack of such complexing agents.

The extensive handling of the simulated feed during feed makeup, filtration (filtered three times) and sampling for turbidity monitoring can lead to absorption of carbon dioxide. The $CO_2$ would react with the free hydroxide to generate carbonate by reaction (1). The net result would be a reduction in free hydroxide and an increase in carbonate. As the free hydroxide declines the amount of aluminate would also be reduced since the aluminate depends directly on the free hydroxide. Calculating a total hydroxide concentration by summing the free hydroxide and twice the carbonate mole concentration results in 3.041 molar free hydroxide in the AW-101 simulant and 3.408 molar free hydroxide in the planned simulant, or about 90% of the planned amount. Therefore, it appears that the in-growth of carbonate has occurred during the feed stabilization period. The same process can occur within the waste tanks due to the vapor space purge to minimize hydrogen flammability concerns.

Solubility problems have been reported previously for Hanford waste supernates such as AW-101 due to presence of double salts of fluoride and phosphate (Calloway et al. 2000). The low results for fluoride, phosphorus and phosphate could be due to the formation of sodium fluorophosphate, which has a low solubility. The long equilibration period prior to the final filtration and submission of the supernate for analysis would allow formation of the double salt, which is known to have slow kinetics of formation. The three filtration steps that the simulant was processed through would remove the double salt.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope A waste tanks. The growth of carbonate within alkaline waste supernate is an expected process as is the precipitation of salts due to the supernate reaching the solubility limits for such things as double salts. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 5.** AW-101 Simulant Feed Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | NM[a] | -- | ICP-ES |
| Al | mg/L | 12150 | 16350 | 74 | ICP-ES |
| B | mg/L | <0.21 | NM | -- | ICP-ES |
| Ba | mg/L | 0.12 | NM | -- | ICP-ES |
| Ca | mg/L | 2.2 | NM | -- | ICP-ES |
| Cd | mg/L | <0.02 | NM | -- | ICP-ES |
| Ce | mg/L | <0.7 | NM | -- | ICP-ES |
| Co | mg/L | <0.05 | NM | -- | ICP-ES |
| Cr | mg/L | 45 | 56 | 81 | ICP-ES |
| Cs | mg/L | 11.8 | 11 | 107 | AA |
| Cu | mg/L | 0.18 | NM | -- | ICP-ES |
| Fe | mg/L | 0.29 | NM | -- | ICP-ES |
| K | mg/L | 22730 | 23000 | 99 | AA |
| La | mg/L | <0.06 | NM | -- | ICP-ES |
| Mg | mg/L | <0.09 | NM | -- | ICP-ES |
| Mn | mg/L | 0.04 | NM | -- | ICP-ES |
| Mo | mg/L | 0.17 | NM | -- | ICP-ES |
| Na | mg/L | 138670 | 148500 | 93 | ICP-ES |
| Na | mg/L | 137530 | 148500 | 93 | AA |
| Nd | mg/L | <0.3 | NM | -- | ICP-ES |
| Ni | mg/L | 0.32 | NM | -- | ICP-ES |
| P | mg/L | 343 | 635 | 54 | ICP-ES |
| Pb | mg/L | 28 | 41 | 68 | ICP-ES |
| Si | mg/L | 125 | 130 | 96 | ICP-ES |
| Sr | mg/L | 0.11 | NM | -- | ICP-ES |
| Ti | mg/L | <0.14 | NM | -- | ICP-ES |
| Zn | mg/L | 15 | 14 | 109 | ICP-ES |
| Zr | mg/L | 0.06 | NM | -- | ICP-ES |
| Chloride | mg/L | 2570 | 3300 | 78 | IC |
| Fluoride | mg/L | 112.0 | 830.0 | 13 | IC |
| Formate | mg/L | <100 | NM | -- | IC |
| Nitrate | mg/L | 105344 | 123000 | 86 | IC |
| Nitrite | mg/L | 59905 | 62750 | 95 | IC |
| Oxalate | mg/L | <100 | NM | -- | IC |
| Phosphate | mg/L | 799 | 1950 | 41 | IC |
| Sulfate | mg/L | 2403 | 1850 | 130 | IC |
| TIC | mg/L | 9620 | 2155 | 446 | $CO_2$ Evolution |
| TOC | mg/L | <200 | NM | -- | $CO_2$ Evolution |
| Carbonate (TIC) | mg/L | 48063 | 10767 | 446 | Calc. from TIC |
| Aluminate | Molar | 0.365 | 0.606 | 60 | Titration |
| Free OH | Molar | 2.133 | 3.050 | 70 | Titration |
| Carbonate | Molar | 0.454 | 0.179 | 254 | Titration |

[a] NM = Not Measured.

### 3.1.3. AN-104 Simulant

The AN-104 simulant recipe is based upon a retrieval scenario in which the entire tank is mixed and then water is added to achieve 50 % dilution by volume (Herting 1998). The resulting supernate contains 7.61 molar sodium and substantially higher concentrations of phosphate, sulfate and carbonate due to dissolution of salts within the solids present in AN-104. A comparison with a supernate based upon the same treatment for AN-105 suggested that the AN-104 simulant is a conservative bounding case and adequately represents AN-105 for the purposes of this study (Herting 1995). The oxalate concentration used in the AN-104 simulant was taken from the AN-105 reference due to the AN-104 measurement being reported as a less than value while oxalate was expected to be present. Due to the addition of water in the presence of the crystallized salts in AN-104, the supernate is likely saturated with carbonates, phosphates and sulfates salts. Similar to the AW-101 simulant, the AN-104 simulant required filtering part way through the equilibrium period and is so noted on Figure 1. Table 6 provides the planned and as "found" composition of the AN-104 simulant. The final feed simulant had a density of 1.342 g/mL. Based upon microwave drying to a constant weight, the total solids in the simulant was 39 wt-%.

There was >20% deviation in concentrations between the "found" and "planned" concentration of the following analytes: Ag, Al, P, F, Oxalate, $PO_4^{3-}$, TIC, $Al(OH)_4^-$, $CO_3^{2-}$, and free hydroxide. The differences can be categorized as being due to: (1) lack of stability for the specific element, (2) the starting reagent, (3) absorption of carbon dioxide during filtering and turbidity monitoring and (4) solubility problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

Silver was supposed to have a concentration of 13 mg/L in the AN-104 feed simulant. The soluble silver, after the feed stability period was complete, was less than detection limits. Since none of the feeds was protected from light, photoreduction of the aqueous silver cation was the probable mechanism by which the silver target concentration was missed. Given the expected low concentration of silver in the Envelope A waste envelope and the ease of reduction, the absence of silver from the tested solutions should not have any impact on the goal of the experiments.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in this study contained ~20 wt-% water. The same trihydroxide source was used in the other A and B Tank simulants (AW-101, AZ-101, and AZ-102). The resulting aluminum levels are still within the range expected for actual Envelope A and B tanks.

The extensive handling of the simulated feed during feed makeup, filtration (filtered three times) and sampling for turbidity monitoring can lead to absorption of carbon dioxide. The $CO_2$ would react with the free hydroxide to generate carbonate by reaction (1). The net result would be a reduction in free hydroxide and an increase in carbonate. As the free hydroxide declined the amount of aluminate would also be reduced since the aluminate depends directly on the free hydroxide. Calculating a total hydroxide concentration by summing the free hydroxide and twice the carbonate mole concentration results in 3.432 molar free hydroxide in the AW-101 simulant and 3.728 molar free hydroxide in the planned simulant, or about 92% of the planned concentration. Therefore, it appears that the ingrowth of carbonate has occurred during the feed stability period. The same process can occur within the waste tanks due to the vapor space purge to minimize hydrogen flammability concerns.

Solubility problems have been reported previously for Hanford waste supernates such as AN-104, due to presence of double salts of fluoride and phosphate (Calloway et al. 2000). The low results for fluoride, phosphorus and phosphate could be due to the formation of sodium fluorophosphate, which has a low solubility. The long equilibration period prior to the final filtration and submission of the supernate for analysis would allow formation of the double salt, which is known to have slow kinetics of formation. The three-filtration steps that the simulant was processed through would remove the double salt.

As mentioned above, the oxalate concentration planned for the AN-104 simulant is not actually based on the AN-104 sample analysis. Since it was desirable to have oxalate present in at least one of the Envelope A simulants, the concentration used came from the supernate of AN-105. Whether the concentration measured in AN-105 supernate is appropriate for composition of AN-104 was not considered. The measured level in the AN-104 simulant could be the correct level for that overall composition.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope A waste tanks. The growth of carbonate within alkaline waste supernate is an expected process as is the precipitation of salts due to the supernate reaching the solubility limits for such things as double salts. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 6.** AN-104 Simulant Feed Composition.

| Component | Units | Found | Target | % of Target | Methods |
|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | 13 | < 2 | ICP-ES |
| Al | mg/L | 16952 | 23200 | 73 | ICP-ES |
| B | mg/L | 33 | 33 | 101 | ICP-ES |
| Ba | mg/L | 5.6 | NM[a] | -- | ICP-ES |
| Ca | mg/L | 2.8 | NM | -- | ICP-ES |
| Cd | mg/L | <0.02 | NM | -- | ICP-ES |
| Ce | mg/L | <0.7 | NM | -- | ICP-ES |
| Co | mg/L | <0.05 | NM | -- | ICP-ES |
| Cr | mg/L | 204 | 248 | 82 | ICP-ES |
| Cs | mg/L | 0.7 | NM | -- | AA |
| Cu | mg/L | 0.14 | NM | -- | ICP-ES |
| Fe | mg/L | 0.31 | NM | -- | ICP-ES |
| K | mg/L | 4320 | 4050 | 107 | AA |
| La | mg/L | <0.06 | NM | -- | ICP-ES |
| Mg | mg/L | <0.09 | NM | -- | ICP-ES |
| Mn | mg/L | <0.009 | NM | -- | ICP-ES |
| Mo | mg/L | 49 | 50 | 98 | ICP-ES |
| Na | mg/L | 164670 | 175000 | 94 | ICP-ES |
| Na | mg/L | 168200 | 175000 | 96 | AA |
| Nd | mg/L | <0.3 | NM | -- | ICP-ES |
| Ni | mg/L | 0.41 | NM | -- | ICP-ES |
| P | mg/L | 444 | 957 | 46 | ICP-ES |
| Pb | mg/L | <0.6 | NM | -- | ICP-ES |
| Si | mg/L | 169 | 153 | 111 | ICP-ES |
| Sr | mg/L | 0.09 | NM | -- | ICP-ES |
| Ti | mg/L | 0.15 | NM | -- | ICP-ES |
| Zn | mg/L | 3.4 | NM | -- | ICP-ES |
| Zr | mg/L | <0.05 | NM | -- | ICP-ES |
| Chloride | mg/L | 5861 | 5100 | 115 | IC |
| Fluoride | mg/L | <200 | 506.0 | <40 | IC |
| Formate | mg/L | <100 | NM | -- | IC |
| Nitrate | mg/L | 85960 | 102000 | 84 | IC |
| Nitrite | mg/L | 62530 | 64500 | 97 | IC |
| Oxalate | mg/L | 160 | 549 | 29 | IC |
| Phosphate | mg/L | 868 | 2930 | 30 | IC |
| Sulfate | mg/L | 5744 | 7120 | 81 | IC |
| TIC | mg/L | 12314 | 7490 | 164 | $CO_2$ Evolution |
| TOC | mg/L | 3628 | NM | -- | $CO_2$ Evolution |
| Carbonate (TIC) | mg/L | 61523 | 37421 | 164 | Calc. from TIC |
| Aluminate | Molar | 0.636 | 0.860 | 74 | Titration |
| Carbonate | Molar | 0.763 | 0.624 | 122 | Titration |
| Free OH | Molar | 1.906 | 2.480 | 77 | Titration |

[a] NM = Not measured.

### 3.1.4. AZ-101 Simulant

The AZ-101 simulant recipe is based on the Best Basis Inventory composition for the AZ-101 supernate as of October 1, 1998. Tank AZ-101 is an Envelope B tank and is a simple simulant with very few minor components in contrast with the more detailed Envelope A and C simulants. No rise in turbidity, suggesting the formation of precipitates, was observed during the feed preparation or equilibration period. The planned and actual composition for the AZ-101 simulant is presented in Table 7. The density of the simulant was 1.227 g/mL and the solids concentration determined by microwave drying was 29.84 wt-%.

There was >20% deviation in concentrations between the "found" and "planned" concentration of the following analytes: Al, Zr, F, TIC, $Al(OH)_4$. The differences can be categorized as being due to: (1) the starting reagent, (2) lack of complexing reagents, and (3) analytical problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in the study contained 20% wt-% water. The same trihydroxide source was used in the other A and B Tank simulants (AN-104, AW-101, and AZ-102). The resulting aluminum levels are still within the range expected for actual A and B envelope tanks. The $Al(OH)_4$ result agrees well with the ICP-ES result for aluminum.

The Best Basis inventory did not provide a basis for adding any organic carbon to the simulant. Therefore, the potential exists for not including the necessary complexing agents to assist in keeping any trace metal such as zirconium soluble. The AZ-101 Tank Characterization report indicates a TOC value of 1030 mg/L based upon a 1995 grab sample (Hodgson 1995). Therefore, a better simulant should include some oxalate and other organic anions.

A comparison of the TIC result with the carbonate titration result, suggests that there was a problem with the TIC measurement on this feed. The carbonate titration result agreed well with the planned carbonate concentration.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope B waste tanks. The growth of carbonate within alkaline waste supernate is an expected process as is the precipitation of salts due to the supernate reaching the solubility limits for such things as double salts. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 7.** AZ-101 Simulant Feed Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Al | mg/L | 7752 | 10668 | 73 | ICP-ES |
| B | mg/L | <0.21 | NM[a] | -- | ICP-ES |
| Ba | mg/L | 0.02 | NM | -- | ICP-ES |
| Ca | mg/L | 3.7 | NM | -- | ICP-ES |
| Ce | mg/L | <0.7 | NM | -- | ICP-ES |
| Cr | mg/L | 648 | 730 | 89 | ICP-ES |
| Cs | mg/L | 41 | 37 | 111 | AA |
| Fe | mg/L | 0.46 | NM | -- | ICP-ES |
| K | mg/L | 4690 | 4624 | 101 | AA |
| La | mg/L | <0.06 | NM | -- | ICP-ES |
| Mg | mg/L | <0.09 | NM | -- | ICP-ES |
| Mn | mg/L | 0.11 | NM | -- | ICP-ES |
| Mo | mg/L | <0.1 | NM | -- | ICP-ES |
| Na | mg/L | 104670 | 108989 | 96 | ICP-ES |
| Na | mg/L | 108990 | 108990 | 100 | AA |
| Ni | mg/L | 0.34 | NM | -- | ICP-ES |
| P | mg/L | 546 | 489 | 112 | ICP-ES |
| Si | mg/L | 5.3 | NM | -- | ICP-ES |
| Zr | mg/L | 0.32 | 3.1 | 10 | ICP-ES |
| Chloride | mg/L | 180 | 200 | 90 | IC |
| Fluoride | mg/L | 760.0 | 1813.0 | 42 | IC |
| Formate | mg/L | <100 | NM | -- | IC |
| Nitrate | mg/L | 60330 | 75630 | 80 | IC |
| Nitrite | mg/L | 61770 | 65060 | 95 | IC |
| Oxalate | mg/L | <100 | NM | -- | IC |
| Phosphate | mg/L | 1318 | 1503 | 88 | IC |
| Sulfate | mg/L | 15740 | 17670 | 89 | IC |
| TIC | mg/L | 8466 | 4620 | 183 | |
| TOC | mg/L | 365 | NM | -- | |
| Carbonate (TIC) | mg/L | 42298 | 23082 | 183 | Calc. from TIC |
| Aluminate | Molar | 0.268 | 0.395 | 68 | Titration |
| Carbonate | Molar | 0.384 | 0.385 | 100 | Titration |
| Free OH | Molar | 0.463 | 0.531 | 87 | Titration |

[a] NM = Not measured.

### 3.1.5. AZ-102 Simulant

The AZ-102 simulant recipe is based upon the recently received Envelope B sample obtained from Hanford tank 241-AZ-102 (Hay 2000) and a core sample (Gray et al. 1993). To insure that the simulant included all of the trace metals, the recipe used the trace metal values from the core sample for the planned composition. The resulting simulant represents a more complete Envelope B simulant than the AZ-101 simulant. Table 8 contains the planned and actual composition of the simulant. No special problems with regards to precipitate formation were encountered during the preparation of this simulant. The density of the simulant was 1.118 g/mL and the total solids in the simulant was 15.76 wt-%.

There was >20% deviation in concentrations between the "found" and "planned" concentration of the following analytes: Ag, Al, Ba, Ca, Cd, Cu, Fe, La, Mg, Mn, Nd, Ni, Pb, Si, Sr, Zr, TIC, and free hydroxide. The differences can be categorized as being due to: (1) the starting reagent, (2) lack of solubility, (3) lack of complexing agents and (4) analytical problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in this study contained 20 wt-% moisture. The same trihydroxide source was used in the other A and B Tank simulants (AN-104, AW-101, and AZ-102). The resulting aluminum levels are still within the range expected for actual A and B envelope tanks. However, the reported concentration of aluminum based on ICP-ES is considerably less than the 80% purity would support. Due to the small amount of free hydroxide, it is not surprising that the soluble aluminum concentration is so low. A small shift in the free hydroxide to a lower concentration due to $CO_2$ absorption could significantly reduce the soluble aluminum level. Note that the aluminate concentration based upon titration does not agree with the ICP result (0.03 M versus 0.01 M).

In an effort to provide a more complete B simulant, the AZ-102 simulant was formulated to include many metals at trace concentrations. The following metals were based upon results from the 1989 core sample of AZ-102 (Gray et al. 1993): Ag, Ba, Cd, Cu, Fe, La, Mg, Mn, Nd, Ni, Pb, Si, Sr, and Zr. For all of these metals except Ag and Nd, the more recent SRTC analysis (Hay 2000) had less than quantifiable levels of these metals. Thus, the "found" values are in better agreement with the results of Hay (2000) than with Gray et al (1993). The neodymium concentration is expected to track the lanthanum concentration and would also be a "less than" value. The chemical properties of silver in the simulant have already been discussed in regards to both the AN-107 and AN-104 simulants and photoreduction probably reduced the soluble silver concentration below the planned level. A contributing factor in the low solubility of these metals could be the relatively high concentration of oxalate present in the AZ-102 supernate. Many of these metals form salts with oxalic acid, which have low solubilities. In particular, calcium oxalate has very limited solubility and could explain the simulant feed having only 4.8 mg/L soluble calcium.

Another contributing factor in the low solubilities of the metals could be the lack of complexing agents other than oxalate anion. The measured TOC for the recent AZ-102 sample was 6.04 g/L (Hay 2000). The measured oxalate anion accounts for only 12% of the TOC. Additional organic characterization might provide a complexing agent sufficient to support the calcium ion concentration observed in the active sample.

The free hydroxide value reported for the AZ-102 simulant could be high due to an interference from the oxalate anion. Part of the analysis procedure involves addition of strontium nitrate to precipitate all of the carbonate prior to titration. Insufficient strontium nitrate addition due to the presence of oxalate might have produced a high hydroxide result and a low carbonate result.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope B waste tanks. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 8.** AZ-102 Simulant Feed Composition.

| Components | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | 6.9 | <4 | ICP-ES |
| Al | mg/L | 230 | 755 | 30 | ICP-ES |
| B | mg/L | 7.3 | 8.4 | 87 | ICP-ES |
| Ba | mg/L | 0.01 | 0.8 | 1 | ICP-ES |
| Ca | mg/L | 4.8 | 108.0 | 4 | ICP-ES |
| Cd | mg/L | 0.05 | 1.9 | 3 | ICP-ES |
| Cr | mg/L | 865 | 1011 | 86 | ICP-ES |
| Cs | mg/L | 1 | NM[a] | -- | AA |
| Cu | mg/L | 0.18 | 3.1 | 6 | ICP-ES |
| Fe | mg/L | 0.23 | 11.20 | 2 | ICP-ES |
| K | mg/L | 3150 | 3167 | 99 | AA |
| La | mg/L | <0.06 | 1.8 | <3 | ICP-ES |
| Mg | mg/L | <0.09 | 0.9 | <10 | ICP-ES |
| Mn | mg/L | <0.009 | 0.8 | <1 | ICP-ES |
| Mo | mg/L | 58 | 58 | 100 | ICP-ES |
| Na | mg/L | 58070 | 60900 | 95 | ICP-ES |
| Na | mg/L | 53000 | 60900 | 87 | AA |
| Nd | mg/L | <0.3 | 5.5 | < 5 | ICP-ES |
| Ni | mg/L | <0.06 | 2.2 | <3 | ICP-ES |
| P | mg/L | 166 | 155 | 108 | ICP-ES |
| Pb | mg/L | <0.6 | 6 | <10 | ICP-ES |
| Si | mg/L | 121 | 559 | 22 | ICP-ES |
| Sr | mg/L | 0.05 | 0.20 | 23 | ICP-ES |
| Zr | mg/L | 0.43 | 4.30 | 10 | ICP-ES |
| Chloride | mg/L | 201 | 248 | 81 | IC |
| Fluoride | mg/L | 1111.0 | 1015.0 | 109 | IC |
| Nitrate | mg/L | 15360 | 16930 | 91 | IC |
| Nitrite | mg/L | 31050 | 30320 | 102 | IC |
| Oxalate | mg/L | 2671 | 2825 | 95 | IC |
| Phosphate | mg/L | 375 | 475 | 79 | IC |
| Sulfate | mg/L | 14848 | 16520 | 90 | IC |
| TIC | mg/L | 8946 | 6135 | 146 | $CO_2$ Evolution |
| TOC | mg/L | 1052 | NM | -- | $CO_2$ Evolution |
| Carbonate (TIC) | mg/L | 44696 | 30652 | 146 | Calc. from TIC |
| Aluminate | Molar | 0.030 | 0.028 | 107 | Titration |
| Carbonate | Molar | 0.464 | 0.511 | 91 | Titration |
| Free OH | Molar | 0.196 | 0.109 | 180 | Titration |

[a] NM = Not Measured.

### 3.1.6. C-106 Caustic Leachate Simulant

Current plans for processing Envelope D sludge includes caustic leaching with 3-M sodium hydroxide to reduce the aluminum content in the Envelope D sludge. The C-106 caustic leachate simulant recipe is based on a 3-M sodium hydroxide leachate of C-106 sludge (Brooks et al. 1997). Since carbonate was not measured on the caustic leachate, carbonate was used to obtain a charge balance. This produces a simulant with a substantial amount of carbonate. A review of the information on the solids from C-106 suggests that carbonate would leach from the solids and is appropriate for this matrix. The planned and as produced composition is presented in Table 9. The density of the simulant was 1.199 g/mL and contained 21.8 wt-% total solids.

There was >20% deviation in concentrations between the “found” and “planned” concentration of the following analytes: Al, $NO_3^-$, TIC, $Al(OH)_4^-$. The differences can be categorized as being due to: (1) the starting reagent and (2) analytical problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in this study contained 20 wt-% moisture. The same trihydroxide source was used in the A and B Tank simulants (AN-104, AW-101, and AZ-102) and in the other caustic leachate simulant. The resulting aluminum levels are still within the range expected for actual Envelope A and B tanks. Since the caustic leachate is a relatively simple caustic solution, it is not surprising that the amount of aluminum based on ICP-ES is so close to the purity of the starting aluminum reagent.

The cause for a lower than expected analytical result for nitrate is not known. The relatively low ionic strength of the caustic leachate simulant should allow complete dissolution of the sodium nitrate used to make the simulant. The caustic leachate simulant was not observed to have produced any solids when it was filtered. One possibility is that the sodium nitrate used may have absorbed some moisture. The absorption of a molecule of water per molecule of sodium nitrate would reduce the nitrate level by about 18% which is close to the amount that was missing. In any case, nitrate is not expected to be a significant portion of the caustic leachate or to participate in solubility problems during waste mixing.

Apparent analytical problems are represented by the results for aluminate and TIC. The aluminate result is only 78% of the ICP-ES value. Aluminate is calculated by taking the difference between two titrations and is subject to increased error when both results are large and nearly equal. The TIC result may be a transcription error since the TOC value is large (no TOC present) and the TIC value is small. However, switching the results gives a TIC value, which does not agree with the carbonate value from titration. The cause for the low TIC and the carbonate (TIC) values are not known. It is known that the carbonate was not inadvertently left out of the recipe because the concentrations of Na, the cation associated with the carbonate salt, existed in the simulant at approximately the targeted concentrations.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope B waste tanks. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 9.** Tank C-106 Caustic Leachate Simulant Feed Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | NM[a] | -- | ICP-ES |
| Al | mg/L | 2460 | 3100 | 79 | ICP-ES |
| B | mg/L | 68 | 67 | 101 | ICP-ES |
| Ba | mg/L | 14.6 | NM | -- | ICP-ES |
| Ca | mg/L | 3.3 | NM | -- | ICP-ES |
| Cr | mg/L | 49 | 58 | 85 | ICP-ES |
| Cs | mg/L | 0.7 | NM | -- | AA |
| Cu | mg/L | 0.06 | NM | -- | ICP-ES |
| Fe | mg/L | 0.24 | NM | -- | ICP-ES |
| K | mg/L | 2.4 | NM | -- | AA |
| Na | mg/L | 105670 | 110000 | 96 | ICP-ES |
| Na | mg/L | 102470 | 110000 | 93 | AA |
| Nd | mg/L | <0.3 | NM | -- | ICP-ES |
| Ni | mg/L | 0.06 | NM | -- | ICP-ES |
| P | mg/L | 125 | 109 | 115 | ICP-ES |
| Pb | mg/L | 26 | 31 | 85 | ICP-ES |
| Si | mg/L | 303 | 295 | 103 | ICP-ES |
| Zn | mg/L | 0.48 | NM | -- | ICP-ES |
| Chloride | mg/L | 105 | NM | -- | IC |
| Fluoride | mg/L | <20 | NM | -- | IC |
| Nitrate | mg/L | 241 | 335 | 72 | IC |
| Nitrite | mg/L | 6589 | 6850 | 96 | IC |
| Oxalate | mg/L | 698 | 2500 | 28 | IC |
| Phosphate | mg/L | 303 | 335 | 90 | IC |
| Sulfate | mg/L | 1570 | 1800 | 87 | IC |
| TIC | mg/L | 3 | 10029 | 0 | |
| TOC | mg/L | 18716 | NM | -- | |
| Carbonate (TIC) | mg/L | 13 | 50110 | 0 | Calc. from TIC |
| Aluminate | Molar | 0.070 | 0.115 | 61 | Titration |
| Carbonate | Molar | 0.881 | 0.835 | 106 | Titration |
| Free OH | Molar | 2.651 | 2.700 | 98 | Titration |

[a] NM = Not Measured.

### 3.1.7. AZ-102 Leachate Simulant

The AZ-102 caustic leachate simulant is based on the resulting supernate produced by leaching AZ-102 sludge with 3-M sodium hydroxide (Herting 1995). Charge balancing the recipe is based on hydroxide since a measured hydroxide concentration was not available for the leachate. Table 10 provides the “found” (actual) and “planned” composition for the simulant feed. The density of the AZ-102 leachate simulant was 1.112 g/mL and the total solids in the simulant was 13.6 wt-%.

There was >20% deviation in concentrations between the “found” and “planned” concentration of the following analytes: Al, F, $NO_3^-$, $PO_4^{3-}$, TIC, $Al(OH)_4^-$, and $CO_3^{2-}$. The differences can be categorized as being due to: (1) the starting reagent and (2) analytical problems. A brief summary for some of the causes that may be responsible for the discrepancies between the planned and found concentrations is presented in Table 2.

The aluminum value as reported by ICP-ES and by titration was lower than planned because the aluminum trihydroxide used in this study had a purity of only 80%, the remaining 20% consisted of water. The same trihydroxide source was used in the A and B Tank simulants (AN-104, AW-101, and AZ-102) and in the other caustic leachate simulant. The resulting aluminum levels are still within the range expected for actual Envelope A and B tanks. Since the caustic leachate is a relatively simple caustic solution, it is not surprising that the amount of aluminum based on ICP-ES is so close to the purity of the starting aluminum reagent.

The cause for the lower than expected analytical result for nitrate is not known. The relatively low ionic strength of the caustic leachate simulant should allow complete dissolution of the sodium nitrate used to make the simulant. The caustic leachate simulant was not observed to have produced any solids when it was filtered. One possibility is that the sodium nitrate used may have absorbed some moisture. The absorption of a molecule of water per molecule of sodium nitrate would reduce the nitrate level by about 18%, which is close to the amount that was missing. In any case, nitrate is not expected to be a significant portion of the caustic leachate or to participate much in solubility problems during waste mixing.

Apparent analytical problems are represented by the results for fluoride, phosphate, aluminate and TIC. The phosphate result from the IC does not agree with the phosphorus result from ICP-ES. Since aluminate is based on a difference between two titrations and the planned aluminate concentration is so small, the production of a less than result is not surprising. The TIC result may be a transcription error since the TOC value is large (no TOC present) and the TIC value is small. However, switching the results gives a TIC value, which does not agree with the planned carbonate concentration of 0.195 molar. The cause for the low TIC value is not known. It is known that the carbonate was not inadvertently left out of the recipe because the concentrations of Na, the cation associated with the carbonate salt, existed in the simulant at approximately the targeted concentrations.

The net impact of these differences on the goal of this study is expected to be small since all of the analytical results are within the range of expected conditions for Envelope B waste tanks. The goal of experiments with waste simulants is to develop knowledge about waste chemistry and to provide some prediction of potential problems. However, since waste characterization is not perfect, the simulant may not exactly duplicate the actual waste. Therefore, results from simulated waste experiments must be confirmed by actual waste studies.

**Table 10.** AZ-102 Caustic Leachate Simulant Composition.

| Component | Units | Found | Planned | % of Target | Methods |
|---|---|---|---|---|---|
| Al | mg/L | 1195 | 1540 | 78 | ICP-ES |
| B | mg/L | 0.25 | NM[a] | -- | ICP-ES |
| Ba | mg/L | 0.01 | NM | -- | ICP-ES |
| Ca | mg/L | 2.2 | NM | -- | ICP-ES |
| Cr | mg/L | 160 | 194 | 82 | ICP-ES |
| Cs | mg/L | 0.2 | NM | -- | AA |
| Cu | mg/L | <0.05 | NM | -- | ICP-ES |
| Fe | mg/L | 0.19 | NM | -- | ICP-ES |
| K | mg/L | 920 | 904 | 102 | AA |
| La | mg/L | <0.06 | NM | -- | ICP-ES |
| Li | mg/L | <0.1 | NM | -- | ICP-ES |
| Mg | mg/L | <0.09 | NM | -- | ICP-ES |
| Mn | mg/L | 0.03 | NM | -- | ICP-ES |
| Mo | mg/L | 14 | 14 | 99 | ICP-ES |
| Na | mg/L | 57070 | 59200 | 96 | ICP-ES |
| Na | mg/L | 57320 | 59200 | 97 | AA |
| Nd | mg/L | <0.3 | NM | -- | ICP-ES |
| Ni | mg/L | <0.06 | NM | -- | ICP-ES |
| P | mg/L | 211 | 194 | 109 | ICP-ES |
| Si | mg/L | 1.4 | NM | -- | ICP-ES |
| Sr | mg/L | 0.03 | NM | -- | ICP-ES |
| Chloride | mg/L | 117 | 22 | 532 | IC |
| Fluoride | mg/L | 100.0 | 136 | 74 | IC |
| Formate | mg/L | <100 | NM | -- | IC |
| Nitrate | mg/L | 4515 | 5940 | 76 | IC |
| Nitrite | mg/L | 7393 | 7930 | 93 | IC |
| Oxalate | mg/L | <100 | NM | -- | IC |
| Phosphate | mg/L | 770 | 594 | 130 | IC |
| Sulfate | mg/L | 4844 | 4850 | 100 | IC |
| TIC | mg/L | <200 | 2340 | <8.5 | $CO_2$ Evolution |
| TOC | mg/L | 8394 | NM | -- | $CO_2$ Evolution |
| Carbonate (TIC) | mg/L | NM | 11690 | -- | Calc. from TIC |
| Aluminate | Molar | <0.01 | 0.057 | <17.5 | Titration |
| Carbonate | Molar | 0.148 | 0.195 | 76 | Titration |
| Free OH | Molar | 1.820 | 1.75 | 104 | Titration |

[a] NM = Not Measured.

### 3.2. *Dilution Experiment*

AN-104 (Envelope A), AW-101 (Envelope A), AZ-101 (Envelope B), AZ-102 (Envelope B) and AN-107 (Envelope C) were diluted with 0.01 M NaOH to 10%, 50%, 90% and 100% (vol.) envelope feed. The average temperature during this study was 21.3 ± 1.7 °C (detailed temperature data is presented in Appendix A). More details of the materials and methods used in this experiment are presented in Section 2.2. Dilution of all simulant feeds with 0.01 M NaOH resulted in decreased turbidity (Figure 2, Figure 3, Figure 4, Figure 5, Figure 6). For the simulants that were not diluted, i.e., 100% simulants, there were varying degrees of increased turbidity with time. This suggests that the simulants were not in true steady state at the start of (or during) the study. The increase turbidity may be the result of slow precipitation kinetics or may have been caused by the repeated introduction of $CO_2$-gas into the simulants while opening the containers to obtain daily turbidity measurements.

There was essentially no turbidity (<14 NTU) for all dilutions of the four Envelope A and B simulants (Figure 2, Figure 3, Figure 4, and Figure 5). However, a significant amount of turbidity was detected in the 100% AN-107 samples (Figure 6). With only a little dilution, 10% 0.01 M NaOH by volume (see 90% AN-107, Figure 6), essentially all the turbidity was eliminated. Additional dilution resulted in only slight incremental decreases in turbidity. One problem with the measurement of turbidity in the AN-107 simulants was that an appreciable amount of precipitate coated the flask and could not be resuspended by shaking the flask. Thus, the turbidity measurements of this sample do not reflect the true amount of solids formed.

Based on XRD analyses of solids collected on a 0.45-µm filter, the solids in the 100% AN-107 were sodium nitrate ($NaNO_3$), sodium nitrite ($NaNO_2$), and sodium hydrogen carbonate hydrate [$Na_3H(CO_3)_2 \cdot x(H_2O)$]. The XRD patterns are presented in Appendix B. Although XRD is capable of detecting and identifying sodium oxalate, it was not detected in these samples. It is important to note that some of these solids may have formed after the solids were collected on the 0.45-µm filter, thereby creating an experimental artifact. Entrained liquid in the solids was evaporated, and likely left a mass of evaporates on the filter. A likely example of such an evaporate, is sodium nitrite. Evidence in support of the contention that evaporates were formed after filtration can be seen by comparing turbidity data with gravimetrically-determined solids concentration collected on the 0.45-µm filters (Table 11). Based on the data in Table 11, one NTU is approximately equal to 20 to 70 mg/L suspended solids, suggesting that appreciably more solids were collected in the filter than would be expected based on turbidity measurements. Additionally, Envelope A and B suspensions had essentially no observable turbidity, yet the gravimetric solids concentrations in these suspensions indicate that between 300 and 1300 mg/L of solids were present; such concentrations would have been easily observed with the naked eye. Apparently, the salt that absorbed into the filters contributes nearly 1 gram of mass, causing an artificially high value for the insoluble solids measurement by this technique.

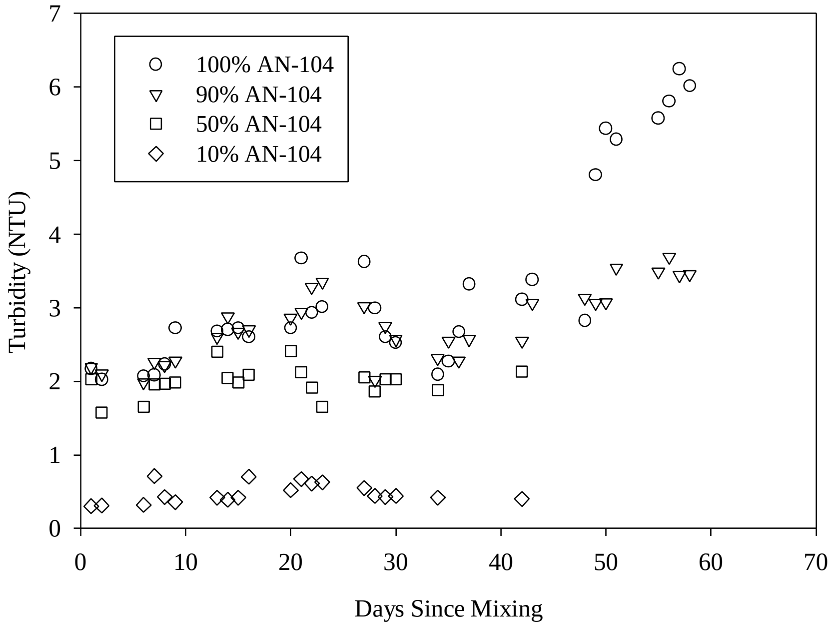

**Figure 2.** Turbidity of AN-104 Diluted with 0.01 M NaOH.

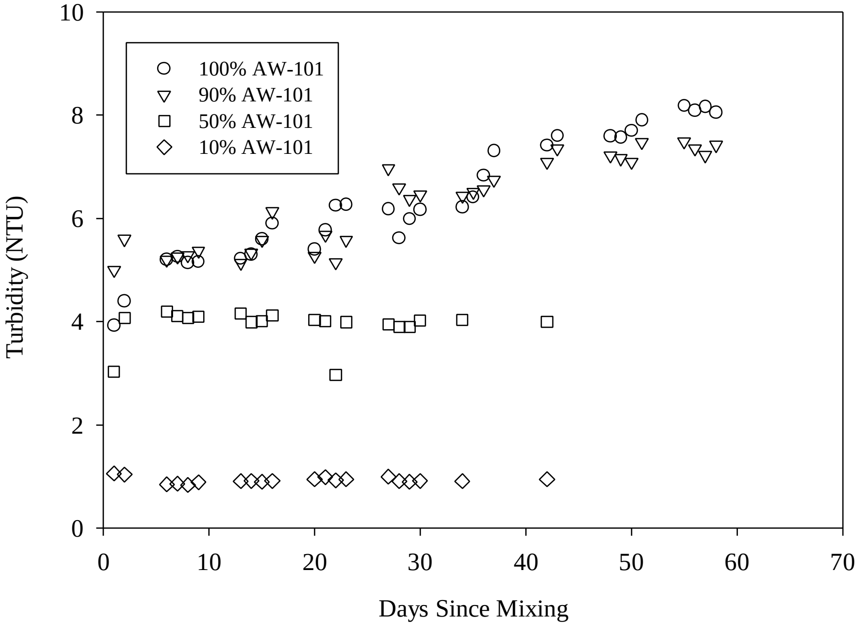

**Figure 3.** Turbidity of AW-101 Diluted with 0.01 M NaOH.

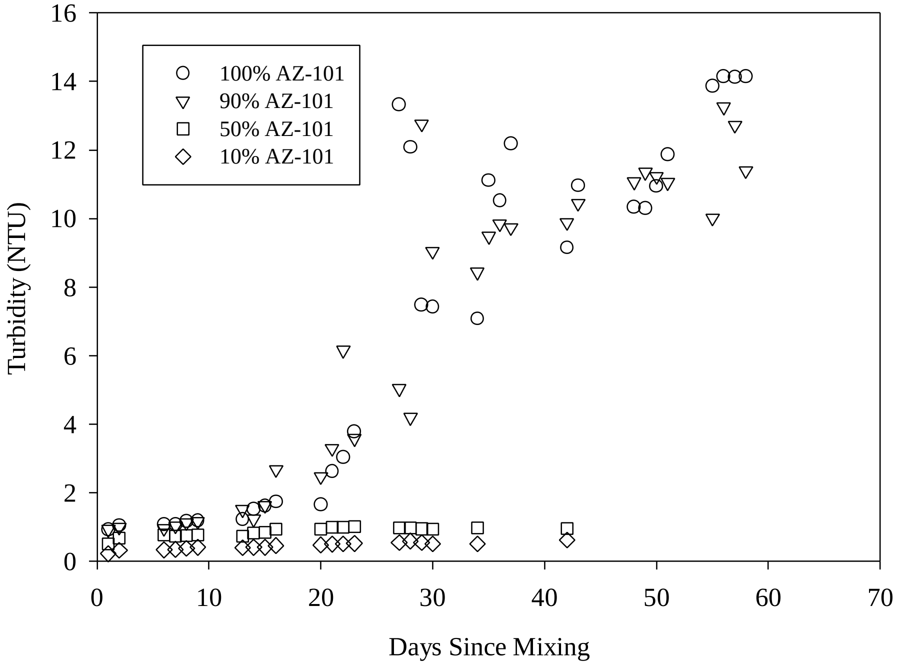

**Figure 4.** Turbidity of AZ-101 Diluted with 0.01 M NaOH.

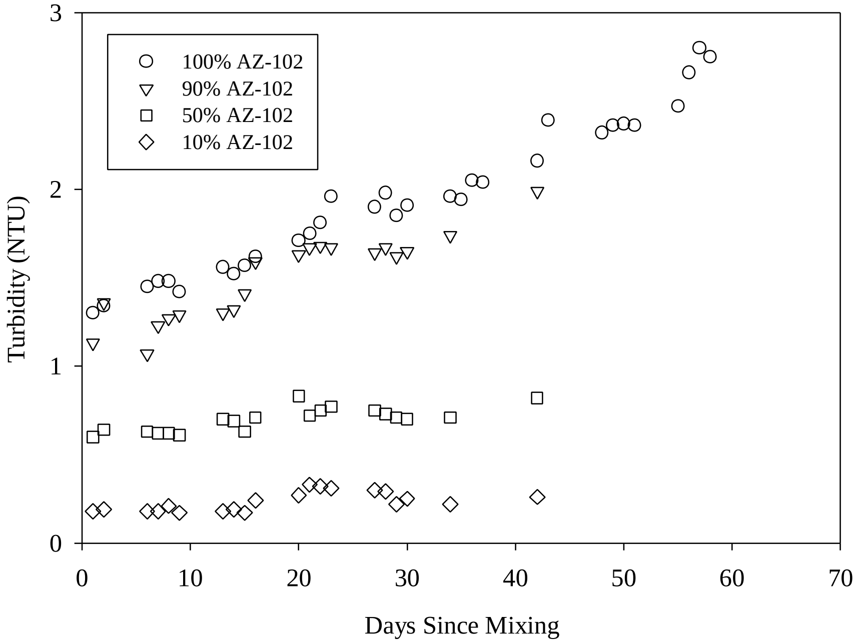

**Figure 5.** Turbidity of AZ-102 Diluted with 0.01 M NaOH.

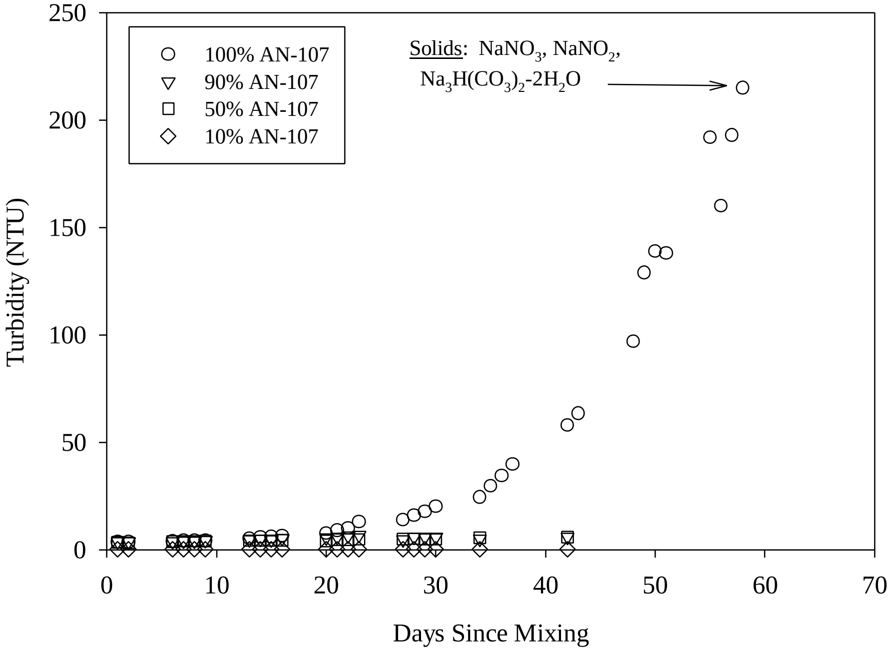

**Figure 6.** Turbidity of AN-107 Diluted with 0.01 M NaOH.

**Table 11.** Turbidity and Solids Concentrations (Collected on a 0.45-Micron Filter) At the End of the 60-Day Equilibration Period.

| **Sample Description** | **Solids Concentration**[a] | **Turbidity** |
|---|---|---|
| | **(mg/L)** | **(NTU)** |
| 100% AN-104 | 1029 | 6.01 |
| 100% AW-101 | 1288 | 8.05 |
| 100% AZ-101 | 681 | 14.14 |
| 100% AZ-102 | 299 | 2.75 |
| 100% AN-107 | 14869 [b] | 215.0 |

[a] Solids concentrations are biased high because of the formation of evaporates during the process of retrieving the solids via filtration.

[b] Not all of the solids could be transferred from the 250-mL flask to the 0.45-μm filter to measure solids concentration. A majority of the solids remained attached to the flask; thus, the reported solids concentration under estimates the true solids concentration for this feed.

## 3.3. *Envelope Mixing Experiment*

It is anticipated that waste will be processed in the following order: AZ-101 (Env. B) or AZ-102 (Env. B), AN-102 (Env. C), AN-104 (Env. A), and finally AN-107 (Env. C; although AN-107 may be substituted for AN-102) (see footnote 1). To reduce the large factorial of tests necessary to simulate all possible mixing scenarios, it was decided to use only one of the two Envelope A simulants (AN-104), one of the two Envelope B simulants (AZ-101), and the only C simulant (AN-107). For this study, the following mixtures were evaluated: 1) 0, 10, 50, and 100% AZ-101 when AZ-101 is mixed into AN-107, and 2) 0, 10, 50, and 100% AN-107 when AN-107 is mixed into AN-104. The average temperature during this study was 21.3 ± 1.7 °C. Detailed temperature information related to this study is presented in Appendix A. Chemical composition data for selected mixtures are presented in Table 12 and Table 13.

**Table 12.** Chemical Composition of Selected Filtrates from Envelope Mixing Study: ICP-ES (mg/L).

| | **100% AN-104** | **100% AZ-101** | **100% AN-107** | **10%AZ-101 90%AN-107** | **50%AZ-101 50%AN-107** | **10%AN-107 90%AN-104** | **50%AN-107 50%AN-104** |
|---|---|---|---|---|---|---|---|
| Al | 16952 | 7752 | 184 | 317 | 4040 | 15950 | 6720 |
| B | 33 | <0.21 | 37 | 31 | 16 | 31 | 25 |
| Ba | 5.6 | 0.02 | 0.03 | 0.026 | 0.033 | 0.049 | 0.045 |
| Ca | 2.8 | 3.7 | 113 | 116 | 71 | 15.0 | 52 |
| Cd | <0.02 | <0.014 | <0.014 | <0.014 | <0.014 | <0.014 | <0.014 |
| Co | <0.044 | <0.044 | <0.044 | <0.044 | <0.044 | <0.044 | <0.044 |
| Cr | 204 | 648 | 154 | 186 | 411 | 198 | 134 |
| Cu | 0.14 | 0.14 | 32 | 27 | 15 | 2.7 | 11.5 |
| Fe | 0.31 | 0.46 | 1660 | 1406 | 734 | 43 | 471 |
| La | <0.06 | <0.06 | 43 | 36 | 21 | 2.4 | 14.4 |
| Li | 0.26 | 0.18 | 0.15 | 0.12 | <0.1 | <0.1 | <0.1 |
| Mg | <0.09 | <0.09 | 20 | 2.33 | 0.45 | <0.084 | <0.084 |
| Mn | <0.009 | 0.11 | 569 | 482 | 217 | 4.9 | 110 |
| Mo | 49 | <0.1 | 37 | 31 | 18 | 47 | 32 |
| Na | 164670 | 104670 | 193972 | 171941 | 148290 | 169578 | 136743 |
| Ni | 0.41 | 0.34 | 517 | 429 | 256 | 51 | 191 |
| P | 444 | 546 | 433 | 402 | 471 | 418 | 321 |
| Pb | <0.6 | <0.06 | 381 | 319 | 179 | 42 | 131 |
| Si | 169 | 5.3 | 1.6 | 1.9 | 3.0 | 145 | 57 |
| Sn | <0.26 | <0.26 | <0.26 | <0.26 | <0.26 | <0.26 | <0.26 |
| Sr | 0.09 | 0.07 | 1.20 | 1.04 | 0.66 | 0.14 | 0.42 |
| Ti | 0.15 | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 |
| V | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 | <0.13 |
| Zn | 3.4 | 4.3 | 45 | 37 | 21.5 | 7.32 | 15.9 |
| Zr | <0.05 | 0.32 | 47 | 39 | 23 | 3.85 | 17 |
| S | 1896 | 5247 | 2675 | 3010 | 4380 | 2480 | 2007 |

**Table 13.** Chemical Composition of Selected Filtrates from Envelope Mixing Study: Other Methods (mg/L).

| | **Analytical Method** | **100% AN-104** | **100% AZ-101** | **100% AN-107** | **10%AZ-101 90%AN-107** | **50%AZ-101 50%AN-107** | **10%AN-107 90%AN-104** | **50%AN-107 50%AN-104** |
|---|---|---|---|---|---|---|---|---|
| Chloride | IC | 5861 | 182 | 2978 | 2750 | 2329 | 5337 | 3174 |
| Fluoride | IC | <200 | 760 | 3813 | 3277 | 2780 | 199 | 1162 |
| Nitrate | IC | 85960 | 60330 | 259453 | 219868 | 162218 | 115107 | 106190 |
| Nitrite | IEC/IPC | 62630 | 61770 | 63578 | 58431 | 70835 | 62579 | 41678 |
| Phosphate | IC | 868 | 1318 | 4684 | 4312 | 3790 | 1134 | 12261 |
| Sulfate | IC | 5744 | 15740 | 9470 | 9542 | 13753 | 7529 | 5608 |
| K | AA | 4320 | 4690 | 1930 | 2005 | 3266 | 4020 | 2240 |
| Free OH (molarity) | Titration | 1.906 | 0.463 | <0.02 | <0.02 | 0.2275 | 1.6524 | 0.4568 |
| Organic C | TIC/TOC | 3628 | 365 | 21640 | 18476 | 11102 | 3008 | 8878 |
| Inorganic C | TIC/TOC | 12314 | 8466 | 25400 | 23200 | 20720 | 32960 | 23020 |
| Formate | IC | <100 | <100 | 12207 | 10184 | 6504 | 1322 | 3746 |
| Oxalate | IC | 160 | <100 | 619 | 572 | 391 | 253 | 226 |
| Citrate | IEC | NBLR | NBLR | 7925 | 6260 | 4782 | 234 | 1800 |
| Glycolate | IEC | 1290 | 1222 | 18225 | 15283 | 9384 | 1994 | 6706 |
| Formate | IEC | 916 | 968 | 10920 | 9198 | 6107 | 1581 | 4547 |
| Acetate | IEC | NBLR | NBLR | 1267 | 1193 | 1087 | NBLR | NBLR |
| HEDTA | IPC | NM | NM | 10749 | 8629 | 5502 | 1033 | 4231 |
| EDTA | IPC | NM | NM | 2109 | 1653 | 938 | 248 | 806 |

[a] NBLR = not baseline resolved during IEC analysis.

[b] NM = not measured.

### 3.3.1. Full-strength Envelope Mixing Experiment

#### 3.3.1.1. AZ-101 and AN-107 Full Strength Mixtures

During the first 30 days, 30 times more precipitates formed in the 10/90 mixture (~500 NTU) than in either control, 100% AZ-101 (14 NTU: Figure 4) or 100% AN-107 (17 NTU; Figure 6). This suggests that the increase in turbidity was the result of new precipitates forming, as opposed to the sum of the precipitates of the two pure simulants.

There was a profound difference in the type of solids formed in the 50/50 and 10/90 mixtures. XRD analysis (which has a detection limit of about 2- wt %) indicated that the 50/50 mixture solids were non-crystalline. The solids also had a somewhat darker coloration than those formed in the 10/90 mixture. EDX analyses indicated the 50/50 solids contained appreciable amounts of iron, manganese, and oxygen (Figure 7 and Figure 8), likely primarily as hydroxide phases. Al, C, Ca, Cl, K, Mg, Na and Pb were present in these solids in lower concentrations. In the 10/90 mixture, XRD analysis indicated that the primary solids formed were similar to those formed in 100% AN-107 alone, namely $NaNO_3$, $NaNO_2$, and $Na_3H(CO_3)_2\text{-}x(H_2O)$ (Figure 6). $NaAl(CO_3)(OH)_2$, formed in the 10/90 mixture, but not in the 100% AN-107 simulant. No sodium oxalate was detected in these samples. The XRD spectra associated with these results are included in Appendix B.

OLI thermodynamic calculations of the solids that would form in these mixtures were conducted using the solution compositions presented in Appendix C. In general, the OLI calculations tended to predict that more different types of solids would precipitate than was detected by XRD (Table 14). In addition, the solids detected by XRD were generally among the list of solids OLI predicted would precipitate. Differences between observed and calculated results could be caused by: 1) XRD having a detection limit of a couple weight percent, thereby not detecting solids existing at concentrations below this rather high limit, 2) the experimental system not being at true equilibrium, the basis of OLI calculations, 3) OLI constants used to predict the solids were incorrect, and 4) an experimental artifact introduced when the entrained liquid in the solids collected on the filters were air-dried, thereby permitting evaporates to form. Regarding the fourth cause, $NaNO_2$ detected by XRD, but not predicted to form by OLI, is very likely an evaporate (Table 14).

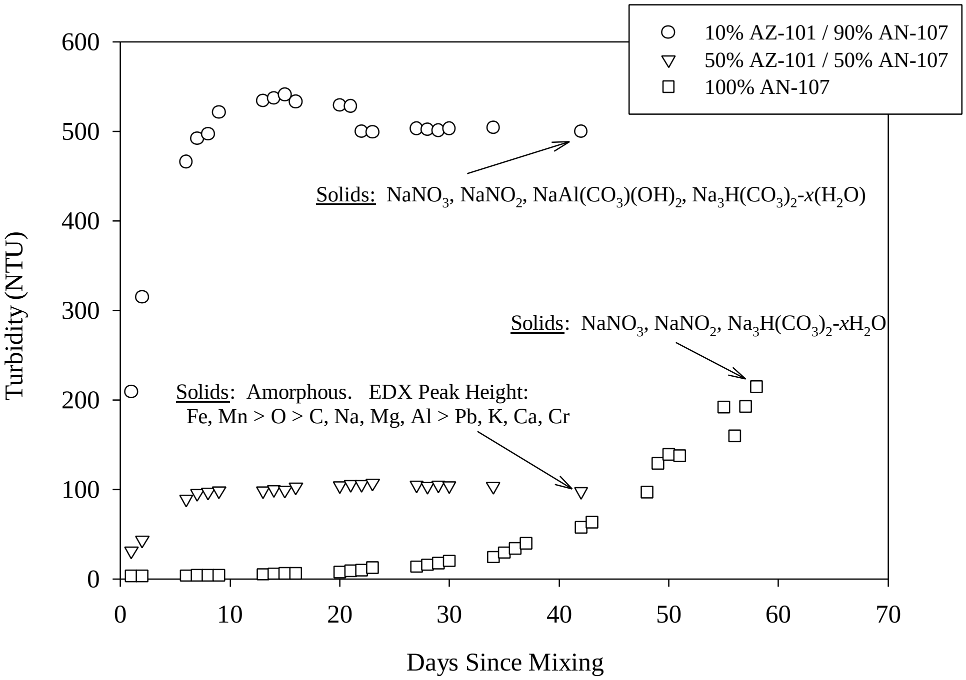

**Figure 7.** Turbidity and Solid Phases Based on XRD and SEM in Mixtures of AZ-101 and AN-107.

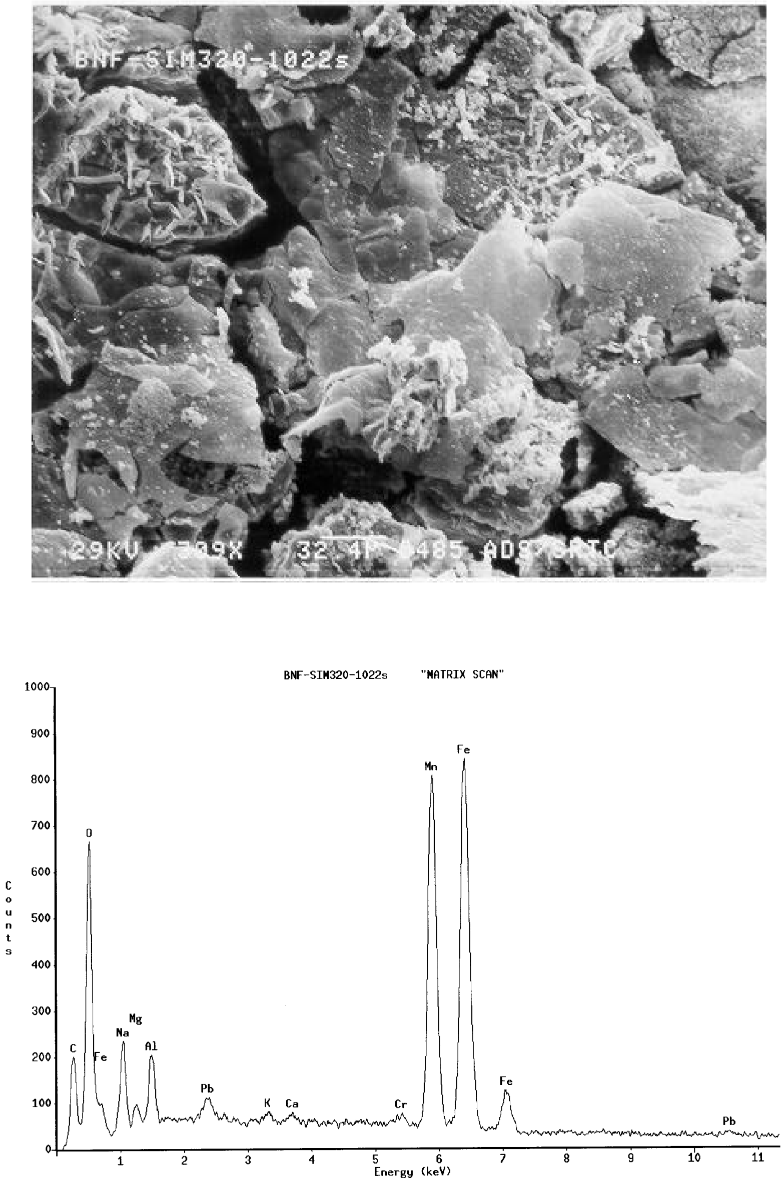

**Figure 8.** SEM image and EDX spectrum of solids recovered at the end of the 50% AZ-101 / 50% AN-107 mixtures. The scale bar in the SEM image represents 32.4-µm. The EDX spot size was about the same as the entire SEM image, thus it represents an average.

**Table 14.** Comparison of the Solids Identified by XRD and those Predicted by OLI in Suspension of Simulant AZ-101 and AN-107.

| Simulant | OLI Precipitate | | XRD Precipitates | Identified by OLI and XRD |
|---|---|---|---|---|
| 100% AZ-101 | $NaHCO_3$ | | Not Determined | |
| | $CaF_2$ | | | |
| | $FePO_4$ | | | |
| | **TOTAL** | | | |
| | | | | |
| 10% AZ-101 & 90% AN-107 | $Fe(OH)_3$ | | $NaNO_3$ | Yes |
| | NaF | | $NaNO_2$ | No |
| | $NaHCO_3$ | | $NaAl(CO_3)(OH)_2$ | Yes |
| | $NaNO_3$ | | $Na_3H(CO_3)_2\text{-}xH_2O$ | Yes (~$NaHCO_3$) |
| | $Ni(OH)_2$ | | | |
| | $CaF_2$ | | | |
| | $NaAlCO_3(OH)_2$ | | | |
| | $Ni_3(PO_4)_2$ | | | |
| | $NiCO_3$ | | | |
| | **TOTAL** | | | |
| | | | | |
| 100% AN-107 | $NaNO_3$ | | $NaNO_3$ | Yes |
| | $NaHCO_3$ | | $NaNO_2$ | No |
| | NaF | | $Na_3H(CO_3)_2\text{-}xH_2O$ | Yes (~$NaHCO_3$) |
| | $NaFSO_4$ | | | |
| | $Fe(OH)_3$ | | | |
| | $PbCO_3$ | | | |
| | **TOTAL** | | | |

#### 3.3.1.2. AN-104 and AN-107 Full Strength Mixtures

During the first 30 days, there was essentially no turbidity (<14 NTU) in the 100% AN-107 (Figure 2) and 100% AN-104 (Figure 6) suspensions. During this same duration, the 50/50 mixture had a turbidity of 110 NTU and the 10/90 mixture had a turbidity of 180 NTU (Figure 9). Since the turbidity values of the mixtures were appreciably greater than the controls, new precipitates must have formed. In support of this observation, Lumetta et al. (2000) reported a significant amount of precipitates formed when AN-107 was mixed with AW-101 at a ratio of 3:30, respectively.

After 60 days, the turbidity in the 100% AN-104 solution was 6.2 NTU (Figure 2), whereas the turbidity in the 100% AN-107 was 200 NTU (Figure 9). At this same time, the 10% AN-107 / 90% AN-104 mixture had approximately as much turbidity as the 100% AN-107 suspension. The different shapes of the turbidity curves suggest that the precipitates in these suspensions originated from different processes and that the solids in the 10/90 mixtures were not simply those from the AN-107 suspension. However, comparison of the XRD patterns suggests that similar solids precipitated from solution: $NaNO_3$, $NaNO_2$, and $Na_3H(CO_3)_2{\cdot}xH_2O$ (Appendix B). Trace amounts of dawsonite, $NaAl(CO_3){\cdot}2H_2O$, was detected in the 10/90 mixture, but not in the 100% AN-107 suspension. Conversely, trace amounts of $Na_2CO_3{\cdot}3H_2O$ was detected in the 100% AN-107 suspension, but not in the 10/90 mixture.

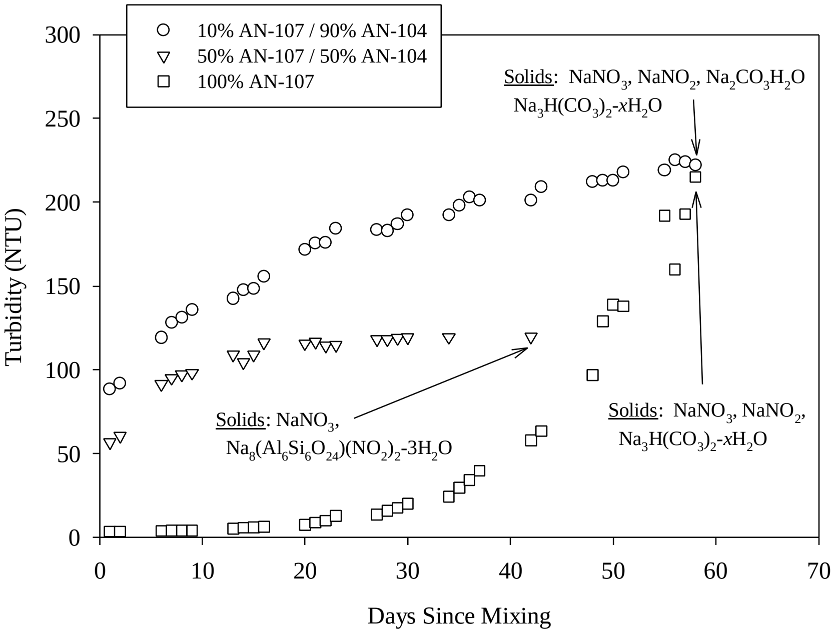

**Figure 9.** Turbidity and solid phases based on XRD and SEM in Mixtures of AN-107 and AN-104.

Only a fraction of the precipitates predicted by OLI to form in the 10/90 mixture was detected by XRD (Table 15). As was observed with the AW-101/AN-107 mixture, $NaNO_2$ was detected by XRD but was not predicted by OLI. Some of the reasons for this apparent discrepancy are discussed above.

**Table 15**. Precipitates Identified by XRD Analyses of 0.45-um Filtrates and by OLI Simulations: AN-104 and AN-107 Mixture.

| **Simulant** | **OLI Precipitate** | | **XRD Precipitates** | **Identified by OLI and XRD** |
|---|---|---|---|---|
| 100% AN-104 | $NaAlCO_3(OH)_2$ | | Not Measured | |
| | $Al(OH)_3$ | | | |
| | $CaCO_3$ | | | |
| | $BaSO_4$ | | | |
| | | | | |
| 10% AN-107 & 90% AN-104 | $Fe(OH)_3$ | | $NaNO_3$ | Yes |
| | $CaF_2$ | | $NaNO_2$ | No |
| | $NaAlCO_3(OH)_2$ | | $Na_2CO_3$-$H_2O$ | Yes (~$NaHCO_3$) |
| | $PbCO_3$ | | $NaH(CO_3)_2$-$xH_2O$ | Yes (~$NaHCO_3$) |
| | $Ni_3(PO_4)_2$ | | | |
| | $NaNO_3$ | | | |
| | $NaHCO_3$ | | | |
| | | | | |
| 100%AN-107 | $NaNO_3$ | | $NaNO_3$ | Yes |
| | $NaHCO_3$ | | $NaNO_2$ | No |
| | NaF | | $Na_3H(CO_3)_2$-$xH_2O$ | Yes (~$NaHCO_3$) |
| | $NaFSO_4$ | | | |
| | $Fe(OH)_3$ | | | |
| | $PbCO_3$ | | | |

### 3.3.2. Dilute Envelope Mixing Experiment

These tests were conducted because no turbidity was visually observed (no turbidity meter was used in the hot cells) when active feed samples were mixed, contrary to the results from the simulant mixing study and those of Lumetta et al (2000). Initially, this inconsistency was believed to be due to differences in feed concentrations; the simulants were more concentrated than the active feed samples. Mixing tests were conducted with simulants that were diluted to the same sodium molar concentrations as the corresponding active feed samples, as described in Table 16 and Table 17. The dilute feed solutions were combined in the same ratios as were used in the active mixing study, i.e., 3/30 on a volume basis. The chemical composition of <0.45-μm filtrates at the end of the 30-day equilibrium period is presented in Table 18 and Table 19. Unfortunately, there was no corresponding concentration data for the active mixtures reported by Hassan et al. (2000).

**Table 16.** Active and Simulant Feed Sodium Concentrations.

| Active Feed | Envelope | Measured Na Concentration (M) |
|---|---|---|
| AN-103 | A | 5.25 |
| AZ-102 | B | 3.16 |
| AN-102 | C | 5.98 |
| | | |
| **Simulant Feed** | **Envelope** | **Measured Na Concentration (M)** |
| AN-107 [a] | C | 8.2 |
| AN-104 [a] | A | 7.3 |
| AW-101 | A | 6 |
| AZ-102 [a] | B | 2.5 |
| AZ-101 | B | 4.7 |

[a] Simulant feeds used in Dilute Envelope Mixing study. Simulants were diluted with water to have similar Na concentrations to corresponding active feed.

**Table 17.** Simulant Dilutions for Dilute Envelope Mixing Study.

| Simulant | Envelope | Final Na Concentration (M) | % of Original Simulant Feed Solution |
|---|---|---|---|
| Dilute AN-107 | C | 5.98 | 73 |
| Dilute AN-104 | A | 5.25 | 72 |
| Dilute AW-101 | A | 5.25 | 88 |
| Dilute AZ-102 | B | 2.65 | 100 |

**Table 18.** Chemical Composition of Selected Filtrates from Dilute Envelope Mixing Study: ICP-ES (mg/L).

| **Solution Description** | **9% dil. AN-107 91% dil. AN-104** | **9% dil. AN-107 91% dil. AW-101** | **9% dil. AN-107 91% dil. AZ-102** |
|---|---|---|---|
| Al | 9970 | 8860 | 232 |
| B | 20 | 2.7 | 7.8 |
| Ba | 0.027 | <0.012 | 0.06 |
| Ca | 8.6 | 8.0 | 12.0 |
| Cd | <0.014 | <0.014 | 0.028 |
| Co | <0.044 | <0.044 | <0.044 |
| Cr | 128 | 43.0 | 812 |
| Cu | 1.7 | 1.7 | 2.1 |
| Fe | 22.6 | 24 | 67 |
| La | 1.2 | 1.4 | 1.9 |
| Li | <0.1 | <0.1 | <0.1 |
| Mg | <0.084 | <0.084 | 0.10 |
| Mn | 2.1 | 2.0 | 11.8 |
| Mo | 30 | 2.3 | 56 |
| Na | 111343 | 116980 | 69381 |
| Ni | 34 | 34 | 44 |
| P | 272 | 278 | 180 |
| Pb | 27 | 50 | 23.7 |
| Si | 91 | 79 | 104 |
| Sn | <0.26 | <0.26 | <0.26 |
| Sr | 0.07 | 0.10 | 0.10 |
| Ti | <0.14 | <0.14 | <0.14 |
| V | <0.13 | <0.13 | <0.13 |
| Zn | 4.7 | 14 | 2.8 |
| Zr | 2.0 | 2.3 | 2.3 |
| S | 1573 | 650 | 5280 |

**Table 19.** Chemical Composition of Selected Filtrates from Dilute Envelope Mixing Study: Other Methods (mg/L).

| | **Analytical Method** | **9%dilAN-107 91%dilAN-104** | **9%dilAN-107 91%dilAW-101** | **9%dilAN-107 91%dilAZ-102** |
|---|---|---|---|---|
| Chloride | IC | 4061 | 3530 | 1825 |
| Fluoride | IC | 193 | 245 | 1054 |
| Nitrate | IC | 79490 | 110019 | 34595 |
| Nitrite | IEC/IPC | 39989 | 48185 | 34200 |
| Phosphate | IC | 844 | 867 | 776 |
| Sulfate | IC | 5590 | 1921 | 16166 |
| K | AA | 2405 | 15881 | 3033 |
| Free OH (molarity) | Titration | 0.8612 | 1.1706 | 0.0714 |
| Organic C | TIC/TOC | 1009 | 2448 | 2256 |
| Inorganic C | TIC/TOC | 23180 | 23480 | 15340 |
| Formate | IC | 945 | 898 | 902 |
| Oxalate | IC | 153 | 33 | 2641 |
| Citrate | IEC | NBLR | NBLR | NBLR |
| Glycolate | IEC | 1290 | 1222 | 1269 |
| Formate | IEC | 916 | 968 | 743 |
| Acetate | IEC | NBLR | NBLR | 507 |
| HEDTA | IPC | 665 | 692 | 757 |
| EDTA | IPC | 185 | 158 | <100 |

There was essentially no turbidity (<3 NTU) in the dilute AN-104, dilute AN-107, and dilute AW-101 simulants. However, once these dilute simulants were mixed together, the turbidity increased appreciably (Figure 10, Figure 11, and Figure 12). For the AN-107/AN-104 mixture, there was more turbidity in the dilute 9/91 mixture than in the corresponding full-strength 10/90 mixtures after the 30-day equilibration period. After 30-days, the dilute 9% AN-107 / 91% dilute AN-104 suspension had a turbidity of ~400 NTU; the full-strength 10% AN-107 / 90% AN-104 had a turbidity of 180 NTU. The cause for this is not known. One possible explanation for this chemical behavior is that the solids formed in this mixture were from Herting's Category II constituents. Herting (1998) organized all tank waste constituents into four categories. Solids associated with constituents in Category II, which included calcium, cadmium, iron, manganese, nickel uranium, zirconium and strontium, tend to increase upon envelope dilution. The cause for this chemical behavior is that the solids containing these constituents dissolve upon dilution, thereby increasing their aqueous concentration. However, the fact that the envelopes did not show an increase in turbidity upon dilution (Figure 2 and Figure 6) is somewhat inconsistent with this explanation.

Although no XRD-detectable crystalline material was identified in the solids generated from the dilute AN-107/AN-104 mixture, some crystalline material was evident in the SEM images (Figure 14). The crystalline material tended to be rich in Mn, Fe, and O. The more abundant amorphous materials consisted primarily of Na and O, with lesser concentrations of C, Al, Mn, and Fe. (Note that SEM concentrations of carbon are not highly reliable due to the need to coat the samples with graphite to allow conduction of electrons.)

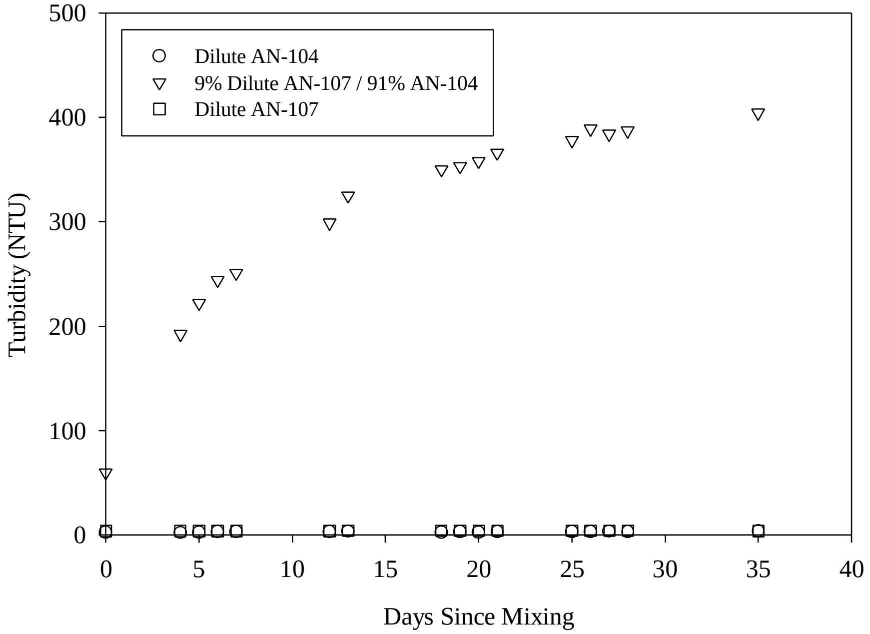

**Figure 10.** Turbidity in Dilute AN-107, Dilute AN-104, and a 9% AN-107 & 91% AN-104 Mixture.

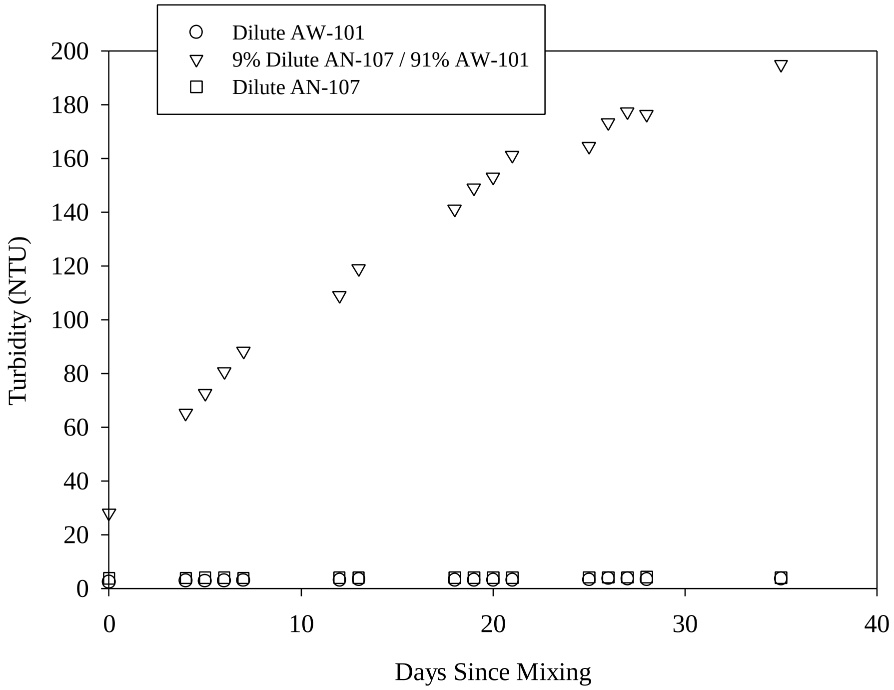

**Figure 11.** Turbidity in Dilute AN-107, Dilute AW-101, and a 9% AN-107 & 91% AW-101 Mixture.

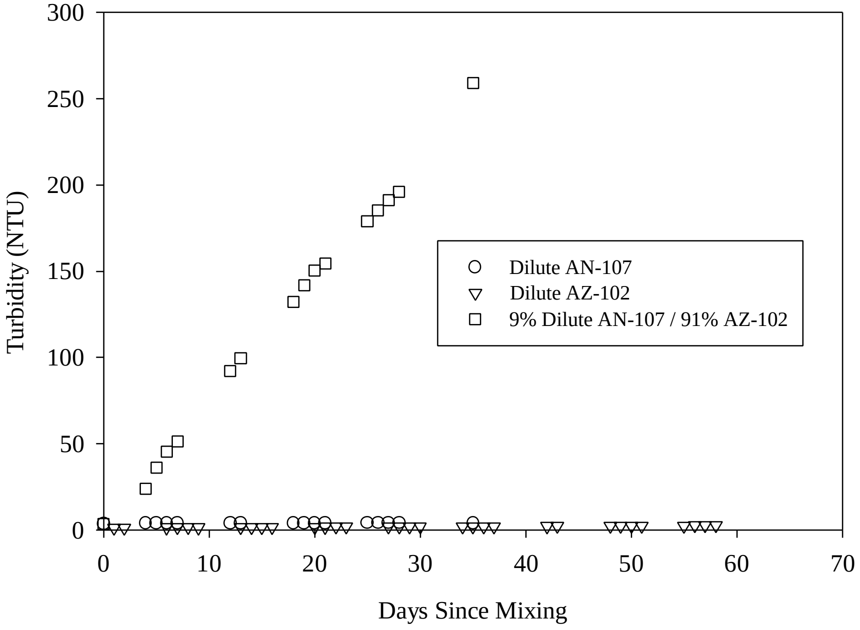

**Figure 12.** Mixture of Dilute AN-107 and Dilute AZ-102.

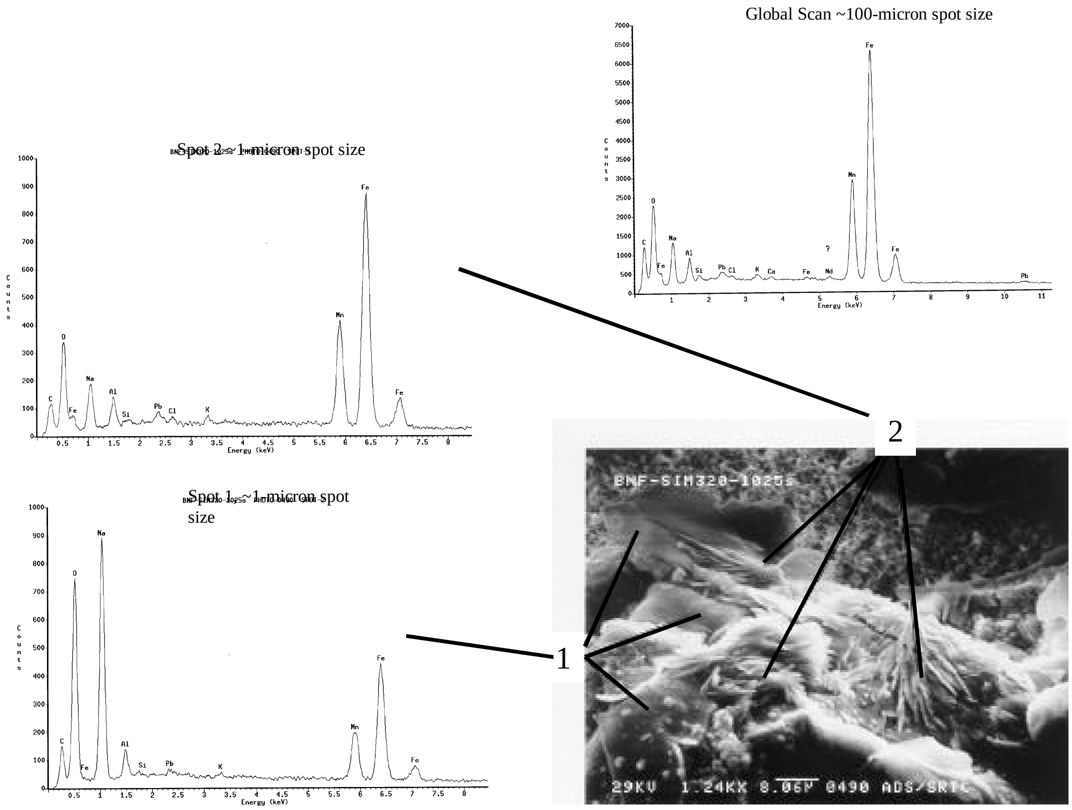

**Figure 13.** SEM image and corresponding EDX spectra of 9% dilute AN-107 / 91% dilute AN-104. Spot 1 is an EDX spectrum taken of large amorphous particles. Spot 2 is an EDX spectrum taken of crystalline particles. A third EDX spectrum is presented of a large spot size, which provides an average elemental composition of several particles.

## 3.4. *Hydroxide-Concentration Experiment*

The hydroxide–concentration experiment varied the concentration of hydroxide from pH 10 to pH 14.5, or over a range of 4.5 orders of magnitude. The experimental design is described in detail in Section 2.4 and in Table 1. The individual test solutions were placed in 250 mL polypropylene bottles and were agitated on an Innova 2300 platform shaker at 80 revolutions per minute. The experiment was run under ambient laboratory temperature. The mean temperature during the monitoring period was 20.8 ± 0.1 °C. The detailed temperature data for this study is presented in Appendix A. The pH was adjusted with either concentration $HNO_3$ or NaOH.

### 3.4.1. Titration Basis for pH Adjustment

Due to the problematic nature of measuring pH in high ionic strength solutions, directly titrating the simulant feeds was not used to adjust the hydroxide concentrations for this experiment. Instead, a measured volume of the feed was diluted with 60 mL of water and titrated with hydrochloric acid using a Mettler DL40GP MemoTitrator and a glass pH electrode calibrated for pH 10. The diluted feed was titrated to a pH of 10. No adjustment of the titration endpoint was made since titration to a pH less than 10 would begin to include significant effects from carbonate, phosphate and other anions. Results of the titrations are listed in Table 20. The column labeled "Used" is the value used to determine the amount of nitric acid or sodium hydroxide to add to each experiment. The samples used for titrations were collected after the feed stability period was complete and correspond with the compositions reported in the simulant formulation portion of this report.

**Table 20.** Titration Results for Simulants.

| | **Sample Vol.**[a] | **Sample 1** | **Sample 1** | **Sample 2** | **Sample 2** | **Average** | **Used** |
|---|---|---|---|---|---|---|---|
| **Feed** | **mL** | **mL 0.1181 M HCl** | **Moles/L** | **mL 0.1181 M HCl** | **Moles/L** | **Moles/L** | **Moles/L** |
| AN-107 | 2 | 5.95 | 0.351 | 6.07 | 0.358 | 0.355 | 0.357 |
| AW-101 | 0.2 | 3.41 | 2.014 | 3.35 | 1.978 | 1.996 | 2.007 |
| AN-104 | 0.2 | 2.835 | 1.674 | 2.77 | 1.636 | 1.655 | 1.665 |
| AZ-101 | 2 | 7.175 | 0.424 | 7.04 | 0.416 | 0.420 | 0.42 |
| AZ-102 | 2 | 5.09 | 0.301 | 4.985 | 0.294 | 0.297 | 0.297 |
| C-106 Leachate | 0.2 | 4.175 | 2.465 | 4.16 | 2.456 | 2.461 | |
| AZ-102 Leachate | 0.2 | 2.68 | 1.583 | 2.585 | 1.526 | 1.554 | |

[a] Sample volume diluted to 60-mL with water.

The titration curve for sample 1 of the AN-107 feed simulant is shown in Figure 14. The curve demonstrates that the feed contains very little free hydroxide and has more of the behavior of a weak base titration curve. In contrast, the titration curves for AN-104, AW-101, and AZ-101, which are displayed in Figure 15, Figure 16, and Figure 17 respectively, are curves for a strong base titration. The final titration curve, AZ-102, (Figure 18) appears to be intermediate in its buffering capacity. The pH levels of the starting solutions are reported in these figures as the pH for the titrations where 0-mL of HCl was added.

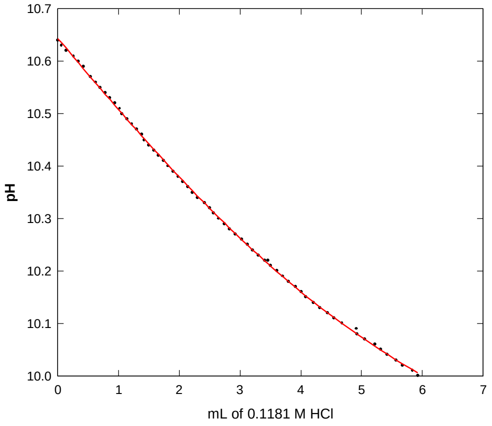

**Figure 14.** Titration Curve for AN-107.

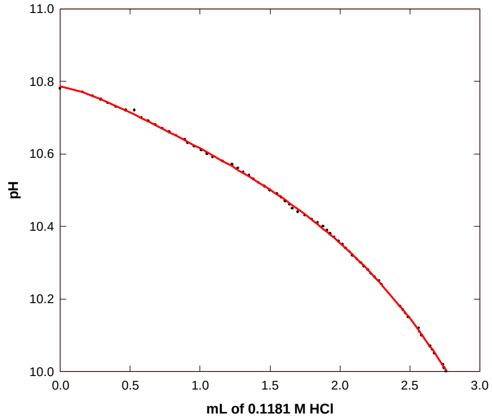

**Figure 15.** Titration Curve for AN-104.

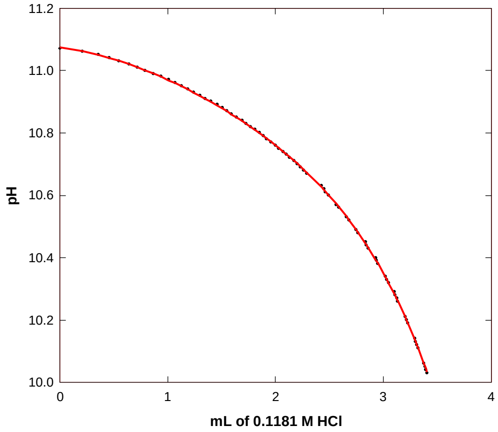

**Figure 16.** Titration Curve for AW-101.

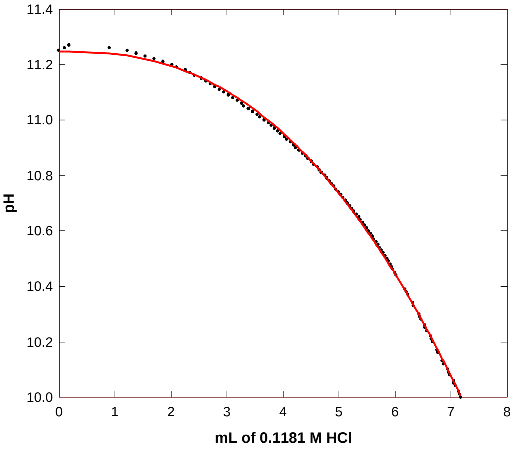

**Figure 17.** Titration Curve for AZ-101.

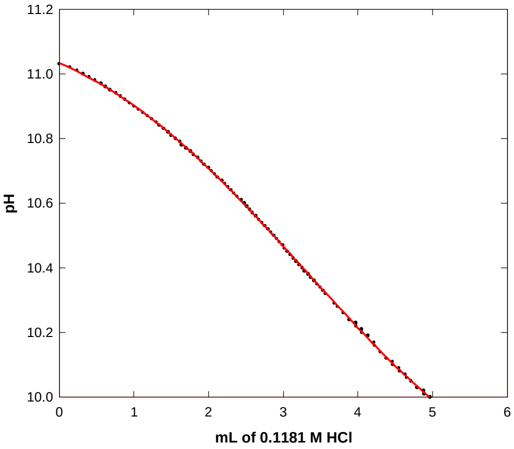

**Figure 18.** Titration Curve for AZ-102.

On a theoretical basis, the amount of acid required to titrate a 1-molar NaOH solution to pH 11 is 99.9 % of the amount to reach pH 10. However, after reviewing the titration curves for all of the feeds, the amount of acid to add to produce the "pH 11" experiments was set at 95% of the total base equivalents. Based on the preliminary titration data, Table 21 specifies the number of moles of nitric acid or sodium hydroxide per liter of feed to add to achieve the different pH goals. The acid or base was added using a transfer pipette while agitating the feed. Nitric acid is added as reagent grade $HNO_3$, 70 weight percent. The pH 14.5 experiment can also be expressed as pOH of –0.5 and is equivalent to a hydroxide concentration of 3.16 molar. For the pH 14.5 test, the sodium hydroxide was added as a 50 weight percent solution to minimize dilution of the feed. Since the AN-107 feed is already below pH 13, NaOH was added to raise the hydroxide concentration to 0.1 molar.

**Table 21.** Based on Preliminary Titration Experiments, Amount of Nitric Acid (70 %) or Sodium Hydroxide (50 wt-%) Required to Adjust pH of Simulants.

| **Feed** | **Base Equivalents** | **$HNO_3$ Added for pH 10** | **$HNO_3$ Added for pH 11** | **$HNO_3$ Added for pH 13** | **NaOH Added for pH 14.5** |
|---|---|---|---|---|---|
| | **(Mol/L)** | **(Mol/L)** | **(Mol/L)** | **(Mol/L)** | **(Mol/L)** |
| AN-107 | 0.357 | 0.357 | 0.33915 | (a) | 3.16 |
| AN-104 | 1.665 | 1.665 | 1.58175 | 1.5 | 1.495 |
| AW-101 | 2.007 | 2.007 | 1.90665 | 1.8 | 1.153 |
| AZ-101 | 0.42 | 0.42 | 0.399 | 0.32 | 2.74 |
| AZ-102 | 0.297 | 0.297 | 0.28215 | 0.197 | 2.863 |

(a) Added 0.1 moles of NaOH instead of Nitric Acid since AN-107 should be less than pH 13.

### 3.4.2. pH Adjustment of AN-107 Simulant

The addition of nitric acid to the AN-107 feed was observed to produce bubbles and a brown gas. The gas is assumed to be $NO_x$ formed from the nitrite anion due to high-localized acid concentrations. More effective mixing might mitigate this gas evolution. Immediate formation of solids was not observed. Addition of NaOH did not produce any observable gas.

Figure 19 displays the result of monitoring turbidity for the pH adjusted AN-107 simulant. Immediate formation of white solids was observed in the targeted pH 10 and 11 bottles.[2] These solids may have redissolved since significant turbidity was not observed until the seventh day after adjustment. As indicated in Figure 19, the pH 14.5

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[2] Final pH levels of the pH-adjusted solutions were not measured because of the analytical problem associated with making this measurement in high ionic strength solutions. Throughout this report, we refer to the various treatments by their targeted pH levels, e.g., pH 10, 11, 13, and 14.5.

(high hydroxide) test had formed solids by day 5. These solids were clearly different from the low hydroxide solids and tended to be thick and gelatinous. The gelatinous solids were difficult to sample and tended to plug the pipette tip. Figure 20 is a photograph of the test solutions and clearly shows the solids at the bottom of the pH 10 and 11 tests. The gelatinous solids in the pH 14.5 test are barely visible in Figure 20 as a darker layer in the bottom third of the solution.

After completion of the turbidity monitoring, the test solutions were passed through a 0.45-μm nylon filter and the supernate chemically characterized (Table 22). As expected, the free hydroxide value for the pH 10 and 11 tests is below detection limit, whereas the pH 13 value is near 0.1-M and the pH 14.5 value is >2-M. The only component concentrations that declined in the acid adjusted tests was Ca and possibly $Al(OH)_4^-$. However, Al by ICP-ES remained constant. The declines in concentration observed for the hydroxide-added test were Fe, Mn, and possibly Ni and $PO_4^{3-}$. The amount of nitrite consumed during acid addition, presumably as $NO_x$, was too small to be detected by chemical analysis.

**Table 22.** Composition of pH-Adjusted AN-107 Simulant.

| Tank Components | Units | Feed Found | pH 10 Found | pH 11 Found | pH 13 Found | pH 14.5 Found | Analysis Method |
|---|---|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | NA[a] | NA | NA | NA | ICP-ES |
| Al | mg/L | 194 | 195 | 197 | 198 | 199 | ICP-ES |
| B | mg/L | 38 | 39 | 39 | 39 | 35 | ICP-ES |
| Ba | mg/L | 0.17 | 0.24 | 0.26 | 0.24 | 0.47 | ICP-ES |
| Ca | mg/L | 138 | 94 | 95 | 140 | 129 | ICP-ES |
| Cd | mg/L | <0.02 | <0.014 | <0.014 | <0.014 | <0.014 | ICP-ES |
| Ce | mg/L | 50.2 | NA | NA | NA | NA | ICP-ES |
| Co | mg/L | 0.39 | <0.044 | <0.044 | <0.044 | <0.044 | ICP-ES |
| Cr | mg/L | 148 | 157 | 158 | 158 | 134 | ICP-ES |
| Cs | mg/L | 22.3 | NA | NA | NA | NA | ICP-ES |
| Cu | mg/L | 32 | 33 | 33 | 33 | 29 | ICP-ES |
| Fe | mg/L | 1623 | 1721 | 1720 | 1740 | 1210 | ICP-ES |
| K | mg/L | 1921 | 2021 | 1984 | 1995 | 1810 | AA |
| La | mg/L | 40 | 42 | 42 | 43 | 34 | ICP-ES |
| Mg | mg/L | 20 | 19 | 20 | 20 | 2 | ICP-ES |
| Mn | mg/L | 564 | 585 | 585 | 592 | 304 | ICP-ES |
| Mo | mg/L | 36 | 38 | 38 | 38 | 35 | ICP-ES |
| Na | mg/L | 188170 | 192899 | 200922 | 195174 | 222725 | ICP-ES |
| Na | mg/L | 201400 | NM | NM | NM | NM | AA |
| Nd | mg/L | 84.4 | NA | NA | NA | NA | ICP-ES |
| Ni | mg/L | 501 | 536 | 539 | 535 | 483 | ICP-ES |
| P | mg/L | 420 | 416 | 420 | 425 | 379 | ICP-ES |
| Pb | mg/L | 364 | 402 | 407 | 402 | 322 | ICP-ES |
| Si | mg/L | 1.4 | 1.5 | 1.5 | 1.7 | 6.8 | ICP-ES |
| Sn | mg/L | <0.26 | <0.26 | <0.26 | <0.26 | <0.26 | ICP-ES |
| Sr | mg/L | 1.3 | 1.1 | 1.1 | 1.3 | 1.08 | ICP-ES |
| Ti | mg/L | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 | ICP-ES |
| Zn | mg/L | 44 | 46 | 46 | 46 | 41 | ICP-ES |
| Chloride | mg/L | 1330 | 2530 | 2602 | 2598 | 2434 | IC |
| Fluoride | mg/L | 3430 | 3496 | 3461 | 3493 | 3079 | IC |
| Formate | mg/L | 11232 | 11972 | 11959 | 11727 | 10997 | IC |
| Nitrate | mg/L | 213930 | 254914 | 251910 | 230079 | 202838 | IC |
| Nitrite | mg/L | 57090 | 58290 | 58497 | 59969 | 54777 | IC |
| Oxalate | mg/L | 335 | 491 | 465 | 483 | 459 | IC |
| Phosphate | mg/L | 1500 | 1899 | 1581 | 1587 | 1291 | IC |
| Sulfate | mg/L | 7280 | 8572 | 8355 | 8418 | 7113 | IC |
| TIC | mg/L | 16100 | 19806 | 19180 | 21320 | 22740 | $CO_2$ Evolution |
| TOC | mg/L | 15800 | 20320 | 22340 | 24800 | 33300 | $CO_2$ Evolution |
| Carbonate(TIC) | mg/L | 80439 | 98940 | 95810 | 106500 | 113600 | Calc. from TIC |
| Aluminate | Molar | 0.054 | 0.0295 | <0.002 | 0.022 | 0.0933 | Titration |
| Carbonate | Molar | 1.052 | NM | NM | NM | NM | Titration |
| Free OH | Molar | 0.039 | <0.02 | <0.02 | 0.064 | 2.19 | Titration |

[a] NM = Not Measured; NA = Not Available.

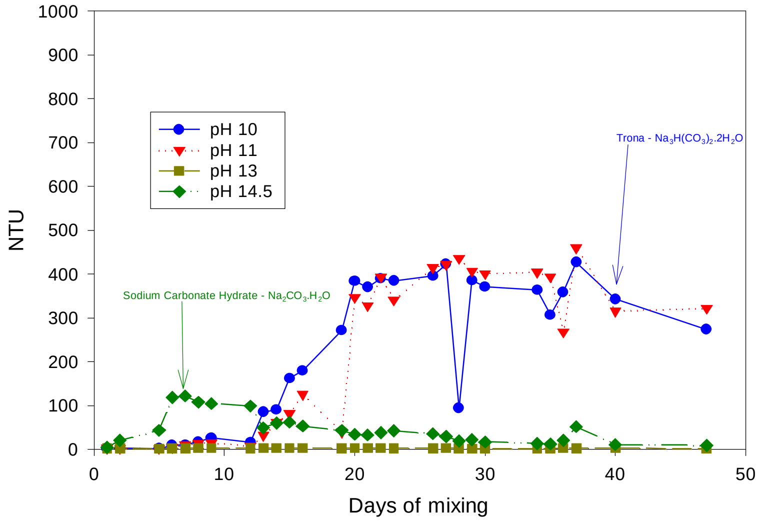

**Figure 19.** Turbidity of pH-Adjusted AN-107 Simulant.

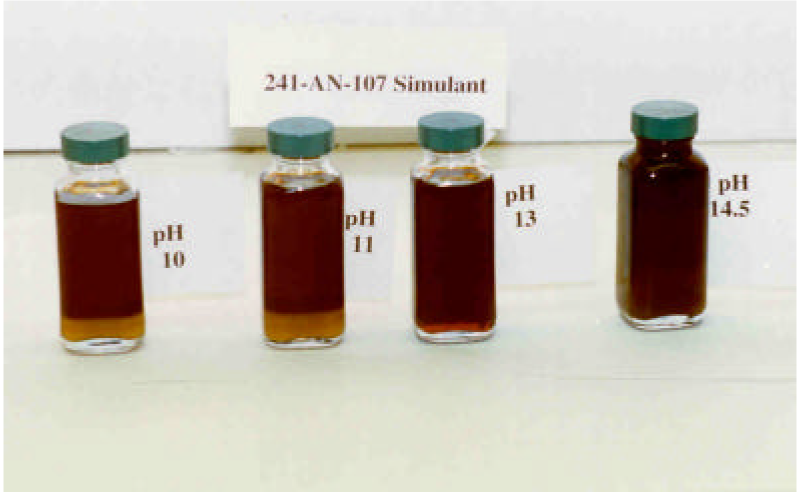

**Figure 20.** AN-107 pH-Adjusted Simulant.

The dried solids from two of the tests, pH 10 and pH 14.5, were submitted for x-ray diffraction analysis (XRD) to identify the solids present. The XRD scan for the acid-adjusted pH 10 test detected the following compounds (see appendix B Figure B13):

trona – $Na_3H(CO_3)_2 \cdot 2H_2O$,
sodium aluminum silicate – $Na_6(AlSiO_4)_6$,
sodium nitrate, and
sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids. The XRD scan for the base-adjusted pH 14.5 test detected the following compounds (see Appendix B Figure B14):

sodium carbonate hydrate – $Na_2CO_3 \cdot H_2O$,
sodium nitrate, and
sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids. Since XRD is dominated by the bulk solids, the lack of identification of Ca, Fe, Mn or $PO_4^{3-}$ species is understandable.

While the addition of only small amounts of hydroxide did not produce solids (pH 13 test), the addition of acid or of molar quantities of hydroxide will produce solids. Table 23 summarizes the observations on pH adjusting AN-107.

**Table 23.** Summary of pH Adjusted AN-107 Observations.

| | | | **Observed** | |
|---|---|---|---|---|
| **Targeted pH** | **Targeted[OH] (M)** | **Measured [OH] (M)** | **Solids** | **Gas** |
| 10 | 0.0001 | <0.01 | Yes | Yes |
| 11 | 0.001 | <0.01 | Yes | Yes |
| 13 | 0.1 | 0.64 | No | No |
| 14.5 | 3.16 | 2.2 | Yes | No |

OLI simulation of the titration is presented in Figure 21. The input chemistry for the AN-107 simulant used in these calculations are presented in Appendix C. The steep slope of the titration curve between 0 and 0.2 mol/L NaOH addition is indicative of the system being very poorly buffered in this relatively narrow range. Outside of this critical range, the simulant appears to be quite well buffered.

A second set of OLI calculations was conducted to provide a comparison with experimental results (insert within Figure 21). The experiments used HCl, instead of

$HNO_3$, as a titrant, to reduce the risk of generating $NO_x$ gases, a potential safety issue. Before discussing the results, some important caveats to this comparison need to be presented. The laboratory titrations were conducted with an equilibration period between each acid addition of generally <15-min. This duration is clearly not long enough for the system to come to equilibrium. Based on turbidity data, some simulants were not at equilibrium even after 60 days. Another important caveat is that a standard pH electrode was used in these studies to provide an estimate of the pH change, and not of the actual pH level. The standard pH electrode cannot accurately measure hydrogen ion activity in high ionic strength solutions, especially at extremely high or low pH levels. However, these measurements were used to provide an indication of the change in pH and to provide some benchmarking, albeit minimal, of OLI. With regards to benchmarking results with OLI, absolute values are certainly less valuable than pH trends.

Rather surprisingly, the pH levels of the experimental and OLI systems were remarkably similar, within 0.4 pH units. However, the trends are quite different; OLI predicts little change in pH, whereas experimental results show a rather large amount of pH change. The solids predicted to precipitate from solution when $HNO_3$ and NaOH are added to AN-107 simulant are presented in Figure 22 and Figure 23.

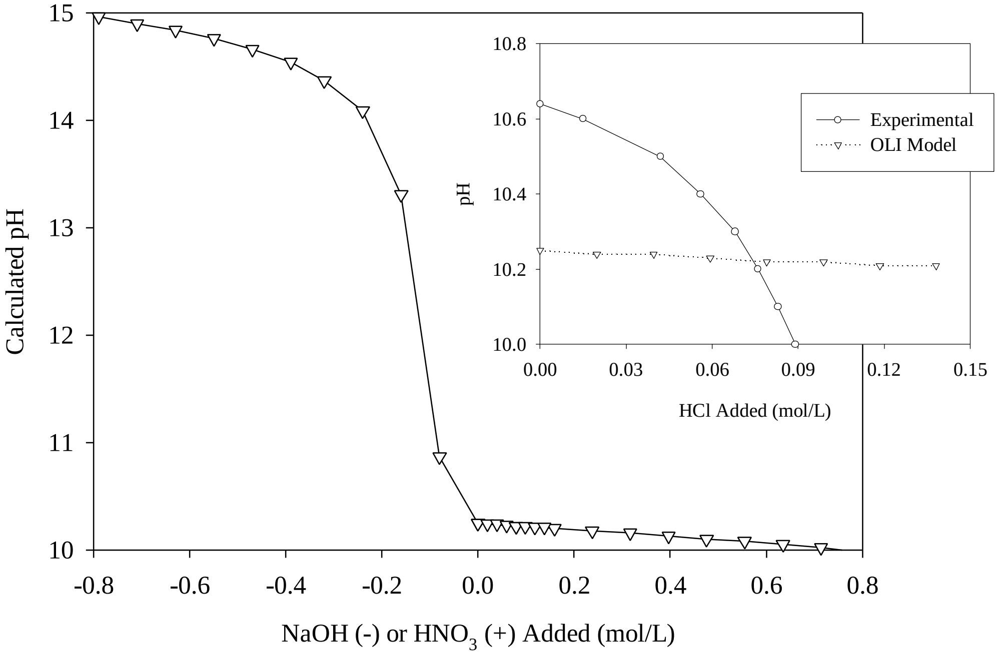

**Figure 21.** OLI Model Results of AN-107 Titration. Insert Compares Experimental (not at Equilibrium) vs. OLI Simulated (at Equilibrium) Results.

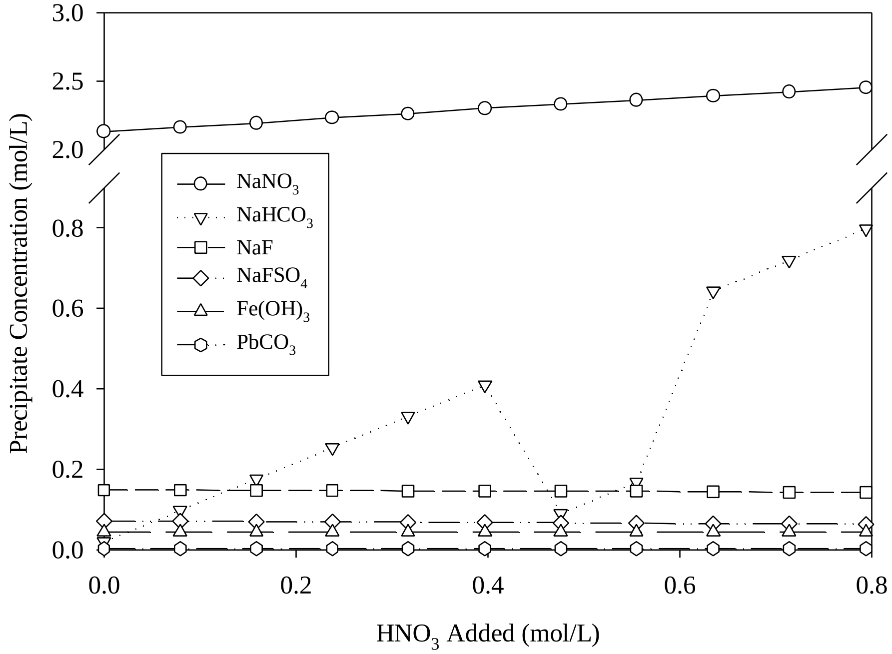

**Figure 22.** Solids Predicted by OLI to Precipitate When Acid is Added to AN-107 Simulant.

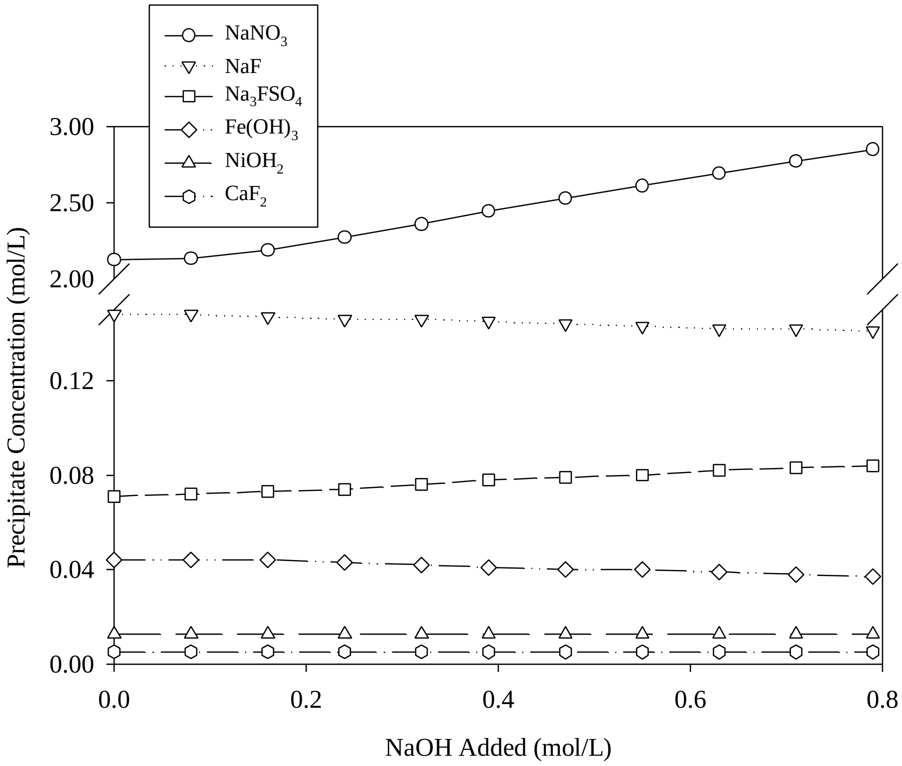

**Figure 23.** Solids Predicted by OLI to Precipitate When NaOH is Added to AN-107 Simulant.

### 3.4.3. pH Adjustment of AN-104 Simulant

The addition of the nitric acid to the AN-104 feed was observed to produce bubbles and a brown gas. The gas is assumed to be $NO_x$ formed from the nitrite anion due to high-localized acid concentrations. More effective mixing might mitigate this gas evolution. Immediate formation of white solids was observed. Addition of sodium hydroxide did not produce any observable gas or solids.

Figure 24 displays the result of monitoring turbidity for the pH adjusted AN-104 simulant. The immediate formation of white solids was observed in the targeted pH 10, 11, and 13 bottles (see footnote 2). These solids after the first few days were observed to settle quickly leading to erratic turbidity readings. This implies that the density and probably the crystallinity of the particles were increasing over time. As indicated in Figure 24, the pH 14.5 (high hydroxide) test did not produce any solids. Figure 25 is a photograph of the test solutions and clearly shows the solids at the bottom of the pH 10 and 11 tests. Only a small amount of solids was present in the pH 13 test and is therefore not clearly visible in Figure 25.

After completion of the turbidity monitoring, the test solutions were filtered using vacuum filtration through a 0.45-micron nylon filter and the supernate submitted for analysis. Table 24 gives the results of the analysis. The filtered solids from the pH 10 experiment were submitted for XRD to identify the solids present. The XRD scan for the acid-adjusted pH 10 test detected the following compounds (see Appendix B, Figure B15):

gibbsite – $Al(OH)_{3,}$
thermonatrite – $Na_2CO_3 \cdot H_2O$,
sodium nitrate, and
sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids. The analysis of the supernate shown in Table 24 confirms the solids characterization since both Al by ICP-ES, $Al(OH)_4^-$ by titration and TIC confirm drops in concentrations for the appropriate metal and anion. The only other components that declined in concentration in the acid adjusted tests were silicon, chloride and nitrite anions, and TOC. The apparent TOC decline may be a poor analysis since almost no organic carbon is in the AN-104 simulant. The decline in nitrite was probably due to the large amount of nitric acid required by the AN-104 simulant (Table 21) as evidenced by the $NO_x$ evolution observed during acid addition. Since XRD is dominated by the bulk solids, the lack of identification of Si or Cl species is understandable.

The most interesting results shown in Table 24 are the free hydroxide results. Nominally, the pH 10, 11, and 13 tests should have had about 0.0001, 0.001 and 0.1 molar free hydroxide levels. Instead, the respective free hydroxide values were 0.83, 0.81 and 0.72 molar. Since the predominant product was the precipitation of gibbsite, $Al(OH)_3$, the following reaction must have occurred:

$$Al(OH)_4^- \longrightarrow Al(OH)_3 + OH^- \qquad (2).$$

As gibbsite slowly precipitates due to the dissociation of the aluminate, free hydroxide is released.

**Table 24.** Composition of pH-Adjusted AN-104 Simulant.

| Tank Components | Units | Feed Found | pH 10 Found | pH 11 Found | pH 13 Found | pH 14.5 Found | Analysis Method |
|---|---|---|---|---|---|---|---|
| Ag | mg/L | <0.03 | NM[a] | NM | NM | NM | ICP-ES |
| Al | mg/L | 16952 | 6920 | 7230 | 16700 | 17700 | ICP-ES |
| B | mg/L | 33 | 31 | 33 | 34 | 32 | ICP-ES |
| Ba | mg/L | 5.6 | <0.04 | 0.05 | 0.11 | 0.23 | ICP-ES |
| Ca | mg/L | 2.8 | <0.04 | 0.4 | 0.9 | 1.9 | ICP-ES |
| Cd | mg/L | <0.02 | <0.014 | <0.014 | <0.014 | <0.014 | ICP-ES |
| Ce | mg/L | <0.7 | NM | NM | NM | NM | ICP-ES |
| Co | mg/L | <0.05 | <0.044 | <0.044 | <0.044 | <0.044 | ICP-ES |
| Cr | mg/L | 204 | 174 | 179 | 179 | 201 | ICP-ES |
| Cs | mg/L | 0.7 | NM | NM | NM | NM | AA |
| Cu | mg/L | 0.14 | <0.05 | <0.05 | <0.05 | <0.05 | ICP-ES |
| Fe | mg/L | 0.31 | 0.38 | 0.14 | 0.23 | 0.76 | ICP-ES |
| K | mg/L | 4320 | 4055 | 4011 | 3941 | 4080 | AA |
| La | mg/L | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | ICP-ES |
| Li | mg/L | 0.26 | 0.12 | 0.11 | <0.1 | 0.12 | ICP-ES |
| Mg | mg/L | <0.09 | <0.084 | <0.084 | <0.084 | <0.084 | ICP-ES |
| Mn | mg/L | <0.009 | 0.024 | <0.009 | <0.009 | 0.07 | ICP-ES |
| Mo | mg/L | 49 | 48 | 51 | 48 | 48 | ICP-ES |
| Na | mg/L | 164670 | 160785 | 157559 | 153602 | 200607 | ICP-ES |
| Na | mg/L | 168200 | NM | NM | NM | NM | AA |
| Nd | mg/L | <0.3 | NM | NM | NM | NM | ICP-ES |
| Ni | mg/L | 0.41 | 2.4 | 2.5 | 2.6 | 2.9 | ICP-ES |
| P | mg/L | 444 | 411 | 443 | 411 | 379 | ICP-ES |
| Pb | mg/L | <0.6 | <0.7 | <0.7 | <0.7 | <0.7 | ICP-ES |
| Si | mg/L | 169 | 77 | 77 | 155 | 160 | ICP-ES |
| Sr | mg/L | 0.09 | <0.002 | 0.006 | 0.05 | 0.09 | ICP-ES |
| Ti | mg/L | 0.15 | <0.14 | <0.14 | <0.14 | <0.14 | ICP-ES |
| Zn | mg/L | 3.4 | <0.37 | <0.37 | <0.37 | 2.8 | ICP-ES |
| Zr | mg/L | <0.05 | <0.05 | 0.16 | 0.11 | 0.05 | ICP-ES |
| Chloride | mg/L | 5861 | 4887 | 4915 | 4902 | 5207 | IC |
| Fluoride | mg/L | <200 | 248 | 249 | 236 | 145 | IC |
| Formate | mg/L | <100 | <100 | <100 | NM | NM | IC |
| Nitrate | mg/L | 85960 | 179766 | 166979 | 165852 | 95374 | IC |
| Nitrite | mg/L | 62530 | 52756 | 50871 | 49066 | 60643 | IC |
| Oxalate | mg/L | 160 | 168 | 178 | 208 | 186 | IC |
| Phosphate | mg/L | 868 | 748 | 764 | 718 | 645 | IC |
| Sulfate | mg/L | 5744 | 6648 | 6660 | 6584 | 6246 | IC |
| TIC | mg/L | 12314 | 8758 | 9239 | 8998 | 11770 | $CO_2$ Evolution |
| TOC | mg/L | 3628 | 586 | 866 | 640 | 396 | $CO_2$ Evolution |
| Carbonate(TIC) | mg/L | 61523 | 43750 | 46150 | 44950 | 58800 | Calc. from TIC |
| Aluminate | Molar | 0.636 | 0.31 | 0.32 | 0.63 | 0.75 | Titration |
| Carbonate | Molar | 0.763 | NM | NM | NM | NM | Titration |
| Free OH | Molar | 1.906 | 0.83 | 0.81 | 0.72 | 2.43 | Titration |

[a] NM = Not Measured.

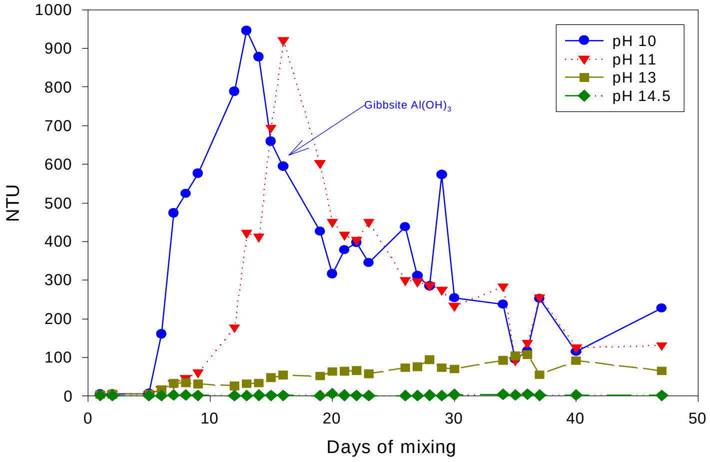

**Figure 24.** Turbidity of pH-Adjusted AN-104 Simulant.

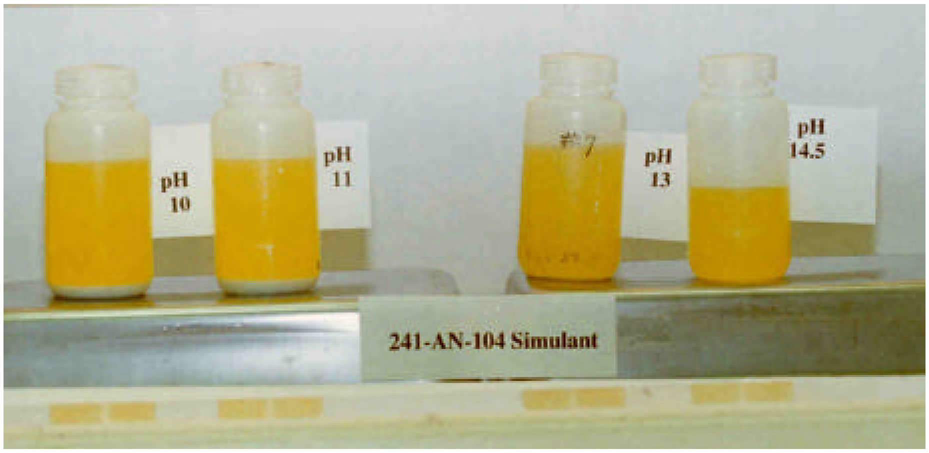

**Figure 25.** pH-Adjusted AN-104 Simulant.

Addition of acid to a high aluminate supernate such as AN-104 will destabilize the aluminate leading to precipitation of gibbsite. Addition of hydroxide to AN-104 does not produce solids. The observations are summarized in Table 25.

**Table 25** Summary of pH-Adjusted AN-104 Observations.

| | | | **Observed** | |
|---|---|---|---|---|
| **Targeted pH** | **Targeted[OH] (M)** | **Measured [OH] (M)** | **Solids** | **Gas** |
| 10 | 0.0001 | ~0.83 | Yes | Yes |
| 11 | 0.001 | ~0.81 | Yes | Yes |
| 13 | 0.1 | ~0.72 | Yes | Yes |
| 14.5 | 3.16 | 2.43 | No | No |

OLI simulated results of titrations of AN-104 are presented in Figure 26 and Figure 27. As was the case in AN-107, AN-104 was poorly buffered in a rather narrow range of HCl additions, between 0.8 and 1.0 $HNO_3$ mol/L (Figure 26). Above this range, the system appears to be very well buffered. OLI and experimental results do not compare favorably. The laboratory titrations were conducted with an equilibration period between each acid addition of generally <15-min. This duration is clearly not long enough for the system to come to equilibration. Based on turbidity data, some simulants were not at equilibrium even after 60 days. Another important caveat is that a standard pH electrode was used in these studies to provide an estimate of the pH change, and not of the actual pH level. The standard pH electrode cannot accurately measure hydrogen ion activity in high ionic strength solutions, especially at extremely high or low pH levels. However, these measurements were used to provide an indication of the change in pH and to provide some benchmarking, albeit minimal, of OLI.

OLI tended to predict a pH more than 2 units greater than the experimental results. In addition, OLI did not capture the experimental pH inflection at 0.09 mol/L HCl added. Only two solid phases were predicted to precipitate from this system upon adding $HNO_3$, $CaCO_3$ and $BaSO_4$ (Figure 27). Concentrations of some solids may have been too low for XRD to detect. The $CaCO_3$ concentration was calculated to exist at ~8e-5 mol/L (0.9 µg/L) and $BaSO_4$ was calculated to exist at ~4e-5 mol/L (0.17 µg/L); both these calculations are below the detection limit of XRD, which is ~2 wt-%. Compared to AN-107, AN-104 contains appreciably lower concentrations of salts, especially of organic carbon salts (Appendix C). Thus, it is not surprising that fewer precipitates were predicted to form.

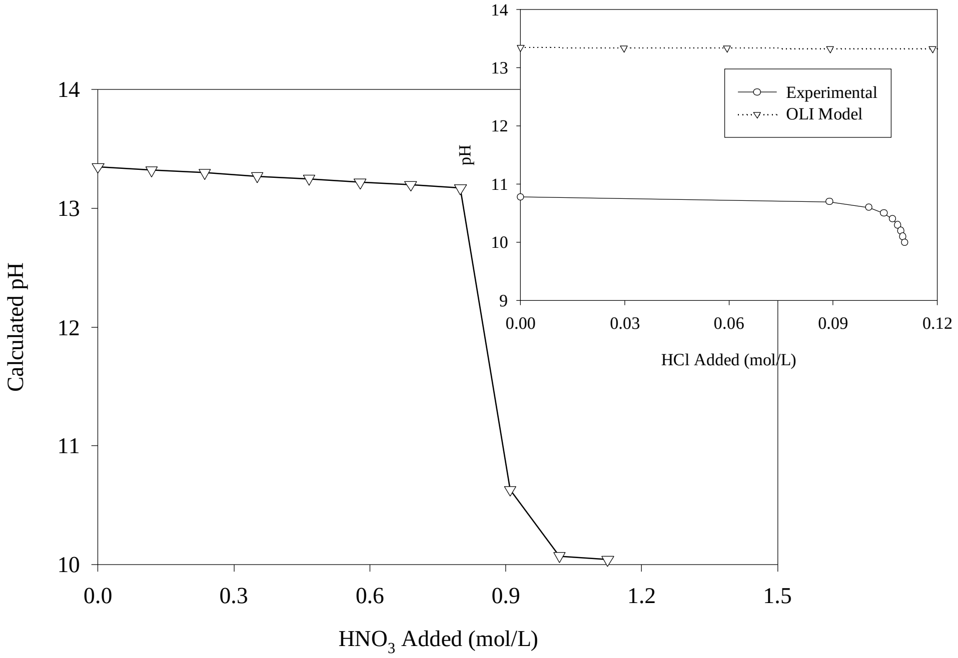

**Figure 26.** OLI Model Results of AN-104 Titration. Insert Compares Experimental (not at Equilibrium) vs. OLI Simulated (at Equilibrium) Results.

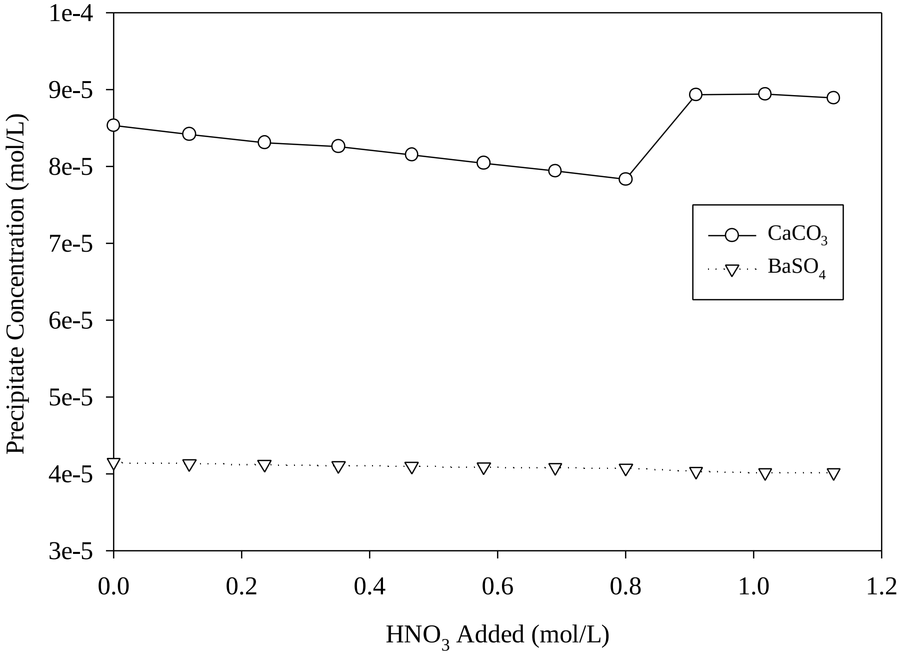

**Figure 27.** Solids Predicted by OLI to Precipitate When Acid is Added to AN-104 Simulant.

### 3.4.4. pH Adjustment of AW-101 Simulant

The addition of the nitric acid to the AW-101 feed was observed to produce bubbles and a brown gas. The gas is assumed to be $NO_x$ formed from the nitrite anion due to high-localized acid concentrations. More effective mixing might mitigate this gas evolution. Immediate formation of white solids during acid addition was observed. Addition of sodium hydroxide did not produce any observable gas or solids.

Figure 28 displays the result of monitoring turbidity for the pH adjusted AW-101 simulant. The immediate formation of white solids was observed in the targeted pH 10, 11, and 13 bottles (see footnote 2). The shape of the curve suggests that solids formation was continuing through the entire monitoring period. The solids after the first few days were observed to settle quickly leading to erratic turbidity readings. This implies that the density and probably the crystallinity of the particles were increasing over time. As indicated in Figure 28, the targeted-pH 14.5 (high hydroxide) test did not produce any solids.

After completion of the turbidity monitoring, the test solutions were filtered using vacuum filtration through a 0.45-micron nylon filter and the supernate submitted for analysis. Table 26 gives the results of the analysis. The filtered solids from the pH 10 experiment were submitted for XRD to identify the solids present. The XRD scan for the acid-adjusted pH 10 test detected the following compounds (see Appendix B, Figure B16):

gibbsite – $Al(OH)_3$,
sodium aluminum,
silicate hydrate – $Na_{96}Al_{96}Si_{96}O_{384}\cdot 216H_2O$,
sodium aluminum silicate hydrate - $Na_2Al_2Si_{2.71}O_{9.42}\cdot 4.39H_2O$,
sodium nitrate, and
sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids. The analysis of the supernate shown in Table 24 confirms the solids characterization since both Al and Si by ICP-ES show decreases in concentrations for the appropriate metal. The only other components that declined in concentration in the acid adjusted tests were sulfate and nitrite anions. The decline in nitrite was probably due to the large amount of nitric acid required by the AW-101 simulant (see Table 21) as evidenced by the $NO_x$ evolution observed during acid addition. Since XRD is dominated by the bulk solids, the absence of peaks corresponding to a sulfate species is surprising. Apparently, the sulfate species was amorphous and did not yield a x-ray pattern.

The most interesting results shown in Table 26 are the free hydroxide results. Nominally, the targeted pH 10, 11, and 13 tests should have had about 0.0001, 0.001 and 0.1 molar free hydroxide levels. Instead the respective free hydroxide values were 0.45, 0.63 and 0.59 molar, respectively. Since the predominant product was the precipitation of gibbsite, $Al(OH)_3$, the previously cited reaction must have occurred:

$$Al(OH)_4^- \longrightarrow Al(OH)_3 + OH^- \qquad (2).$$

As gibbsite slowly precipitates due to the dissociation of the aluminate, free hydroxide is released.

**Table 26.** pH Adjustment Results for AW-101 Simulant.

| Tank Components | Units | Feed Found | pH 10 Found | pH 11 Found | pH 13 Found | pH 14.5 Found | Analysis Method |
|---|---|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | NM[a] | NM | NM | NM | ICP-ES |
| Al | mg/L | 12150 | 10870 | 10917 | 10850 | 11760 | ICP-ES |
| B | mg/L | <0.21 | 0.7 | 0.28 | 0.32 | 0.38 | ICP-ES |
| Ba | mg/L | 0.12 | 0.14 | 0.13 | 0.15 | 0.18 | ICP-ES |
| Ca | mg/L | 2.2 | 0.55 | 0.8 | 0.79 | 0.9 | ICP-ES |
| Cd | mg/L | <0.02 | <0.014 | <0.014 | <0.014 | <0.014 | ICP-ES |
| Ce | mg/L | <0.7 | NM | NM | NM | NM | ICP-ES |
| Co | mg/L | <0.05 | <0.044 | <0.044 | <0.044 | <0.044 | ICP-ES |
| Cr | mg/L | 45 | 32 | 36 | 37 | 45 | ICP-ES |
| Cs | mg/L | 11.8 | NM | NM | NM | NM | AA |
| Cu | mg/L | 0.18 | <0.05 | <0.05 | <0.05 | <0.05 | ICP-ES |
| Fe | mg/L | 0.29 | 0.34 | 0.3 | 0.31 | 0.73 | ICP-ES |
| K | mg/L | 22730 | 21182 | 19590 | 20720 | 21710 | AA |
| La | mg/L | <0.06 | <0.061 | <0.061 | <0.061 | <0.061 | ICP-ES |
| Li | mg/L | 0.24 | <0.1 | <0.1 | <0.1 | 0.11 | ICP-ES |
| Mg | mg/L | <0.09 | <0.084 | <0.084 | <0.084 | <0.084 | ICP-ES |
| Mn | mg/L | 0.04 | 0.04 | 0.025 | 0.029 | 0.1 | ICP-ES |
| Mo | mg/L | 0.17 | 0.34 | <0.1 | <0.1 | <0.1 | ICP-ES |
| Na | mg/L | 138670 | 128134 | 124647 | 127454 | 153500 | ICP-ES |
| Na | mg/L | 137530 | NM | NM | NM | NM | AA |
| Nd | mg/L | <0.03 | NM | NM | NM | NM | ICP-ES |
| Ni | mg/L | 0.32 | 0.62 | 0.64 | 0.73 | 0.94 | ICP-ES |
| P | mg/L | 343 | 297 | 292 | 297 | 262 | ICP-ES |
| Pb | mg/L | 28 | 28 | 29 | 28 | 30 | ICP-ES |
| Si | mg/L | 125 | 57 | 72 | 73 | 110 | ICP-ES |
| Sr | mg/L | 0.11 | 0.08 | 0.078 | 0.075 | 0.11 | ICP-ES |
| Ti | mg/L | <0.14 | <0.14 | <0.14 | <0.14 | <0.14 | ICP-ES |
| Zn | mg/L | 15 | 7.8 | 12 | 12 | 15 | ICP-ES |
| Zr | mg/L | 0.06 | <0.048 | 0.11 | <0.048 | 0.5 | ICP-ES |
| Chloride | mg/L | 2570 | 3430 | 3205 | 3439 | 3583 | IC |
| Fluoride | mg/L | 112 | 430 | 386 | 457 | 456 | IC |
| Formate | mg/L | <100 | <100 | <100 | <100 | <100 | IC |
| Nitrate | mg/L | 105344 | 210322 | 184258 | 201678 | 109016 | IC |
| Nitrite | mg/L | 59905 | 42576 | 43293 | 47905 | 56742 | IC |
| Oxalate | mg/L | <100 | <100 | <100 | <100 | <100 | IC |
| Phosphate | mg/L | 799 | 657 | 638 | 666 | 510 | IC |
| Sulfate | mg/L | 2403 | 1479 | 1353 | 1497 | 1596 | IC |
| TIC | mg/L | 9620 | 3995 | 4394 | 4838 | 8355 | $CO_2$ Evolution |
| TOC | mg/L | <200 | 378 | 183 | 167 | <100 | $CO_2$ Evolution |
| Carbonate(TIC) | mg/L | 48063 | 19960 | 21950 | 24170 | 41740 | Calc. from TIC |
| Aluminate | Molar | 0.365 | 0.44 | 0.43 | 0.43 | 0.54 | Titration |
| Carbonate | Molar | 0.454 | NM | NM | NM | NM | Titration |
| Free OH | Molar | 2.133 | 0.45 | 0.63 | 0.59 | 2.64 | Titration |

[a] NM = Not Measured.

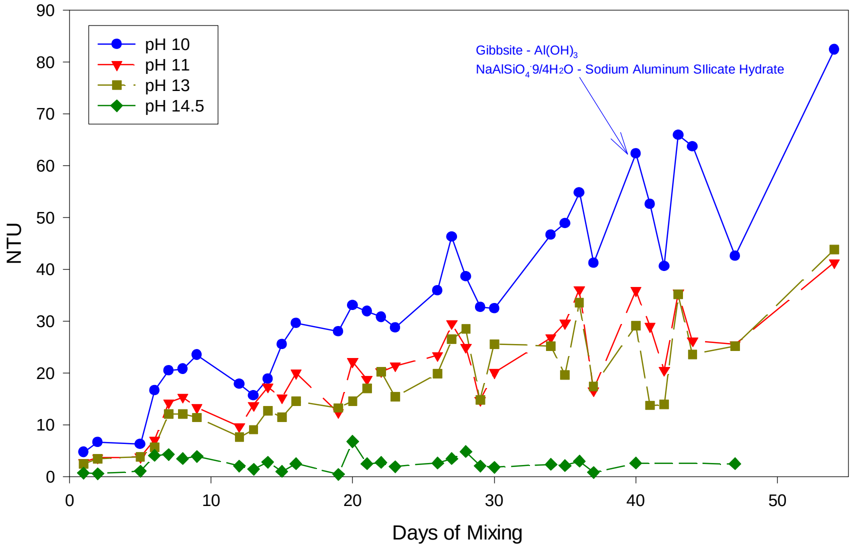

**Figure 28.** Turbidity of pH-Adjusted AW-101 Simulant.

Addition of acid to a high aluminate supernate such as AW-101 will destabilize the aluminate leading to precipitation of Gibbsite. If sufficient soluble silicon is present, sodium aluminosilicates will also precipitate. Addition of hydroxide to AW-101 does not produce solids. The observations are summarized in Table 27.

**Table 27.** Summary of pH Adjusted AW-101 Observations.

|  |  |  | **Observed** |  |
|---|---|---|---|---|
| **Targeted pH** | **Targeted[OH] (M)** | **Measured [OH] (M)** | **Solids** | **Gas** |
| 10 | 0.0001 | ~0.45 | Yes | Yes |
| 11 | 0.001 | ~0.63 | Yes | Yes |
| 13 | 0.1 | ~0.59 | Yes | Yes |
| 14.5 | 3.16 | 2.64 | No | No |

OLI simulated results of titrations of AW-101 are presented in Figure 29 and Figure 30. Compared to AN-104 and AN-107, AW-101 was more evenly buffered throughout the entire acid addition range evaluated (Figure 29). OLI and experimental results do not compare favorably. The laboratory titrations were conducted with an equilibration period between each acid addition of generally <15-min. This duration is clearly not long enough for the system to come to equilibration. Based on turbidity data, some simulants were not at equilibrium even after 60 days. Another important caveat is that a standard pH electrode was used in these studies to provide an estimate of the pH change, and not of the actual pH level. The standard pH electrode cannot accurately measure hydrogen ion activity in high ionic strength solutions, especially at extremely high or low pH levels. However, these measurements were used to provide an indication of the change in pH and to provide some benchmarking, albeit minimal, of OLI.

OLI tended to predict a pH more than 3 units greater than the experimental results. In addition, OLI did not capture the experimental pH inflection at 0.09 mol/L HCl added. Three solid phases were predicted to precipitate from this system upon adding $HNO_3$, $Al(OH)_3$, $CaCO_3$, and $Ca(OH)_2$ (Figure 30). Compared to AN-107, AW-101 contains fewer different constituents and appreciably lower concentrations of salts, especially of organic carbon salts (Appendix C). Thus, it is not surprising that fewer precipitates were predicted to form in AW-101 than in AN-107.

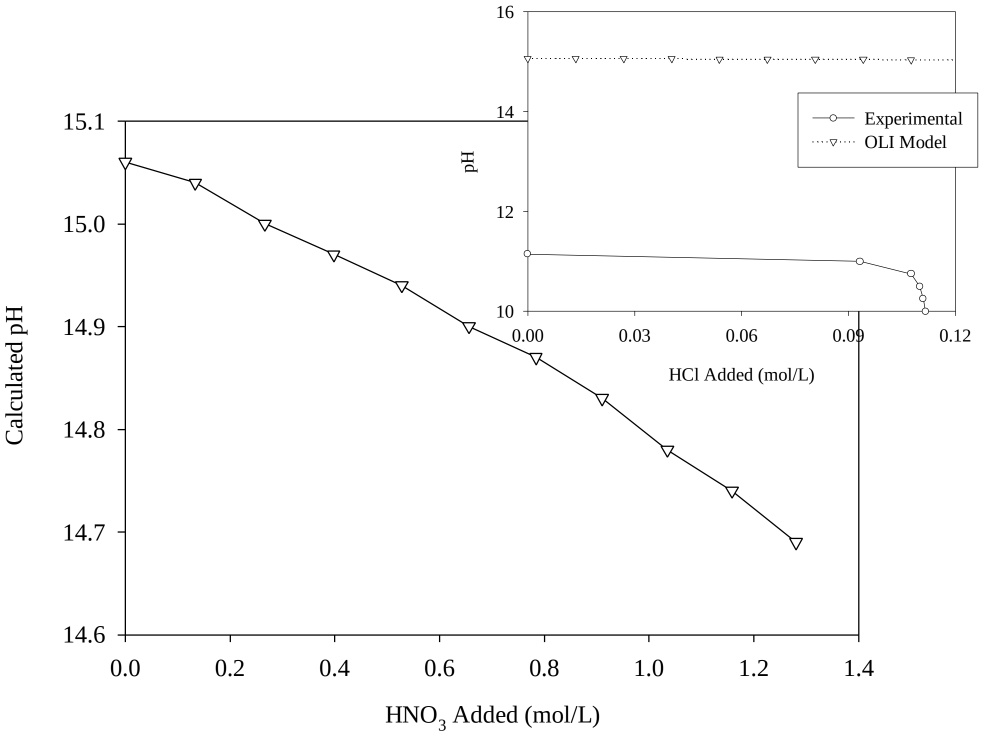

**Figure 29.** OLI Model Results of AW-101 Titration. Insert Compares Experimental (not at Equilibrium) vs. OLI Simulated (at Equilibrium) Results (note scale changes)**.**

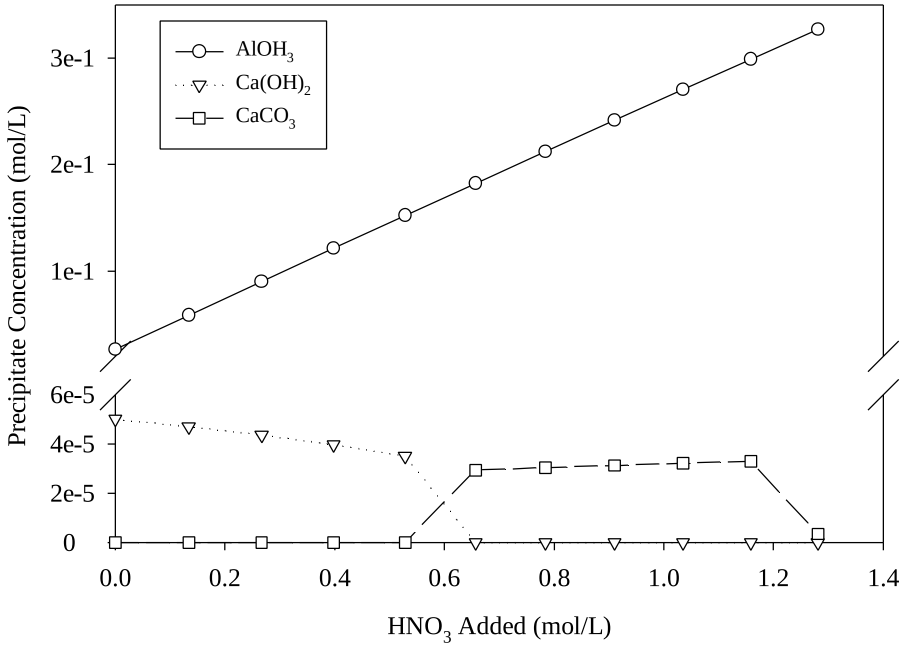

**Figure 30.** Solids Predicted by OLI to Precipitate When Acid is Added to AW-101 Simulant.

### 3.4.5. pH Adjustment of AZ-101 Simulant

Brown gas formed when nitric acid was added to the AZ-101 feed. The gas is assumed to be $NO_x$ formed from the nitrite anion due to high-localized acid concentrations. More effective mixing might mitigate this gas evolution. Immediate formation of white solids during acid addition was observed. Addition of sodium hydroxide did not produce any observable gas.

Figure 31 displays the result of monitoring turbidity for the pH adjusted AZ-101 simulant. The immediate formation of white solids was observed in the targeted pH 10 and 13 bottles (see footnote 2). The solids after the first few days were observed to settle quickly leading to erratic turbidity readings. This implies that the density and probably the crystallinity of the particles were increasing over time. The shape of the curve clearly supports the observation. Unlike the two A envelope simulants, the pH 14.5 test shown in Figure 31 indicates the formation of solids due to hydroxide addition. The data while erratic was supported by visible observations.

After completion of the turbidity monitoring, the tests solutions were filtered using vacuum filtration through a 0.45-micron nylon filter and the supernate submitted for analysis. Table 28 gives the results of the analysis. The filtered solids from the targeted pH 10 experiment were submitted for XRD to identify the solids present. The XRD scan for the acid-adjusted pH 10 test detected the following compounds (see appendix B Figure B17):

> Gibbsite – $Al(OH)_{3,}$
> sodium nitrate, and
> sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids. The analysis of the supernate shown in Table 28 confirms the solids characterization since Al by ICP-ES and $Al(OH)_4^-$ by titration drop in concentration. The only other components that declined in concentration in the acid adjusted tests were Si and TIC. Since XRD is dominated by amorphous or low-crystalline solids, the absence of sharp peaks associated with Si species is understandable. This suggests that the precipitated Si formed non-crystalline precipitates. The components that declined in concentration in the high hydroxide adjustment were fluoride, phosphate and sulfate. This suggests that the solids may have been double salts of the fluorophosphate and fluorosulfate type.

Nominally, the pH 10, 11, and 13 tests should have had about 0.0001, 0.001 and 0.1 molar free hydroxide levels Table 28). Instead the respective free hydroxide values were 0.16, 0.18 and 0.33 molar. Since the predominant product was the precipitation of Gibbsite, $Al(OH)_3$, the previously cited reaction must have occurred:

$$\mathrm{Al(OH)_4^-} \longrightarrow \mathrm{Al(OH)_3} + \mathrm{OH^-} \qquad (2)$$

As Gibbsite slowly precipitates due to the dissociation of the aluminate, free hydroxide is released.

**Table 28.** Composition of pH-Adjusted AZ-101 Simulant.

| **Tank Components** | **Units** | **Feed Found** | **pH 10 Found** | **pH 11 Found** | **pH 13 Found** | **pH 14.5 Found** | **Analysis Method** |
|---|---|---|---|---|---|---|---|
| Al | mg/L | 7752 | 1611 | 1750 | 1960 | 7691 | ICP-ES |
| B | mg/L | <0.21 | <0.21 | <0.21 | <0.21 | <0.21 | ICP-ES |
| Ba | mg/L | 0.02 | <0.012 | <0.012 | <0.012 | 0.11 | ICP-ES |
| Ca | mg/L | 3.7 | 0.12 | 0.14 | 0.09 | 1.6 | ICP-ES |
| Ce | mg/L | <0.7 | NM[a] | NM | NM | NM | ICP-ES |
| Cr | mg/L | 648 | 657 | 651 | 650 | 627 | ICP-ES |
| Cs | mg/L | 41 | NM | NM | NM | NM | ICP-ES |
| Fe | mg/L | 0.46 | <0.044 | <0.044 | <0.044 | 0.43 | ICP-ES |
| K | mg/L | 4690 | 4728 | 4791 | 4785 | 4368 | AA |
| La | mg/L | <0.06 | <0.06 | <0.06 | <0.06 | <0.06 | ICP-ES |
| Li | mg/L | 0.18 | <0.1 | <0.1 | <0.1 | <0.1 | ICP-ES |
| Mg | mg/L | <0.09 | <0.09 | <0.09 | <0.09 | <0.09 | ICP-ES |
| Mn | mg/L | 0.11 | <0.009 | <0.009 | <0.009 | <0.009 | ICP-ES |
| Mo | mg/L | <0.1 | 6.5 | <0.1 | <0.1 | <0.1 | ICP-ES |
| Na | mg/L | 104670 | 104740 | 109238 | 110376 | 145997 | ICP-ES |
| Na | mg/L | 108990 | NM | NM | NM | NM | AA |
| Ni | mg/L | 0.34 | 7.3 | 7.2 | 7.0 | 7.6 | ICP-ES |
| P | mg/L | 546 | 486 | 536 | 525 | 505 | ICP-ES |
| Si | mg/L | 5.3 | <0.7 | <0.7 | <0.7 | <0.7 | ICP-ES |
| Zr | mg/L | 0.32 | 0.54 | 0.3 | 0.16 | 0.22 | ICP-ES |
| Chloride | mg/L | 180 | 1540 | 1541 | 1561 | 1493 | IC |
| Fluoride | mg/L | 760 | 1709 | 1838 | 2007 | 479 | IC |
| Formate | mg/L | <100 | <100 | <100 | <100 | <100 | IC |
| Nitrate | mg/L | 60330 | 92095 | 98074 | 93977 | 67967 | IC |
| Nitrite | mg/L | 61770 | 57993 | 62251 | 62641 | 55853 | IC |
| Oxalate | mg/L | <100 | 310 | <100 | <100 | <100 | IC |
| Phosphate | mg/L | 1318 | 1223 | 1327 | 1341 | 935 | IC |
| Sulfate | mg/L | 15740 | 16925 | 17036 | 17207 | 9907 | IC |
| TIC | mg/L | 8466 | 6911 | 7163 | 8028 | 11430 | $CO_2$ Evolution |
| TOC | mg/L | 365 | 222 | 188 | <100 | 173 | $CO_2$ Evolution |
| Carbonate(TIC) | mg/L | 42298 | 34525 | 35780 | 40105 | 57100 | Calc. from TIC |
| Aluminate | Molar | 0.268 | 0.13 | 0.12 | 0.13 | 0.36 | Titration |
| Carbonate | Molar | 0.384 | NM | NM | NM | NM | Titration |
| Free OH | Molar | 0.463 | 0.16 | 0.18 | 0.33 | 2.31 | Titration |

[a] NM = Not Measured.

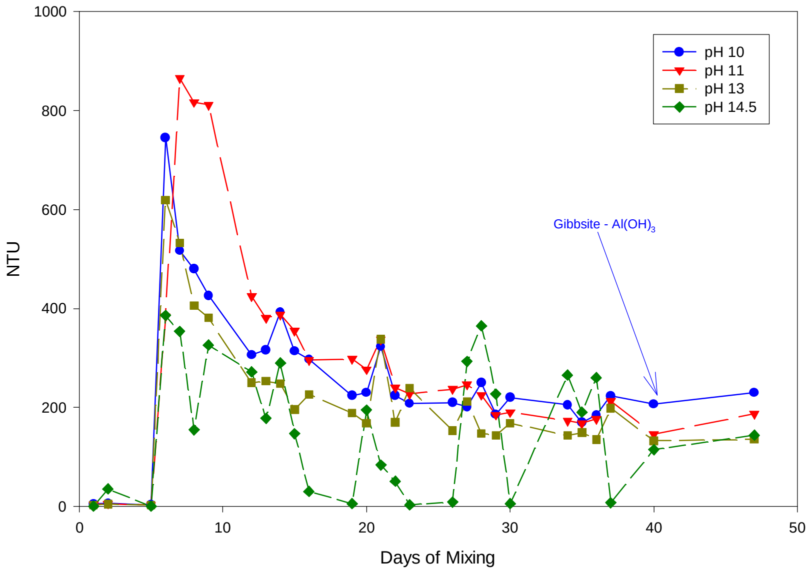

**Figure 31.** Turbidity of pH-Adjusted AZ-101 Simulant.

Addition of acid to a high aluminate supernate such as AZ-101 will destabilize the aluminate leading to precipitation of Gibbsite. Addition of hydroxide to AZ-101 does produce solids. Since the AZ-101 simulant is based upon the Best Basis Inventory and not an actual sample analysis, a better test of B envelope feed will be the AZ-102 simulant. The observations are summarized in Table 29.

**Table 29**. Summary of pH Adjusted AZ-101 Observations.

| | | | Observed | |
|---|---|---|---|---|
| **Targeted pH** | **Targeted[OH] (M)** | **Measured [OH] (M)** | **Solids** | **Gas** |
| 10 | 0.0001 | ~0.16 | Yes | Yes |
| 11 | 0.001 | ~0.18 | Yes | Yes |
| 13 | 0.1 | 0.33 | Yes | Yes |
| 14.5 | 3.16 | 2.31 | Yes | No |

OLI simulated results of titrations of AZ-101 are presented in Figure 32 and Figure 33. Compared to the previous simulants, AZ-101 was more like AW-101 than AN-104 or AN-107 insofar that it was evenly buffered throughout the entire acid-addition range evaluated (Figure 32). OLI and experimental results do not compare favorably. The laboratory titrations were conducted with an equilibration period between each acid addition of generally <15-min. This duration is clearly not long enough for the system to come to equilibrium. Based on turbidity data, some simulants were not at equilibrium even after 60 days. Another important caveat is that a standard pH electrode was used in these studies to provide an estimate of the pH change, and not of the actual pH level. The standard pH electrode cannot accurately measure hydrogen ion activity in high ionic strength solutions, especially at extremely high or low pH levels. However, these measurements were used to provide an indication of the change in pH and to provide some benchmarking, albeit minimal, of OLI.

Discussion of the cause for this poor agreement between experimental and OLI predicted results are presented above. Unlike the previously discussed simulants, OLI tended to underestimate the measured pH. Also, OLI did not capture the experimental pH inflection at 0.08 mol/L HCl added. Three solid phases were predicted to precipitate from this system upon adding $HNO_3$, $NaHCO_3$, $NaAlCO_3(OH)_2$, and $CaF_2$ (Figure 33).

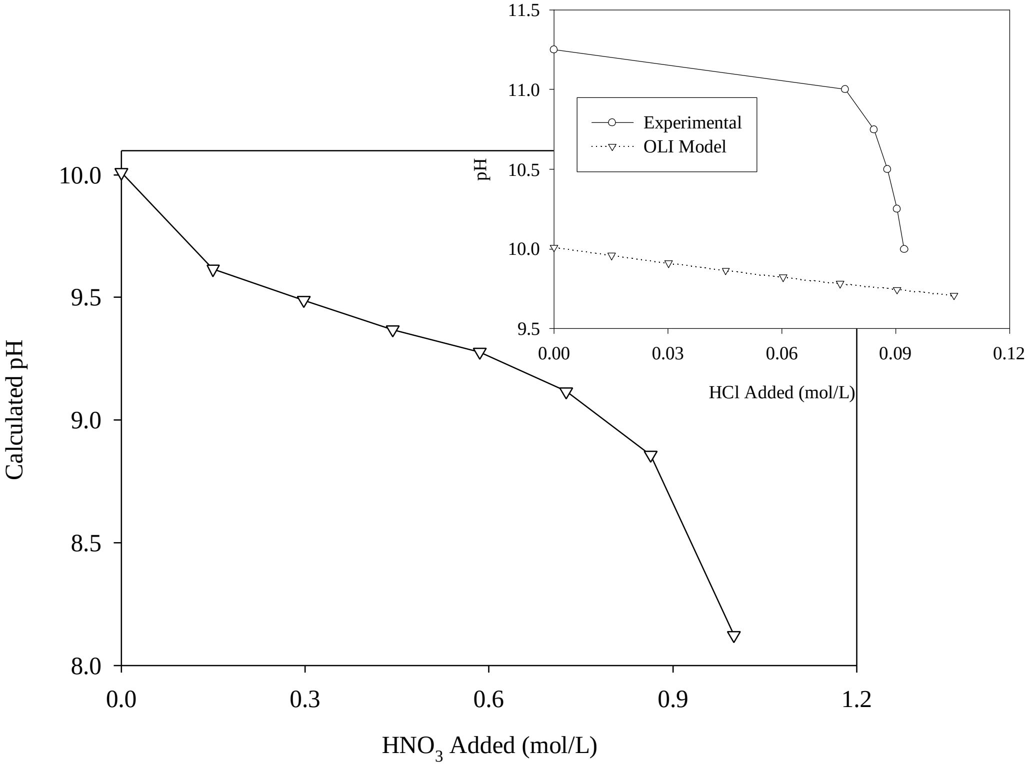

**Figure 32.** OLI Model Results of AZ-101 Titration. Insert Compares Experimental (not at Equilibrium) vs. OLI Simulated (at Equilibrium) Results.

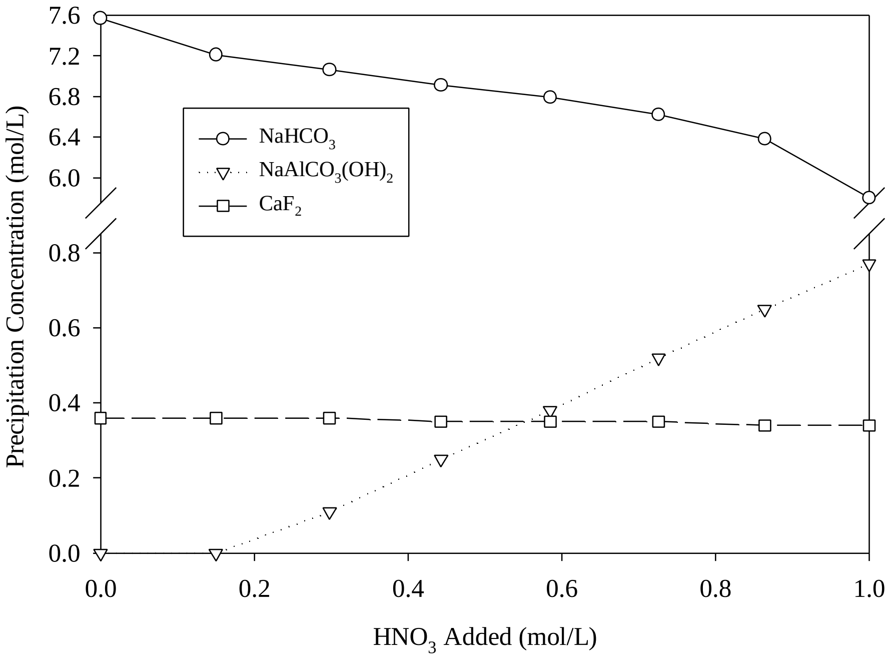

**Figure 33.** Solids Predicted by OLI to Precipitate When Acid is Added to AZ-101 Simulant.

### 3.4.6. pH Adjustment of AZ-102 Simulant

Brown gas was observed when nitric acid was added to the AZ-102 feed. The gas is assumed to be $NO_x$ formed from the nitrite anion due to high-localized acid concentrations. More effective mixing might mitigate this gas evolution. Immediate formation of white solids during acid addition was observed. Addition of sodium hydroxide did not produce any observable gas or solids.

Figure 34 displays the result of monitoring turbidity for the pH adjusted AZ-102 simulant. Fine solids were observed in all three pH adjusted tests from the very first day of monitoring. The apparent delay in turbidity was the result of not swirling the bottle before removing a sample for turbidity measurements. Once gentle agitation was used, the readings became stable and agreed with the visual observations. The turbidity plot also indicates that fewer solids were probably present in the targeted pH 13 test than in the other two acid-adjusted tests. As indicated in Figure 34, the pH 14.5 (high hydroxide) test did not produce any solids in contrast to the AZ-101 test.

After completion of the turbidity monitoring, the test solutions were filtered using vacuum filtration through a 0.45-micron nylon filter and the supernate submitted for analysis. Table 30 gives the results of the analysis. The filtered solids from the pH 11 experiment were submitted for XRD to identify the solids present. The XRD scan for the acid-adjusted pH 11 test detected the following compounds (see Appendix B, Figure B18):

> gibbsite – $Al(OH)_3$,
> sodium aluminum silicate – $Na_{1.84}Al_2Si_{2.88}O_{9.68}$,
> sodium nitrate, and
> sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids as XRD-detectable evaporates. The analysis of the supernate shown in Table 30 confirms the solids identified by XRD, since both Si by ICP-ES and $Al(OH)_4$ by titration show drops in concentration. The only other components that declined in concentration in the acid adjusted tests were Ca and TIC. Despite the observation of $NO_x$, no evidence of a decline in nitrite concentration can be found in Table 30. Since XRD patterns were dominated by the presence of amorphous or poorly crystalline solids, the lack of Ca and carbonate solids in the XRD pattern is understandable. XRD identifies only crystalline minerals, thus few of the precipitates formed during the study could be identified by XRD. Since the aluminate level was so low in the AZ-102 simulant, the free hydroxide concentrations were less than detection limit as planned for this experiment.

**Table 30.** Composition of pH-Adjusted AZ-102 Simulant.

| Tank Components | Units | Feed Found | pH 10 Found | pH 11 Found | pH 13 Found | pH 14.5 Found | Analysis Method |
|---|---|---|---|---|---|---|---|
| Ag | mg/L | <0.3 | NM[a] | NM | NM | NM | ICP-ES |
| Al | mg/L | 230 | 9.7 | 290 | 149 | 223 | ICP-ES |
| B | mg/L | 7.3 | 6.6 | 5.8 | 7.1 | 6.8 | ICP-ES |
| Ba | mg/L | 0.01 | <0.012 | <0.012 | <0.012 | 0.09 | ICP-ES |
| Ca | mg/L | 4.8 | 2.9 | 1.2 | 0.6 | 4.3 | ICP-ES |
| Cd | mg/L | 0.05 | <0.014 | <0.014 | <0.014 | 0.04 | ICP-ES |
| Ce | mg/L | <0.7 | NM | NM | NM | NM | ICP-ES |
| Co | mg/L | <0.05 | <0.044 | <0.044 | <0.044 | <0.044 | ICP-ES |
| Cr | mg/L | 865 | 831 | 822 | 872 | 803 | ICP-ES |
| Cs | mg/L | 1 | NM | NM | NM | NM | ICP-ES |
| Cu | mg/L | 0.18 | <0.05 | <0.05 | <0.05 | 0.09 | ICP-ES |
| Fe | mg/L | 0.23 | 0.06 | <0.044 | 0.05 | 0.58 | ICP-ES |
| K | mg/L | 3150 | 3150 | 3422 | 3224 | 2914 | AA |
| La | mg/L | <0.06 | <0.061 | <0.061 | <0.061 | <0.061 | ICP-ES |
| Li | mg/L | 0.12 | <0.1 | <0.1 | <0.1 | <0.1 | ICP-ES |
| Mg | mg/L | <0.09 | <0.084 | <0.084 | <0.084 | <0.084 | ICP-ES |
| Mn | mg/L | <0.009 | <0.009 | <0.009 | <0.009 | 0.013 | ICP-ES |
| Mo | mg/L | 58 | 58 | 51 | 59 | 53 | ICP-ES |
| Na | mg/L | 58070 | 62137 | 65248 | 61590 | 111131 | ICP-ES |
| Na | mg/L | 53000 | NM | NM | NM | NM | AA |
| Nd | mg/L | <0.3 | NM | NM | NM | NM | ICP-ES |
| Ni | mg/L | <0.06 | 9.2 | 9.2 | 9.8 | 9.5 | ICP-ES |
| P | mg/L | 166 | 150 | 201 | 162 | 148 | ICP-ES |
| Pb | mg/L | <0.6 | <0.7 | <0.7 | <0.7 | 1.4 | ICP-ES |
| Si | mg/L | 121 | 4.1 | 5.6 | 21 | 118 | ICP-ES |
| Sn | mg/L | <0.26 | <0.26 | <0.26 | <0.26 | <0.26 | ICP-ES |
| Sr | mg/L | 0.05 | 0.013 | 0.014 | 0.006 | 0.07 | ICP-ES |
| Ti | mg/L | <0.14 | <0.014 | <0.014 | <0.014 | <0.014 | ICP-ES |
| V | mg/L | <0.13 | <0.013 | <0.013 | <0.013 | <0.013 | ICP-ES |
| Zn | mg/L | <0.37 | <0.37 | <0.37 | <0.37 | <0.37 | ICP-ES |
| Zr | mg/L | 0.43 | 0.31 | 0.17 | 0.78 | 0.44 | ICP-ES |
| Chloride | mg/L | 201 | 280 | 280 | 282 | 188 | IC |
| Fluoride | mg/L | 1111 | 1001 | 1019 | 938 | 821 | IC |
| Formate | mg/L | <100 | <100 | <100 | <100 | <100 | IC |
| Nitrate | mg/L | 15360 | 35640 | 42978 | 28782 | 14808 | IC |
| Nitrite | mg/L | 31050 | 31099 | 35079 | 31289 | 28496 | IC |
| Oxalate | mg/L | 2671 | 2568 | 2271 | 2597 | 763 | IC |
| Phosphate | mg/L | 375 | 488 | 584 | 513 | 505 | IC |
| Sulfate | mg/L | 14848 | 15507 | 15568 | 15570 | 14051 | IC |
| TIC | mg/L | 8946 | 6778 | 7188 | 7466 | 12720 | $CO_2$ Evolution |
| TOC | mg/L | 1052 | 930 | 932 | 988 | 386 | $CO_2$ Evolution |
| Carbonate(TIC) | mg/L | 44696 | 33864 | 35913 | 37302 | 63551 | Calc. from TIC |
| Aluminate | Molar | 0.030 | <0.02 | <0.02 | <0.02 | 0.146 | Titration |
| Carbonate | Molar | 0.464 | NM | NM | NM | NM | Titration |
| Free OH | Molar | 0.196 | <0.02 | <0.02 | <0.02 | 2.17 | Titration |

[a] NM = Not Measured.

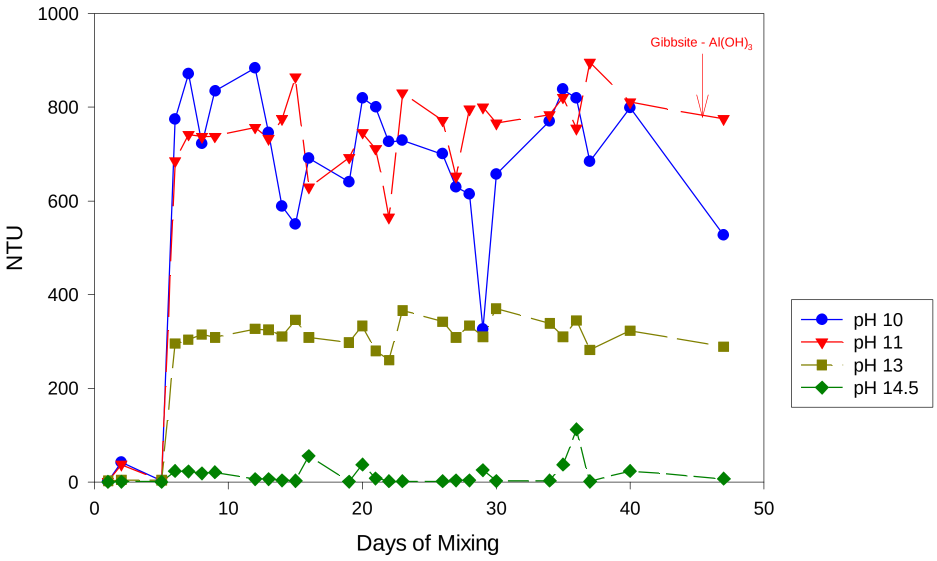

**Figure 34.** Turbidity of pH-Adjusted AZ-102 Simulant.

Addition of acid to an Envelope B supernate such as AZ-102 will destabilize the aluminate leading to precipitation of Gibbsite and production of aluminosilicates. Addition of hydroxide to AZ-102 does not produce solids. The observations are summarized in Table 31.

**Table 31.** Summary of pH Adjusted AZ-102 Observations.

|  |  |  | **Observed** |  |
|---|---|---|---|---|
| **Targeted pH** | **Targeted[OH] (M)** | **Measured [OH] (M)** | **Solids** | **Gas** |
| 10 | 0.0001 | <0.02 | Yes | Yes |
| 11 | 0.001 | <0.02 | Yes | Yes |
| 13 | 0.1 | <0.02 | Yes | Yes |
| 14.5 | 3.16 | 2.17 | No | No |

OLI simulated results of titrations of AZ-102 are presented in Figure 35 and Figure 36. The titration curve of AZ-102 did not have any point of sharp inflection, similar to AW-101 and AZ-101, suggesting that it is evenly buffered throughout the entire acid-addition range evaluated (Figure 32). OLI and experimental results do not compare favorably. The laboratory titrations were conducted with an equilibration period between each acid addition of generally <15-min. This duration is clearly not long enough for the system to come to equilibration. Based on turbidity data, some simulants were not at equilibrium even after 60 days. Another important caveat is that a standard pH electrode was used in these studies to provide an estimate of the pH change, and not of the actual pH level. The standard pH electrode cannot accurately measure hydrogen ion activity in high ionic strength solutions, especially at extremely high or low pH levels. However, these measurements were used to provide an indication of the change in pH and to provide some benchmarking, albeit minimal, of OLI.

OLI tended to predict larger pH values than were measured experimentally. The pH trends, near constant, were similar in the experimental and OLI model systems. OLI predicted that several solids would precipitate upon the addition of $HNO_3$; the majority of the precipitates were composed of $NaHCO_3(OH)_2$ and $Na_2C_2O_4$ (Figure 33).

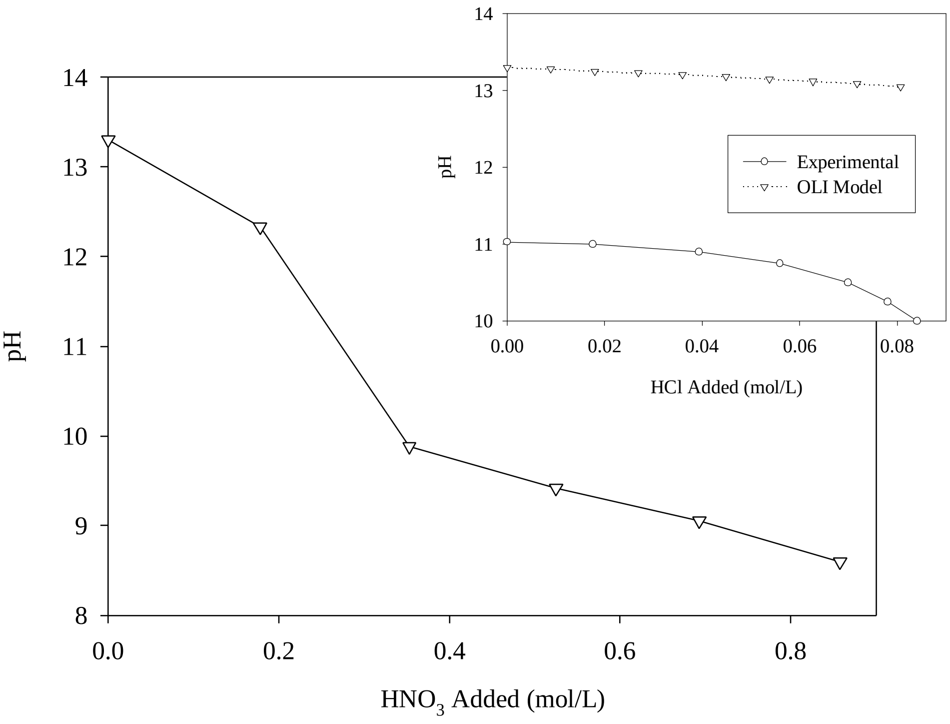

**Figure 35.** OLI Model Results of AZ-102 Titration. Insert Compares Experimental (not at Equilibrium) vs. OLI Simulated (at Equilibrium) Results.

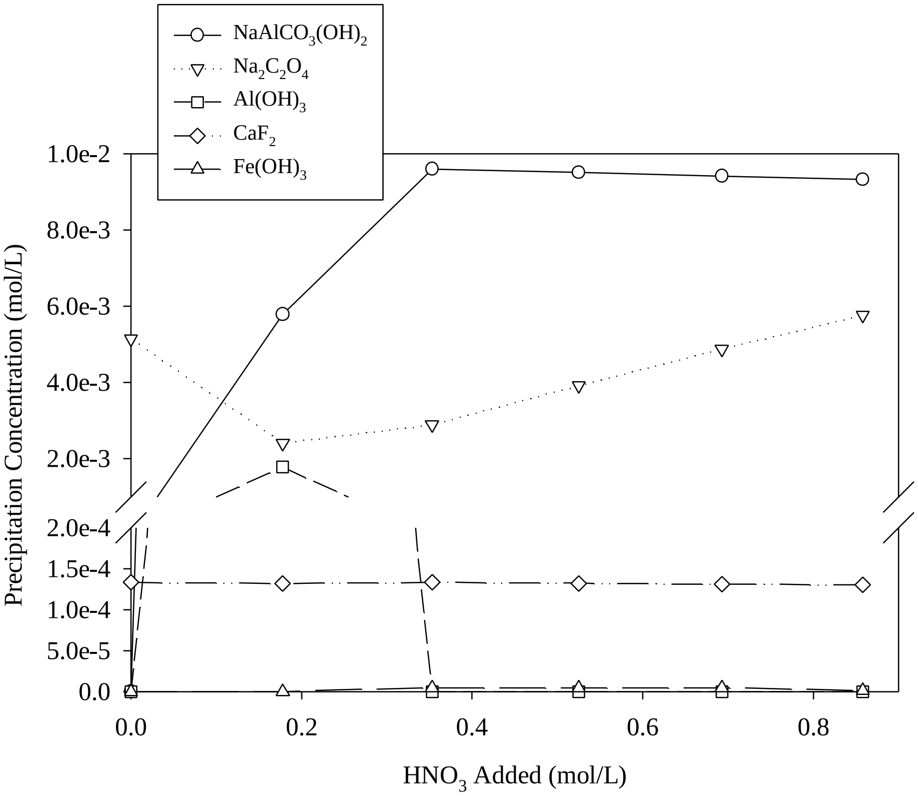

**Figure 36.** Solids Predicted by OLI to Precipitate When Acid is Added to AZ-102 Simulant.

## 3.5. *Envelope-D Leachate Mixing Experiment*

This group of experiments is designed to evaluate whether the recycle of leachate from caustic washing of Envelope D sludge will produce solids upon addition to feed tanks containing Envelope A, B or C supernates. The specific mixtures tested are listed in the experimental design in Table 1. The experimental methodology is presented in more detail in Section 2.5. Only results for AN-107 and C-106 caustic leachate mixtures are discussed in detail because the other mixtures did not result in appreciably amounts of precipitation. These other tests confirm and mimic results obtained from caustic testing with Envelopes A and B; the AN-107 and C-106 mixtures did not mimic results from caustic testing.

### 3.5.1. AN-107 and C-106 Caustic Leachate Mixtures

Two of the test mixtures began to show solids after one day of mixing. Figure 37 displays the turbidity data for the undiluted simulants and for the mixtures. The 50:50 mixture and the 10% AN-107:90% C-106 mixture showed rapid increases in turbidity. These solids tended to cling to the walls of containers and to cling to pipette tips, leading to variable results. This behavior is similar to that reported for the pH adjusted (high hydroxide) experiment (see Section 3.4.2). The agreement between these experiments is excellent considering that the small addition of hydroxide did not produce solids (pH 13 test), and the similar 90% AN-107:10% C-106 also did not produce solids. Near the end of the monitoring period, the 100% AN-107 feed began to show signs of solids formation. It appears that the addition of a small amount of additional free hydroxide may be capable of stabilizing the AN-107 simulant.

After completion of the turbidity monitoring, the test solutions were filtered using vacuum filtration through a 0.45-micron nylon filter and the supernate for the 50:50 mixture submitted for analysis. Table 32 provides the results of the analysis. The filtered solids from the 50:50 mixture were submitted for XRD to identify the solids present. The XRD scan for the 50:50 mixture detected the following compounds (see Appendix B, Figure B19):

sodium aluminum silicate hydrate – $Na_{12.8}Al_{7.2}Si_{16.8}O_{48}(H_2O)_{6}$,
sodium carbonate hydrogen peroxide – $Na_2CO_3(H_2O_2)_{1.5}$,
sodium nitrate, and
sodium nitrite.

Since the solids were not washed, the sodium nitrate and sodium nitrite salts could be due to the residual supernate, which dried on the solids as XRD-detectable evaporates. However, analysis of the 50:50 supernate shown in Table 32 shows a lower nitrate concentration possibly due to the production of sodium nitrate crystals. Components with concentration significantly less than the postulated 50:50 mixture value included: Ca, Mn, F, oxalate, $PO_4^{3-}$, $SO_4^{2-}$, and possibly TOC. Additional testing of these mixtures may be necessary to give answers that are more definitive.

Confirmation of the solids generation in AN-107 upon addition caustic feeds can be found in the Envelope Mixing tests also documented in this report and in actual waste tests. When an actual waste sample from AN-107 was mixed with AW-101 or with a leach solution from C-104 washing, solids formation was observed (Lumetta et al. 2000).

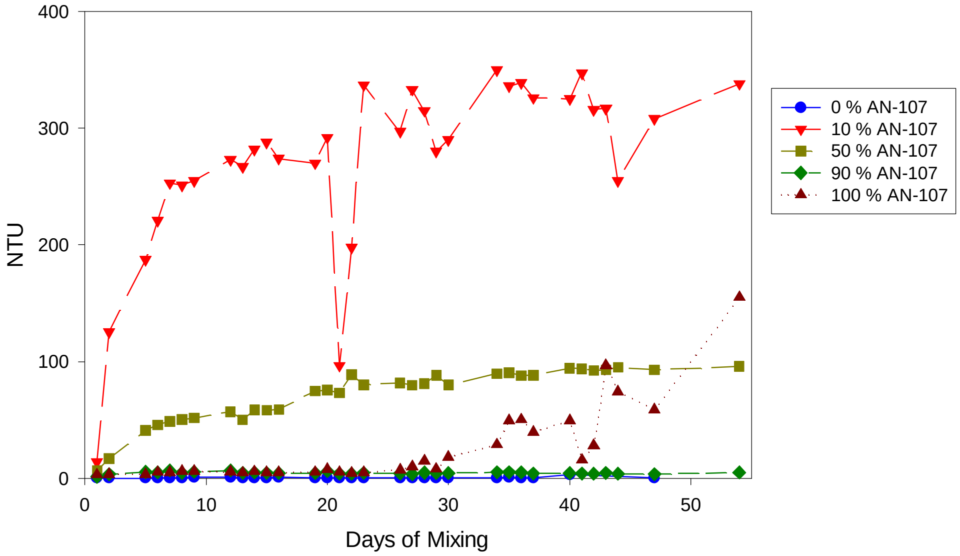

**Figure 37.** Turbidity of AN-107 & C-106 Leachate Simulant Mixtures.

**Table 32.** Composition of 50:50 Mixture of AN-107 and C-106 Leachate.

| Tank | Units | AN-107 Found | C-106 Leachate Found | 50% Mix Expected | 50% Mix Found | % of Expected in 50% Mixture |
|---|---|---|---|---|---|---|
| Al | mg/L | 194 | 2460 | 1349 | 1360 | 101 |
| B | mg/L | 38 | 68 | 54 | 56 | 104 |
| Ba | mg/L | 0.17 | 14.6 | 7 | 0.16 | 2 |
| Ca | mg/L | 138 | 3.3 | 72 | 83 | 115 |
| Cd | mg/L | <0.02 | <0.02 | <0.02 | <0.014 | NA |
| Ce | mg/L | 50.2 | <0.7 | 26 | NM* | NA |
| Co | mg/L | 0.39 | <0.05 | 0.2 | <0.044 | NA |
| Cr | mg/L | 148 | 49 | 100 | 110 | 110 |
| Cs | mg/L | 22.3 | 0.7 | 12 | NM | NA |
| Cu | mg/L | 32 | 0.06 | 16 | 21 | 131 |
| Fe | mg/L | 1623 | 0.24 | 825 | 675 | 82 |
| K | mg/L | 1921 | 2.4 | 978 | 11990 | 1226 |
| La | mg/L | 40 | <0.06 | 21 | 20 | 95 |
| Mg | mg/L | 20 | <0.09 | 10 | 1 | 10 |
| Mn | mg/L | 564 | 0.02 | 287 | 146 | 51 |
| Mo | mg/L | 36 | <0.1 | 18 | 21 | 117 |
| Na | mg/L | 188170 | 105670 | 149385 | 161228 | 108 |
| Na | mg/L | 201400 | 102470 | 154484 | NM | NA |
| Nd | mg/L | 84.4 | <0.3 | 43 | NM | NA |
| Ni | mg/L | 501 | 0.06 | 255 | 297 | 116 |
| P | mg/L | 420 | 125 | 278 | 308 | 111 |
| Pb | mg/L | 364 | 26 | 198 | 199 | 101 |
| Si | mg/L | 1.4 | 303 | 155 | 138 | 89 |
| Sr | mg/L | 1.3 | 0.06 | 0.7 | 0.62 | 89 |
| Zn | mg/L | 44 | 0.48 | 23 | 25 | 109 |
| Zr | mg/L | 45 | <0.05 | 23 | 25 | 109 |
| Chloride | mg/L | 1330 | 105 | 676 | 2552 | 378 |
| Fluoride | mg/L | 3430 | <20 | 1744 | 306 | 18 |
| Formate | mg/L | 11232 | <100 | 5710 | <100 | NA |
| Nitrate | mg/L | 213930 | 241 | 108882 | 64845 | 60 |
| Nitrite | mg/L | 57090 | 6589 | 32374 | 37304 | 115 |
| Oxalate | mg/L | 335 | 698 | 525 | 366 | 70 |
| Phosphate | mg/L | 1500 | 303 | 917 | 572 | 62 |
| Sulfate | mg/L | 7280 | 1570 | 4499 | 1747 | 39 |
| TIC | mg/L | 16100 | 3 | 8186 | 14500 | 177 |
| TOC | mg/L | 15800 | 18716 | 17548 | 1713 | 10 |
| Carbonate(TIC) | mg/L | 80439 | 13 | 40901 | 72434 | 177 |
| Aluminate | Molar | 0.054 | 0.070 | 0.063 | 0.38 | 603 |
| Carbonate | Molar | 1.052 | 0.881 | 0.983 | -- | NA |
| Free OH | Molar | 0.039 | 2.651 | 1.368 | 2.02 | 148 |

[a] NM = Not Measured; NA = Not Available.

### 3.5.2. A and B Envelopes Mixed with Caustic Leachates

The following mixtures did not produce any significant solids under the mixing ratios tested:

AW-101:C-106 Leachate (Figure 38),
AZ-102:AZ-102 Leachate (Figure 39),
AZ-101:AZ-102 Leachate (Figure 40), and
AN-104:C-106 Leachate (Figure 41).

In general, these tests agree with the targeted pH 14.5 adjustment tests for the Envelope A and B tanks.

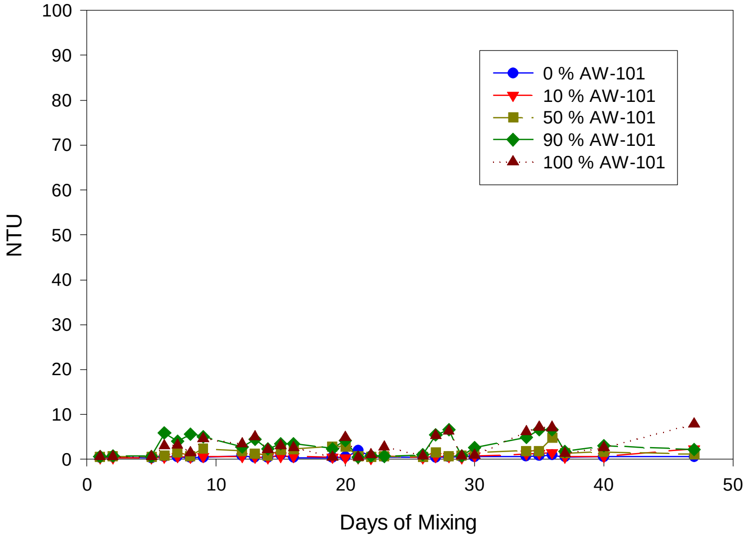

**Figure 38.** Turbidity of AW-101 & C-106 Leachate Simulant Mixtures.

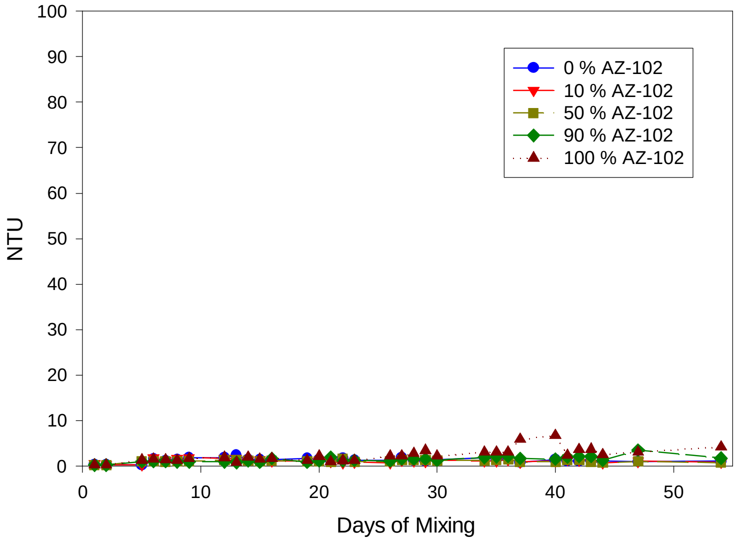

**Figure 39.** Turbidity of AZ-102 & AZ-102 Leachate Mixtures.

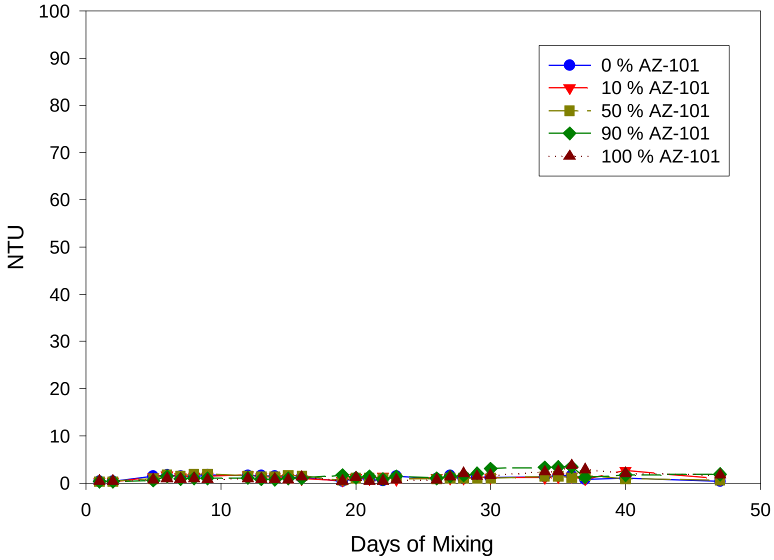

**Figure 40.** Turbidity of AZ-101 and AZ-102 Leachate Mixtures.

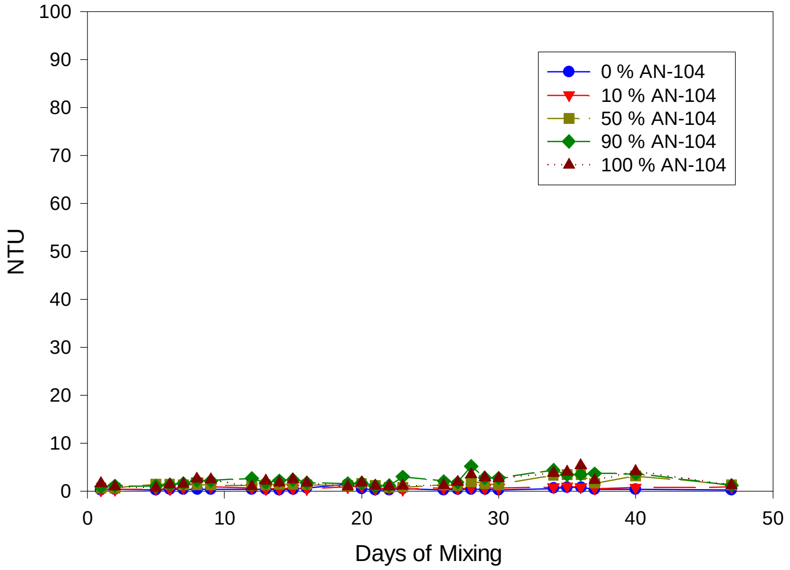

**Figure 41.** Turbidity of AN-104 and C-106 Leachate Mixtures.

# 4. CONCLUSIONS AND IMPLICATIONS

Neither diluting simulants nor mixing Envelope A or B simulants with AZ-102 Caustic Leachate simulant caused an increase in turbidity. Conversely, mixing Envelope A or B or C-106 Caustic leachate with Envelope C simulants and decreasing the pH of the simulants resulted in an appreciable increase in turbidity.

A summary of the solids formed during the various experiments is presented in Table 33. The solids identified are consistent with previously reported solids with one notable exception, that sodium oxalate was not identified among the solids formed (Herting 1997, 1998, Kaplan et al. 1999). It is likely that some XRD-detectable evaporates formed while the filtered solids were air-dried. Another experimental problem associated with quantifying and identifying the solid phases in these studies was that some of the precipitates plated onto the glassware, this is especially true of AN-107 suspensions and acidified suspensions. This caused an experimental artifact, insofar that these plated precipitates were not represented in the turbidity measurements and were not sampled for the XRD and SEM/EDX analyses. The dominant precipitates formed were sodium nitrate, sodium nitrite, and various types of sodium carbonate phases containing silicate, hydroxide, hydrogen, or aluminum. Upon acidification, gibbsite ($Al(OH)_3$) and other Al-containing phases tended to precipitate.

AN-107 was especially unstable with regards to forming precipitates. Although the simulant was filtered several times prior to use in the mixing studies, unaltered AN-107 continued to form precipitates for an additional two months. Upon mixing AN-107 with AN-104 or AZ-101, a great deal of insoluble solids were created. Acid additions to AN-107 also created an enormous amount of precipitates. These precipitates tended to plate to the glassware. Based on these results, slight chemical perturbation of this simulant will result in precipitate formation.

Mixing Envelopes A or B with AN-107 (Envelope C) is likely to generate a lot of precipitates. Upon mixing envelopes, a significant amount of solids may form that can compromise the efficiency and/or capacity of the filters and ion exchange resins. It may be possible to reduce such adverse effects by reducing tank heel volumes, flushing tanks, etc. A review of the process schedule and sequence is needed to determine which approach is best. The effect of mixing Envelopes A and B together on solids formation were not evaluated in this study. Further work is needed, once the tank waste retrieval schedule is confirmed so that appropriate simulant mixtures can be prepared.

**Table 33.** XRD-Identified Solids Formed in Simulants that had High Turbidity.

| **Treatment** | **Final Turbidity (NTU)** | **Solids Formed** |
|---|---|---|
| 100% AN-107 | 245 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>$Na_3H(CO_3)_2\text{-}x(H_2O)$[a] |
| 10% AZ-101 / 90% AN-107 | 500 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>$Na_3H(CO_3)_2\text{-}x(H_2O)$,<br>$NaAl(CO_3)(OH)_2$ |
| 50% AZ-101 / 50% AN-107 | 97 | Amorphous: primarily Fe-Mn-O phase(s) |
| 10% AN-107 / 90% AN-104 | 222 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>$Na_3H(CO_3)_2\text{-}x(H_2O)$<br>Sodium $Na_2CO_3H_2O$ |
| 50% AN-107 / 50% AN-104 | 120 | Sodium Nitrate - $NaNO_3$<br>$Na_8(Al_6Si_6O_{24})(NO_2)_2\text{-}3H_2O$ |
| 9% dilute AN-107 / 91% dilute AN-104 | 404 | $Na_8(Al_6Si_6O_{24})(NO_2)_2\text{-}3H_2O$<br>Amorphous: primarily Fe-Mn-O phase(s), trace Na-O phase(s) |
| 9% dilute AN-107 / 91% dilute AW-101 | 195 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>$Na_8(Al_6Si_6O_{24})(NO_2)_2\text{-}3H_2O$,<br>$Na_2CO_3\text{-}H_2O$ |
| 9% dilute AN-107 / 91% AZ-102 | 259 | Sodium Nitrate, $NaNO_3$<br>Sodium Nitrite, $NaNO_2$<br>$Na_8(Al_6Si_6O_{24})(NO_2)_2\text{-}3H_2O$, |
| AN-104 (pH 10) | 250 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>Gibbsite – $Al(OH)_3$<br>Thermonatrite – $Na_2CO_3 \bullet H_2O$ |
| AN-107 (pH 10) | 285 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>$Na_3H(CO_3)_2\text{-}2H_2O$<br>$Na_6(AlSiO_4)_6$<br>Gibbsite – $Al(OH)_3$ |
| AW-101 (pH 10) | 85 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>Gibbsite – $Al(OH)_3$<br>Sodium Aluminum Silicate Hydrate –$Na_{96}Al_{96}Si_{96}O_{384} \cdot 216H_2O$<br>Sodium Aluminum Silicate Hydrate –$Na_2Al_2Si_{2.71}O_{9.42} \cdot 4.39H_2O$ |
| AZ-101 (pH 10) | 230 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>Gibbsite – $Al(OH)_3$ |
| AZ-102 (pH 10) | 540 | Sodium Nitrate - $NaNO_3$<br>Sodium Nitrite, - $NaNO_2$<br>Gibbsite – $Al(OH)_3$<br>Sodium Aluminum Silicate – $Na_{1.84}Al_2Si_{2.88}O_{9.68}$ |

[a] The degree of hydration will vary based on conditions solids were stored. Energy of hydration is very small between monohydrate and di-hydrate species.

As expected, acidifying the feed simulants greatly increased the amount of solids formed. Between a targeted pH of 13.5 to 10, incremental decreases in pH resulted in incremental increases in turbidity. Some instances in the pretreatment process where acidic solutions may be introduced into feed include: 1) cleaning solutions from LAW ultrafiltration system are mixed with the Envelope A, B, or C feed, 2) HLW melter off-gas condensate mixes with Envelope D feed, 3) LAW melter off-gas condensate mixes with pretreated LAW feed to the evaporator, and 4) LAW melter off-gas condensate mixes with LAW feed. Depending on the acid concentration and ratio of volumes, these streams may require neutralization before mixing with feed.

Based on these studies, dilution of the feed solutions will incrementally reduce the amount of solids formed. It appears that the dilution resulting from such dilutions does not reduce the pH of the suspension sufficiently to cause the aluminum phases to precipitate from solution. Dilution of the feed is expected to occur at various places in the process, including where 1) HLW permeate wash solutions are introduced into the feed, and 2) dilute NaOH and water flushes of the Cs or Tc ion exchange columns are reintroduced into the feed.

In general, it appears that particular attention will have to be directed at processing AN-107. AN-107 was very prone to precipitation and only slight changes to the system resulted in the formation of precipitates. The 100% AN-107 simulant continued to generate increasing amounts of precipitates during the study, perhaps the result of absorbing atmospheric $CO_2$-gas into the system. This simulant generated significant quantities of solids when acidified or mixed with as little as 10% of Envelopes A or B. While it appeared that a small addition of caustic may have stabilized the undiluted AN-107 simulant, the preferred option would be to dilute AN-107 with dilute caustic to prevent premature solids formation.

OLI modeling tended to identify more different types of solids than were experimentally determined by conducting XRD analysis of filter cakes. This apparent discrepancy could have been the result of a number of things, including issues related to the constants used in the OLI calculations, the high detection limit of the XRD, the difficulty of sampling the filter cake, the fact that OLI calculates systems at equilibrium while many experimental mixtures were shown not to be at true equilibrium, and the presence of evaporates in the filter-cakes. Perhaps one of the key problems in applying OLI modeling to the pretreatment waste processing system will be that the feed stream will take a great deal of time, in the range of weeks to months, to come to equilibrium (based on this study’s turbidity data). The various perturbations of the feed stream will likely force the feed stream out of equilibrium through-out the pretreatment process. The OLI software appears to be conservative with respect to prediction of more solids than experimentally observed. It is recommended that the software be used to guide stream mixing parameters, but experiments are needed to confirm behaviors. While these results do not impact the current design, understanding precipitation kinetics is essential for developing guidelines for operations, such as when tanks or vessels must be flushed.

Further work is planned which will examine the effect of mixing other waste tank simulants, once the tank retrieval sequence is finalized. Similarly, other internal recycle stream testing is planned (e.g., submerged bed scrubber recycle). Also, since Na-Al-Si precipitates were formed, there is a need to determine whether radionuclides sorb to these solids. Using the results reported herein, a review of the planned operation is needed to ensure avoidance of undesirable precipitates. Testing with actual waste tank samples is needed to confirm the observations reported here.

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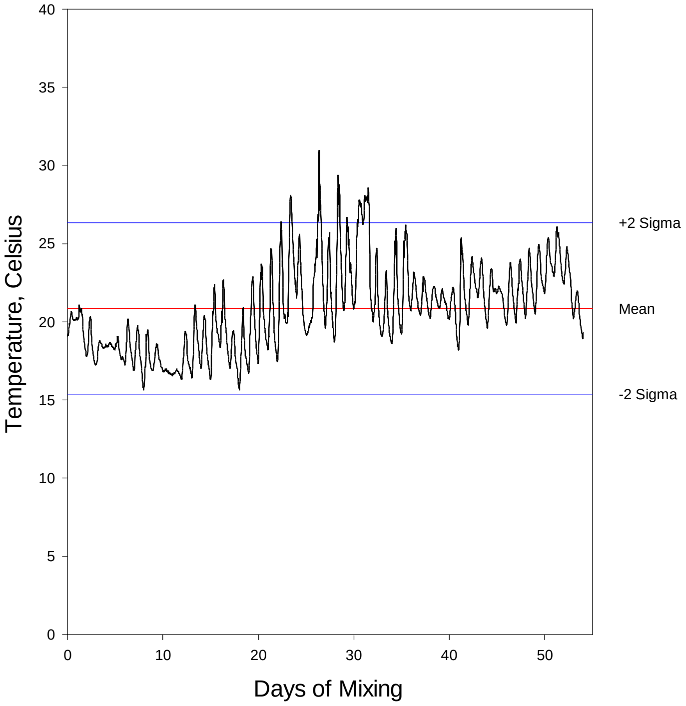
# 6. APPENDIX A: TEMPERATURE DATA

**Table A1.** Suspension Temperatures During Dilution and Envelope Mixing Experiments.

| Date | Day since Mixing | Degrees C | Date | Day since Mixing | Degrees C |
|---|---|---|---|---|---|
| 1/12/00 | 1 | 23 | 2/14/00 | 34 | 21 |
| 1/13/00 | 2 | 23 | 2/15/00 | 35 | 20 |
| 1/17/00 | 6 | 23 | 2/16/00 | 36 | 20 |
| 1/18/00 | 7 | 22 | 2/17/00 | 37 | 20 |
| 1/19/00 | 8 | 22 | 2/22/00 | 42 | 20 |
| 1/20/00 | 9 | 22 | 2/23/00 | 43 | 20 |
| 1/24/00 | 13 | 25 | 2/28/00 | 48 | 20 |
| 1/25/00 | 14 | 26 | 2/29/00 | 49 | 20 |
| 1/26/00 | 15 | 26 | 3/1/00 | 50 | 20 |
| 1/27/00 | 16 | 23 | 3/2/00 | 51 | 21 |
| 1/31/00 | 20 | 21 | 3/6/00 | 55 | 20 |
| 2/1/00 | 21 | 21 | 3/7/00 | 56 | 20 |
| 2/2/00 | 22 | 20 | 3/8/00 | 57 | 21 |
| 2/3/00 | 23 | 20 | 3/9/00 | 58 | 21 |
| 2/7/00 | 27 | 20 | 3/16/00 | 35 | 21 |
| 2/8/00 | 28 | 20 | | | |
| 2/9/00 | 29 | 20 | | | |
| 2/10/00 | 30 | 20 | AVERAGE | 21.3 | |
| 2/14/00 | 34 | 21 | STD DEV | 1.7 | |

Figure A1. Temperature Variations during the Hydroxide Adjustment and Leaching Mixing Studies.



# 7. APPENDIX B. XRD DATA

Figure B1. XRD Spectrum of Solids from 100% AN-107.

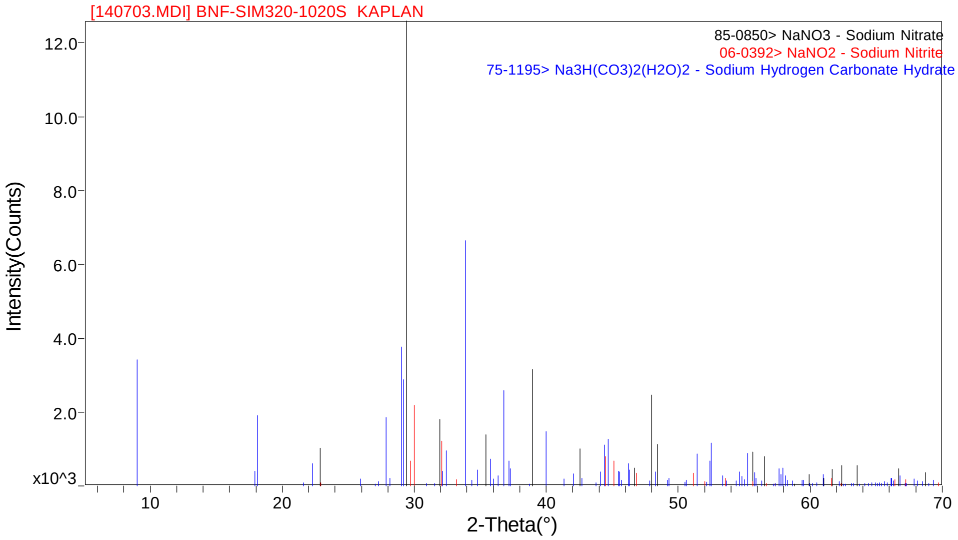


Figure B2. XRD Spectrum of Solids from 10% AZ-101 / 90% AN-107.

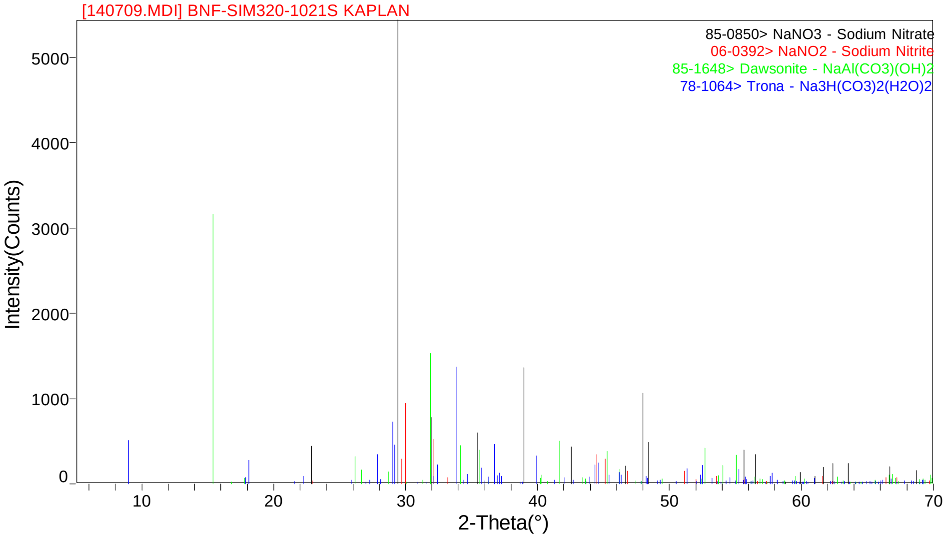


Figure B3. XRD Spectrum of Solids from 50% AZ-101 / 50% AN-107.

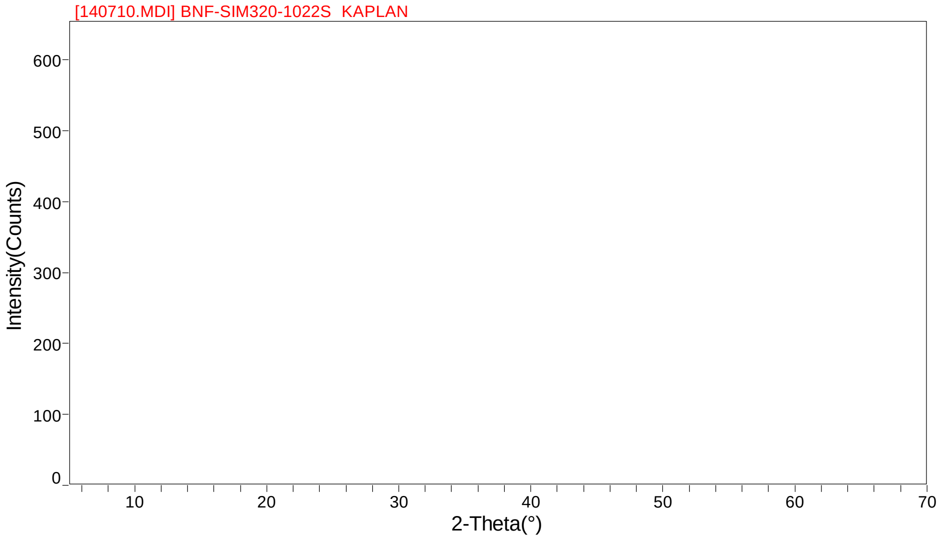


Figure B4. XRD Spectrum of Solids from 10% AN-107 / 90% AN-104.

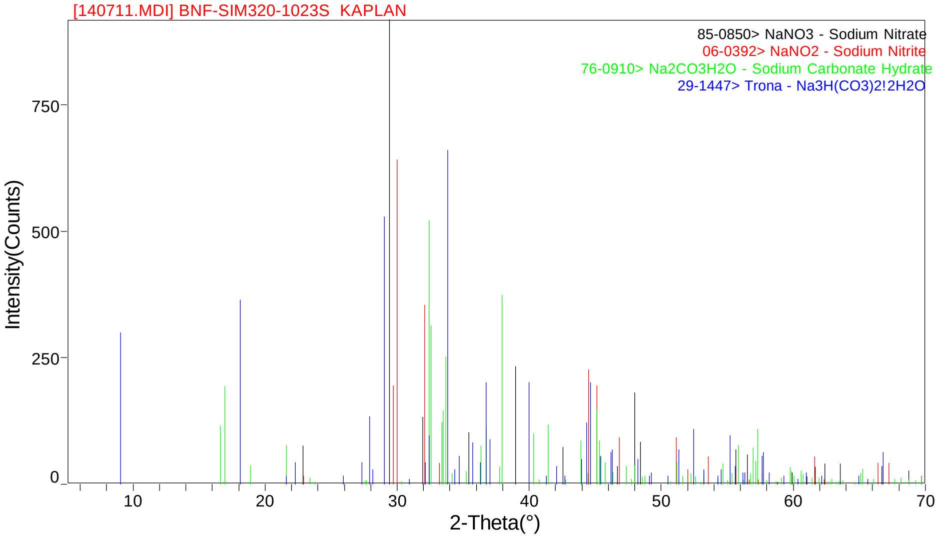


Figure B5. XRD Spectrum of Solids from 50% AN-107 / 50% AN-104.

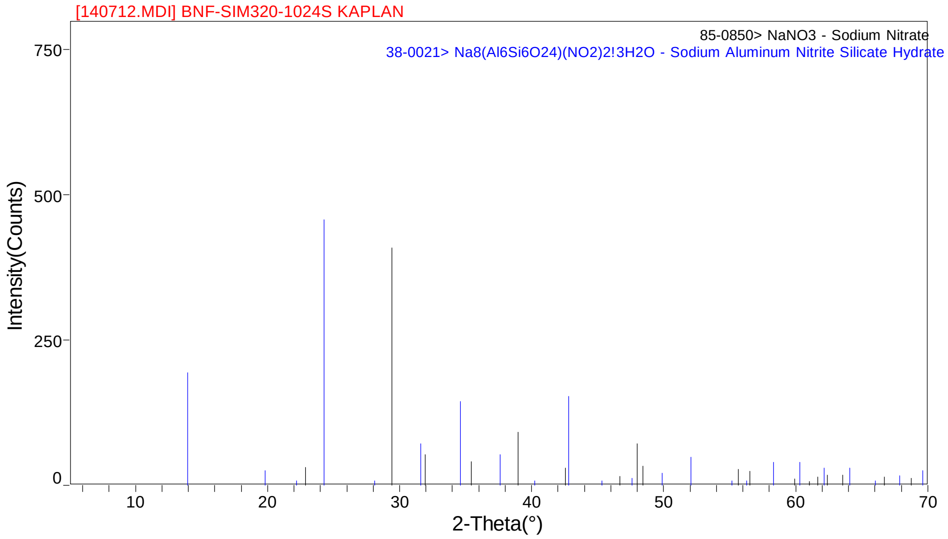


Figure B6. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AN-104.

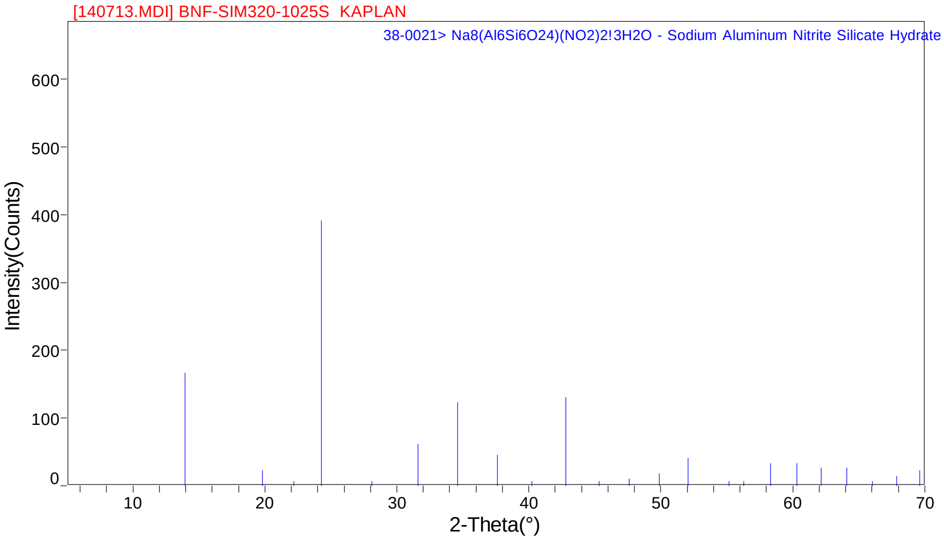


Figure B7. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AW-101.

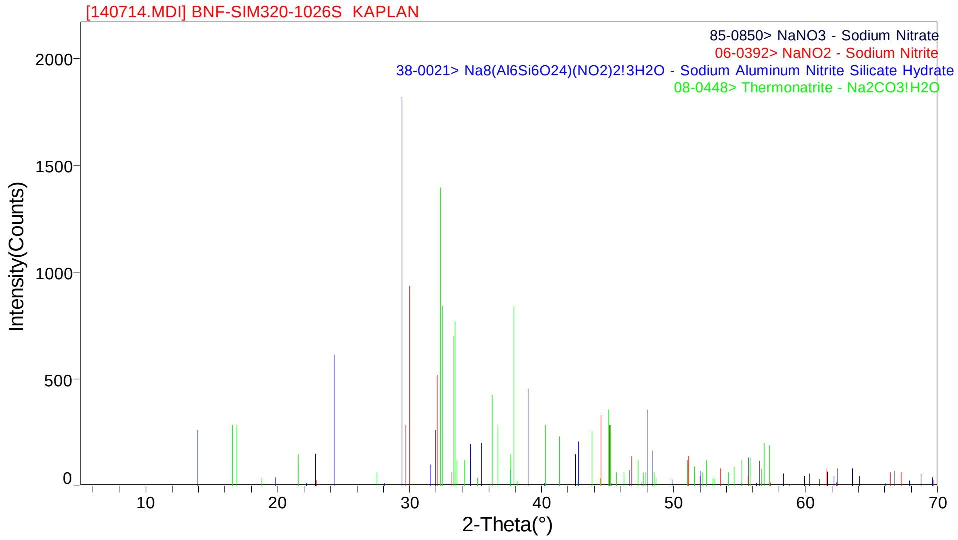


Figure B8. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AZ-102.

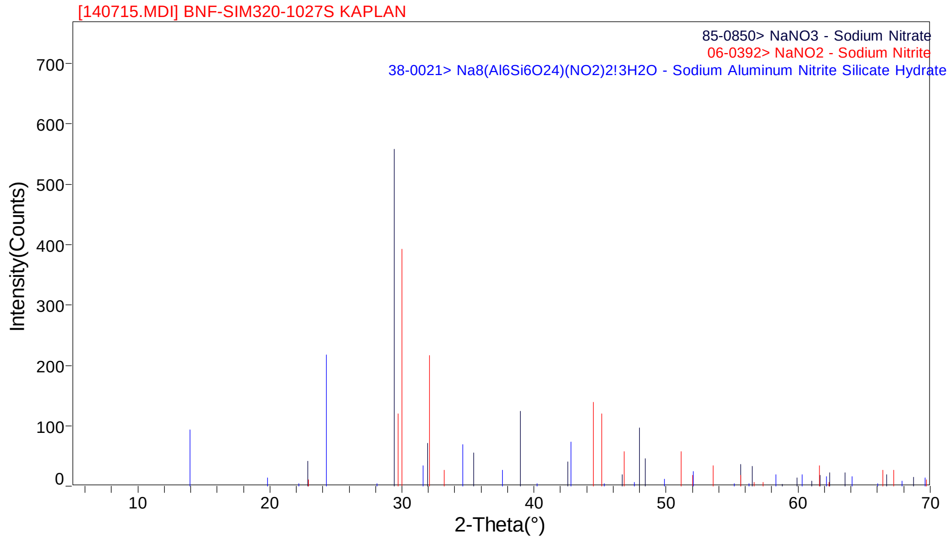


Figure B9. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AN-104.

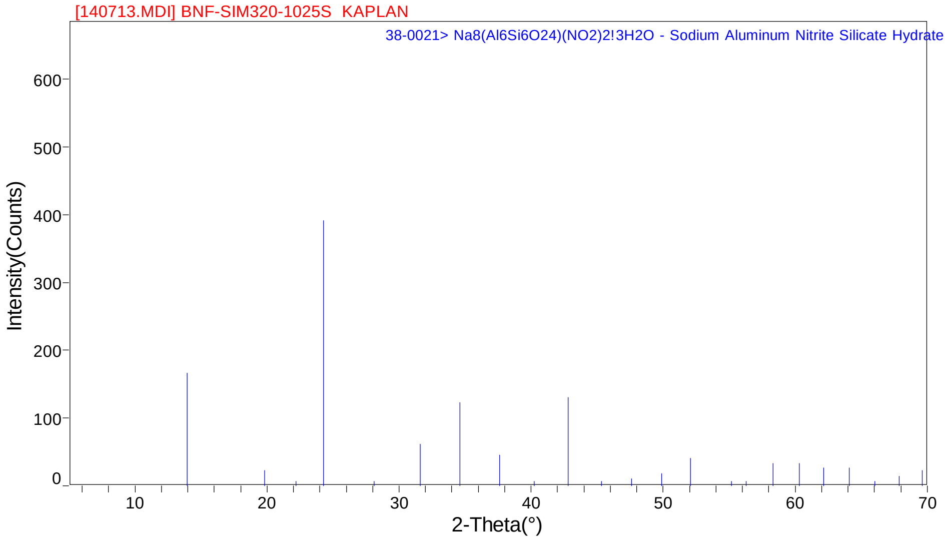


Figure B10. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AW-101.

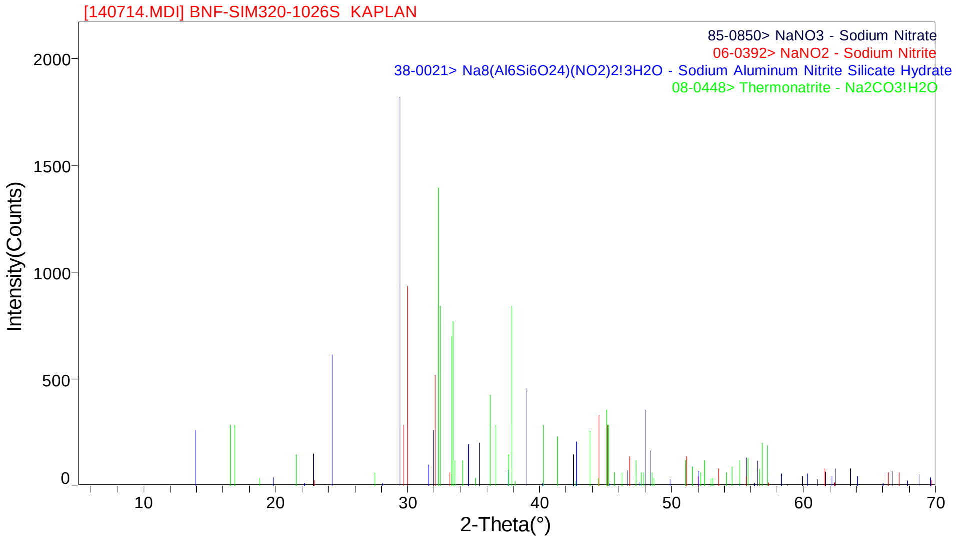


Figure B11. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AZ-102.

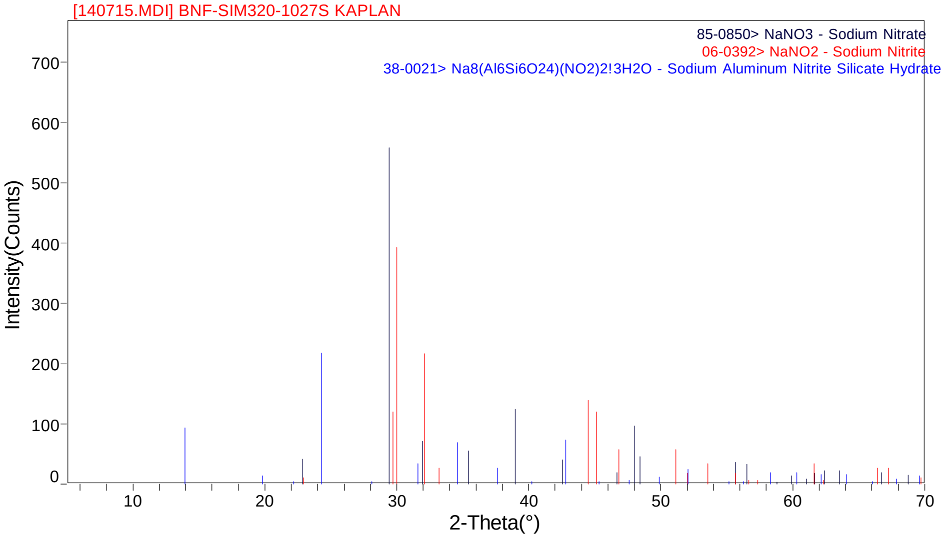


Figure B12. XRD Spectrum of Tabular Crystals from AN-107 Simulant Feed.

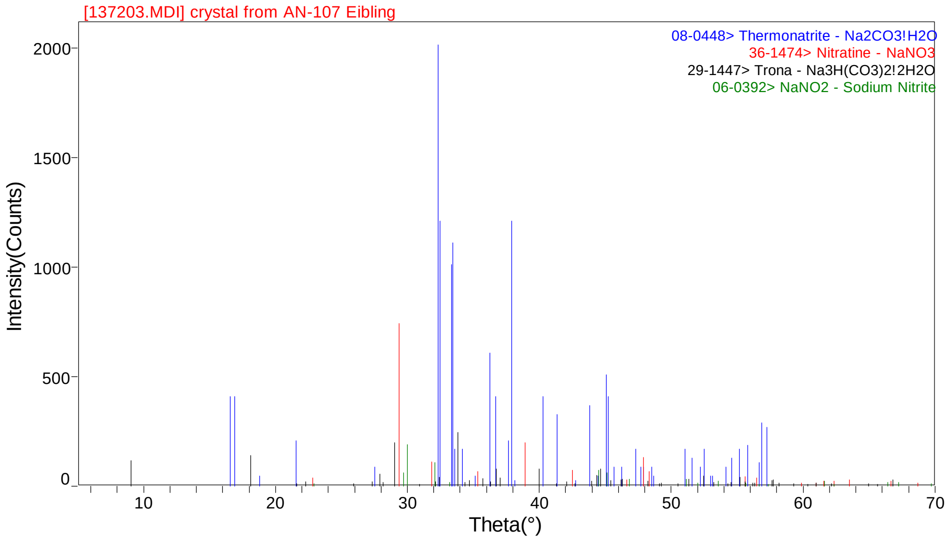


Figure B13. XRD Spectrum of Solids from pH 10 Adjusted AN-107 Simulant.

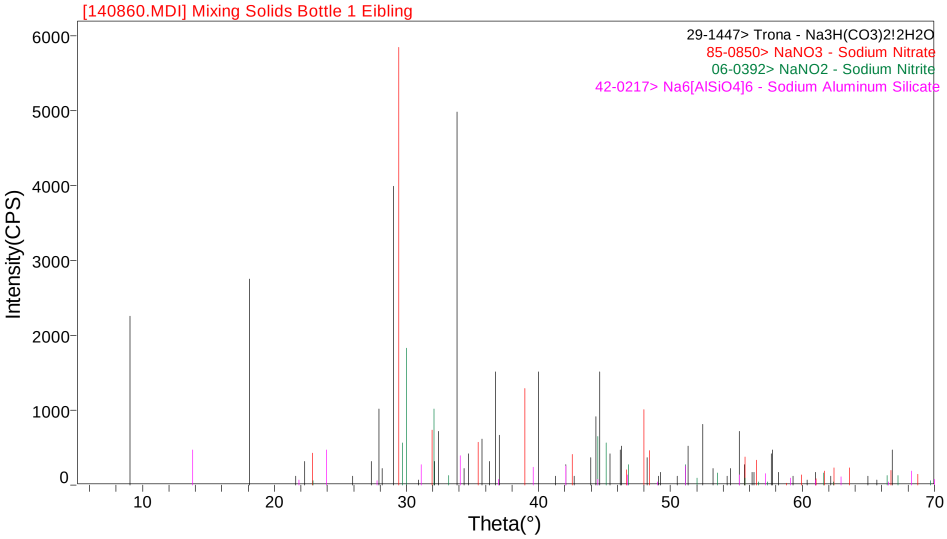


Figure B14. XRD Spectrum of Solids from pH 14.5 Adjusted AN-107 Simulant.

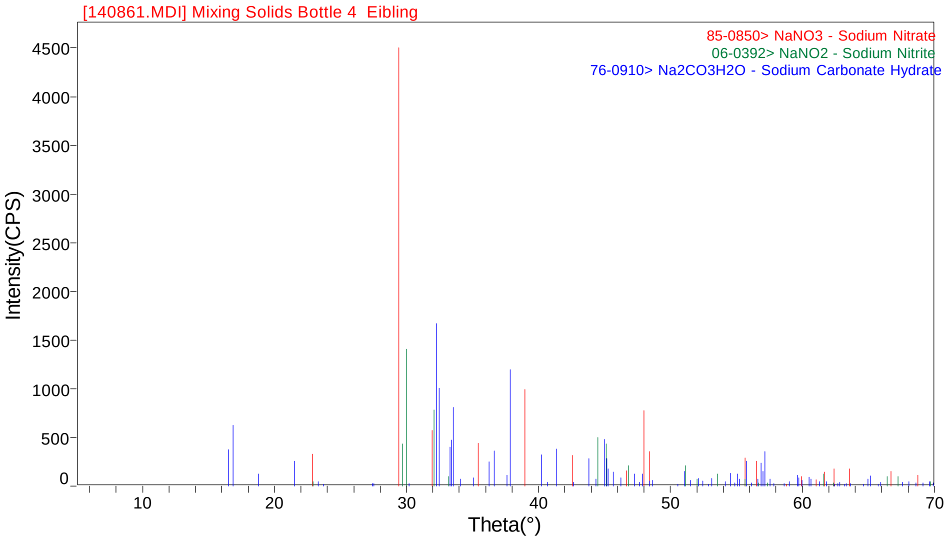


Figure B15. XRD Spectrum of Solids from pH 10 Adjusted AN-104 Simulant.

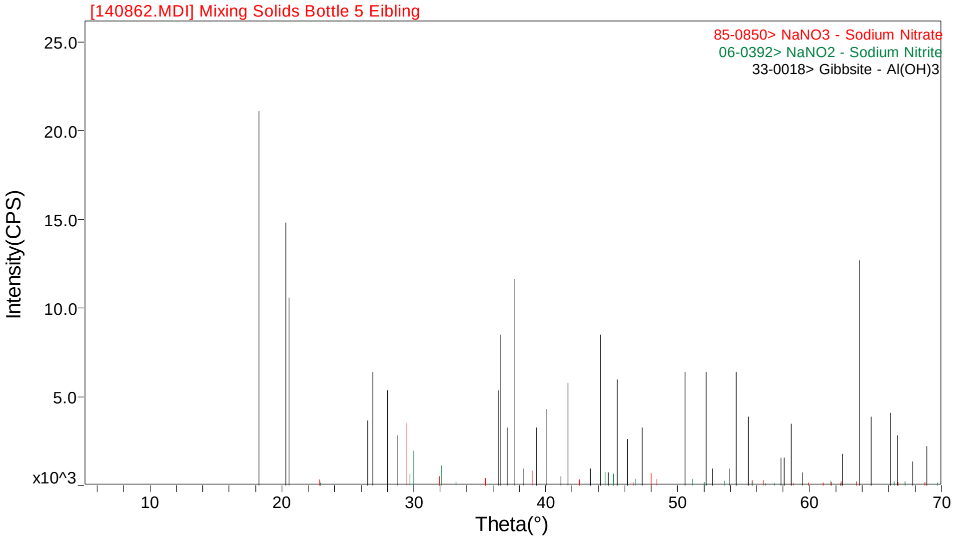


Figure B16. XRD Spectrum of Solids from pH 10 Adjusted AW-101 Simulant.

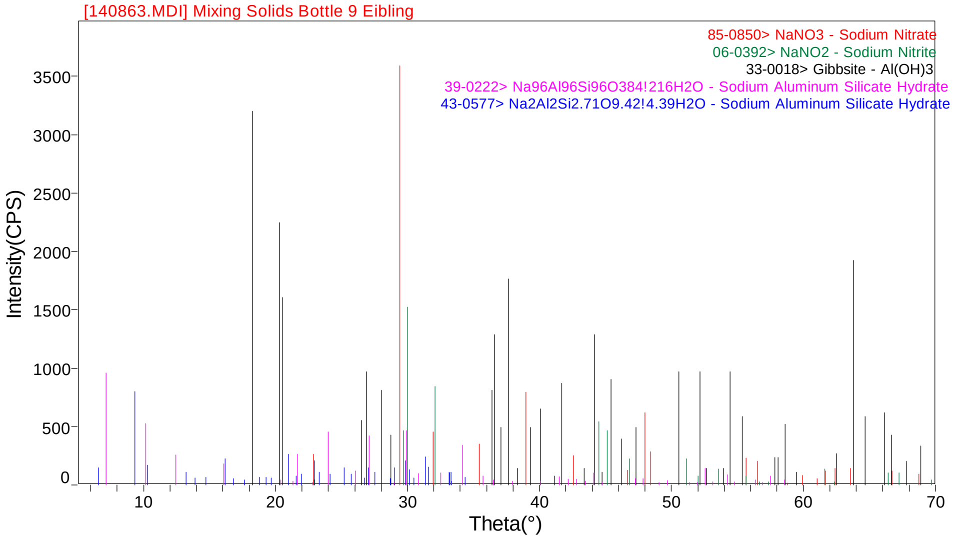


Figure B17. XRD Spectrum of Solids from pH 10 adjusted AZ-101 Simulant.

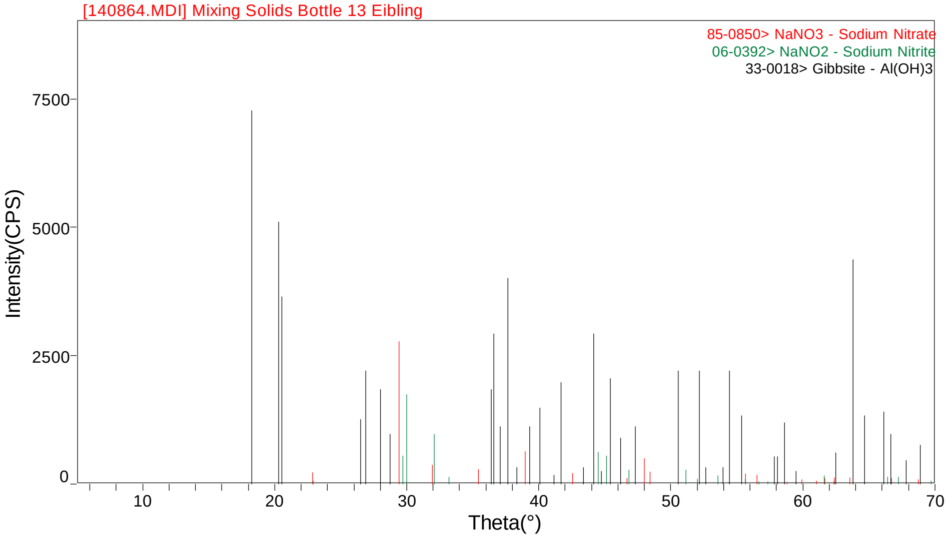


Figure B18. XRD Spectrum of Solids from pH 11 Adjusted AZ-102 Simulant.

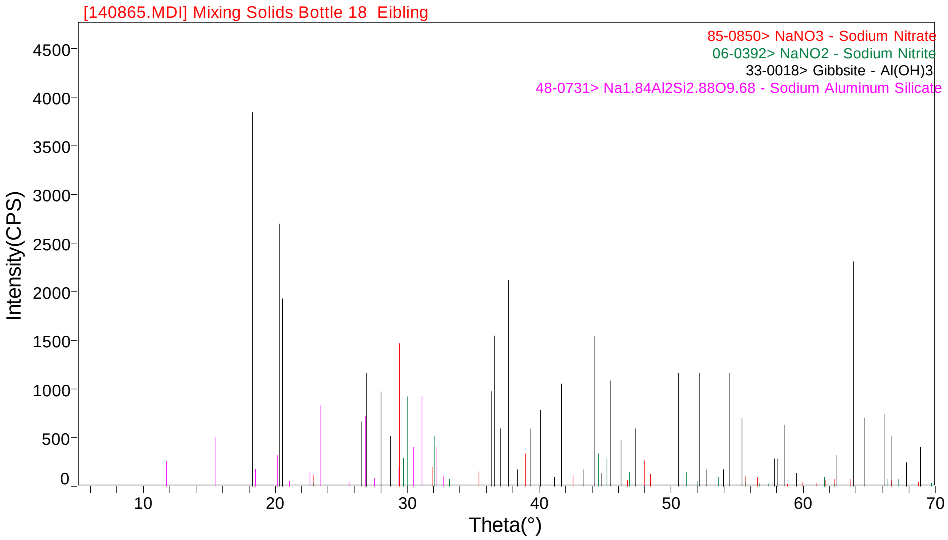
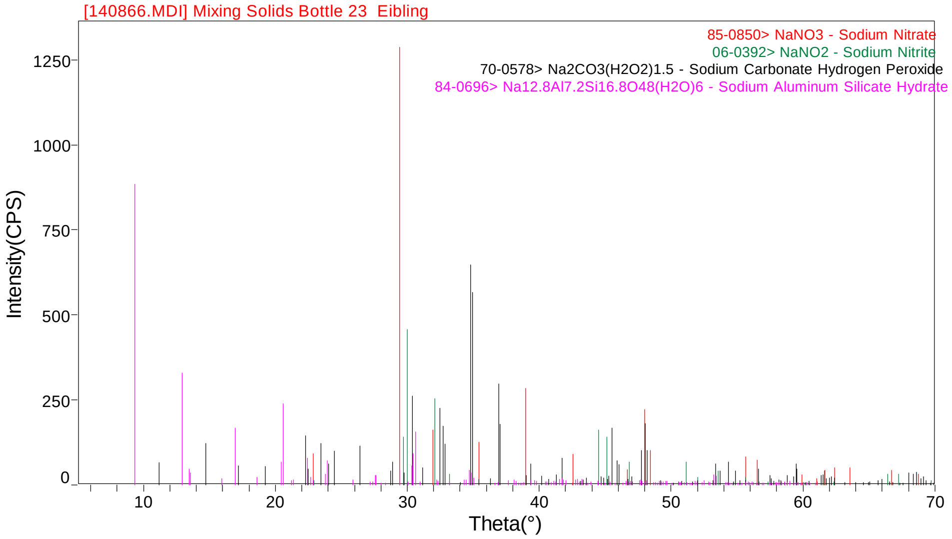


Figure B19. XRD Spectrum of Solids from 50% AN-107 and 50% C-106 Caustic Leachate.



# 8. APPENDIX C: OLI INPUT

**Table C1.** Chemical Composition of AN-107 Simulant and Justification for Dropping Analytes from OLI Calculations.[a]

| | **AN-107 (mg/L)** | **AN-107 (mol/L)** | **Reason for Dropping Analyte from OLI Input** |
|---|---|---|---|
| Ag | <0.3 | -- | 1 |
| Al | 193.5 | 0.007 | |
| B | 37.703 | 0.0034 | 5 |
| Ba | 0.17 | 1.23E-06 | 2 |
| Ca | 138.09 | 0.0034 | |
| Cd | <0.02 | -- | 1 |
| Ce | 50.2 | 0.00035 | 2 |
| Co | 0.39 | 6.61E-06 | 2 |
| Cr | 148.36 | 0.0028 | |
| Cu | 31.91 | 0.00050 | 2 |
| Fe | 1623.2 | 0.029 | |
| La | 40.33 | 0.00029 | 2 |
| Li | 0.52 | 7.49E-05 | 2 |
| Mg | 19.655 | 0.00080 | 2 |
| Mn | 563.62 | 0.01026 | |
| Mo | 35.96 | 0.00037 | 2 |
| Na | 188170 | 8.1848 | 3 |
| Nd | 84.4 | 0.00091 | 2&4 |
| Ni | 500.92 | 0.00853 | |
| P | 420.49 | 0.01357 | 3 |
| Pb | 364.11 | 0.00176 | |
| Si | 1.43 | 5.09E-05 | 2 |
| Sn | <0.26 | -- | 1 |
| Sr | 1.295 | 1.47E-05 | 2 |
| Ti | <0.14 | -- | 1 |
| Zn | 43.943 | 0.00067 | 2 |
| Cs | 22.3 | 0.00017 | 2 |
| K | 1921 | 0.04913 | |
| Na | 201400 | 8.760 | |
| Fluoride | 3430 | 0.180 | |
| Formate | 11232 | 0.249 | |
| Nitrate | 213930 | 3.39 | |
| Nitrite | 57090 | 1.214 | |
| Oxalate | 335 | 0.0038 | |
| Phosphate | 1500 | 0.0158 | |
| Sulfate | 7280 | 0.0909 | |
| TIC | 16100 | 1.342 | 3 |
| TOC | 15800 | 1.317 | 3 |
| Carbonate(TIC) | 80439 | 1.828 | |
| Aluminate | | 0.054 | 3 |
| Carbonate | | 1.052 | 3 |
| Free OH | 668.1 | 0.039 | |

[a] OLI can only conduct calculations on ~16 ionic input analytes. Justification for dropping analytes from OLI simulant: 1 = below detection limit, 2 = low concentration, 3 = repetitive of another Analyte, 4 = limited OLI database & low concentration, 5 = generally soluble, not likely to form precipitates. All analytes without a justification for dropping, were included in the OLI calculation.

**Table C2.** Chemical Composition of AZ-101 Simulant and Justification for Dropping Analytes from OLI Calculations.[a]

| | **AZ-101 (mg/L)** | **AZ-101 (mol/L)** | **Reason for Dropping Analyte from OLI Input** |
|---|---|---|---|
| Ag | <0.3 | -- | 1 |
| Al | 7752 | 2.87E-01 | |
| B | <0.21 | -- | 1 |
| Ba | 0.02 | 1.46E-07 | 2 |
| Ca | 3.7 | 9.19E-05 | |
| Cd | <0.02 | -- | 1 |
| Ce | <0.7 | -- | 1 |
| Co | <0.05 | -- | 1 |
| Cr | 648 | 1.25E-02 | |
| Cu | <0.05 | -- | 1 |
| Fe | 0.46 | 8.18E-06 | |
| La | <0.06 | -- | 1 |
| Li | 0.18 | 2.59E-05 | 2&5 |
| Mg | <0.09 | -- | 1 |
| Mn | 0.11 | 2.06E-06 | |
| Mo | <0.1 | -- | 1 |
| Na | 104670 | 4.55E+00 | 3 |
| Nd | <0.3 | -- | 1 |
| Ni | 0.34 | 5.79E-06 | |
| P | 546 | 1.76E-02 | 3 |
| Pb | <0.6 | -- | 1 |
| Si | 5.3 | 1.88E-04 | |
| Sn | <0.26 | -- | 1 |
| Sr | 0.08 | 8.56E-07 | 2 |
| Ti | <0.14 | -- | 1 |
| V | <0.13 | -- | 1 |
| Zn | <0.37 | -- | 1 |
| Zr | 0.32 | 3.51E-06 | 2 |
| Cs | 41 | 3.09E-04 | |
| K | 4690 | 1.20E-01 | |
| Na | 108990 | 4.74E+00 | |
| Fluoride | 760.0 | 4.00E-02 | |
| Formate | <100 | -- | 1 |
| Nitrate | 60330 | 9.58E-01 | |
| Nitrite | 61770 | 1.31E+00 | |
| Oxalate | <100 | -- | 1 |
| Phosphate | 1318 | 1.39E-02 | |
| Sulfate | 15740 | 1.97E-01 | |
| TIC | 8466 | 7.06E-01 | 3 |
| TOC | 365 | 3.04E-02 | 3 |
| Carbonate(TIC) | 42298 | 9.61E-01 | |
| Aluminate | | 0.268 | 3 |
| Carbonate | | 0.384 | 3 |
| Free OH | 7871 | 0.463 | |

[a] OLI can only conduct calculations on ~16 ionic input analytes. Justification for dropping analytes from OLI simulant: 1 = below detection limit, 2 = low concentration, 3 = repetitive of another analyte, 4 = limited OLI database & low concentration, 5 = generally soluble, not likely to form precipitates. All analytes without a justification for dropping, were included in the OLI calculation.

**Table C3.** Chemical Composition of AZ-102 Simulant and Justification for Dropping Analytes from OLI Calculations.[a]

| | **AZ-102 (mg/L)** | **AZ-102 (mol/L)** | **Reason for Dropping Analyte from OLI Input** |
|---|---|---|---|
| Ag | <0.3 | -- | 1 |
| Al | 230 | 0.0085 | |
| B | 7.3067 | 0.00068 | |
| Ba | 0.01 | 7.3E-08 | 2 |
| Ca | 4.8133 | 0.00012 | |
| Cd | 0.05 | 4.4E-07 | 2 |
| Ce | <0.7 | -- | 1 |
| Co | <0.05 | -- | 1 |
| Cr | 864.69 | 0.0167 | |
| Cu | 0.18 | 2.8E-06 | |
| Fe | 0.23 | 4.1E-06 | |
| La | <0.06 | -- | 1 |
| Li | 0.12 | 1.7E-05 | |
| Mg | <0.09 | -- | 1 |
| Mn | <0.009 | -- | 1 |
| Mo | 57.727 | 0.0006 | |
| Na | 58070 | 2.52588 | 3 |
| Nd | <0.3 | -- | 1 |
| Ni | <0.06 | -- | 1 |
| P | 166.49 | 0.0054 | 3 |
| Pb | <0.6 | -- | 1 |
| Si | 121.25 | 0.00432 | |
| Sn | <0.26 | -- | 1 |
| Sr | 0.045 | 5.1E-07 | 2 |
| Ti | <0.14 | -- | 1 |
| V | <0.13 | -- | 1 |
| Zn | <0.37 | -- | 1 |
| Zr | 0.425 | 4.7E-06 | 2 |
| Cs | 1 | 7.5E-06 | 2 |
| K | 3150 | 0.0806 | |
| Na | 53000 | 2.305 | |
| Fluoride | 1111 | 0.058 | |
| Formate | <100 | -- | 1 |
| Nitrate | 15360 | 0.244 | |
| Nitrite | 31050 | 0.660 | |
| Oxalate | 2671 | 0.0301 | |
| Phosphate | 375 | 0.0039 | |
| Sulfate | 14848 | 0.1854 | |
| TIC | 8946 | 0.746 | 3 |
| TOC | 1052 | 0.0877 | 3 |
| Carbonate(TIC) | 44696 | 1.0158 | |
| Aluminate | | 0.03 | 3 |
| Carbonate | | 0.464 | 3 |
| Free OH | 3332 | 0.196 | |

[a] OLI can only conduct calculations on ~16 ionic input analytes. Justification for dropping analytes from OLI simulant: 1 = below detection limit, 2 = low concentration, 3 = repetitive of another analyte, 4 = limited OLI database & low concentration, 5 = generally soluble, not likely to form precipitates. All analytes without a justification for dropping, were included in the OLI calculation.

**Table C4.** Chemical Composition of AW-101 Simulant and Justification for Dropping Analytes from OLI Calculations.[a]

| | **AW-101 (mg/L)** | **AW-101 (mol/L)** | **Reason for Dropping Analyte from OLI Input** |
|---|---|---|---|
| Ag | <0.3 | -- | 1 |
| Al | 12150 | 0.4503 | |
| B | <0.21 | -- | 1 |
| Ba | 0.115 | 8.4E-07 | 2 |
| Ca | 2.2333 | 5.6E-05 | |
| Cd | <0.02 | -- | 1 |
| Ce | <0.7 | -- | 1 |
| Co | <0.05 | -- | 1 |
| Cr | 45.357 | 0.00087 | |
| Cu | 0.175 | 2.8E-06 | 2 |
| Fe | 0.29 | 5.2E-06 | |
| La | <0.06 | -- | 1 |
| Li | 0.24 | 3.5E-05 | 2&5 |
| Mg | <0.09 | -- | 1 |
| Mn | 0.04 | 7.3E-07 | 2 |
| Mo | 0.1667 | 1.7E-06 | 2 |
| Na | 138670 | 6.0317 | 3 |
| Nd | <0.3 | -- | 1 |
| Ni | 0.32 | 5.45E-06 | 2 |
| Pb | 27.81 | 0.00013 | |
| Si | 125.25 | 0.0044 | |
| Sn | <0.26 | -- | 1 |
| Sr | 0.105 | 1.2E-06 | 2 |
| Ti | <0.14 | -- | 1 |
| V | <0.13 | -- | 1 |
| Zn | 15.277 | 0.00023 | |
| Cs | 11.8 | 8.88E-05 | 2 |
| K | 22730 | 0.581 | |
| Na | 137530 | 5.98 | |
| Fluoride | 112 | 0.0059 | |
| Formate | <100 | -- | 1 |
| Nitrate | 105344 | 1.672 | |
| Nitrite | 59905 | 1.274 | |
| Oxalate | <100 | -- | 1 |
| Phosphate | 799 | 0.0084 | |
| Sulfate | 2403 | 0.030 | |
| TIC | 9620 | 0.801 | 3 |
| TOC | <200 | -- | 1&3 |
| Carbonate(TIC) | 48063 | 1.092 | |
| Aluminate | | 0.365 | 3 |
| Carbonate | | 0.454 | 3 |
| Free OH | 36261 | 2.133 | |

[a] OLI can only conduct calculations on ~16 ionic input analytes. Justification for dropping analytes from OLI simulant: 1 = below detection limit, 2 = low concentration, 3 = repetitive of another analyte, 4 = limited OLI database & low concentration, 5 = generally soluble, not likely to form precipitates. All analytes without a justification for dropping, were included in the OLI calculation.

**Table C5.** Chemical Composition of AN-104 Simulant and Justification for Dropping Analytes from OLI Calculations.[a]

| | **AN-104 (mg/L)** | **AN-104 (mol/L)** | **Reason for Dropping Analyte from OLI Input** |
|---|---|---|---|
| Ag | <0.3 | -- | 1 |
| Al | 16952 | 0.628 | |
| B | 33.437 | 0.0031 | 4 |
| Ba | 5.55 | 4.04E-05 | |
| Ca | 2.83 | 7.06E-05 | |
| Cd | <0.02 | -- | 1 |
| Ce | <0.7 | -- | 1 |
| Co | <0.05 | -- | 1 |
| Cr | 203.69 | 0.00391 | |
| Cu | 0.135 | 2.12E-06 | 2 |
| Fe | 0.31 | 5.55E-06 | 2 |
| La | <0.06 | -- | 1 |
| Li | 0.26 | 3.74E-05 | 2&5 |
| Mg | <0.09 | -- | 1 |
| Mn | <0.009 | -- | 1 |
| Mo | 49.193 | 0.00051 | |
| Na | 164670 | 7.16267 | 3 |
| Nd | <0.3 | -- | 1 |
| Ni | 0.41 | 6.98E-06 | 2 |
| P | 444.15 | 0.01434 | 3 |
| Pb | <0.6 | -- | 1 |
| Si | 169.25 | 0.00602 | |
| Sn | <0.26 | -- | 1 |
| Sr | 0.085 | 9.70E-07 | 2 |
| Ti | 0.15 | 3.13E-06 | 2 |
| Zn | 3.4233 | 5.23E-05 | 2 |
| Cs | 0.7 | 5.26E-06 | 2 |
| K | 4320 | 0.11049 | |
| Na | 168200 | 7.316 | |
| Fluoride | 100 | 0.00526 | |
| Formate | <100 | -- | 1 |
| Nitrate | 85960 | 1.36 | |
| Nitrite | 62530 | 1.330 | |
| Oxalate | 160 | 0.0018 | |
| Phosphate | 868 | 0.0091 | |
| Sulfate | 5744 | 0.0717 | |
| TIC | 12314 | 1.026 | 3 |
| TOC | 3628 | 0.302 | 3 |
| Carbonate(TIC) | 61523 | 1.39 | |
| Aluminate | | 0.63 | 3 |
| Carbonate | | 0.76 | 3 |
| Free OH | 32402 | 1.90 | |

[a] OLI can only conduct calculations on ~16 ionic input analytes. Justification for dropping analytes from OLI simulant: 1 = below detection limit, 2 = low concentration, 3 = repetitive of another analyte, 4 = limited OLI database & low concentration, 5 = generally soluble, not likely to form precipitates. All analytes without a justification for dropping, were included in the OLI calculation.

# 9. DISTRIBUTION

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