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Milestone M4900: Simulant Mixing Analytical Results

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Aiken, SC 29808



SAVANNAH RIVER SITE

Prepared for the U.S. Department of Energy under Contract No. DE-AC09-96SR18500

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1. SUMMARY

This report addresses Milestone M4900, “Simulant Mixing Sample Analysis Results,” and contains the data generated during the “Mixing of Process Heels, Process Solutions, and Recycle Streams: Small-Scale Simulant” task. The Technical and Quality Assurance Plan for this task is BNF-003-98-0079A.

The overall objective of this small-scale simulant mixing study was to identify the processes that generate precipitates and to identify the 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
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, HNO₃ addition, or caustic leachate addition. Turbidity and temperature was measured for 1 to 2 months after treatment. After this period of monitoring turbidity and temperature, 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 Selective Electrode; ISE), anions (Ion Chromatography; IC), formate, glycolate, acetate, and oxalate (Ion Exchange Chromatography; IEC), and EDTA/HEDTA (Ion Paired Chromatography; IPC). Solids were analyzed by X-ray Diffraction (XRD) to identify crystalline phases, and Energy Dispersive X-ray Analysis/Scanning Electron Microscopy (EDX/SEM) to measure the chemical composition and morphology of amorphous solid phases. This report includes the analytical results from these studies. A report with a narrative description and discussion of this data and OLI thermodynamic modeling will be issued separately.

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2. INTRODUCTION

2.1. *Background*

This report addresses Milestone M4900, “Simulant Mixing Sample Analysis Results,” and contains the data generated during the “Mixing of Process Heels, Process Solutions, and Recycle Streams: Small-Scale Simulant” task. The Task Technical and Quality Assurance Plan for this task is BNF-003-98-0079A. A report with a narrative description and discussion of the data will be issued separately. A brief description of the objectives, scope and general approaches follow. The data are organized by the experiments conducted for this task.

2.2. *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 Low-Activity Waste (LAW) feed solutions may need to be diluted with 0.01 M NaOH solution prior to transfer to the River Protection Project – Waste Treatment Plant (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 High-Level Waste (HLW) solids with the LAW feed solutions, to address the potential range of these mixtures as identified in the RPP-WTP flowsheet.

2.3. 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

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.

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).

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 melter. 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.

2.4. 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 Pair 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.

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.

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.	

3. EXPERIMENTAL

3.1. *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- μ m 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.

3.2. *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.

3.3. *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.

3.4. *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 $\text{pH} > 13$ 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 4.4.1.
2. – 8. These steps are identical to those in the Dilution Experiment.

3.5. *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.

4. RESULTS

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. All experiment temperature data is presented in Appendix A and all X-ray Diffraction data is presented in Appendix B.

4.1. *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. This filtration process does not mimic any WTP process. 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.

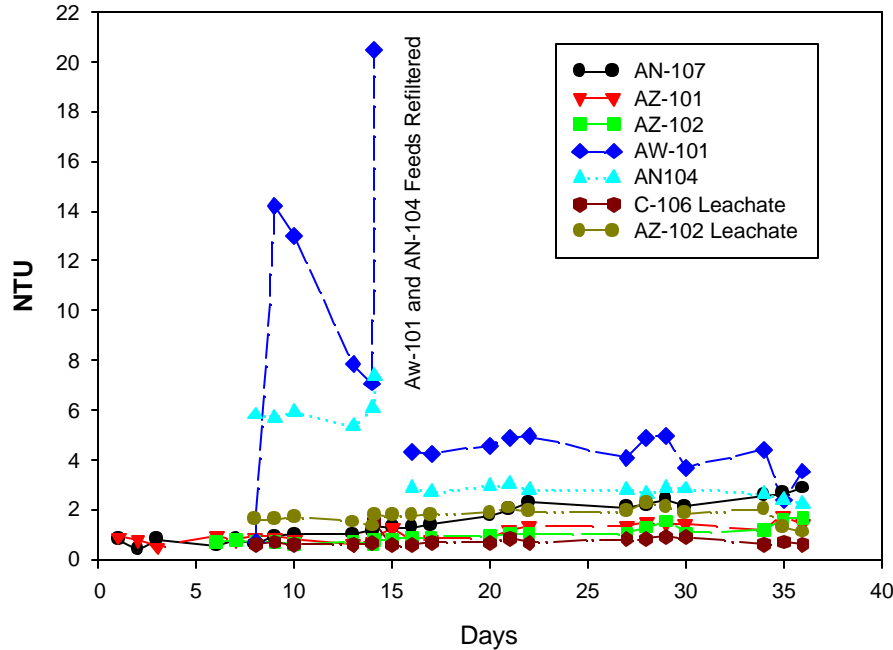


Figure 1. Simulant Turbidity (NTU) During Equilibration Period Prior to Mixing.

4.1.1. 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 ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) (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 ethylenediaminetetraacetic 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)ethylenediaminetriacetic 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 $\text{Al}(\text{OH})_3$. (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

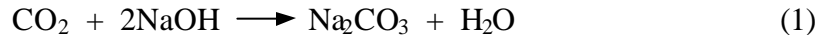
The divalent metal cations that were present at less than the target concentration are generally characterized as forming insoluble carbonates and phosphates, but also stable complexes with chelating agents such as EDTA. Since the carbonate level was sufficiently high in the AN-107 simulant to generate 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.

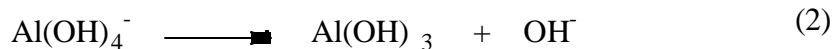
The measured values for three of the complexing agents differed significantly from the planned target values: EDTA less than planned, and HEDTA and IDA greater than planned (Table 3). One possible reason for the difference could be an analytical problem since both of the methods used (ion exclusion chromatography 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 CO₂ from the air with the free hydroxide to generate carbonate:



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:



The form of zirconium used for the simulant recipe was zirconyl nitrate, ZrO(NO₃)₂·xH₂O, 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 CO₂ 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

4.1.2. 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- μ m 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, $\text{Al}(\text{OH})_4^-$, 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.

4.1.3. 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, $\text{Al}(\text{OH})_4^-$, 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.

4.1.4. 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, $\text{Al}(\text{OH})_4$. 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 $\text{Al}(\text{OH})_4$ 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. It is not known why the “found” fluorine concentration was only 42% of the “planned” 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.

4.1.5. 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 CO₂ 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. The neodymium concentration is expected to track the lanthanum concentration and would 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.

4.1.6. 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, $\text{Al}(\text{OH})_4^-$. 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.

4.1.7. 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, $\text{Al}(\text{OH})_4^-$, 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.

4.2. *Dilution Experiment*

The reader is directed to Kaplan et al. (2000; SRT-RPP-2000-00016) for discussion, details and conclusions concerning this experiment. The analytical results presented in this section are for general information and the final report (Kaplan et al. 2000) should be consulted before using or trying to interpret these results.

These tests were added because no turbidity was visually observed (no turbidity meter was used) when active feed samples were mixed, contrary to the results from the simulant mixing study. 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. 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

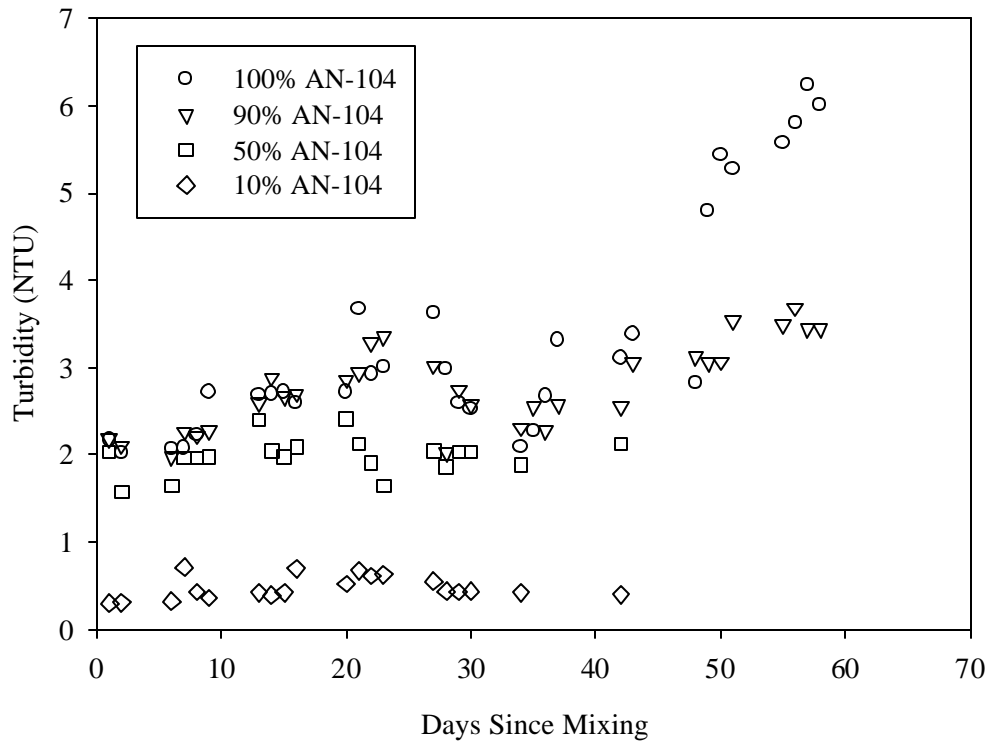


Figure 2. Turbidity of AN-104 Diluted with 0.01 M NaOH.

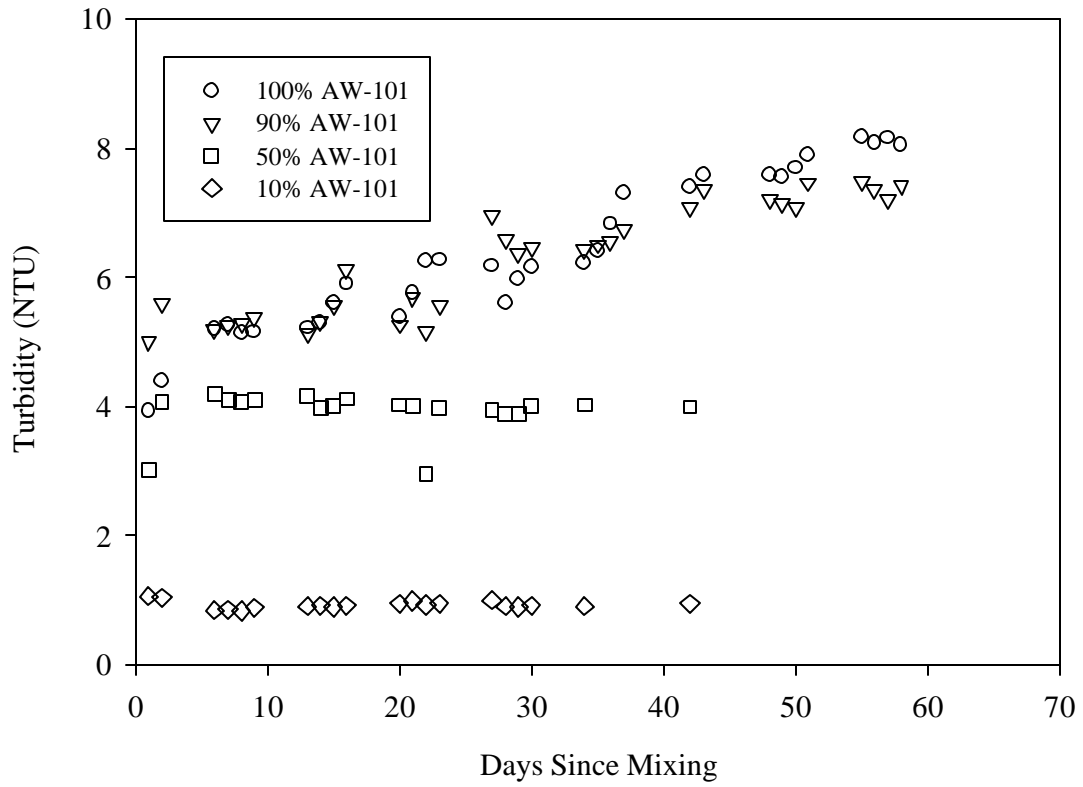


Figure 3. Turbidity of AW-101 Diluted with 0.01 M NaOH.

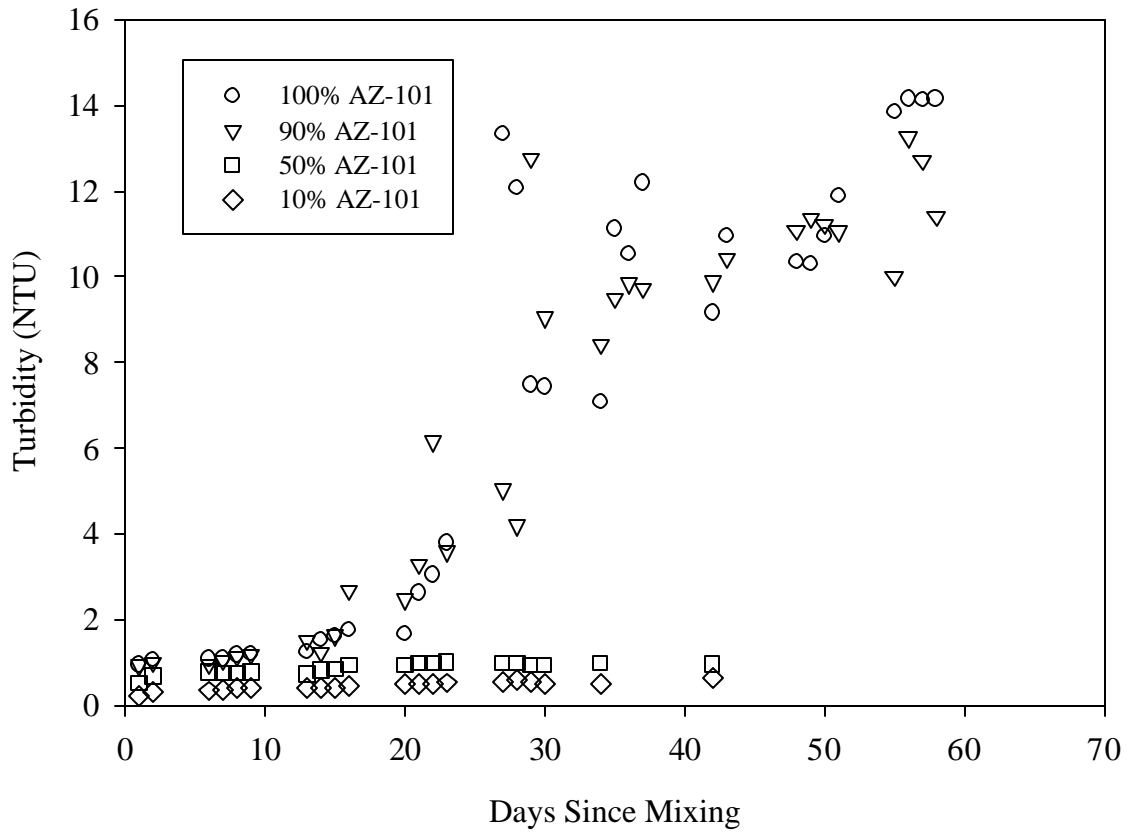


Figure 4. Turbidity of AZ-101 Diluted with 0.01 M NaOH.

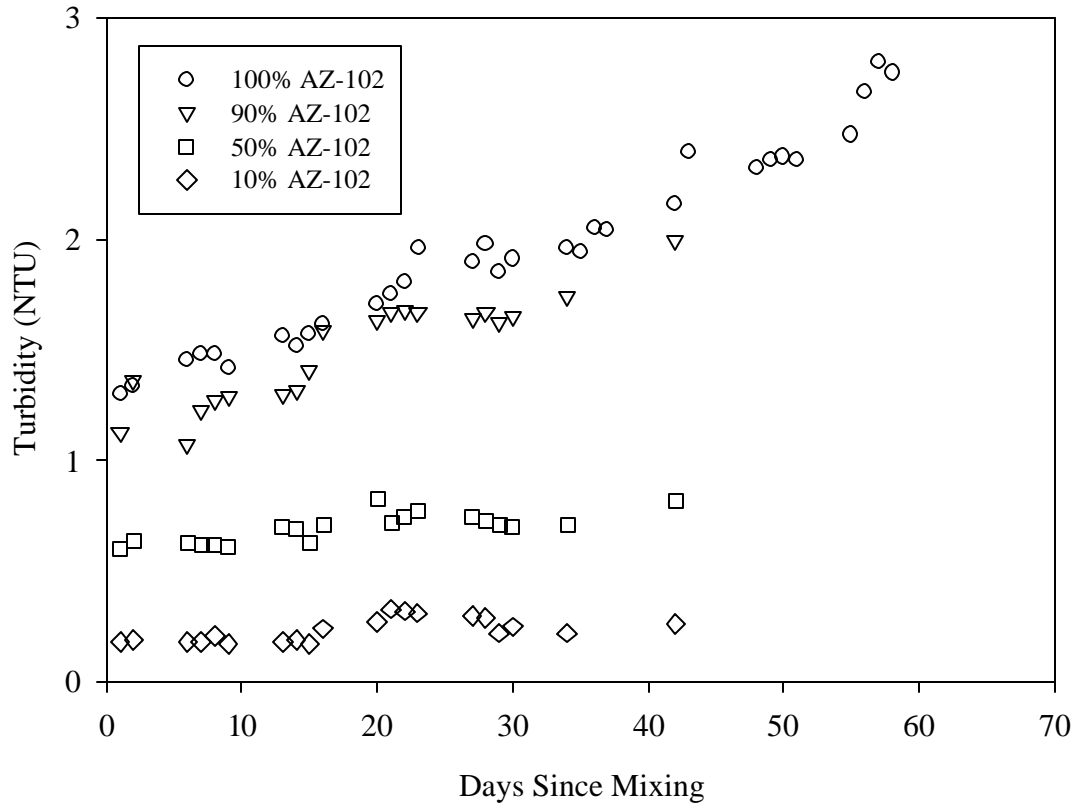


Figure 5. Turbidity of AZ-102 Diluted with 0.01 M NaOH.

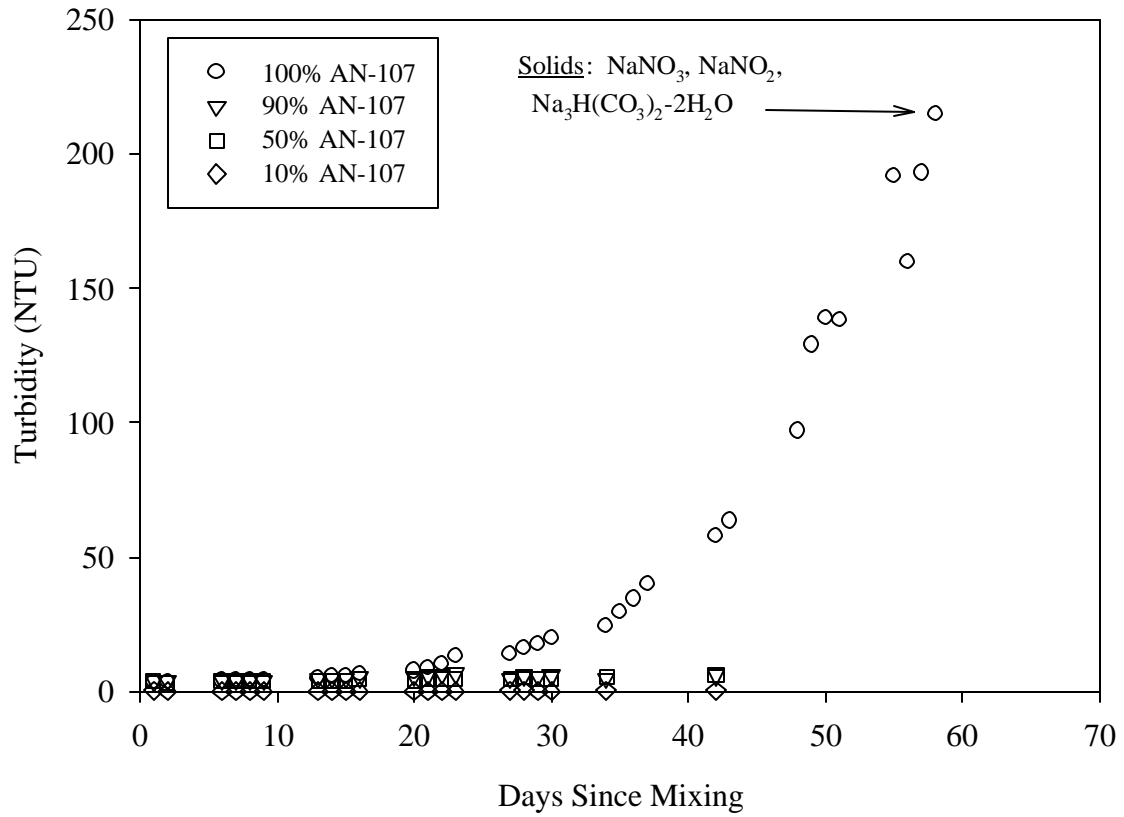


Figure 6. Turbidity of AN-107 Diluted with 0.01 M NaOH.

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- μ m 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.

4.3. Envelope Mixing Experiment

The reader is directed to Kaplan et al. (2000; SRT-RPP-2000-00016) for discussion, details and conclusions concerning this experiment. The analytical results presented in this section are for general information and the final report (Kaplan et al. 2000) should be consulted before using or trying to interpret these results.

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.

4.3.1. Full-strength Envelope Mixing Experiment

4.3.1.1. AZ-101 and AN-107 Full Strength Mixtures

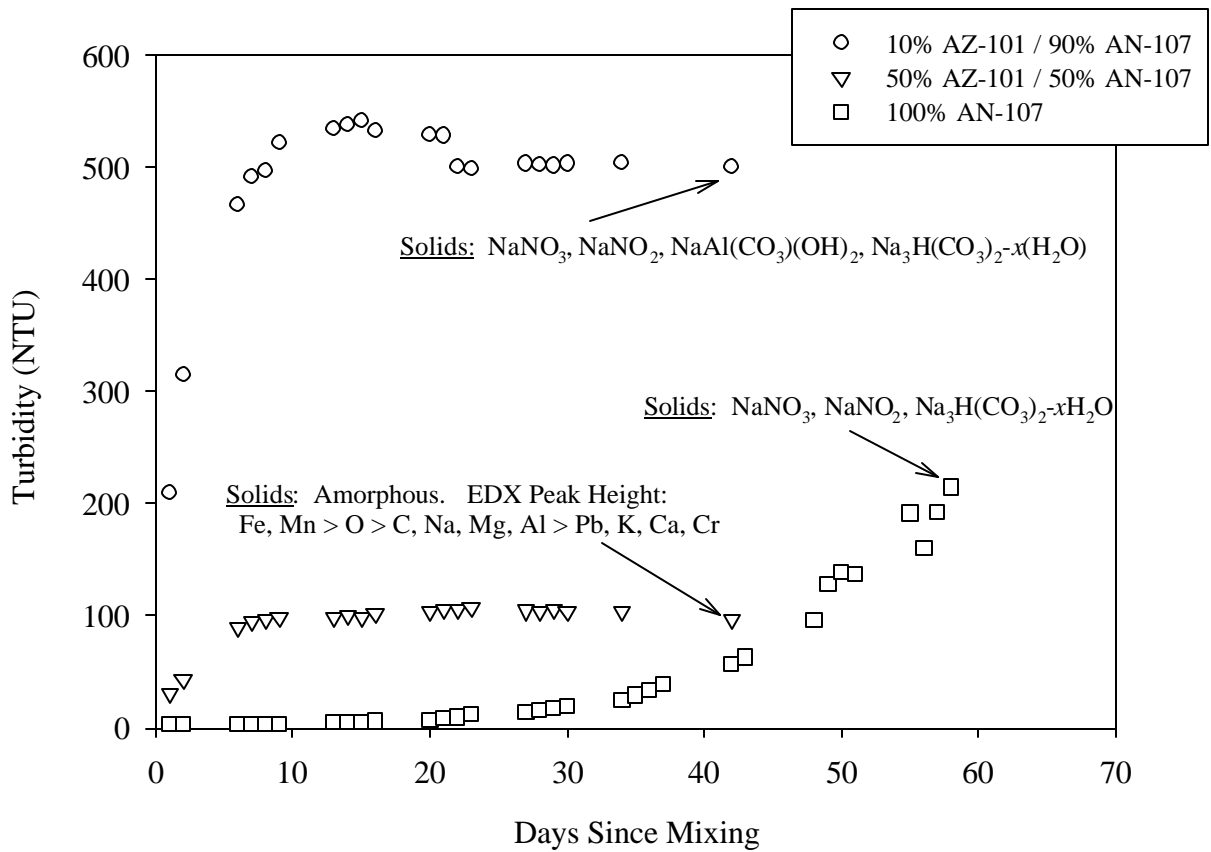


Figure 7. Turbidity and Solid Phases Based on XRD and SEM in Mixtures of AZ-101 and AN-107.

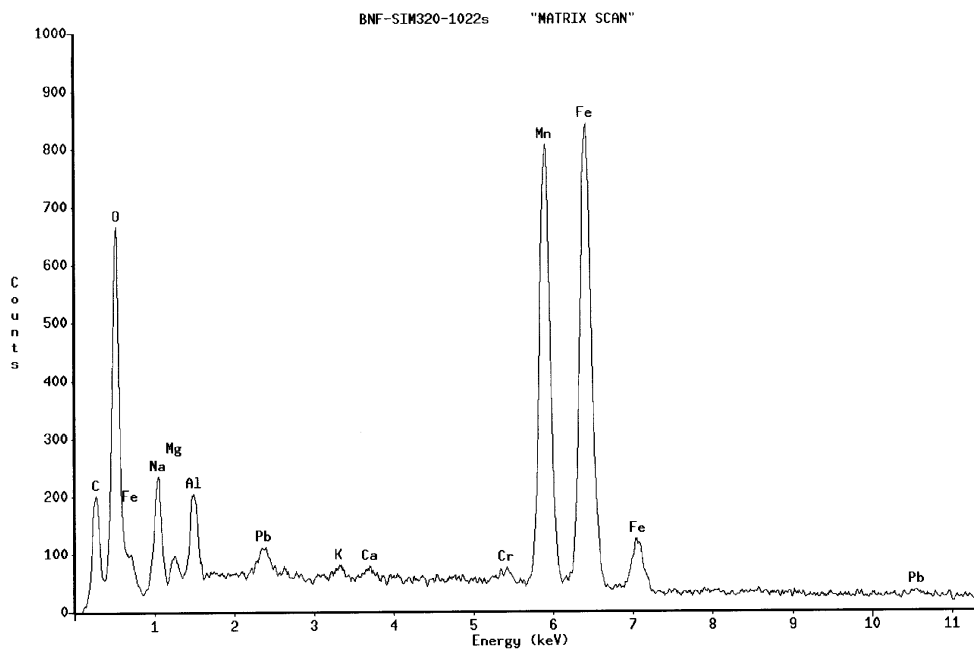
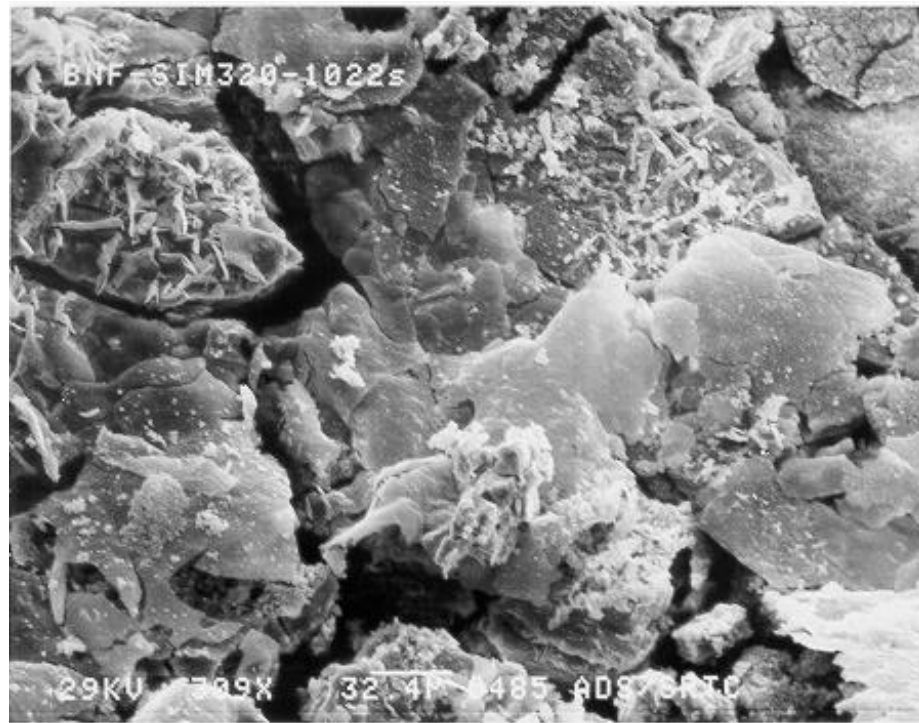


Figure 8. SEM image and EDX spectrum of solids recovered at the end of the 50% AZ-101 / 50% AN-107 mixtures. The scale bar in the SEM image represents 32.4- μm . The EDX spot size was about the same as the entire SEM image, thus it represents an average.

4.3.1.2. AN-104 and AN-107 Full Strength Mixtures

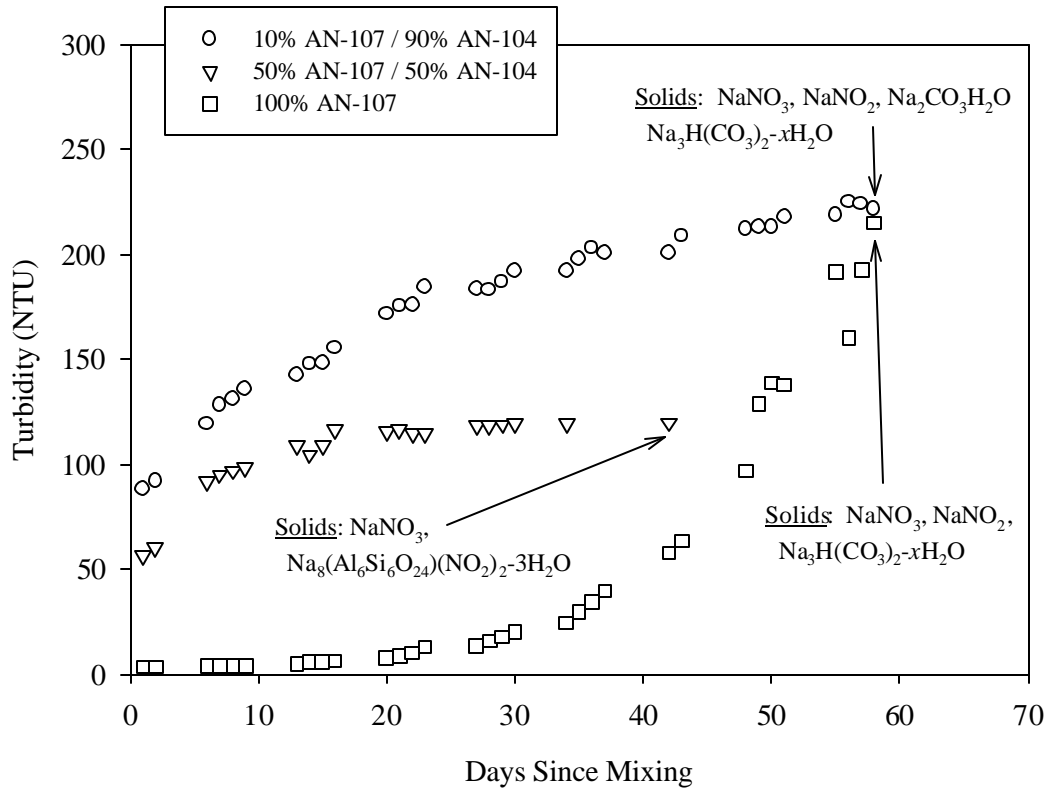


Figure 9. Turbidity and solid phases based on XRD and SEM in Mixtures of AN-107 and AN-104.

4.3.2. Dilute Envelope Mixing Experiment

These tests were added because no turbidity was visually observed (no turbidity meter was used) when active feed samples were mixed, contrary to the results from the simulant mixing study. 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 14 and Table 15. 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.

Table 14. 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 15. 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 16. 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 17. 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

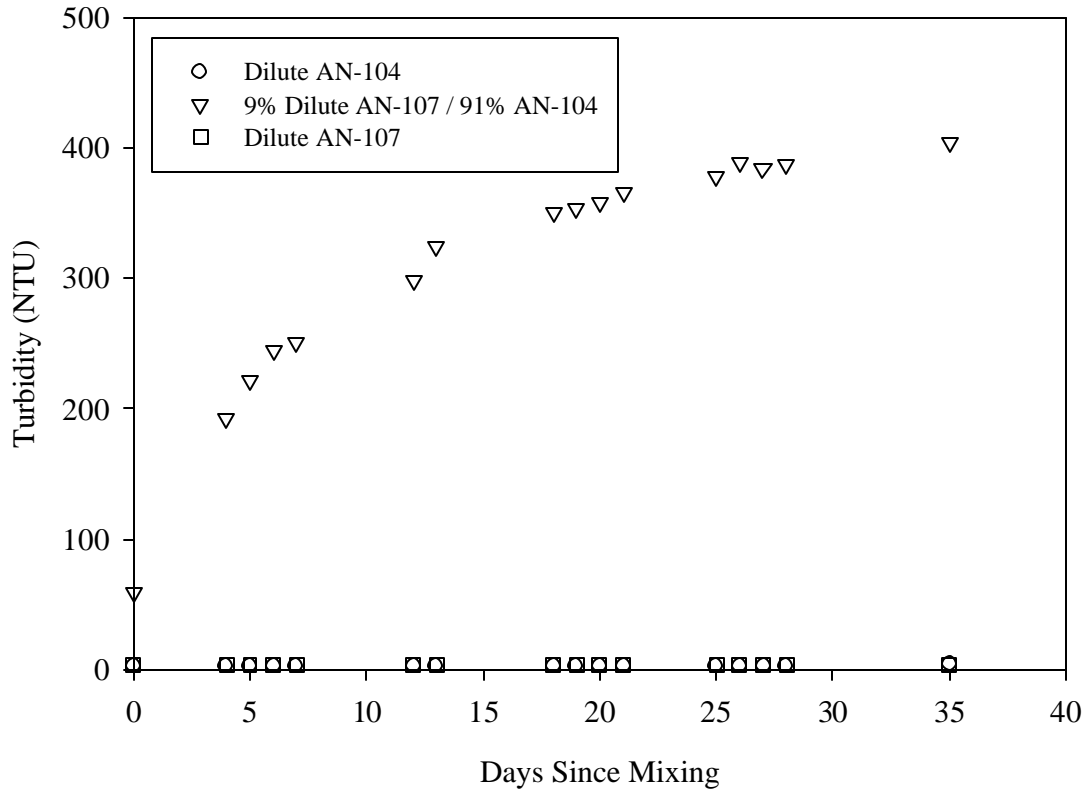


Figure 10. Turbidity in Dilute AN-107, Dilute AN-104, and a 9% AN-107 & 91% AN-104 Mixture.

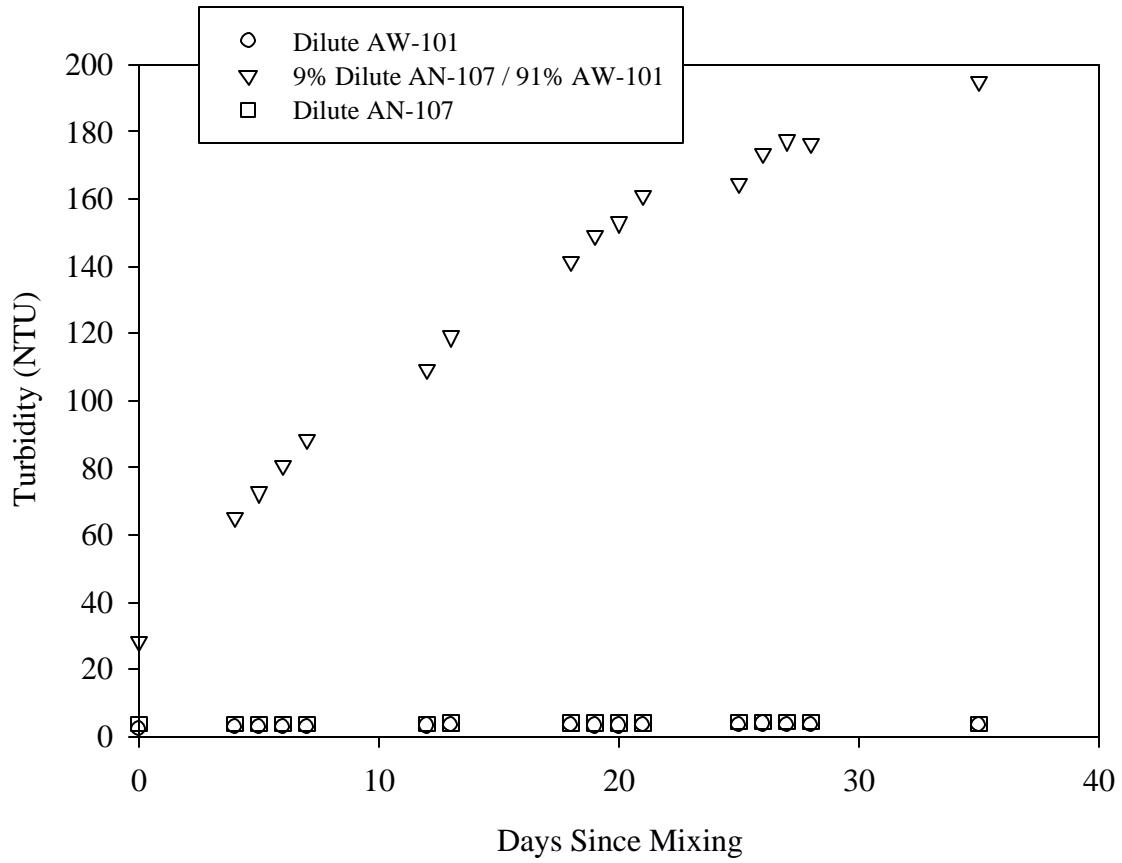


Figure 11. Turbidity in Dilute AN-107, Dilute AW-101, and a 9% AN-107 & 91% AW-101 Mixture.

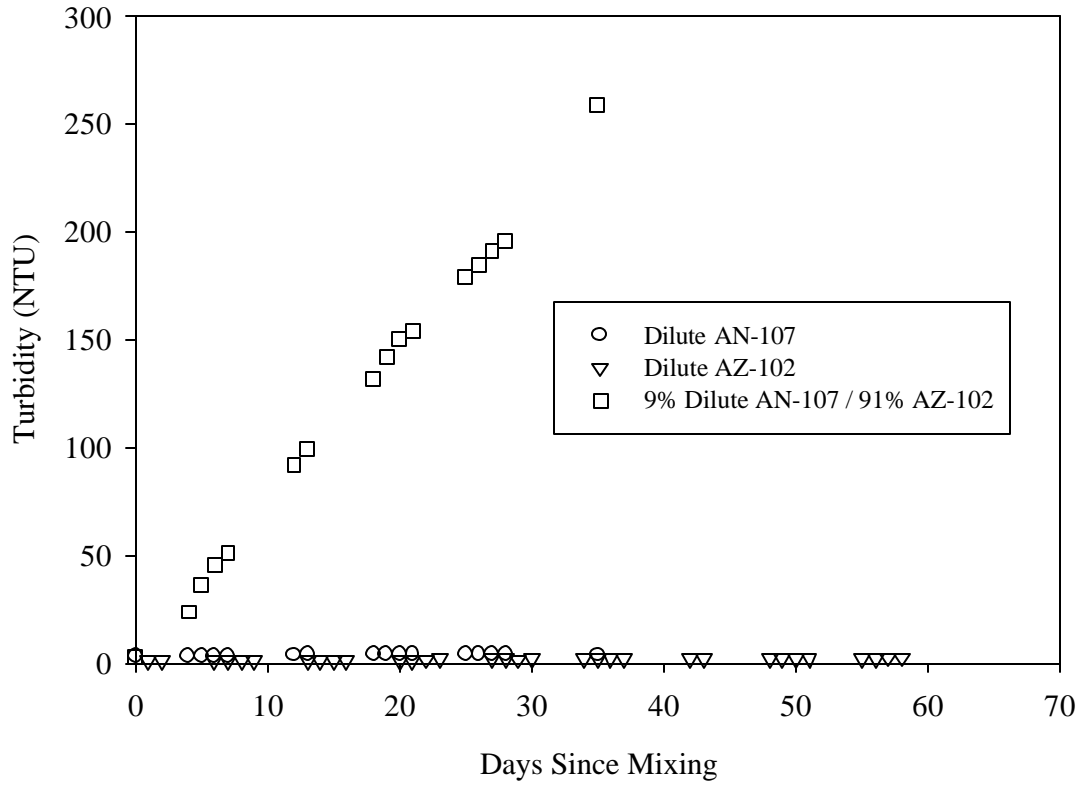


Figure 12. Mixture of Dilute AN-107 and Dilute AZ-102.

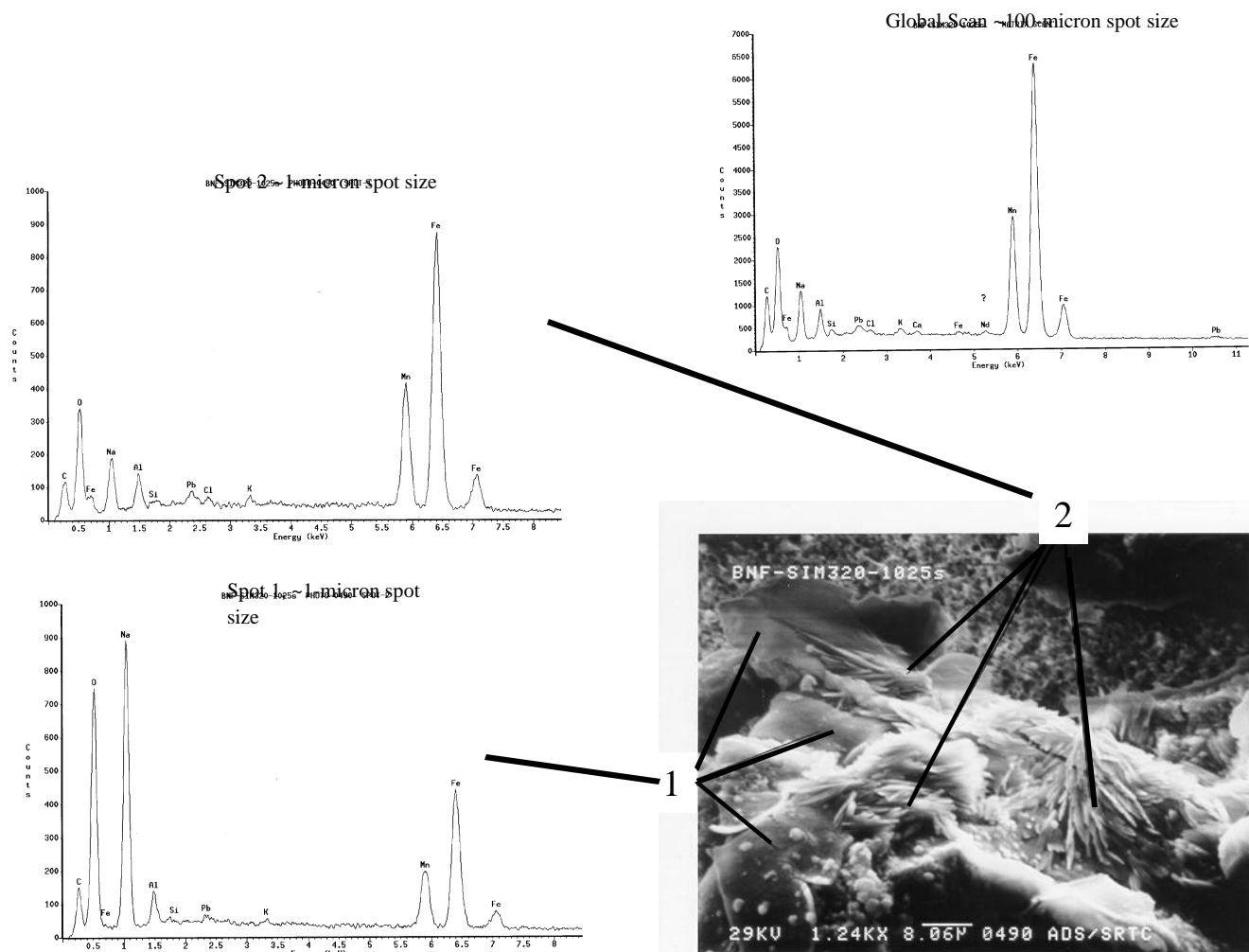


Figure 13. SEM image and corresponding EDX spectra of 9% dilute AN-107 / 91% dilute AN-104. Spot 1 is an EDX spectrum taken of large amorphous particles. Spot 2 is an EDX spectrum taken of crystalline particles. A third EDX spectrum is presented of a large spot size, which provides an average elemental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

4.4. Hydroxide-Concentration Experiment

The reader is directed to Kaplan et al. (2000; SRT-RPP-2000-00016) for discussion, details and conclusions concerning this experiment. The analytical results presented in this section are for general information and the final report (Kaplan et al. 2000) should be consulted before using or trying to interpret these results.

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 3.4 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.

4.4.1. Titration Basis for pH Adjustment

Table 18. 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.

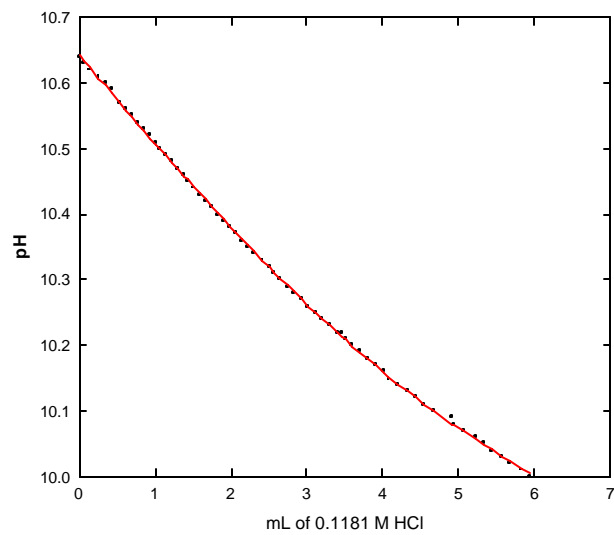


Figure 14. Titration Curve for AN-107.

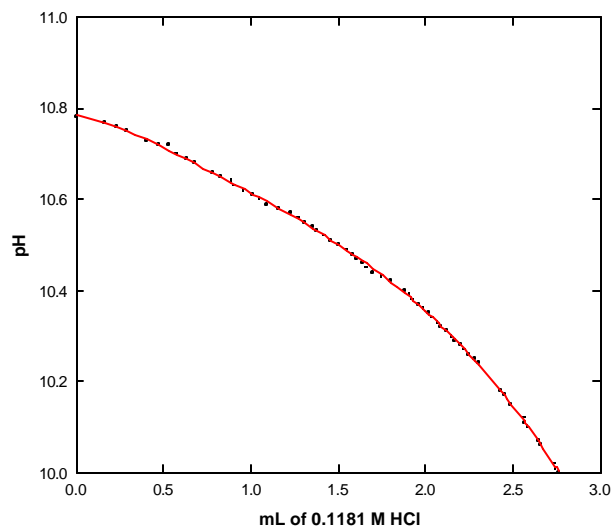


Figure 15. Titration Curve for AN-104.

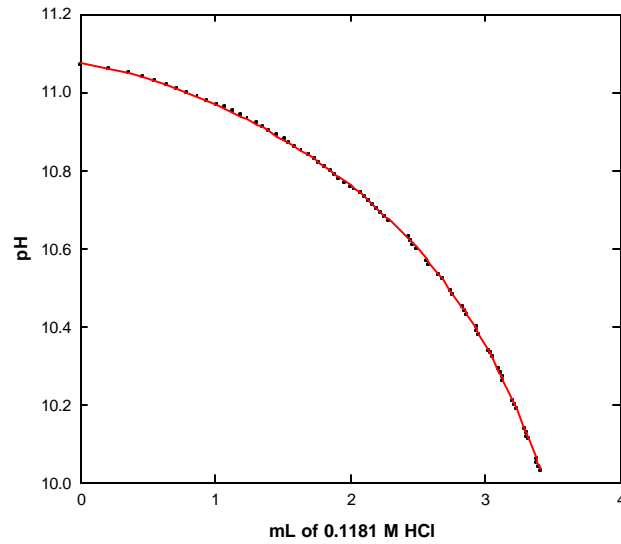


Figure 16. Titration Curve for AW-101.

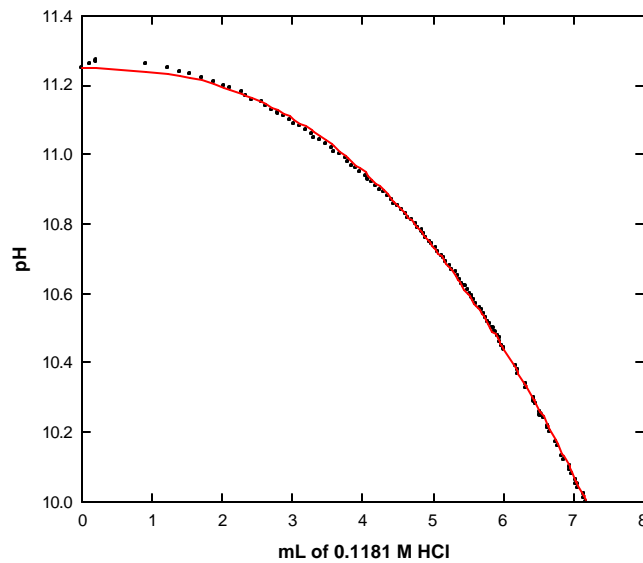


Figure 17. Titration Curve for AZ-101.

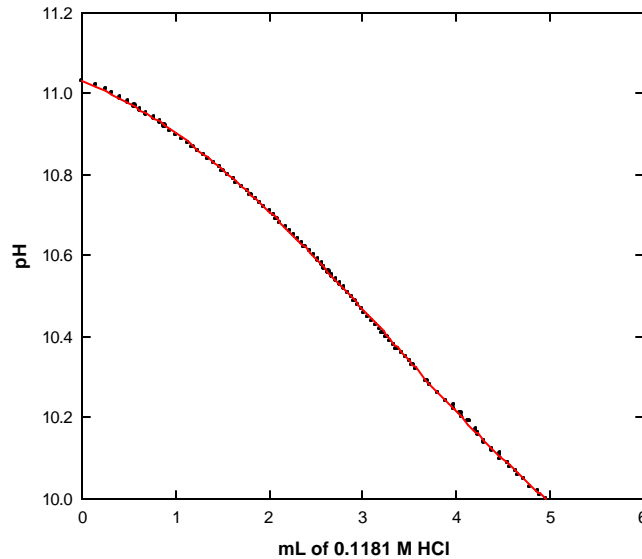


Figure 18. Titration Curve for AZ-102.

Table 19. 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.

4.4.2. 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 (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 20). 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 $>2\text{-M}$. The only component concentrations that declined in the acid adjusted tests was Ca and possibly $\text{Al}(\text{OH})_4^-$. 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.

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.

Table 20. Composition of pH-Adjusted AN-107 Simulant.

Tank		Feed	pH 10	pH 11	pH 13	pH 14.5	Analysis
Components	Units	Found	Found	Found	Found	Found	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.

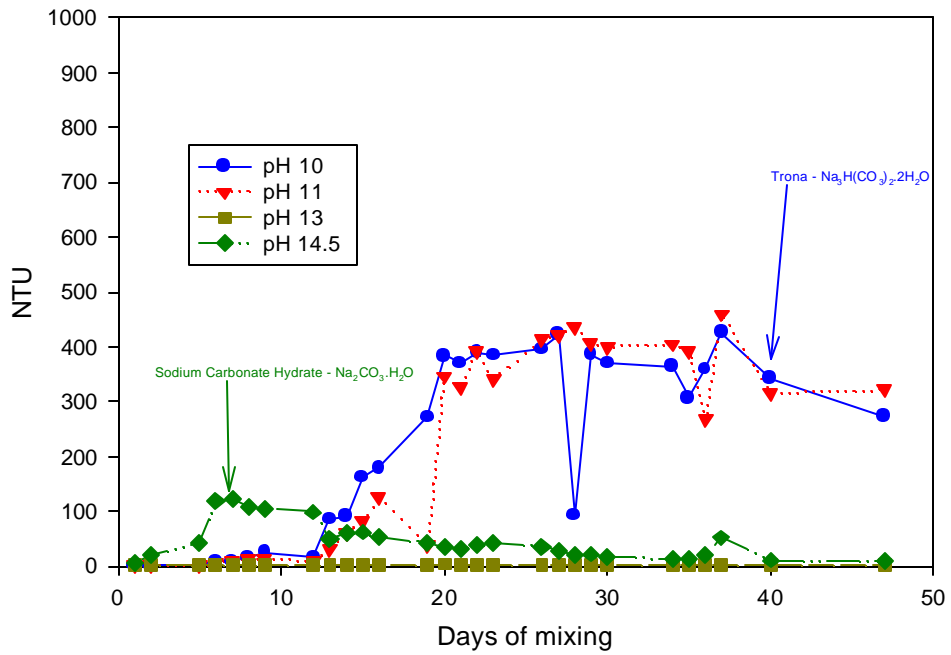


Figure 19. Turbidity of pH-Adjusted AN-107 Simulant.

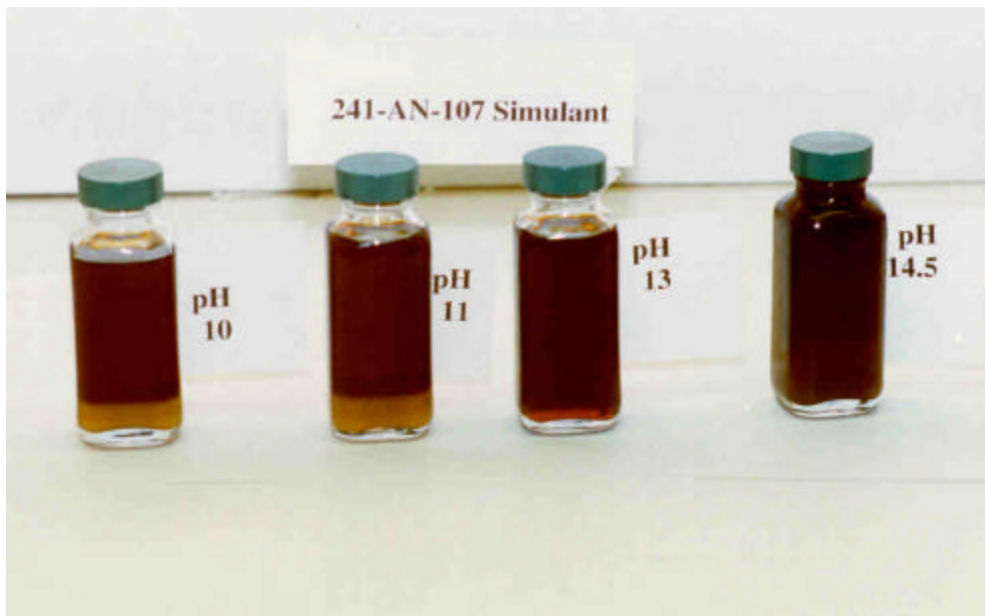


Figure 20. AN-107 pH-Adjusted Simulant.

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 – $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$,
 sodium aluminum silicate – $\text{Na}_6(\text{AlSiO}_4)_6$,
 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 – $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$,
 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 21 summarizes the observations on pH adjusting AN-107.

Table 21. Summary of pH Adjusted AN-107 Observations.

Targeted pH	Targeted[OH] (M)	Measured [OH] (M)	Observed	
			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

4.4.3. 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.

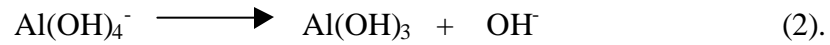
Figure 21 displays the result of monitoring turbidity for the pH adjusted AN-104 simulant. The immediate formation of white solids was observed in the targeted pH 10, 11, and 13 bottles (see footnote 2). These solids after the first few days were observed to settle quickly leading to erratic turbidity readings. This implies that the density and probably the crystallinity of the particles were increasing over time. As indicated in Figure 21, the pH 14.5 (high hydroxide) test did not produce any solids. Figure 22 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 22.

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 22 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 – $\text{Al}(\text{OH})_3$,
thermonatrite – $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$,
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 22 confirms the solids characterization since both Al by ICP-ES, $\text{Al}(\text{OH})_4^-$ 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 19) 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 22 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, $\text{Al}(\text{OH})_3$, the following reaction must have occurred:



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

Table 22. 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.

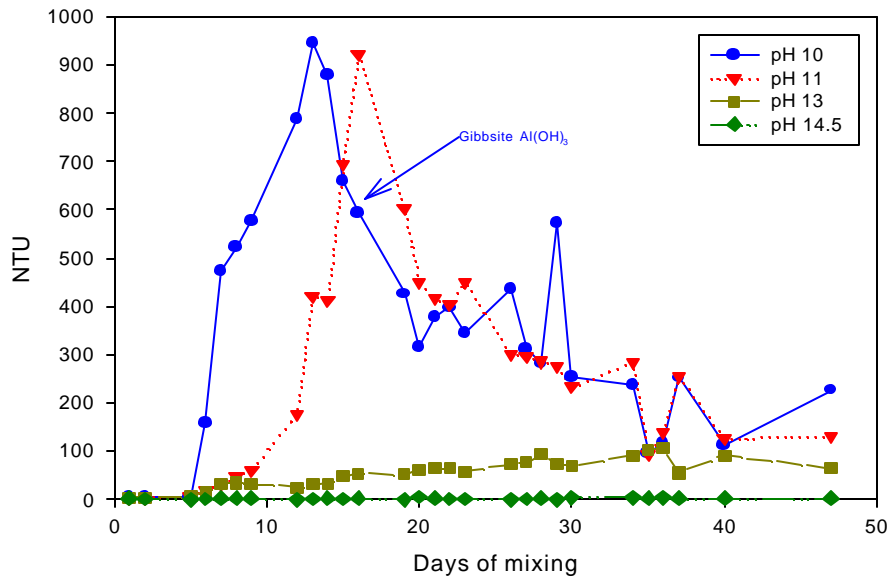


Figure 21. Turbidity of pH-Adjusted AN-104 Simulant.

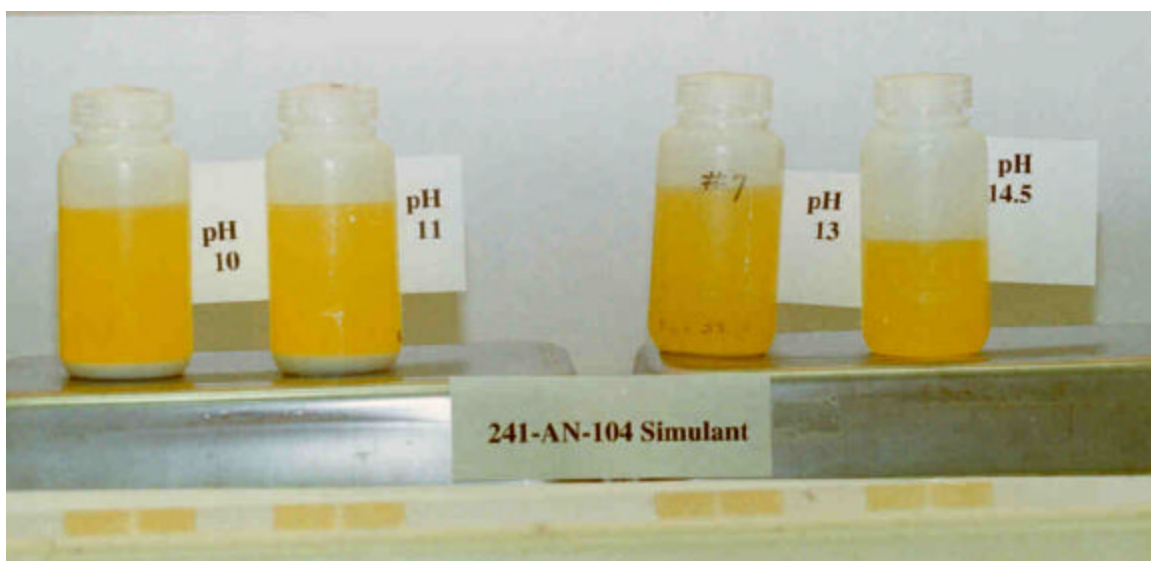


Figure 22. pH-Adjusted AN-104 Simulant.

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 23.

Table 23 Summary of pH-Adjusted AN-104 Observations.

Targeted pH	Targeted[OH] (M)	Measured [OH] (M)	Observed	
			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

4.4.4. 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.

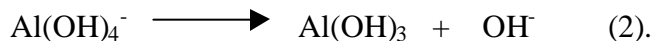
Figure 23 displays the result of monitoring turbidity for the pH adjusted AW-101 simulant. The immediate formation of white solids was observed in the targeted pH 10, 11, and 13 bottles (see footnote 2). The shape of the curve suggests that solids formation was continuing through the entire monitoring 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 23, 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 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 B16):

gibbsite – $\text{Al}(\text{OH})_3$,
 sodium aluminum,
 silicate hydrate – $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot 216\text{H}_2\text{O}$,
 sodium aluminum silicate hydrate - $\text{Na}_2\text{Al}_2\text{Si}_{2.71}\text{O}_{9.42}\cdot 4.39\text{H}_2\text{O}$,
 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 22 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 19) 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 24 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, $\text{Al}(\text{OH})_3$, the previously cited reaction must have occurred:



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

Table 24. 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.

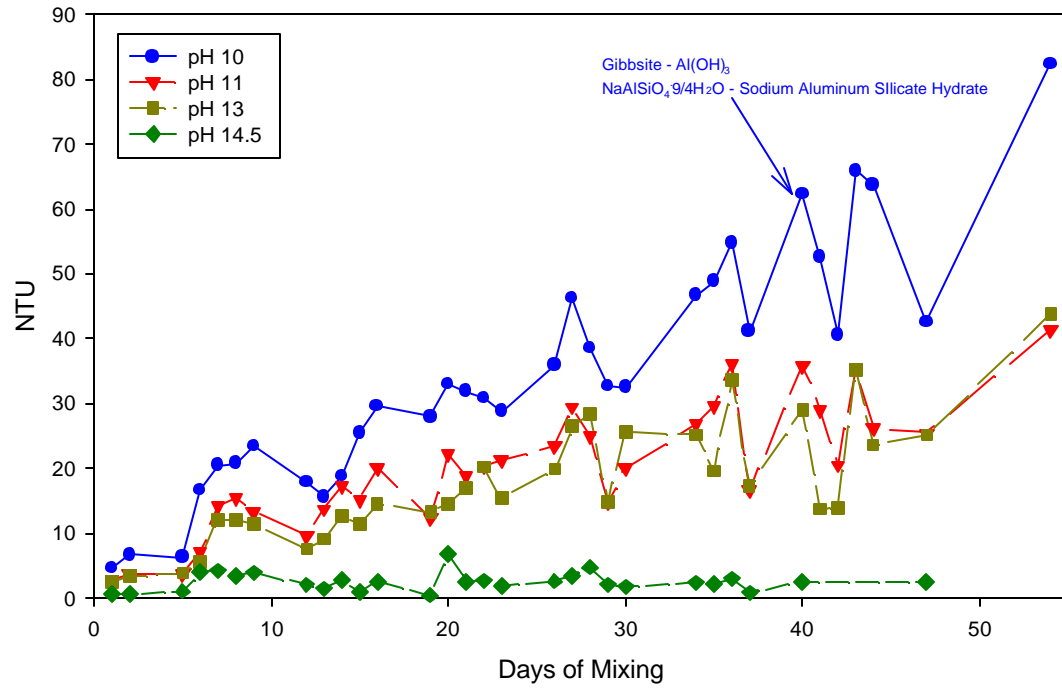


Figure 23. Turbidity of pH-Adjusted AW-101 Simulant.

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 25.

Table 25. Summary of pH Adjusted AW-101 Observations.

Targeted pH	Targeted[OH] (M)	Measured [OH] (M)	Observed	
			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

4.4.5. 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.

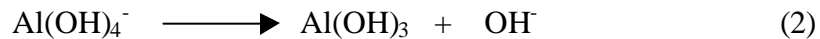
Figure 24 displays the result of monitoring turbidity for the pH adjusted AZ-101 simulant. The immediate formation of white solids was observed in the targeted pH 10 and 13 bottles (see footnote 2). The solids after the first few days were observed to settle quickly leading to erratic turbidity readings. 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 24 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 26 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 26 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 26). 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:



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

Table 26. 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.

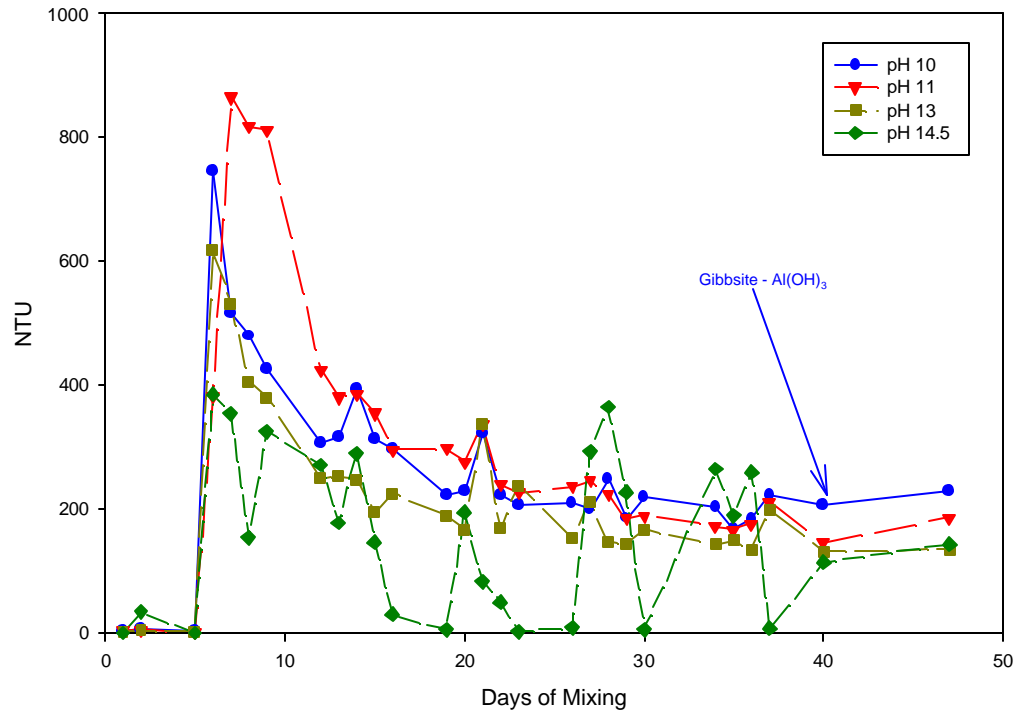


Figure 24. Turbidity of pH-Adjusted AZ-101 Simulant.

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 27.

Table 27. Summary of pH Adjusted AZ-101 Observations.

Targeted pH	Targeted[OH] (M)	Measured [OH] (M)	Observed	
			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

4.4.6. 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 25 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 25, 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 28 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}Al₂Si_{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 28 confirms the solids identified by XRD, since both Si by ICP-ES and $\text{Al}(\text{OH})_4$ 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 28. 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 28. 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.

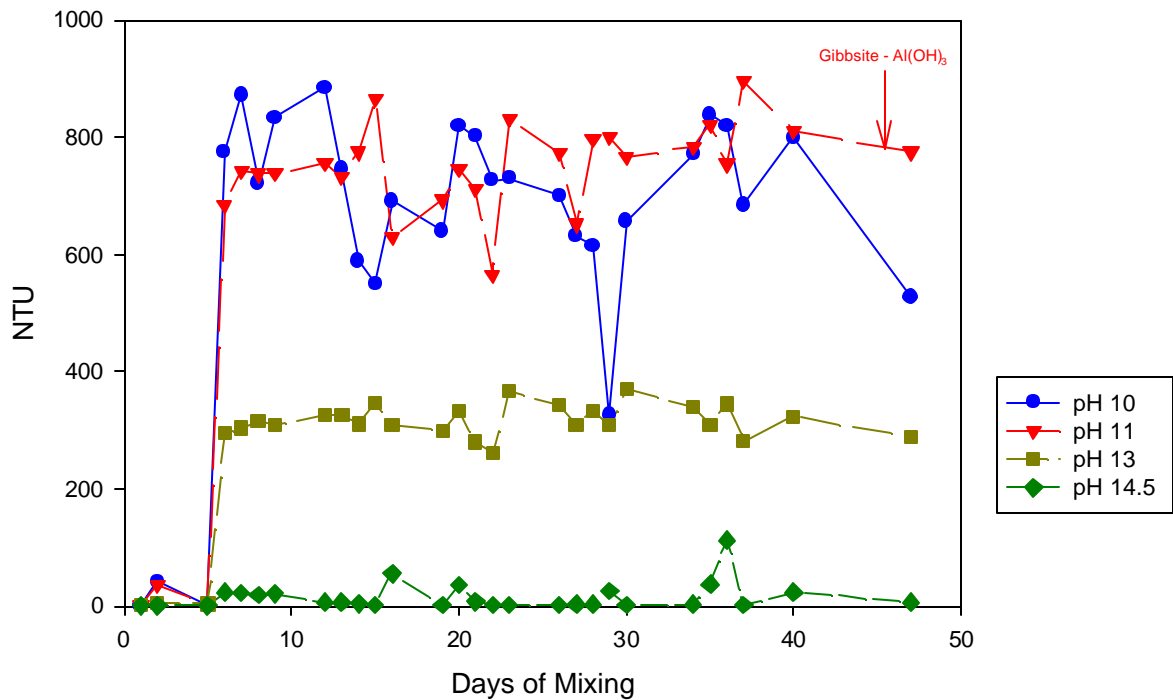


Figure 25. Turbidity of pH-Adjusted AZ-102 Simulant.

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 29.

Table 29. Summary of pH Adjusted AZ-102 Observations.

Targeted pH	Targeted[OH] (M)	Measured [OH] (M)	Observed	
			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

4.5. *Envelope-D Leachate Mixing Experiment*

The reader is directed to Kaplan et al. (2000; SRT-RPP-2000-00016) for discussion, details and conclusions concerning this experiment. The analytical results presented in this section are for general information and the final report (Kaplan et al. 2000) should be consulted before using or trying to interpret these results.

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 3.5. Only results for AN-107 and C-106 caustic leachate mixtures are discussed in detail because the other mixtures did not result in appreciable 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.

4.5.1. AN-107 and C-106 Caustic Leachate Mixtures

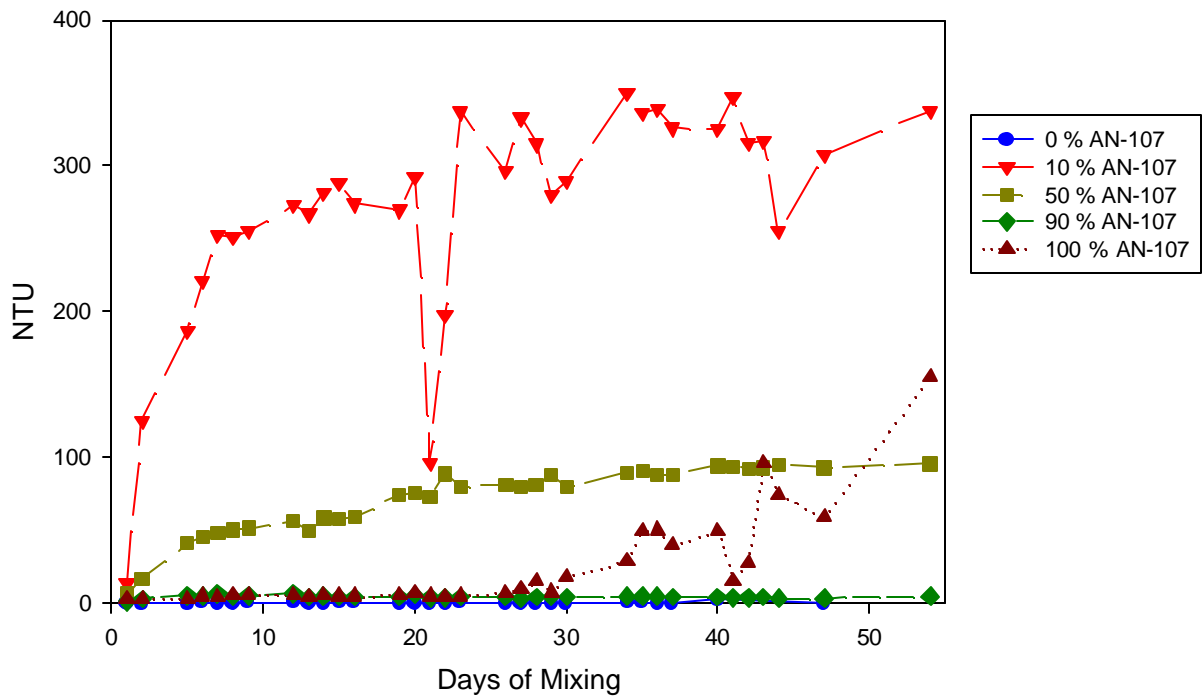


Figure 26. Turbidity of AN-107 & C-106 Leachate Simulant Mixtures.

X-Ray Diffraction Results for Filtered Solids from the 50:50 Mixture of AN-107 and C-106 Leachate

Sodium Aluminum Silicate Hydrate – $\text{Na}_{12.8}\text{Al}_{7.2}\text{Si}_{16.8}\text{O}_{48}(\text{H}_2\text{O})_6$

Sodium Carbonate Hydrogen Peroxide – $\text{Na}_2\text{CO}_3(\text{H}_2\text{O}_2)_{1.5}$

Sodium Nitrate and Sodium Nitrite were also detected but since the solids were not washed this would be due to the residual supernate which dried on the solids.

Table 30. 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.

4.5.2. A and B Envelopes Mixed with Caustic Leachates

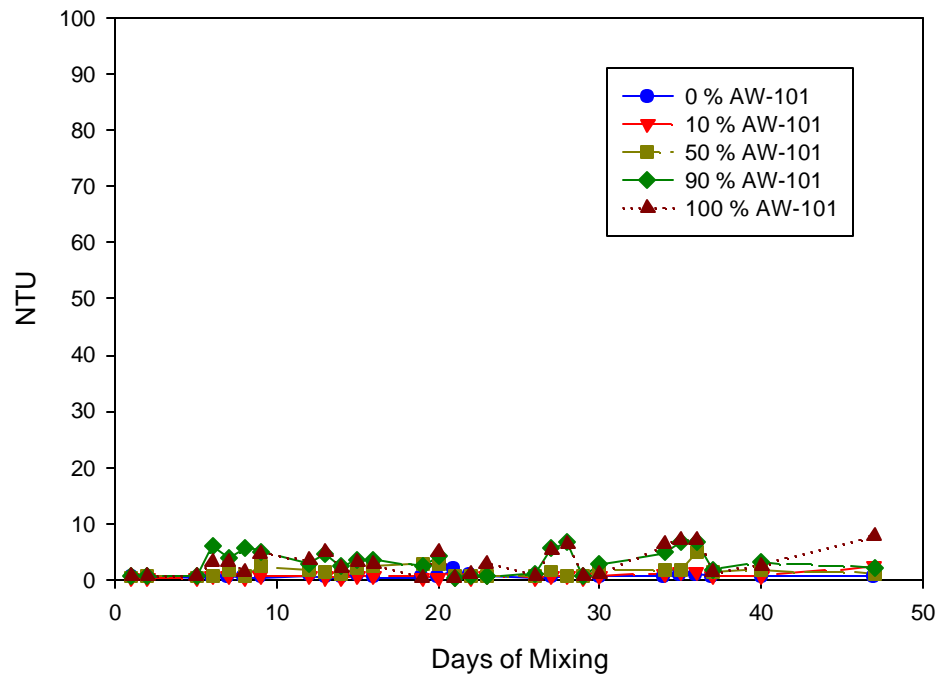


Figure 27. Turbidity of AW-101 & C-106 Leachate Simulant Mixtures.

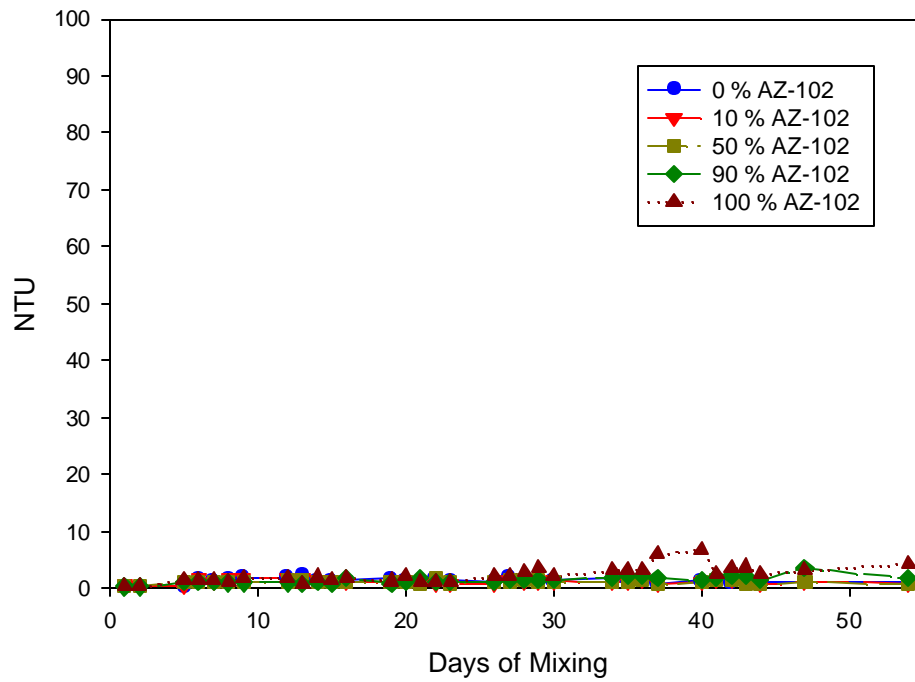


Figure 28. Turbidity of AZ-102 & AZ-102 Leachate Mixtures.

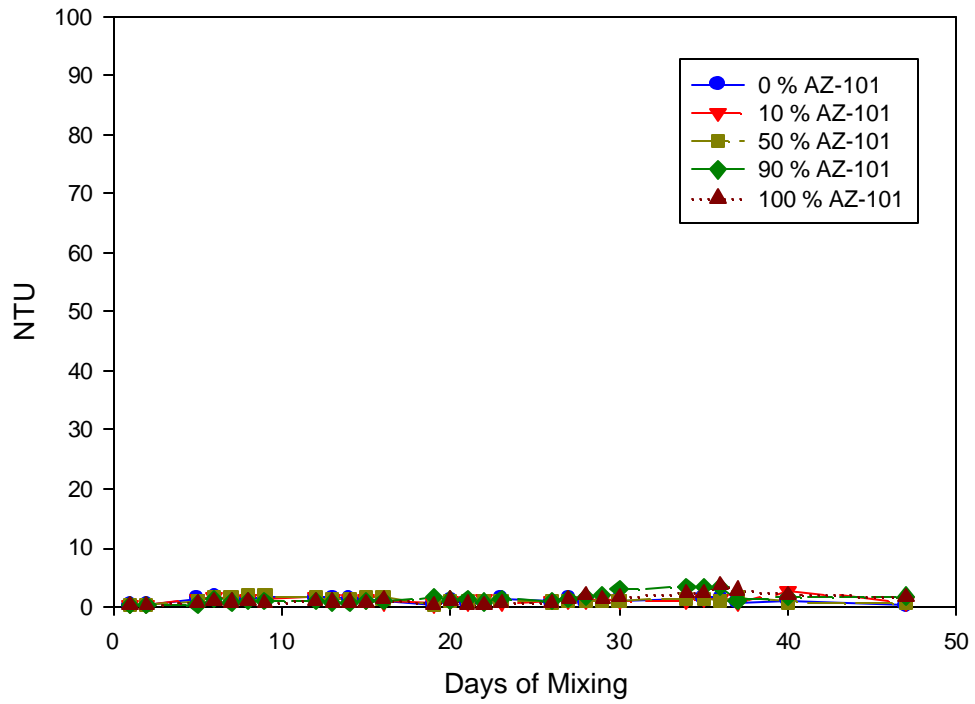


Figure 29. Turbidity of AZ-101 and AZ-102 Leachate Mixtures.

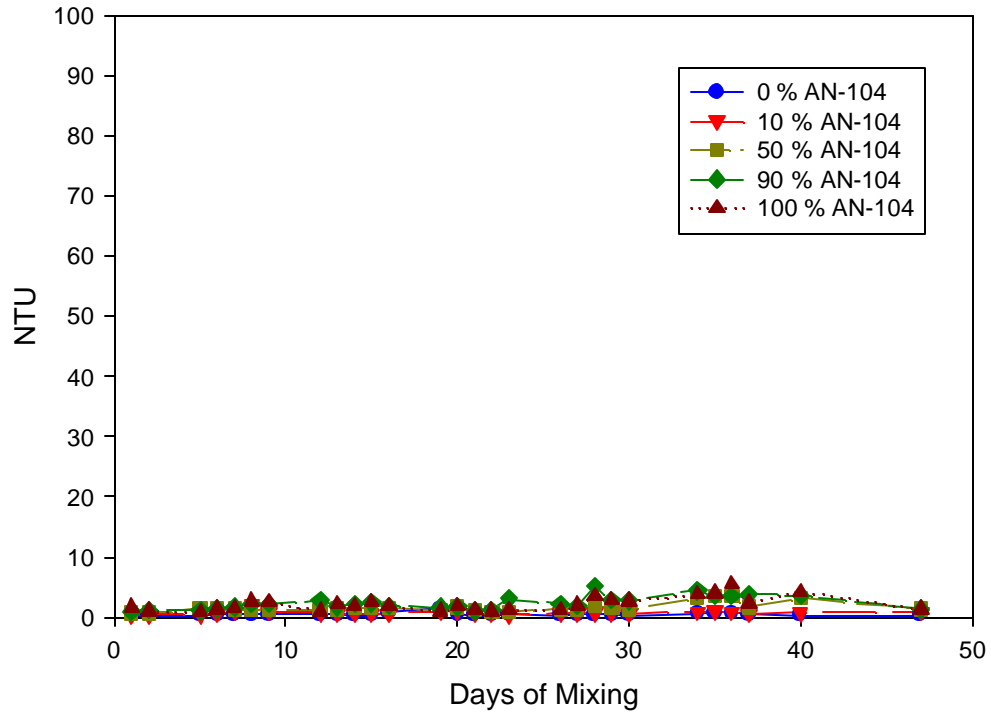


Figure 30. Turbidity of AN-104 and C-106 Leachate Mixtures.

5. REFERENCES

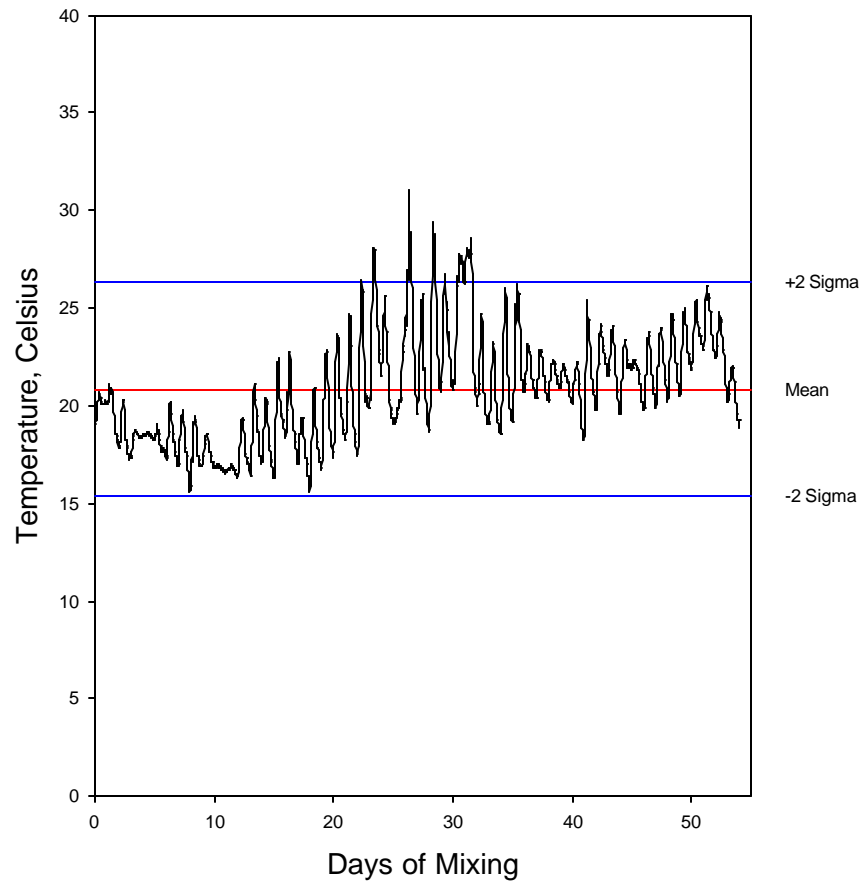
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6. APPENDIX A: TEMPERATURE DATA

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.

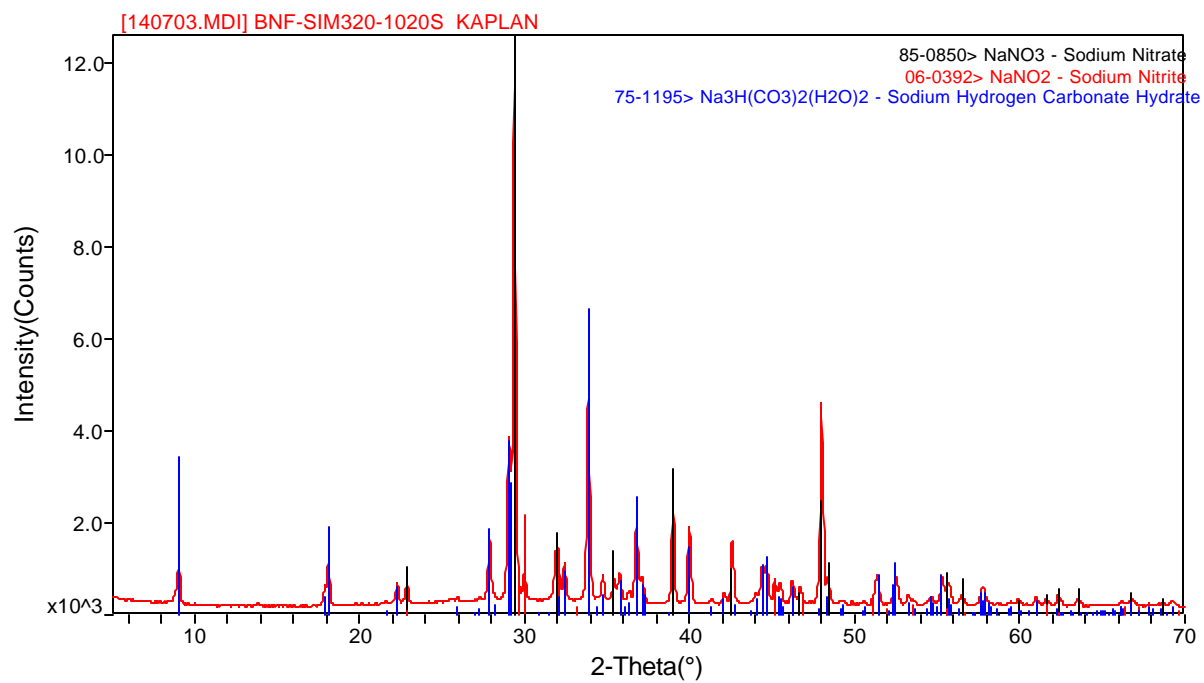


Figure B2. XRD Spectrum of Solids from 10% AZ-101 / 90% AN-107.

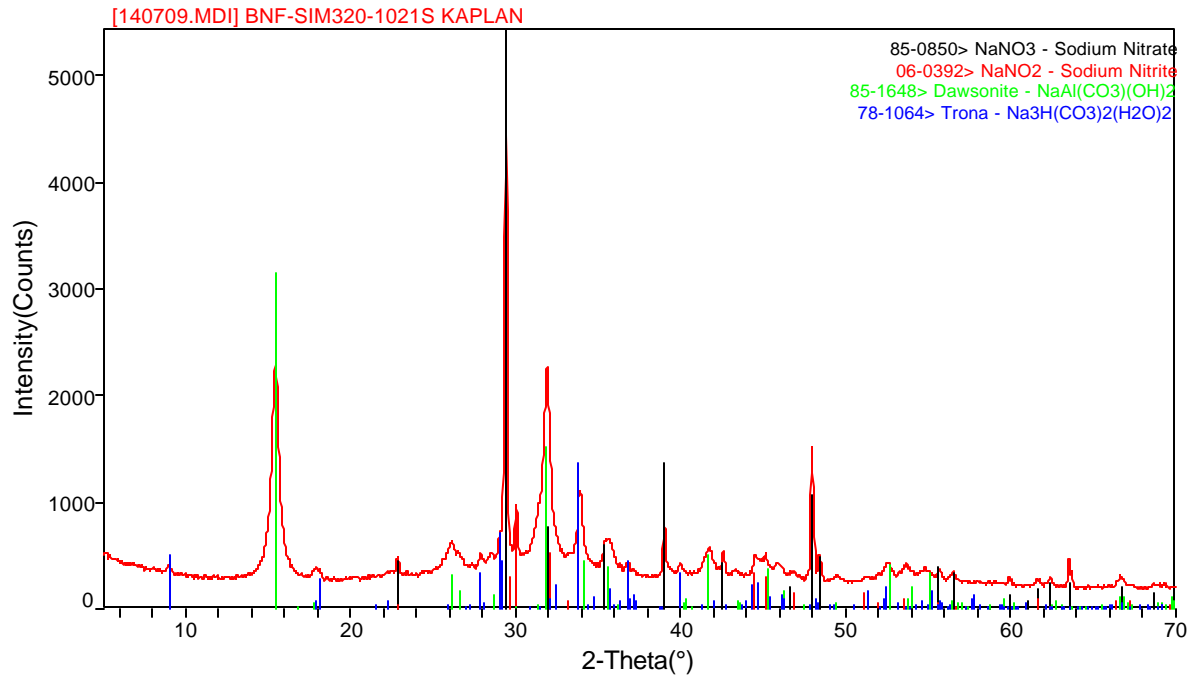


Figure B3. XRD Spectrum of Solids from 50% AZ-101 / 50% AN-107.

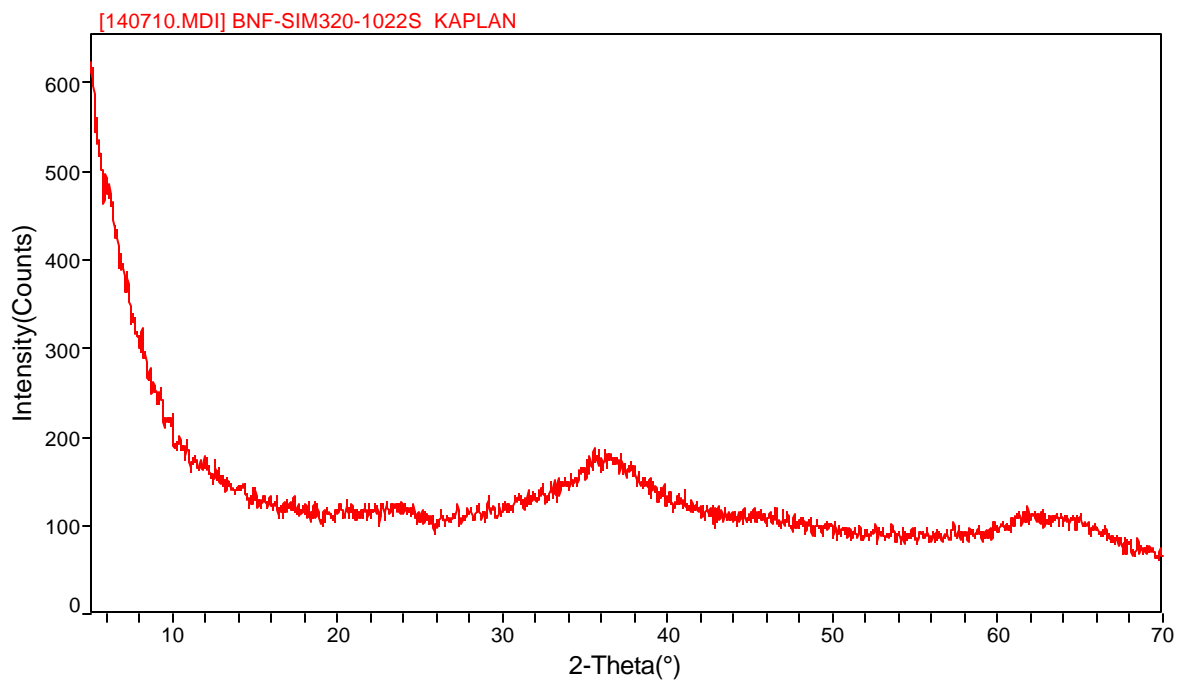


Figure B4. XRD Spectrum of Solids from 10% AN-107 / 90% AN-104.

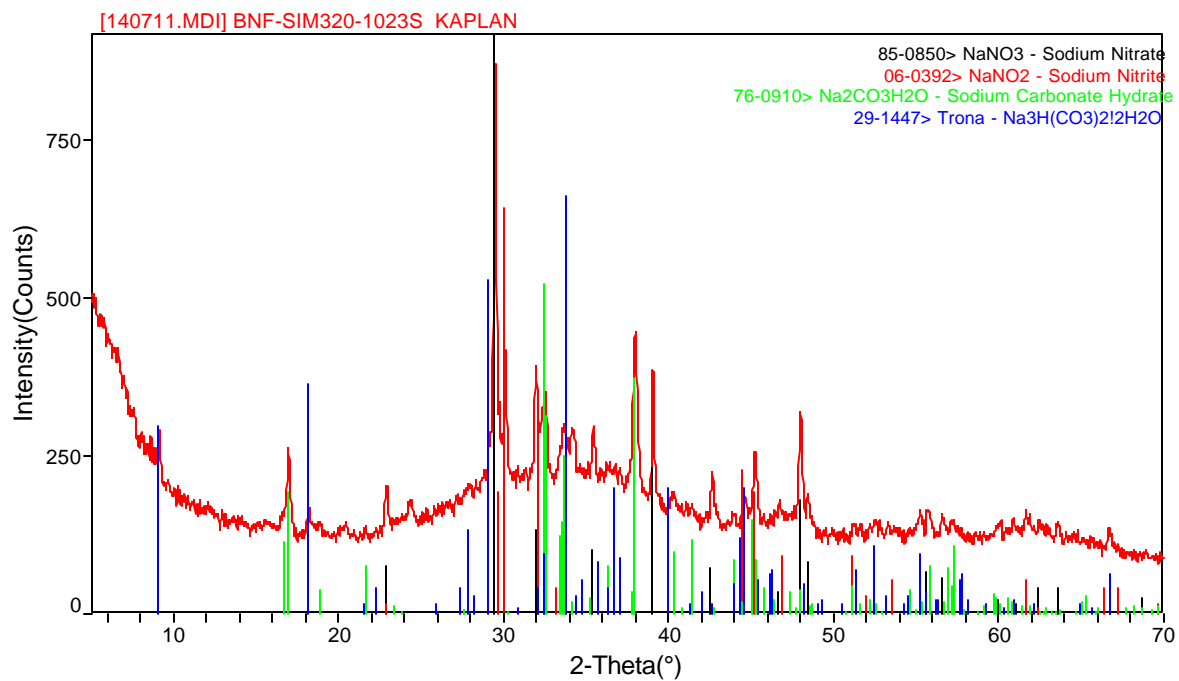


Figure B5. XRD Spectrum of Solids from 50% AN-107 / 50% AN-104.

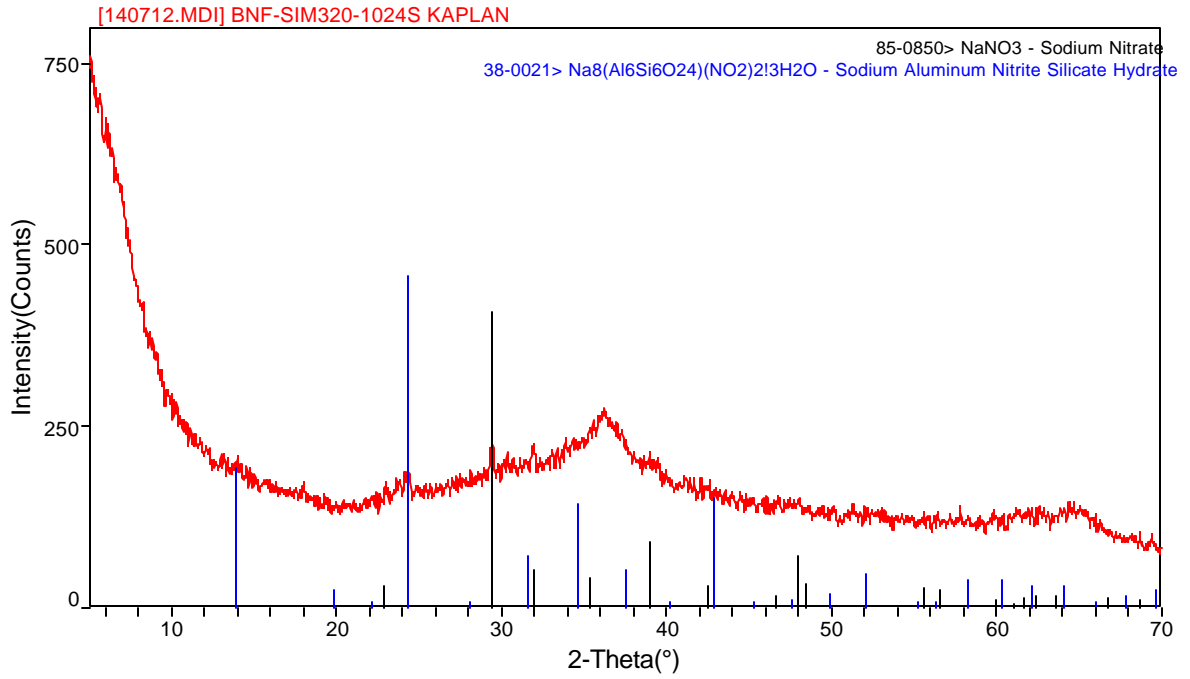


Figure B6. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AN-104.

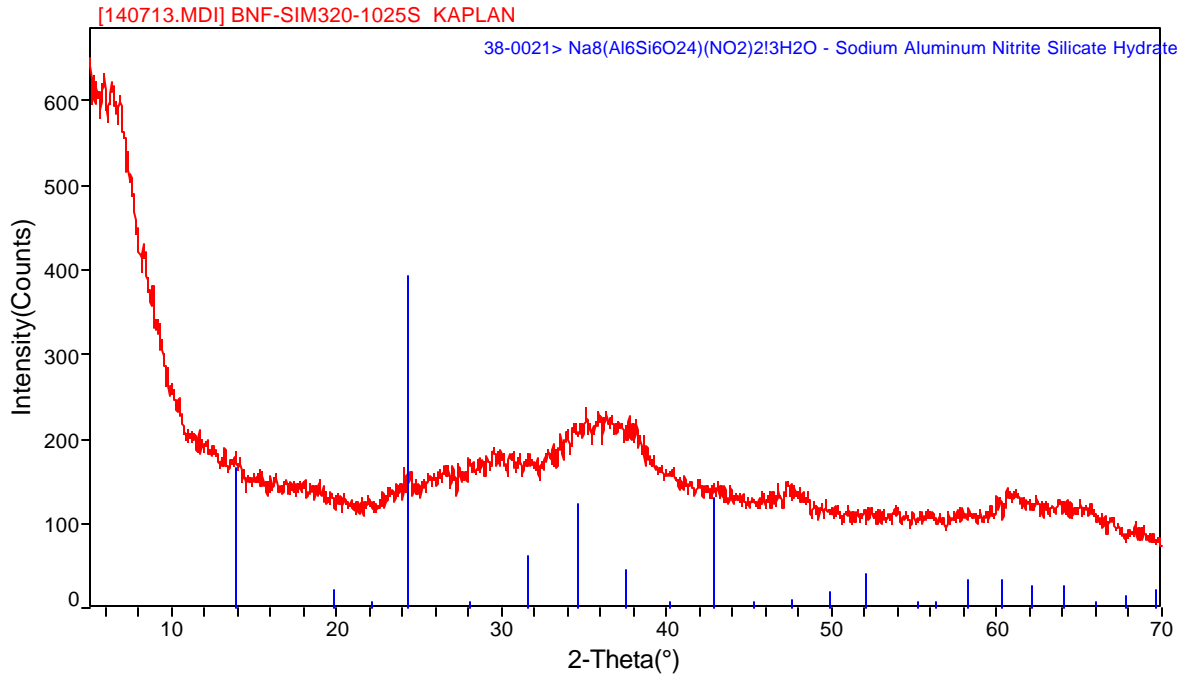


Figure B7. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AW-101.

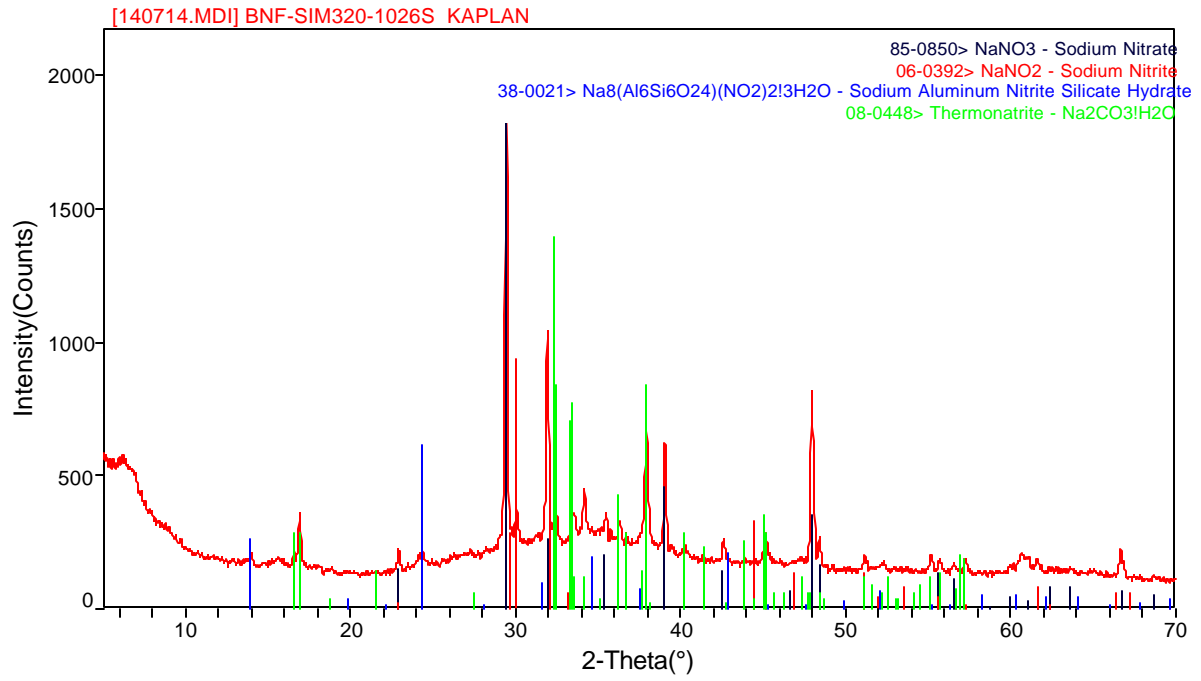


Figure B8. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AZ-102.

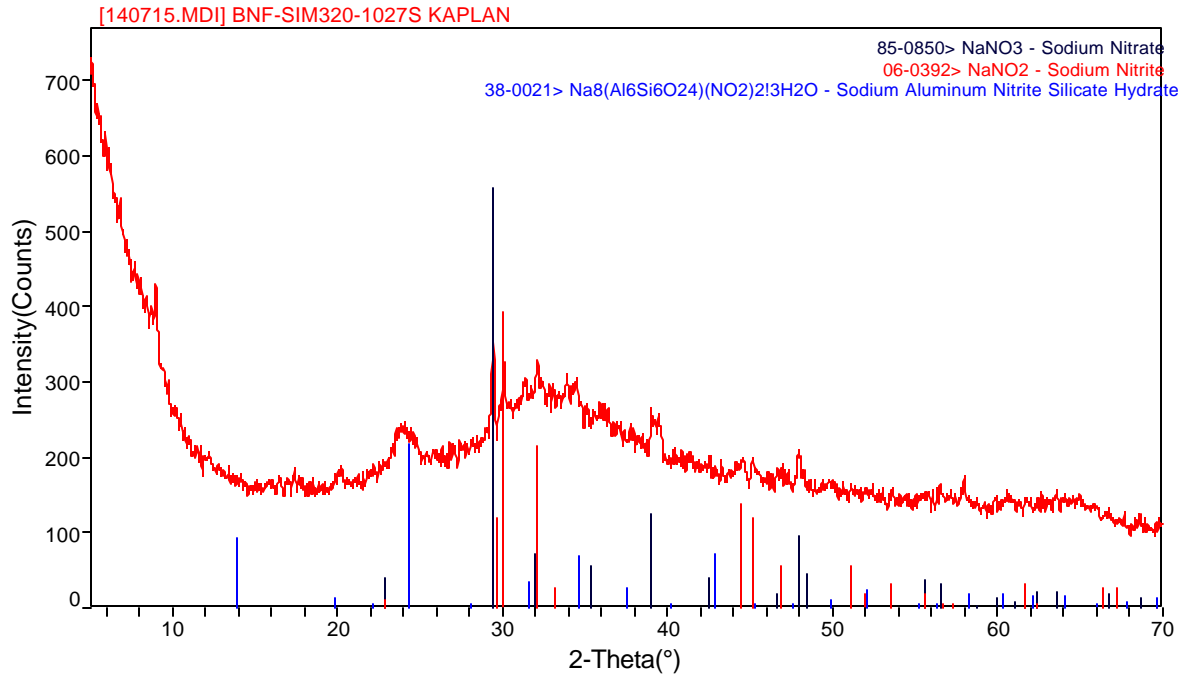


Figure B9. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AN-104.

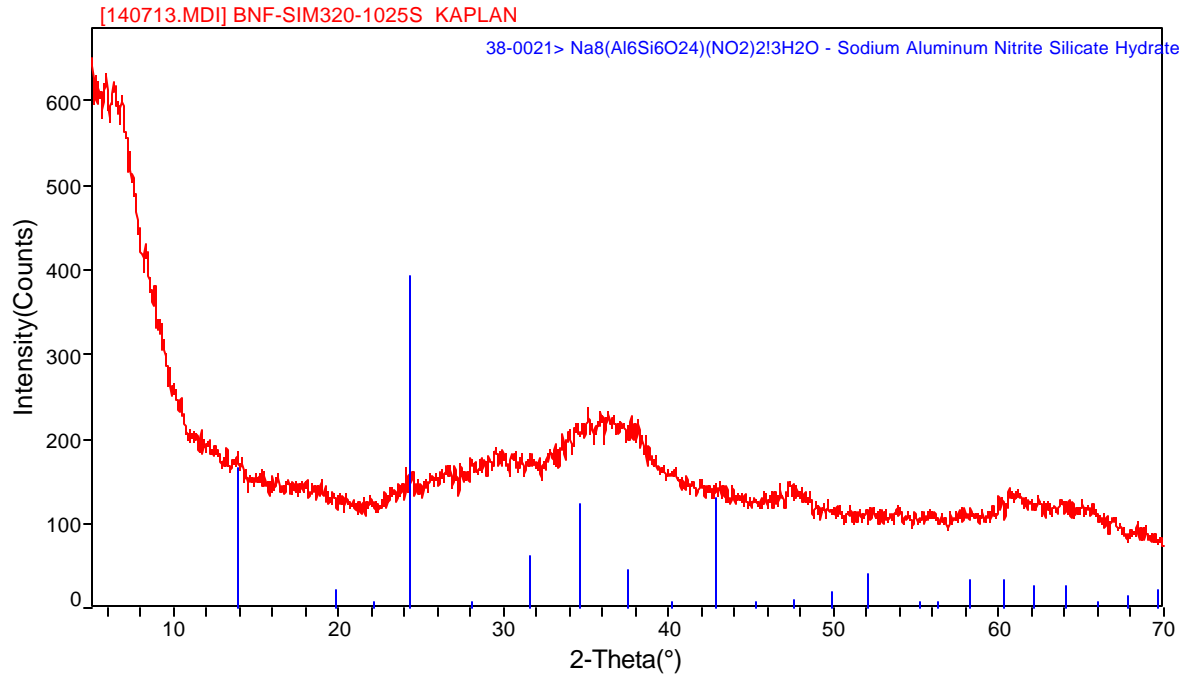


Figure B10. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AW-101.

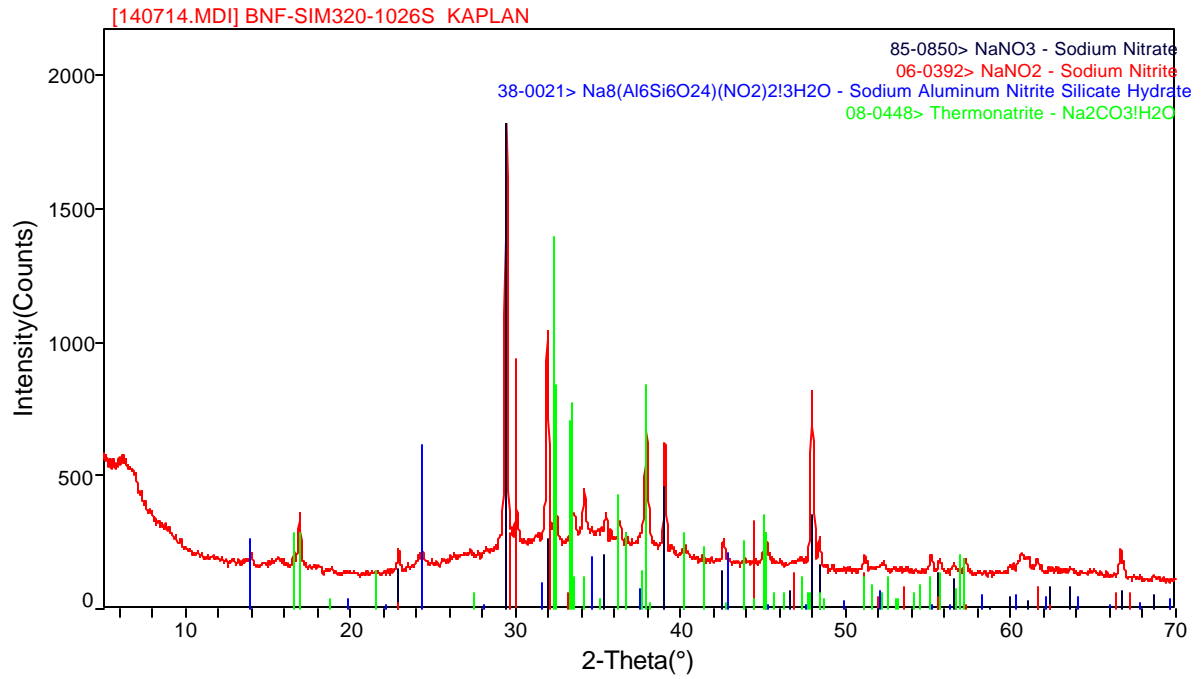


Figure B11. XRD Spectrum of Solids from 9% dilute AN-107 / 91% AZ-102.

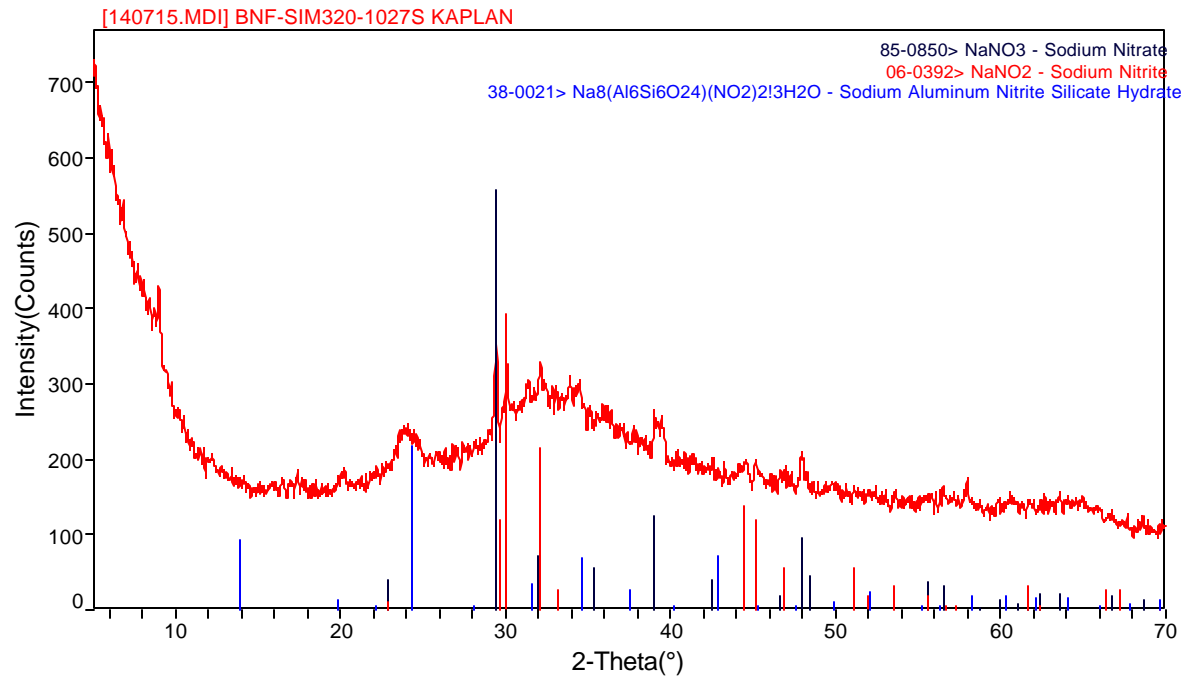


Figure B12. XRD Spectrum of Tabular Crystals from AN-107 Simulant Feed.

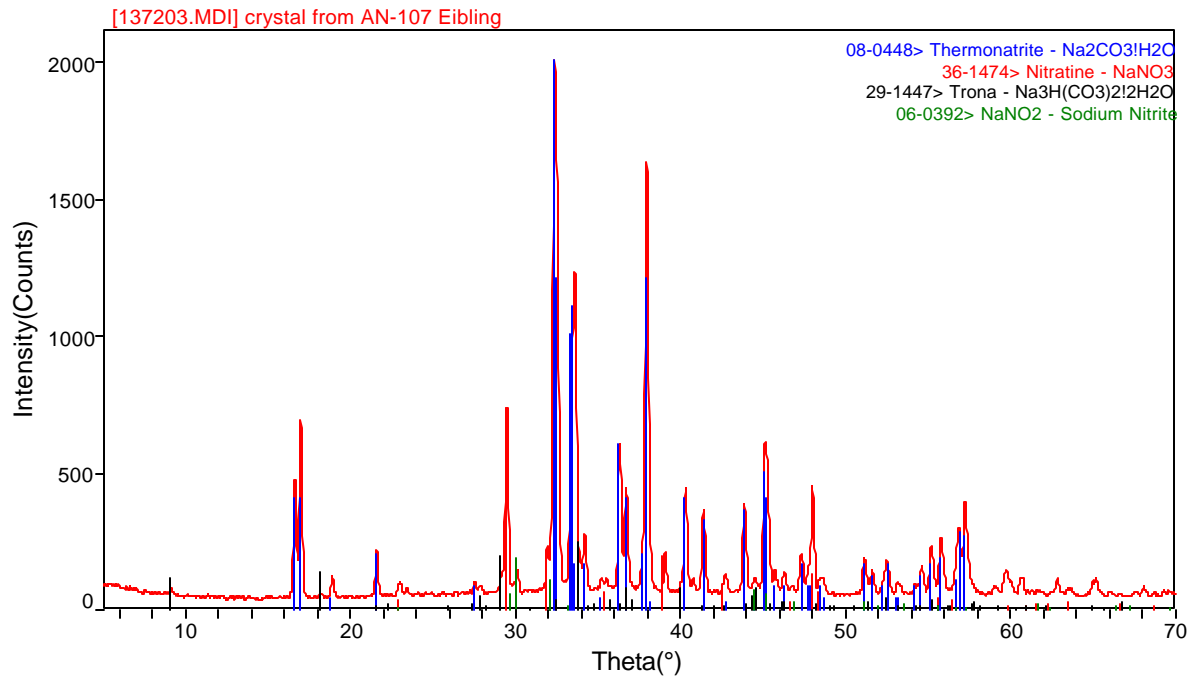


Figure B13. XRD Spectrum of Solids from pH 10 Adjusted AN-107 Simulant.

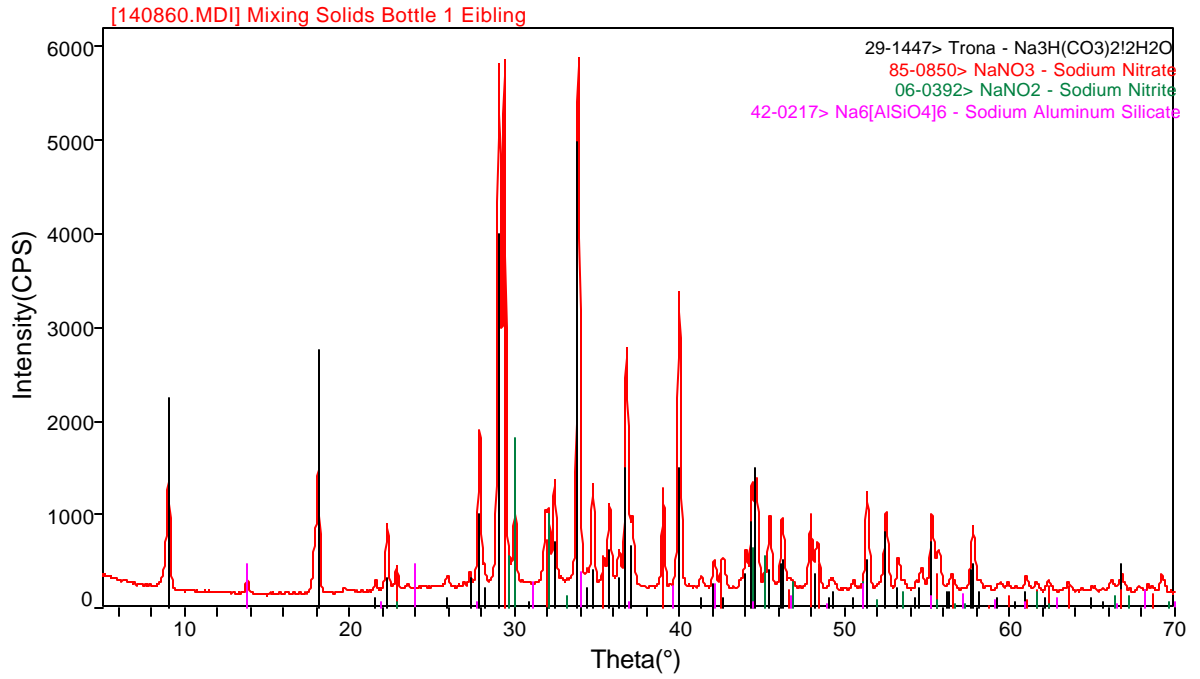


Figure B14. XRD Spectrum of Solids from pH 14.5 Adjusted AN-107 Simulant.

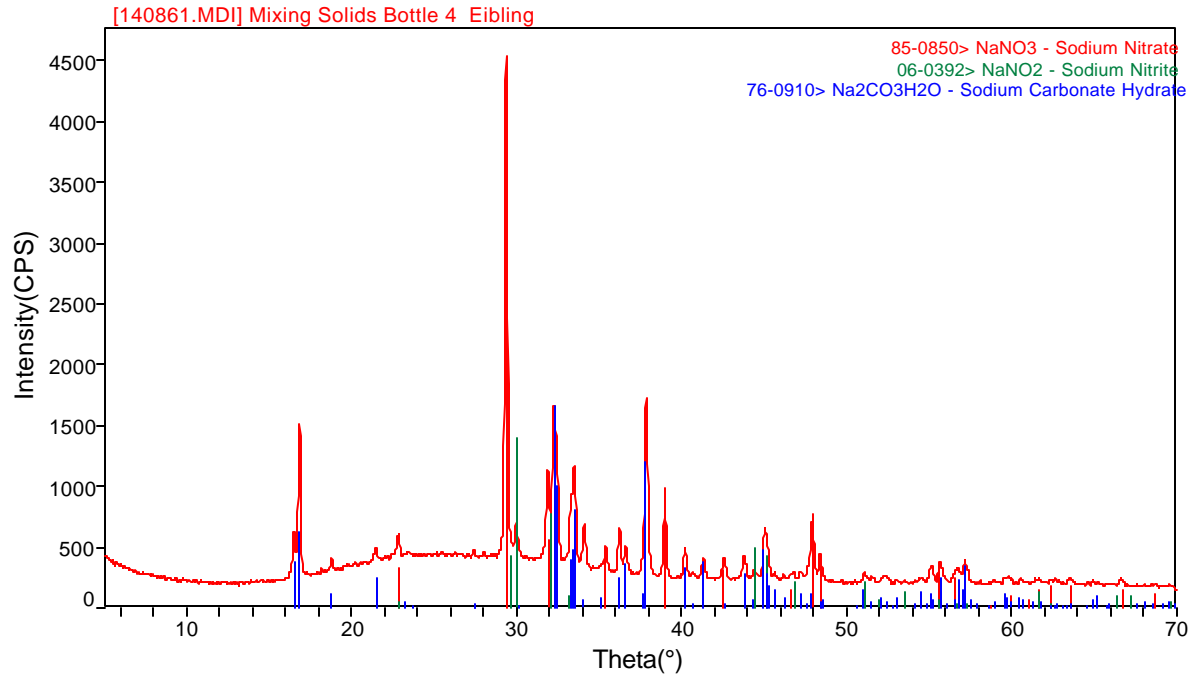


Figure B15. XRD Spectrum of Solids from pH 10 Adjusted AN-104 Simulant.

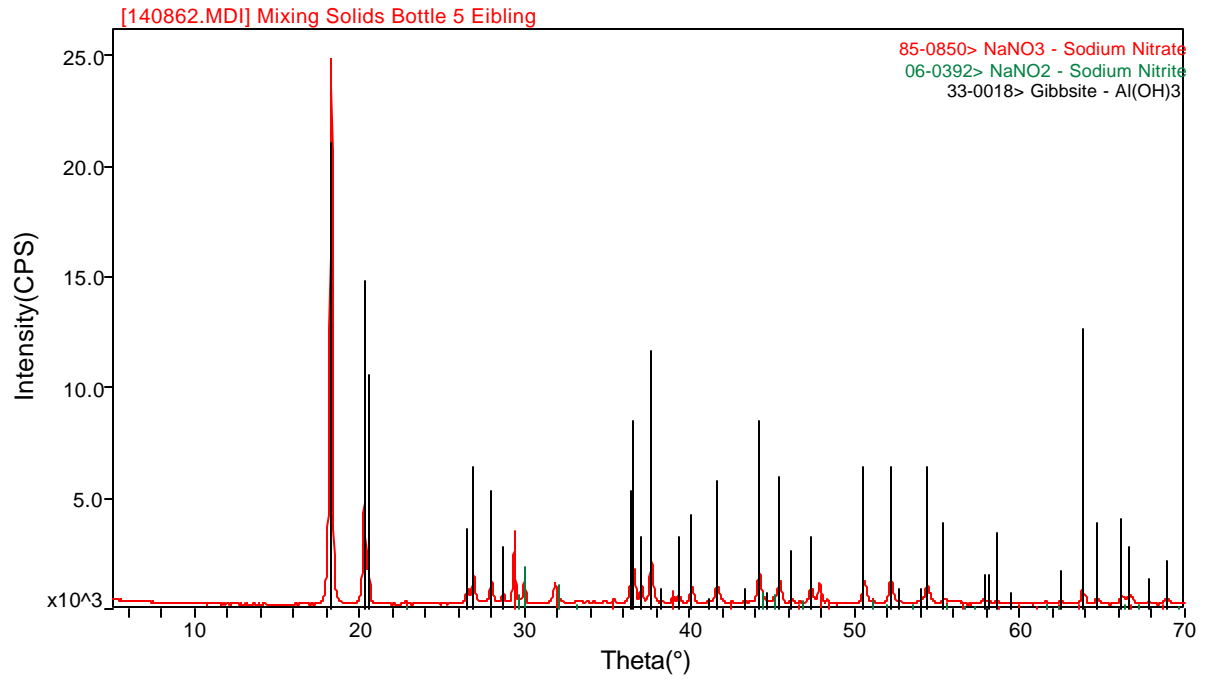


Figure B16. XRD Spectrum of Solids from pH 10 Adjusted AW-101 Simulant.

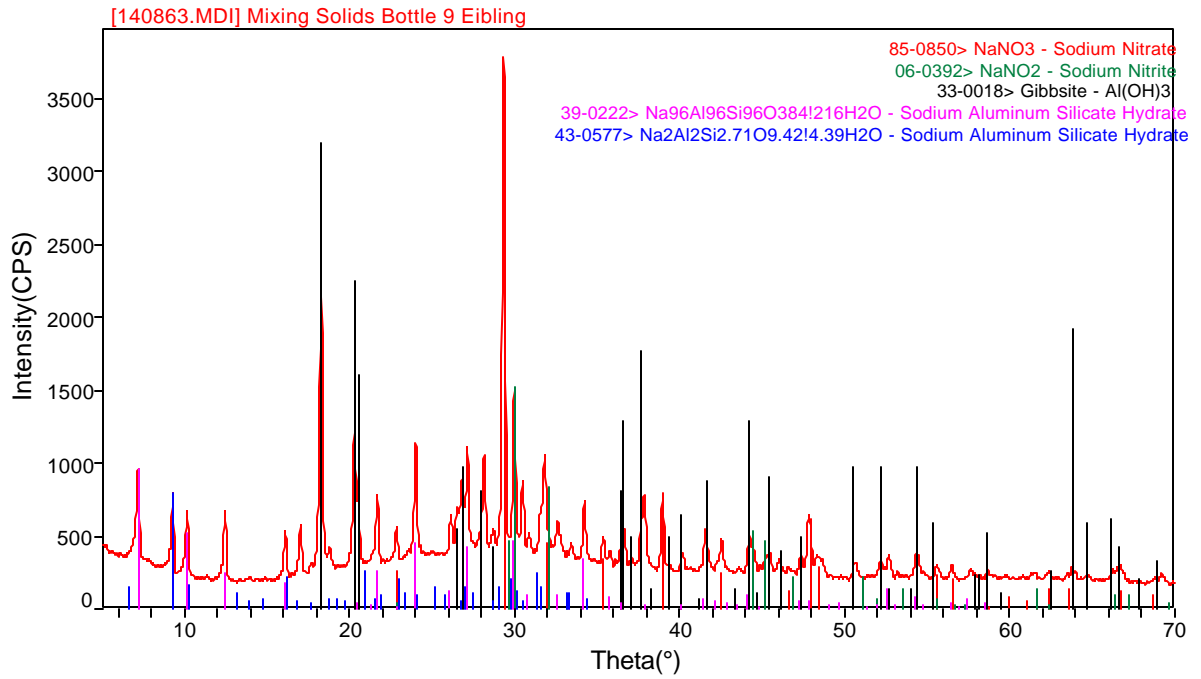


Figure B17. XRD Spectrum of Solids from pH 10 adjusted AZ-101 Simulant.

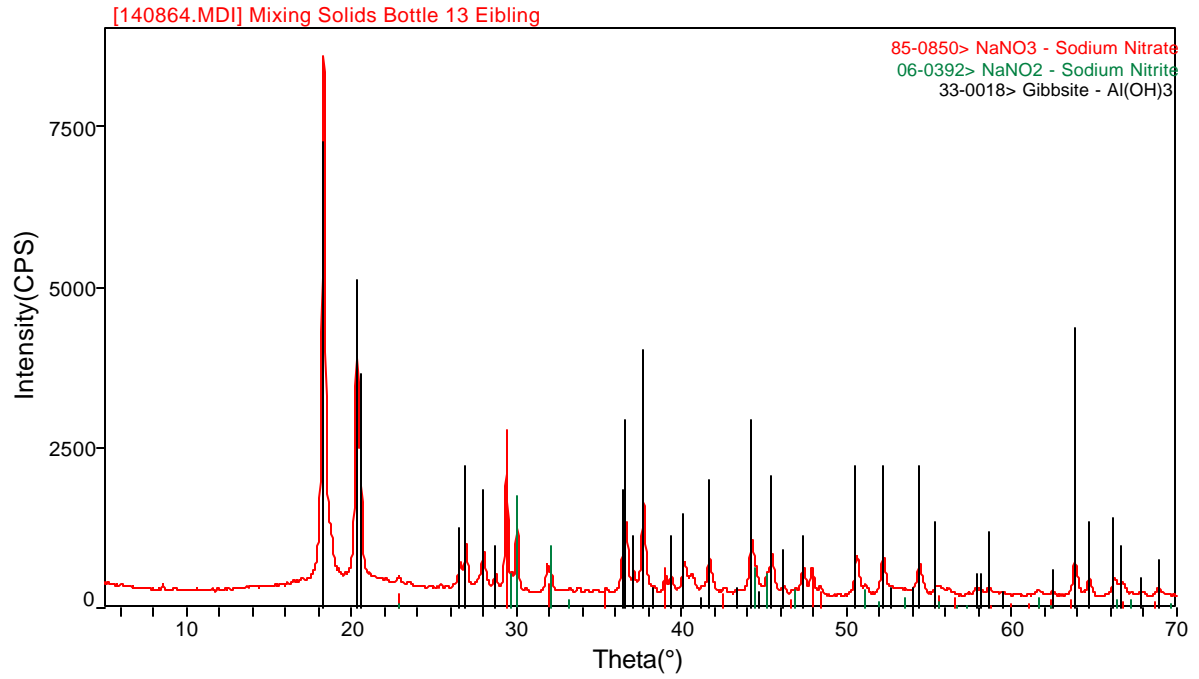


Figure B18. XRD Spectrum of Solids from pH 11 Adjusted AZ-102 Simulant.

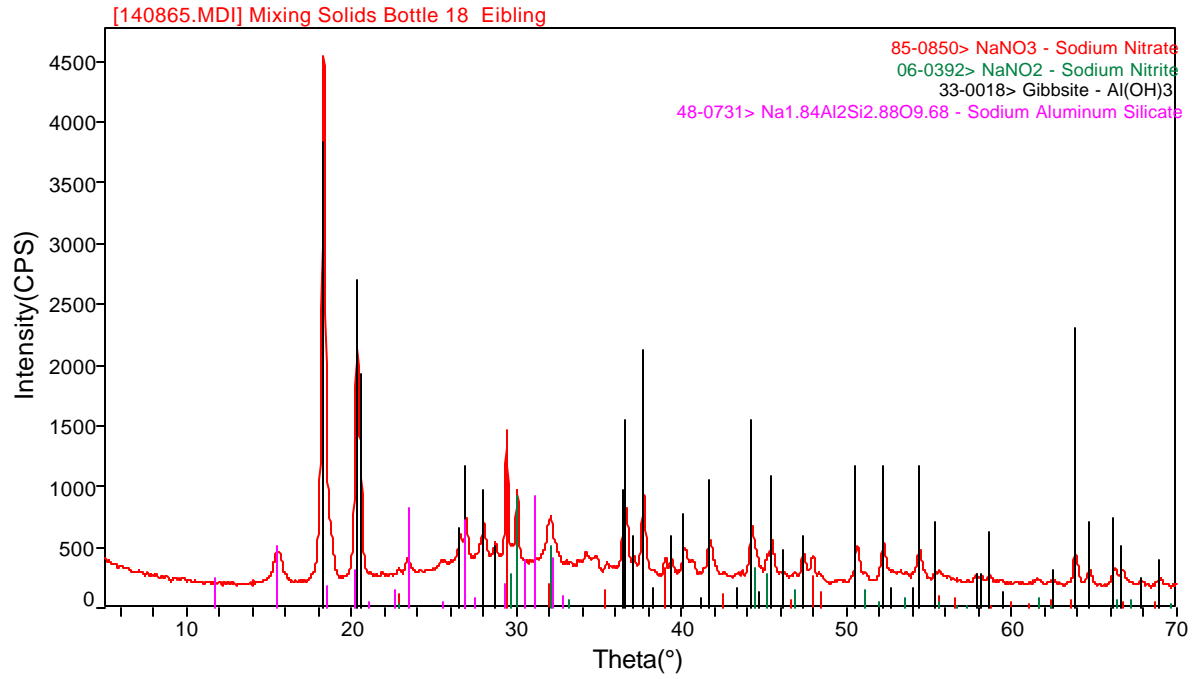
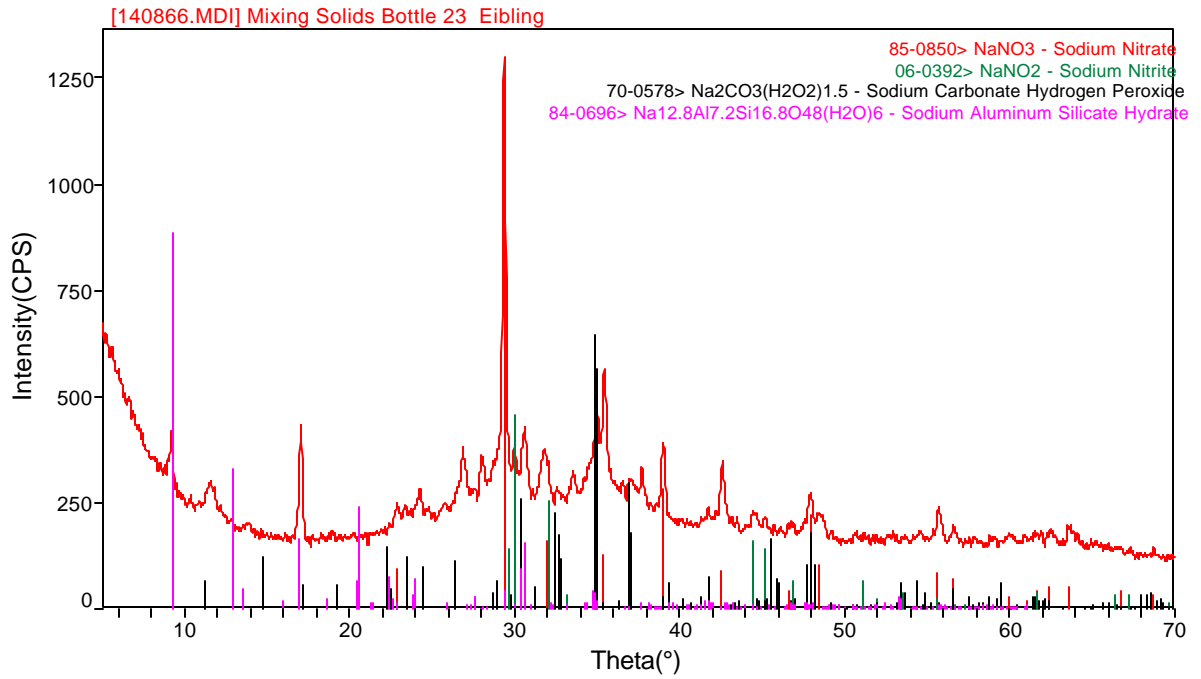


Figure B19. XRD Spectrum of Solids from 50% AN-107 and 50% C-106 Caustic Leachate.



8. DISTRIBUTION

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