WSRC-TR-2002-00387
Revision 0

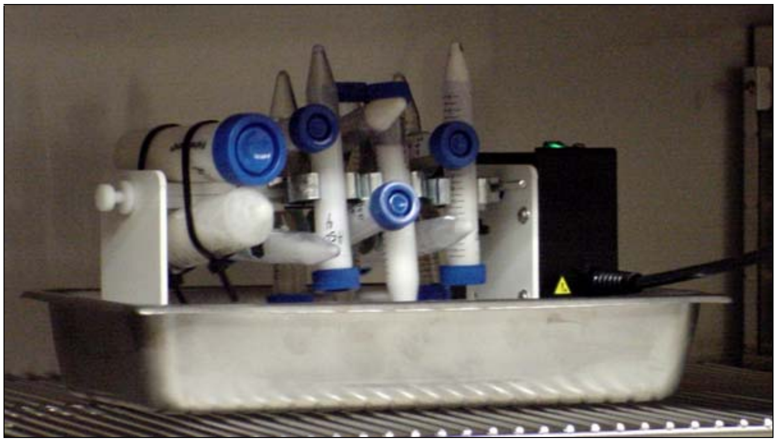
Keywords: Waste Removal
Salt
Solubility
Equilibrium

Retention: Permanent

Saltcake Dissolution Simulant Tests

C. J. Martino
M. R. Poirier
N. E. Gregory

Publication date: December 11, 2002



Westinghouse
Savannah River Company
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

Abstract

Small-scale (15 to 50 mL) dissolution equilibrium tests were performed on surrogate waste representing typical saltcake at the Savannah River and Hanford Sites. The primary objectives of this study were to gain a better understanding of the solid-liquid equilibrium of simulated-waste saltcakes and chemistry of the dissolved salt solutions. These tests were performed in preparation for similar dissolution tests with actual-waste saltcakes.

Two types of tests (single-wash and multiple-wash) were performed at two temperatures (25 °C and 50 °C) for each saltcake simulant. The compositions of the supernatant fluids are provided for both types of dissolution tests, and profiles of the elution of each salt component are provided for the multiple-wash tests.

The conclusions from these tests follow:

- For both salt waste surrogates, dissolution of the soluble components was achieved at less than a 2:1 mass ratio of inhibited water to saltcake during multiple-wash tests.
- Dissolution of the Hanford S-112 simulant resulted in a relatively large weight percentage of residual insoluble material (4.2 wt. %), which was identified as a mixture of $Al(OH)_3$ phases (bayerite and gibbsite).
- The profiles for the relative elution of anions from saltcake during dissolution exhibit distinctions that are dependent upon the dissolution temperature and the initial saltcake composition.

Table of Contents

List of Figures

List of Tables

Introduction

Salt Dissolution Research Program

The Savannah River Site (SRS) has 49 carbon steel tanks that currently house 37 million gallons of High Level Waste (HLW). The waste takes the form of sludge (solids insoluble at high pH), saltcake, and salt supernate. The current inventory of saltcake will be dissolved and processed in the future Salt Waste Processing Facility (SWPF) and the proposed low-Curie salt process. The bulk of the sodium salts that compose saltcake will be ultimately disposed as saltstone, a cement-based waste form. Though there have been several full-scale demonstrations, the full behavior of salt dissolution and removal is not known. There is the need to investigate the influence of chemistry on tank waste properties and behavior during feed preparation, retrieval, transport, and receipt, and the impacts of these operations on downstream processes. Of particular interest are the equilibrium thermodynamics and the resulting physical and chemical properties of the dissolved salt solution.

The salt in SRS HLW tanks is formed from the concentrate of atmospheric-pressure evaporators. The hot aqueous concentrate stream is lifted from the pot and drained to a designated 1.3 million gallon waste tank. As this concentrated salt solution cools, salts precipitate and saltcake is formed. The cake consists of the solid precipitates and an interstitial saturated salt solution. The cake is covered by a supernatant salt solution that is recycled back as feed to the evaporator. This process forms wet saltcakes that contain interstitial liquid of approximate composition of the supernatant fluid at the time of cake formation. The varying feeds to the evaporators, the location of the drains to the salt tanks, and the tendency for salt to crystallize on cool surfaces cause both vertical and horizontal variances in cake composition and properties.

The solubility of each individual salt in a high ionic-strength matrix will usually be lower than its individual solubility due to the common ion effect. During batch-wise salt dissolution schemes with mixing, the most soluble salts and components in the interstitial liquid are mainly removed in initial batches and the least soluble salts dissolve in the later batches. This leads to a variation in composition of the dissolved salt stream fed to subsequent processing steps.

Working with the Tanks Focus Area, SRTC performed saltcake dissolution tests with SRS and Hanford surrogate HLW. Personnel performed a series of small-scale (15 to 50 mL) saltcake dissolution studies to determine solid-liquid equilibrium in HLW surrogates. These simulant tests were performed in advance of similar tests with actual-waste saltcake from SRS Tank 31H. The purposes of this stage of testing are to establish estimates of the salt dissolution chemistry of SRS HLW saltcake, to reproduce the Hanford actual-waste solubility data, to check the experimental technique and equipment for SRS actual-waste dissolution tests, and to provide information for engineering-scale saltcake dissolution tests. The data collected during these tests could be used to validate equilibrium chemistry models for their use in larger salt dissolution, evaporator system, and integrated tank farm models.

Research Background

Salt dissolution has been investigated in a variety of ways at SRS and Hanford. The focus of actual-waste salt dissolution tests at SRS has been in support of criticality analysis.[1,2,3,4,5] The goal of these criticality tests was the characterization of the residual insoluble material after the sodium salts had been removed completely. The insoluble material was prepared by washing salt with an excess (typically, one wash with 3:1 by mass and two washes with between 0.5:1 and 3:1 by mass) of inhibited water (typically 0.015 M NaOH). These dissolutions for criticality characterization were not performed and analyzed in a manner that provides useful salt solubility profiles. Additional information can be gleaned from the limited data obtained during the several SRS full-scale salt dissolution demonstrations (e.g., Tanks 10H, 19F, 20F, 22H, 33F). At SRS, the primary engineering salt dissolution studies were performed in support of Tank 41H corrosion inhibition planning.[6,7] The dissolution of stratified saltcake simulant was studied using tens of liters of material in both a vertical tube and a trough. Rather than focusing on equilibrium thermodynamics, these tests provided information on the dissolution kinetics and physical phenomena.

At Hanford, a series of studies were conducted on simulants to formulate solubility correlations.[8,9,10] While not direct studies of salt dissolution, they are valuable to an understanding of component solubility over a wide range of conditions. Of more use to this study is the methodology devised for a recent program involving actual-waste salt dissolution of numerous Hanford tanks.[11,12,13] This methodology involves saltcake-dissolution tests that fall into three general categories: series of single-wash tests, multiple-wash tests, and feed stability tests. The tests contained in this task plan are modeled after the first two of these categories of Hanford's saltcake dissolution experiments. The series of single-wash tests are of particular interest to thermodynamic modelers. The multiple-wash tests are very small-scale versions of the full in-tank dissolution process, and thus are of more interest to engineers and planners. The analyses performed reflected the goals of the individual tests, with typical analyses including ion chromatography (IC) for anion concentration and gamma counting for the concentration of key radionuclides (^{137}Cs and ^{99}Tc).

Experimental

Test outline

One of the purposes of these tests is to provide a dry run for the actual-waste tests to be performed in the SRTC shielded cells. For that reason, personnel in the Waste Processing Technology (WPT) Section used a protocol that resembled the expected apparatus and procedure for actual-waste tests. As a consequence of this, these simulant tests did not have the greatest precision of temperature control and volume determination. These tests were performed over a wider range of conditions than practical for the actual-waste tests because of the relatively large amount of simulated saltcake that was available. The test design used aspects from previous saltcake dissolution studies performed at Hanford.[11,12,13]

Table 1 contains the factors that were varied between each test and the levels of each factor. Two different saltcake simulants were prepared: "Average SRS" mimicked typical SRS waste and "Hanford S-112" represented a Hanford single-shell tank waste. Dissolutions were performed at two temperatures, the ambient laboratory temperature of approximately 25 °C and an elevated temperature of 50 °C. The dissolution fluid was inhibited water (IW), which was deionozed water with 0.01 M NaOH and 0.011 M $NaNO_2$.

Table 1: Experimental Matrix of Salt Dissolution Tests

Factor	Level
Saltcake	2 (Average SRS and Hanford S-112)
Temperature	2 (25 °C and 50 °C)
Dissolution Fluid	1 (Inhibited Water)

Simulant Preparation

Saltcake simulants were prepared by evaporating excess water from fully soluble salt solutions. Table 2 provides the recipes used for the preparation of “Average SRS” and “Hanford S-112” saltcakes. The Average SRS saltcake was created from a surrogate of similar composition to the information contained in the Waste Characterization System (WCS) for saltcake in most SRS salt tanks. The composition of the starting soluble material has the same composition as the Average SRS simulant developed for the dissolved salt feed of a cesium removal process.[14] The Hanford Tank S-112 saltcake simulant was prepared using the chemical composition in a recipe provided by Rodney Hunt of Oak Ridge National Laboratory, but the preparation procedure was tailored to match that of the SRS surrogate waste. The composition of the saltcake simulants differs by a few key aspects. The SRS saltcake includes additional cations (potassium and cesium) and several of the trace anions (chloride, fluoride, molybdate, silicate, and oxalate). The Hanford simulant had a much greater amount of phosphate and a much larger ratio of aluminate to hydroxide.

Table 2: Saltcake composition based on initial solution makeup.

	Average SRS Simulant		Hanford S-112 Simulant	
Ion	(M / M Na^+)	(dry wt. %)	(M / M Na^+)	(dry wt. %)
Na^+	1.00	34.16	1.00	32.08
K^+	0.00269	0.156	0	0
Cs^+	0.00003	0.0050	0	0
OH^-	0.341	8.62	0.156	3.70
NO_3^-	0.382	35.21	0.406	35.15
NO_2^-	0.0930	6.35	0.116	7.43
AlO_2^-	0.0554	7.81	0.0795	10.54
CO_3^{2-}	0.0286	2.55	0.0669	5.60
SO_4^{2-}	0.0268	3.83	0.0156	2.09
PO_4^{3-}	0.00448	0.633	0.0257	3.41
Cl^-	0.00448	0.236	0	0
F^-	0.00574	0.162	0	0
$C_2O_4^{2-}$	0.00143	0.187	0	0
SiO_3^{2-}	0.000717	0.0810	0	0
MoO_4^{2-}	0.000035	0.0084	0	0

The soluble salt solutions were prepared in the following manner: NaOH was dissolved gradually in deionized (DI) water in one beaker, $Al(NO_3)_3 * 9H_2O$ was dissolved in DI water in another beaker, and the remaining salts were added (not all were dissolved) to DI water in a third beaker. While agitating briskly, the solution containing aluminum was added gradually to the NaOH solution. The solution with the rest of the salts was added to the mixture, the solution volume was brought up to the target volume for a 5M Na^+ solution, and the solution was mixed until all of the salts had dissolved. Four liters of each simulant were prepared.

Two 1L portions of each soluble simulant were heated in 1.2 L stainless steel beakers. The beakers were placed in an oven at a temperature range from 125 to 145 °C for a period of several 10-hour shifts. Water was driven off until the solution volume was reduced to about 20% to 25% of its original volume. Some solids formed in the hot liquor, but the bulk fluid became solid saltcake when the slurries were removed from the oven and allowed to cool. This simulated saltcake material was ground with a mortar and pestle, stirred with a spatula, and stored in polystyrene containers for use in the salt dissolution tests. This procedure of evaporation, cooling, and grinding produces a saltcake that does not mimic the physical properties and inhomogeneities of actual-waste saltcake. It should produce saltcake, however, that is a good chemical simulant adequate for solid-liquid equilibrium testing.

Dissolution Test Protocol

For each combination of factors in Table 1, saltcake dissolution tests were performed using each of two schemes: a series of single-wash dissolutions and one multiple-wash dissolution. Figure 1 provides a pictorial representation of a series of single-wash tests. A separate portion of the composite saltcake sample was added to six 15-mL polyethylene terephthalate (PET) centrifuge tubes. Appropriate amounts of dissolution fluid were added to each tube to provide mixtures with a range of sample-to-inhibited water ratios. The centrifuge tubes were capped, shaken overnight, and centrifuged. Volume fractions of the supernate and saltcake fractions are noted. The supernatant liquid is decanted, measured for density, diluted when necessary, and submitted to ADS for analysis. The packed solids are analyzed for density and weight percent solids. Figure 2 gives a schematic of a multiple-wash dissolution test. A 60-g portion of saltcake is added to one 50mL polypropylene (PP) centrifuge tube. An aliquot of inhibited water is added, the mixture is shaken overnight, the tube is centrifuged, the volume of each phase is noted, and the liquid is decanted. This process of washing is repeated six to eight times, with each wash contacting the remaining solids with an additional aliquot of dissolution fluid. The liquid samples are analyzed for density, diluted, and sent to ADS for analysis. The residual insoluble solid may be dried and sent to ADS for analysis. Note that the number of washes and mass ratios of Diluent:Saltcake included in Figure 1 and Figure 2 are guides that were used to design the tests, but the actual values for this study are included in the data presented in the results section.

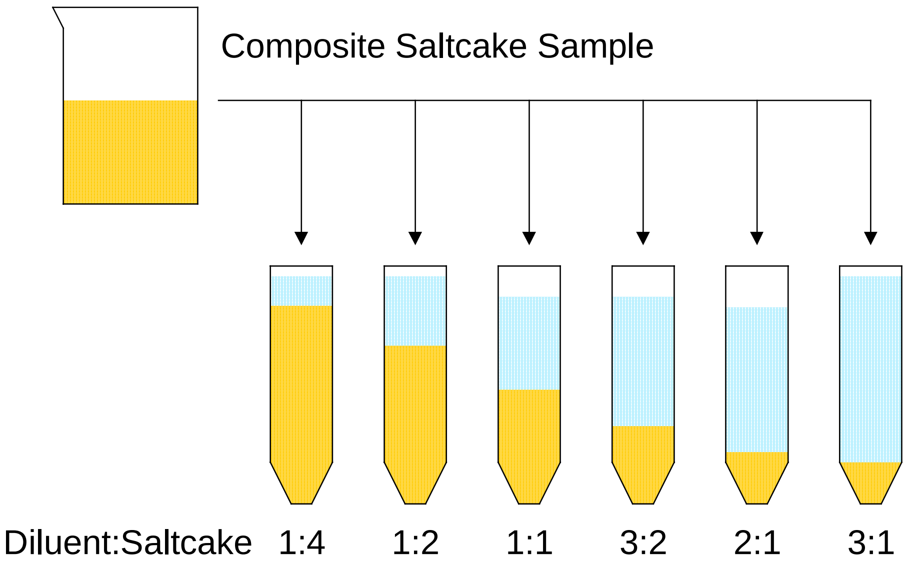


Figure 1: Series of single-wash dissolution tests (the actual Diluent:Saltcake mass ratios vary between different series of tests and are reported with the results).

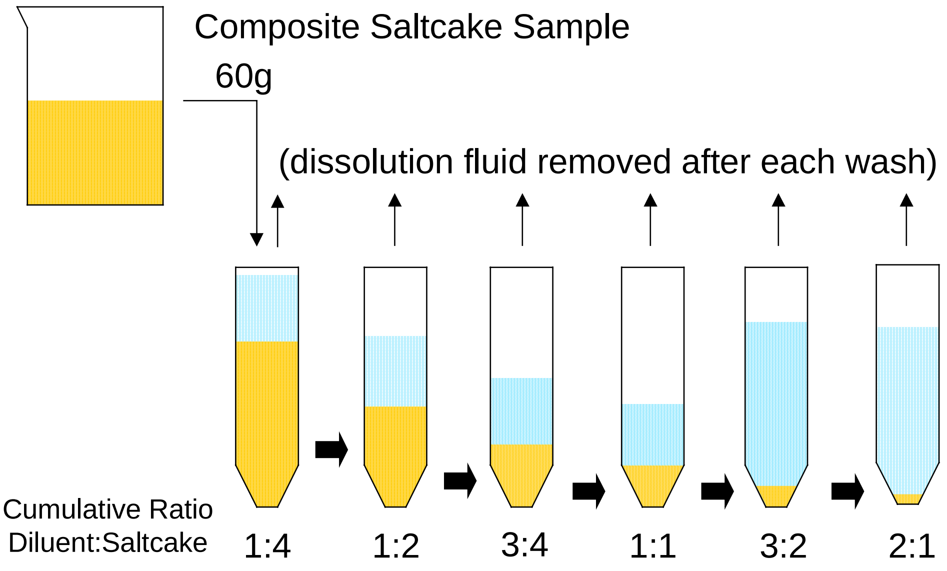


Figure 2: Multiple-wash dissolution test (the actual number of contacts and cumulative Diluent:Saltcake mass ratios vary between different tests and are reported with the results).

Solutions in the ambient temperature tests were mixed on the bench-top and solutions in the 50 °C tests were mixed in a 50 °C oven. Since a temperature-controlled centrifuge was not used in these tests, solution temperature was measured again after the completion of centrifuging. For the 50 °C tests, the centrifuge basket and adapter sleeves were heated to the dissolution temperature. The centrifuging of the 50 °C solutions had to be performed by several short (5 min) periods of centrifuging separated by periods (30 to 60 minutes) of heating in order to maintain temperature of > 40 °C throughout the process. Temperature had again reached 50 °C during decanting, density measurement, and ADS sample preparation.

Analytical Protocol

Table 3 contains the sample analyses and corresponding analytes that were requested of the Analytical Development Section (ADS). ADS analyzed five-fold dilutions made from the supernatant liquid decanted from each of the centrifuge tubes. The primary purpose of the liquid sample analysis was the characterization of the major ionic components. ADS personnel analyzed the aqueous samples by inductively coupled plasma – emission spectroscopy (ICP-ES), ion chromatography (IC) for anions, and a wet chemistry titration. There were redundant analyses for aluminum/aluminate, sulfur/sulfate, and phosphorous/phosphate. The $Al(OH)_4^-$ concentrations were converted from the ICP-ES results for Al rather than from the wet chemistry titration. The sulfate and phosphate results converted from the ICP-ES results for sulfur and phosphate were averaged with the sulfate and phosphate results measured by the IC anions analysis. The concentrations of SiO_3^{2-} and MoO_4^{2-} were calculated from ICP-ES results for Si and Mo, respectively.

The solids remaining from the final wash of the 25 °C multiple-wash test of the Hanford S-112 saltcake were submitted to ADS for X-ray diffraction (XRD) analysis. Additionally, WPT personnel analyzed the solids using Fourier transform infrared (FTIR) spectroscopy.

Table 3: Sample analysis

Analysis	Analyte
Liquid Samples	
ICP-ES	Na, K, Al, Si, Mo, S, P
IC Anions	NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, F^-, PO_4^{3-}, $C_2O_4^{2-}$
Wet Chemistry	AlO_2^-, OH^-, CO_3^{2-}
Solid Samples	
XRD	Identification of crystalline phases
FTIR (by WPT personnel)	Identification of crystalline phases

WPT personnel performed measurements of the density and weight percent total solids of the original saltcake and the liquid and solid phases after dissolution. The liquid supernate density was measured at the dissolution temperature using glass 2 mL volumetric flasks. The original saltcake density was measured by displacement at 20 °C using 10 mL volumetric flasks. The residual solid density was estimated by observation of the volume and mass of solid remaining in the centrifuge tube after the supernatant fluid was decanted. The percent total solids for each material was determined by drying a small amount of material (< 5 g) to a constant mass at 120 °C.

Column Test Protocol

A column of salt was prepared in a 250 mL graduated cylinder. The cylinder was approximately 12.5 inches tall and 1.5 inches in diameter, and capable of holding approximately 320 mL of material. A ¼ inch port was fashioned at the 10 mL level (from bottom) to allow for the drainage and removal of material. A column of saltcake was produced from 1L of the soluble 5 M Na+ Average SRS solution. One liter of the solution was heated in a stainless steel beaker at 120 to 145 °C until the final volume was approximately 320 mL. The hot slurry (some solids had already formed) was transferred to the graduated cylinder and allowed to cool to room temperature and settle for three days. The bottom portion of the graduated cylinder contained 170 mL of saltcake and the top portion of the cylinder contained 150 mL of saturated supernate. The supernatant liquid was removed and the dissolution test proceeded with the addition of 50 mL aliquots of inhibited water.

Results and Discussion

Saltcake Simulant Composition

The saltcake surrogates were chemical rather than physical simulants of HLW saltcake. In preparation of the saltcakes by evaporation of water from the solutions at 125 to 145 °C, solids were noted to form while the temperature was still elevated. These solids formed in layers at the bottom and top of the high-temperature solution. Personnel periodically mixed the solids into the bulk solution. After the removal of the desired amount of water, the solutions were allowed to cool. After cooling, both surrogates formed hard, immobile saltcake with no free liquid. Each saltcake was chiseled from its stainless steel beaker, transferred into a ceramic mortar, crushed with a pestle, and mixed with a spatula. Upon crushing and mixing, each surrogate took on a wet appearance and was able to flow like a viscous liquid, although no free liquid was evident. After transferring into a polystyrene storage container, the Hanford S-112 saltcake became hard and immobile again within a few days, but the Average SRS saltcake retained a degree of fluidity even after one week. The difference in appearance of the two saltcake surrogates is shown in Figure 3, which contains images taken at the initiation of the ambient temperature tests (approximately one week of aging). At the start of the 50 °C dissolution tests, the additional three weeks of aging caused the SRS saltcake to take on a hard and dry appearance similar to that of the Hanford saltcake.

Personnel noted corrosion of the stainless steel beakers used for the preparation of the SRS saltcake. The slight orange color and the analytical confirmation of iron in the dissolved saltcake samples reinforced this observation. No such corrosion was noted during the preparation of the Hanford simulant.

Figure 3: "Average SRS" (left) and "Hanford S-112" (right) saltcake simulants at start of ambient temperature dissolution tests.

The change in the physical nature of the saltcake during initial mixing was partially due to changes in the saltcake moisture. This did not occur in the same manner for both saltcakes because of the different hydroxide concentrations. Small samples of Hanford and SRS simulants were observed to behave differently when left uncovered in the lab hood. The Hanford S-112 simulant appeared to get dryer and harder, while the SRS simulant was hygroscopic, condensing water from the lab atmosphere and developing a supernatant liquid.

The weight percent total solids in the saltcake surrogates were measured near the end of the testing. The Average SRS simulant had a total solids of 86.7 ± 0.3 wt. % and the Hanford S-112 simulant has a total solids of 82.1 ± 0.7 wt. %. Densities were estimated by displacement to be 1.98 ± 0.02 g/cm^3 for the Average SRS simulant and 1.91 ± 0.11 g/cm^3 for the Hanford S-112 simulant. The ranges reported are the standard deviations of three measurements.

The initial compositions of the two saltcake simulants are reported on a dry basis in Table 4. The columns labeled target composition contain the predicted values of the ions in the saltcake from the initial solution makeup (as in Table 2). The remaining two columns of data for each simulant are estimates of the saltcake composition form the analysis of the dissolved salt during the dissolution testing. These are calculated from the analyses of the solutions with the largest diluent to saltcake ratio from each series of single wash tests. During the preparation of the soluble Hanford S-112 solution, a significant quantity of aluminum hydroxide precipitation was noted. A portion of this aluminum hydroxide was present in the saltcake at the start of each test. Thus, the actual aluminate composition of the Hanford saltcake is much less than the target. An approximation of the amount of aluminum hydroxide precipitant present in the saltcake is contained in Table 5. Also of note, all of the measured saltcake hydroxide concentrations are lower than the target values and all of the measured carbonate concentrations are higher than the target values. This suggests that during the course of saltcake surrogate preparation and aging, carbon dioxide may have been absorbed from the laboratory atmosphere.

Table 4: Saltcake target composition and dissolved saltcake analysis (dry basis).

	Average SRS Simulant			Hanford S-112 Simulant		
ion	target composition (dry wt%)	est. from 25 °C test (dry wt%)	est. from 50 °C test (dry wt%)	target composition (dry wt%)	est. from 25 °C test (dry wt%)	est. from 50 °C test (dry wt%)
Na^+	34.2	32.6	33.7	32.1	30.4	28.5
K^+	0.156	0.201	0.182	0	0	0
Cs^+	0.0050	n.d	n.d	0	0	0
OH^-	8.62	6.10	5.55	3.70	2.86	1.586
NO_3^-	35.2	36.4	37.2	35.2	36.4	36.3
NO_2^-	6.35	6.58	7.04	7.43	7.81	8.37
$Al(OH)_4^-$	7.81	8.24	8.03	10.54	3.61	3.03
CO_3^{2-}	2.55	4.95	3.24	5.60	6.34	7.04
SO_4^{2-}	3.83	4.16	4.22	2.09	2.27	2.19
PO_4^{3-}	0.633	0.245	0.245	3.41	2.84	2.83
Cl^-	0.236	0.173	0.194	0	0	0
F^-	0.162	0.141	0.148	0	0	0
$C_2O_4^{2-}$	0.187	0.171	0.165	0	0	0
SiO_3^{2-}	0.0810	n.d	n.d	0	0	0
MoO_4^{2-}	0.0084	0.0085	0.0079	0	0	0

n.d. = not determined

Table 5: Saltcake percent moisture and aluminum hydroxide

	Average SRS Simulant			Hanford S-112 Simulant		
	est. from 25 °C test (wt%)	est. from 50 °C test (wt%)	measured after tests (wt%)	est. from 25 °C test (wt%)	est. from 50 °C test (wt%)	measured after tests (wt%)
H_2O	23.5	19.6	13.3	20.4	23.0	17.9
$Al(OH)_3$[a]	~ 0	~ 0		7.45	10.2	

[a] $Al(OH)_3$ weight percent in the saltcake is reported on a dry basis.

Table 5 contains estimates of moisture content and water-insoluble $Al(OH)_3$ in the two saltcake simulants. The saltcake percent moisture at the time of dissolution testing was estimated as the amount of water required to complete the mass balance of the single-wash test samples. The weight percent moisture measured at the end of the tests (100% minus the weight percent total solids) is provided for comparison. In addition, Table 5 contains an estimate of the quantity of $Al(OH)_3$ in the Hanford S-112 saltcake simulant.

Single- and Multiple-Wash Dissolution Data

This section and the appendix contain the results for the simulant saltcake dissolution tests. Table 6 indexes the presentation of results to the experiments that were performed. The single-wash dissolution tests are presented only in tabular form contained in the appendix (Table 7 through Table 10). The single-wash dissolution tests with the highest diluent to saltcake ratio are also used to estimate the saltcake composition and moisture in Table 4. Data from the multiple-wash dissolution tests better illustrate salt dissolution principles, and thus are given a more thorough treatment within the report. In addition to the tabulated data contained in the appendix (Table 11 through Table 14), the multiple-wash dissolution data is used to trend the physical and chemical characteristics of the dissolved salt solution throughout the dissolution process. A series of figures are provided that allow for the estimation of the fractional removal of each component (Figure 6 through Figure 9) and supernatant fluid composition (Figure 10 through Figure 13) at stages of a progressive dissolution.

Table 6: Index of results

Saltcake	Average SRS Simulant		Hanford S-112 Simulant	
Temperature	25 °C	50 °C	25 °C	50 °C
Single Wash	Table 7 Table 4	Table 8 Table 4	Table 9 Table 4	Table 10 Table 4
Multiple-Wash	Table 11 Figure 4 Figure 5 Figure 6 Figure 10	Table 12 Figure 4 Figure 5 Figure 7 Figure 11	Table 13 Figure 4 Figure 5 Figure 8 Figure 12	Table 14 Figure 4 Figure 5 Figure 9 Figure 13

Test Conditions

Although the test temperatures are reported as 25 °C (ambient) or 50 °C (elevated), the true temperatures of the tests were somewhat transient. During inhibited water addition, mixing, centrifuging, and subsequent measurement, several temperature changes were encountered.

The 25°C tests were performed by adding ambient-temperature, nominally 20 °C, fluid to the saltcake. After mixing overnight, the temperature of the salt slurry was measured to be approximately 20 °C. The slurry was centrifuged at 4000 rpm for three periods of 15 minutes, causing its temperature to increase to between 25 and 30 °C. When the supernate was decanted for submittal to ADS, the temperature of the fluid was lower. The decanted solution, however, was likely above ambient temperature because salt crystals formed in many of the decanted supernates after equilibration of the fluid at room temperature. Thus, the data from the ambient test were obtained on a sample that was higher than the ambient 20 °C temperature. The actual test temperature was nominally 25 °C.

During the 50 °C heated tests, the opposite trend was noted during centrifuging. The centrifuge could only be operated for a short time (5 minutes) in order to keep the sample temperature above 40 °C, after which the sample was placed in the oven for 30 minutes to re-heat to 50 °C. This was repeated several times in order to achieve effective solid-liquid separation while maintaining the temperature near 50 °C. Density glassware and the insulating centrifuge-tube sheaths were also kept at 50 °C to assure that separation and density measurement would occur near the target equilibrium temperature.

Physical Data

Figure 4 and Figure 5 represent trends that are noted in the physical data from the multiple-wash dissolution of the simulated HLW saltcakes. Data are presented against an abscissa of the cumulative amount of diluent (0.01M NaOH and 0.011M $NaNO_2$) added per the original mass of saltcake on a mass-per-mass basis. Figure 4 displays the mass fraction of saltcake remaining during the progressive multiple-wash dissolution. As expected, salt dissolution at 50 °C allowed for a greater degree of dissolution than salt dissolution at 25 °C with the same amount of added fluid. At a given temperature and amount of dissolution fluid, a greater fraction of the SRS saltcake surrogate was dissolved than the Hanford saltcake surrogate. At both dissolution temperatures, the Hanford S-112 surrogate had a larger amount of residual insoluble solids than did the Average SRS surrogate.

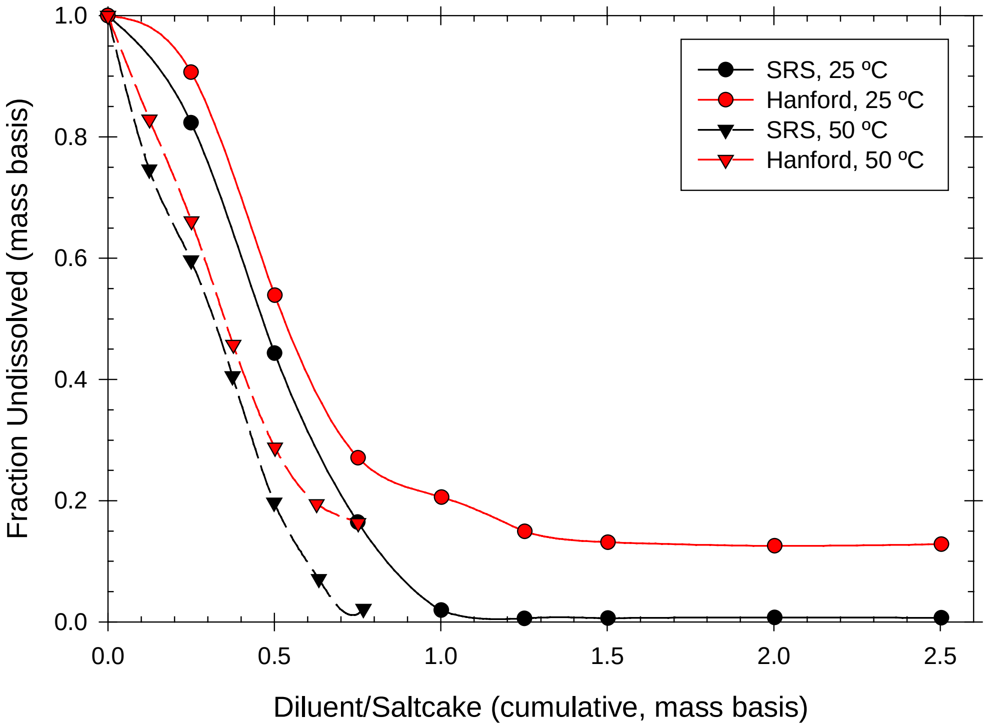


Figure 4: The weight fraction of saltcake that remains undissolved during multiple-wash tests as a function of the cumulative weight of inhibited water added (and subsequently removed) normalized by the weight of original saltcake.

Figure 5 tracks the density of the supernatant liquors removed from the multiple-wash tests. In the 25 °C tests, the supernatant fluid removed during the initial dissolution stages of both saltcake simulants had specific gravities (SpG) from 1.4 to 1.45. In the 50 °C tests, the supernatant SpG of the initial dissolution stages are 1.5 to 1.55. Additional physical data, including the approximate solid-phase density and the percent total solids in the supernatant liquid and residual solid, are contained in the Appendix.

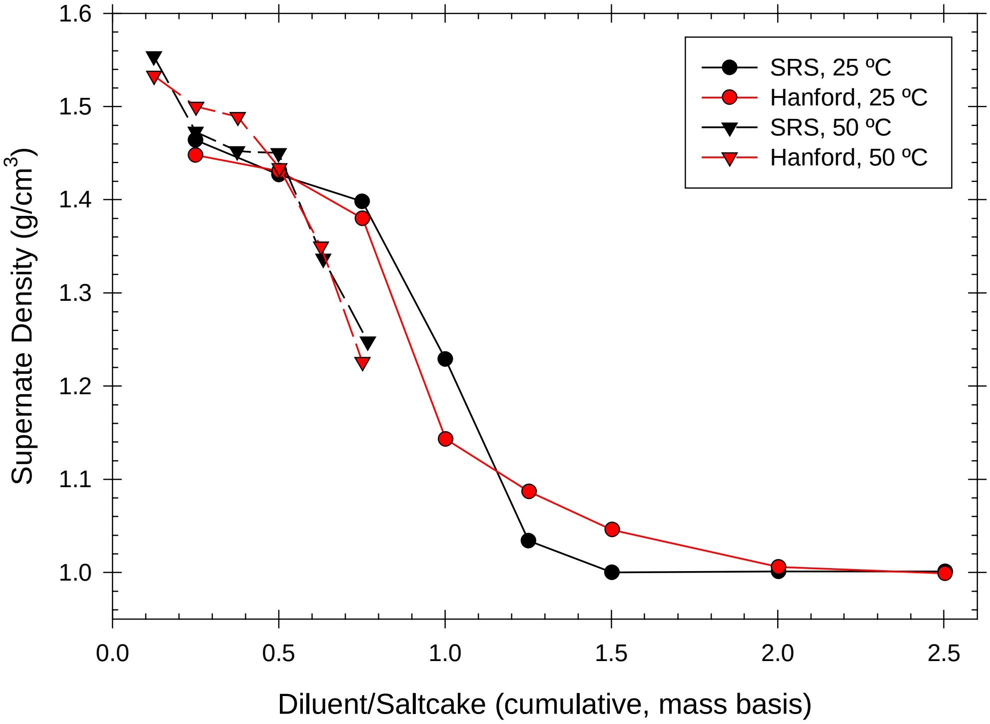


Figure 5: The density of the supernatant liquor decanted multiple-wash tests (Average SRS and Hanford S-112 simulant dissolutions at 25 °C and 50 °C).

<u>Single-Wash Tests</u>

A series of six single wash tests were performed for each of the two waste surrogates at two temperatures, and the results are presented in Table 7 through Table 10 in the appendix. For each single-wash test, the mass of dissolution fluid added per mass of saltcake is reported as “Diluent/Saltcake (mass basis)”. “Solid in Tube” is the volume percentage of the material that is solid plus interstitial liquid after salt dissolution was accomplished and the tubes were centrifuged. The volume percentage of clear supernatant fluid is 100% minus “Solid in Tube”. The solid volume percentages are not reported for one of the SRS saltcake 50 °C tests and two of the Hanford saltcake 50 °C tests due to leakage of material from the tubes. The “Undissolved Saltcake” value is either the volume or weight percentage of the original saltcake that remained undissolved, as measured after decanting the clear supernatant fluid. The supernatant fluid density measurement was repeatable to within ± 0.005 g/cm^3. The density estimate of the residual solid plus interstitial fluid was only reliable to about ± 0.1 g/cm^3 due to inefficient decanting and uncertainties in volume measurement. Solid volume percent values that were below what could be measured reliably, preceded by “<”, led to under-estimates of solid densities, preceded by “>”. The percent total solids content of the undissolved solid and the supernatant fluid are also reported. The results of analyses that could not be reported are detailed in the notes associated with each table.

The tables contain the result of the supernate composition analyses outlined in Table 3. Analytes present in samples at concentrations below their minimum detection limits are preceded by “<”. The charge balance is defined as the percentage of the as-analyzed cations (Na^+ and K^+) that are balanced by the as-analyzed anions. A charge balance under 100% signifies an anion deficiency, while a charge balance over 100% signifies an anion surplus. With the exception of a few suspicious results identified in the notes for each table, the charge balance falls between 85% and 104%.

For the SRS surrogate saltcake, an approximately 1.5:1 mass ratio of dissolution fluid to saltcake led to mixtures with a solid fractions < 1 vol. % for both the ambient and elevated temperature tests. This corresponds to the dissolution of > 95 vol. % of the original saltcake. At 25 °C, there was noticeably depressed solubility of nitrate, carbonate, sulfate, phosphate, fluoride, and oxalate in the high sodium matrix of the low Diluent/Saltcake tests. This was most pronounced for fluoride and oxalate. Similar results are obtained for dissolution temperature 50 °C, with the exception of phosphate, which exhibits a higher solubility in this high ionic strength matrix at the higher temperature. The dissolution of the Hanford surrogate waste at both temperatures resulted in a large portion (23 to 24 vol. %, 18 to 24 wt. %) of solids insoluble at high Diluent/Saltcake.

Multiple-Wash Tests

A multiple-wash test was performed for each of the two waste surrogates at two temperatures, and the results are presented in Table 11 through Table 14 in the appendix. The results of the multiple-wash dissolutions are presented graphically in Figure 6 through Figure 13 (see Table 6 for details). These progressive salt dissolution results should allow for engineering approximations based on subsequent additions of dissolution fluid. The multiple-wash tests contact saltcake with a series of relatively small aliquots of dissolution fluid in order to simulate a dissolution process with a continuous inflow of dissolution fluid and outflow of saturated salt supernate.

Data for the multiple-wash tests are provided in the appendix (Table 11 through Table 14) in a format similar to the presentation of the single-wash test data. The multiple-wash data is reported as a function of the cumulative mass ratio of Diluent:Saltcake. This ratio is obtained from the reported mass of inhibited water diluent used and the original wet mass of saltcake (60.00 g for the 25 °C tests, 60.19 g for the 50 °C test of Average SRS, and 60.05 g for the 50 °C test of Hanford S-112). The early stages of multiple-wash dissolutions exhibit the same good charge balance as obtained in the single-wash tests, but the later stages of multiple-wash dissolutions often have charge imbalances due to the much lower concentration of most ionic species and the influence of the detection limits.

Additional irregularities are noted in Table 12 and Table 14. As mentioned previously, several tube leakages occurred during the 50 °C tests. During the fourth wash of the SRS saltcake, a portion of the slurry leaked from the centrifuge tube while mixing overnight. The amount of salt/supernate slurry lost was estimated as 7.1 % and the Diluent/Saltcake values of the subsequent washes were adjusted to remain on a basis of cumulative mass of dissolution fluid added per mass of original saltcake. For both the dissolution of the SRS and Hanford simulants at 50 °C, slurry leakage was noted during the sixth wash upon the initiation of heating and mixing. The solutions were allowed to come to equilibrium at room temperature, and the liquid was analyzed by the same methods as the previous washes. The solids were washed with a large excess of inhibited water, and the soluble portion of these solids is reported.

The data from the multiple wash tests are presented in two different graphical formats. First, the dissolution profiles of the salt surrogate components are presented in Figure 6 through Figure 9. These figures indicate what mass fraction of each saltcake component has been removed as a function of the amount of diluent added. Dissolved salt samples that contained a component at less than the detectable limit are reported as contributing nothing to the cumulative mass fraction of that component's removal. Second, the composition of each of the supernates are presented in Figure 10 through Figure 13. This indicates the changing dissolved salt concentration as a function of the cumulative diluent mass added.

In Figure 6 through Figure 9, the cumulative mass fraction of dissolution of a component does not include the contribution from washes that contained the component at less than the detectable limit. For the 50 °C tests, the composition of the solid remaining after the sixth wash was used to calculate the total fraction of each component removed during the first six washes. With the exception of the gibbsite and bayerite remaining after the dissolution of the Hanford S-112 simulant, no analyses were performed on the residual solids from the 25 °C tests. Thus, the total fractional removal for all components except aluminum are normalized to unity for the 25 °C tests.

Several observations can be made from the dissolution profiles of Figure 6 through Figure 9:

- Hydroxide, nitrite, potassium, chloride, and molybdate are eluted at the earliest stages of the multiple-wash dissolution. This indicates that these ions are resident in the interstitial fluid of the original saltcake rather than in solid salt crystals. These components are eluted at comparable fractions, so they are denoted as a single curve (X) in Figure 6 through Figure 9. The aluminate also follows this trend for the Average SRS simulant, but the large quantity of insoluble aluminum resulting from the Hanford S-112 saltcake dissolution causes a significant fraction of the aluminum to not be eluted during dissolution.

- Phosphate dissolution exhibits a strong temperature effect . While phosphate elutes in the later stages of dissolution at 25 °C, it elutes in the early stages of dissolution at 50 °C. This trend is more evident for the Hanford S-112 surrogate, where phosphate comprises a greater portion of the saltcake. The impact of temperature on phosphate dissolution is noted regardless of the presence of fluoride ion.

- The latest eluting components of the SRS surrogate waste are oxalate, fluoride, and sulfate.

- For both saltcakes, temperature is seen to affect the relative elution of nitrate, carbonate, phosphate, sulfate, and fluoride.

- A significant portion of the silicon was not recovered from the dissolution of SRS saltcake, suggesting that the solids may contain a silicon-rich phase.

The ambient multiple-wash dissolution test of the Hanford S-112 saltcake resulted in a relatively large amount of residual insoluble material (12.8 wt. % wet insoluble solids per original wet saltcake). These solids, however, contained a large amount of interstitial liquid. Accounting for the low percent total solids content (32.8 %), the residual insoluble solid material was 4.2 wt. % of the original Hanford S-112 saltcake. The ambient multiple-wash dissolution of the Average SRS saltcake resulted in a small amount of material (< 0.7 wt. % of wet insoluble solids per original wet saltcake), so further analyses could not be performed. The 50 °C multiple-wash tests for both saltcake surrogates were stopped prematurely, so the residual solid material contained some of the less soluble sodium salts in addition to the material typically considered insoluble in inhibited water.

The presence of a relatively large quantity of residual insoluble material from the dissolution of Hanford S-112 simulant in comparison with Average SRS simulant was noted at both dissolution temperatures and in both types of dissolution tests. The insoluble material from the 25 °C multiple-wash dissolution of Hanford S-112 saltcake is was analyzed by FTIR and XRD. From Figure 16 contained in the Appendix, the material showed similarity to, but not an exact mach of, a gibbsite reference. As seen in Figure 17, XRD identified the residual insoluble solids as a mixture of two crystalline phases of aluminum trihydroxide ($Al(OH)_3$), namely bayerite and gibbsite. Recent actual-waste dissolution tests of other Hanford single-shell tank saltcakes also identified the bayerite phase of $Al(OH)_3$ as a component of the water-insoluble solids.[13] The residual solids from the dissolution of Average SRS surrogate were not submitted for analysis due to the small quantity. From a mass balance, the SRS residual solids likely contained Si, which was likely present as a sodium aluminosilicate.

An additional phenomenon was noted while performing measurements during the 50 °C tests. After the completion of the density measurements of the supernatant fluid from the Hanford S-112 simulant tests at 50 °C, the saturated solutions had cooled by about 10 °C. At that point, the 40 °C solutions temporarily became gels, most likely due to phosphate precipitation. This gel was not noted for the SRS simulant, possibly due to the lower amount of phosphate and the presence of fluoride contributing to a the formation of a different phosphate salt.

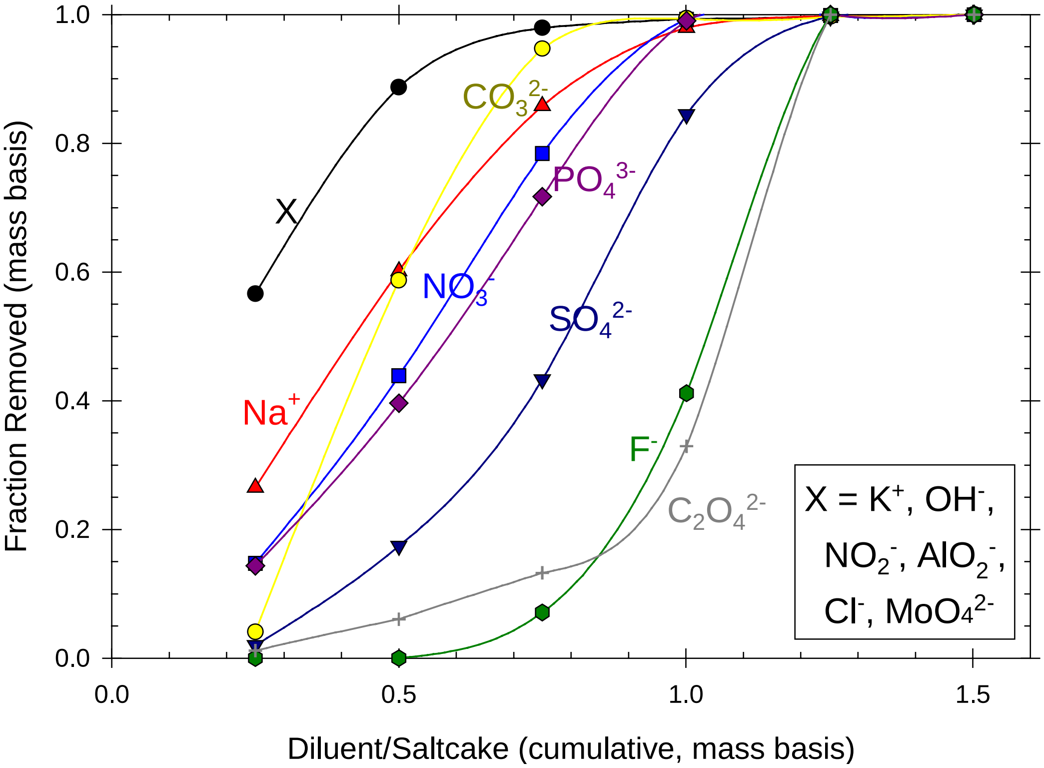


Figure 6: Cumulative fraction of component dissolved during multiple-wash dissolution of Average SRS saltcake simulant at 25 °C.

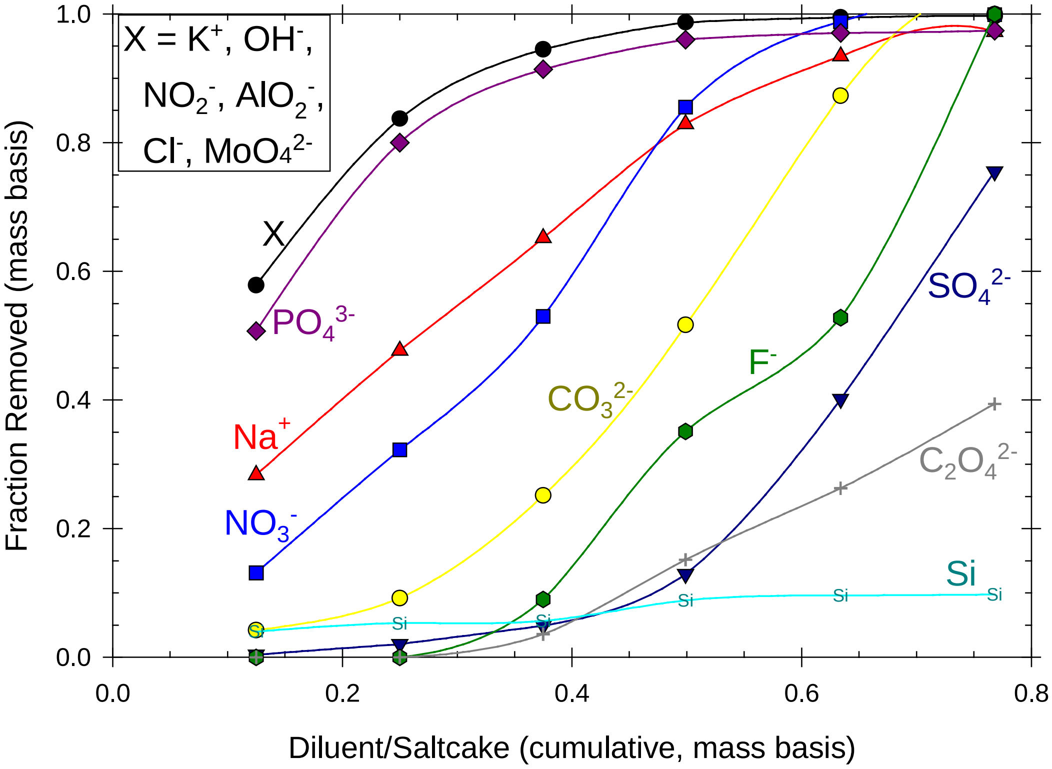


Figure 7: Cumulative fraction of component dissolved during multiple-wash dissolution of Average SRS saltcake simulant at 50 °C.

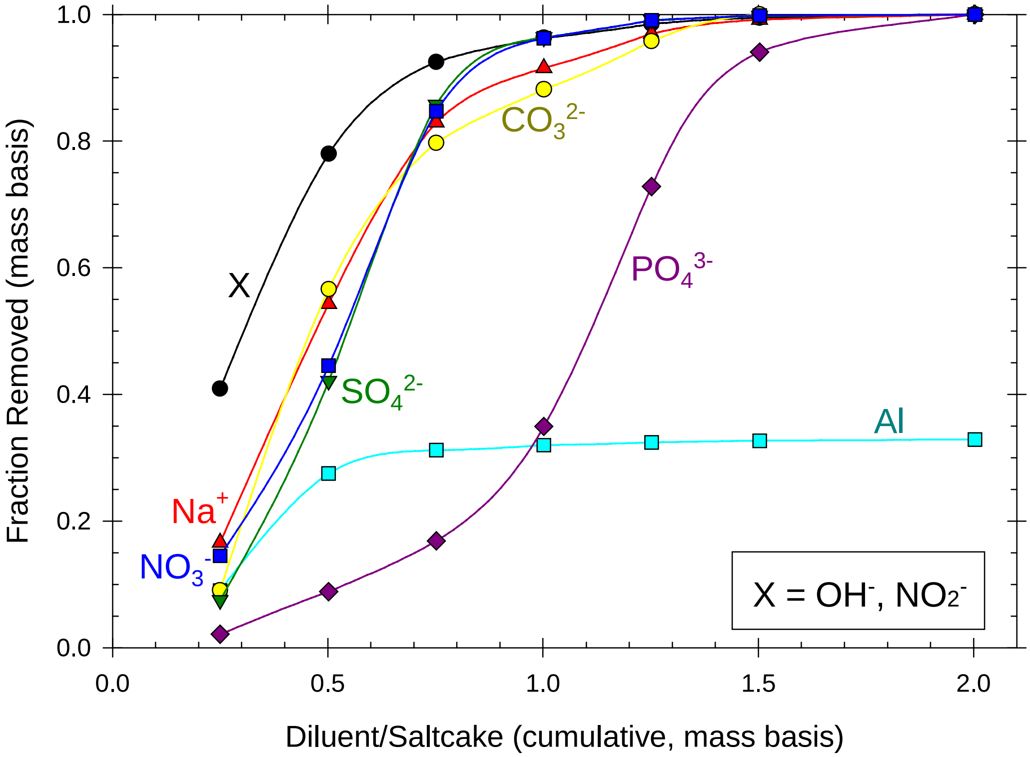


Figure 8: Cumulative fraction of component dissolved during multiple-wash dissolution of Hanford S-112 saltcake simulant at 25 °C.

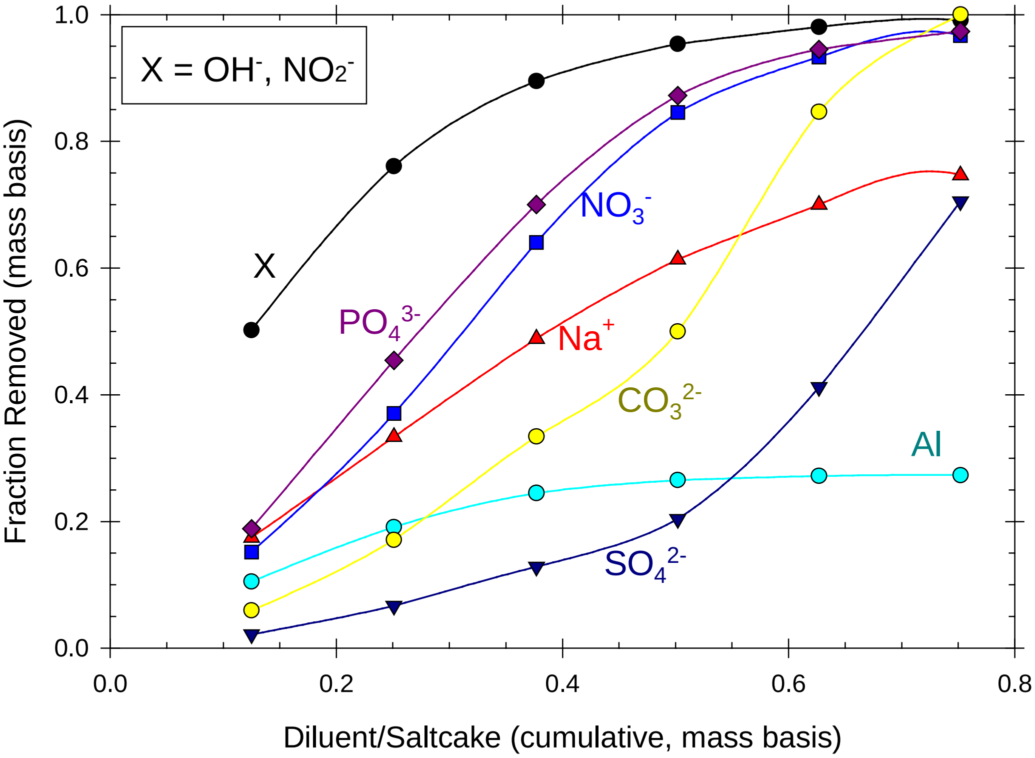


Figure 9: Cumulative fraction of component dissolved during multiple-wash dissolution of Hanford S-112 saltcake simulant at 50 °C.

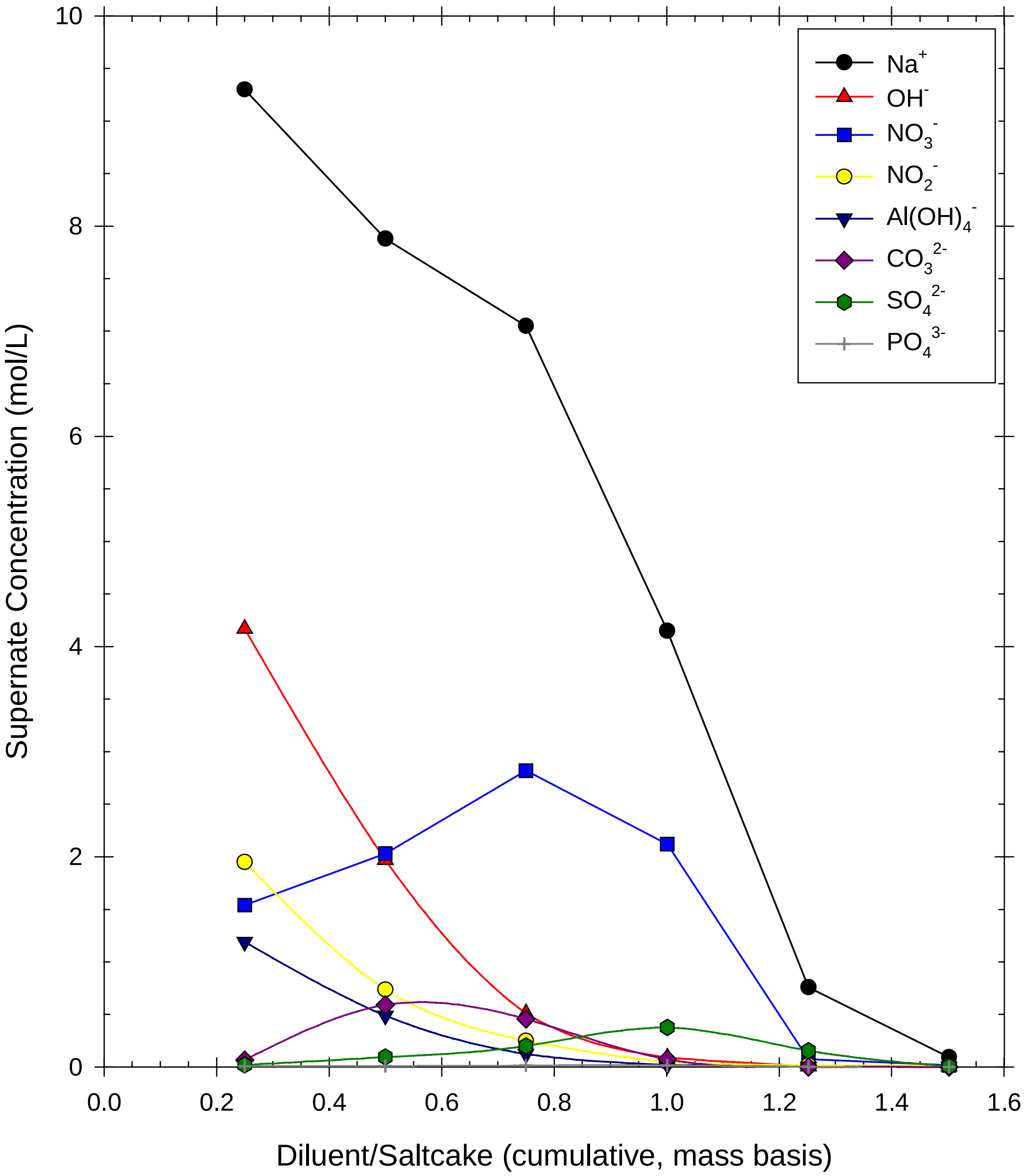


Figure 10: Component concentrations of decanted liquor during multiple-wash dissolution of Average SRS saltcake simulant at 25 °C.

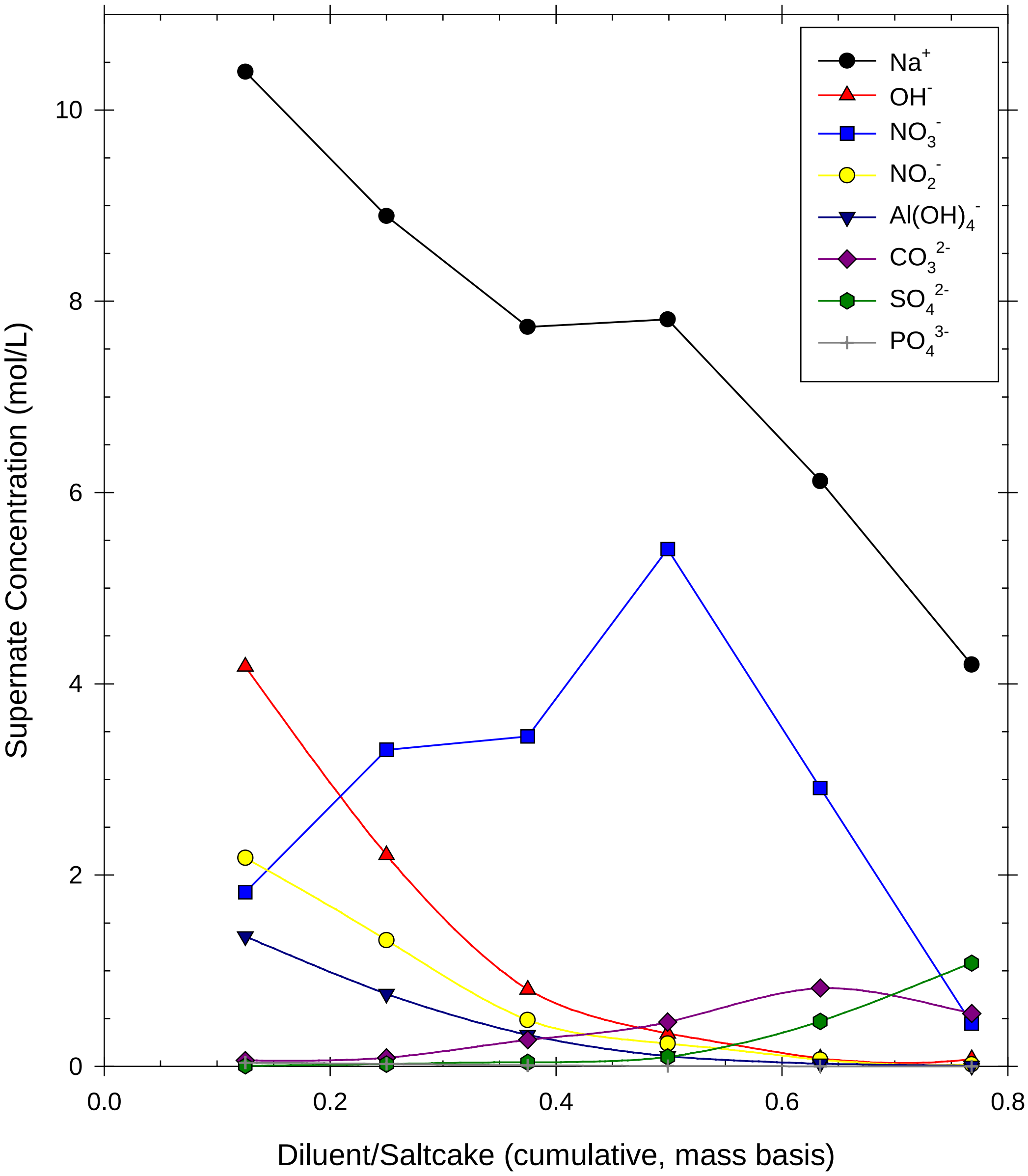


Figure 11: Component concentrations of decanted liquor during multiple-wash dissolution of Average SRS saltcake simulant at 50 °C.

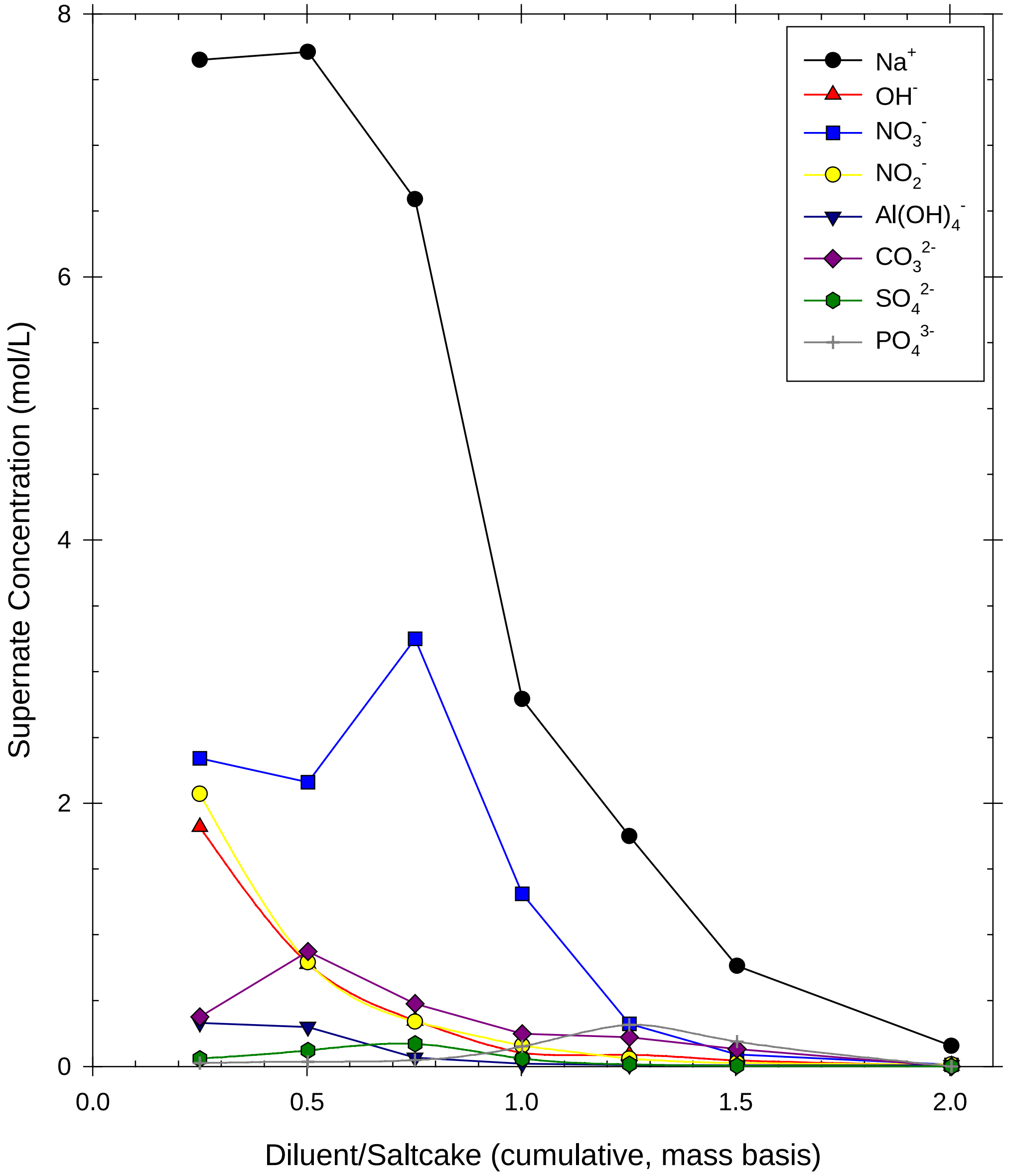


Figure 12: Component concentrations of decanted liquor during multiple-wash dissolution of Hanford S-112 saltcake simulant at 25 °C.

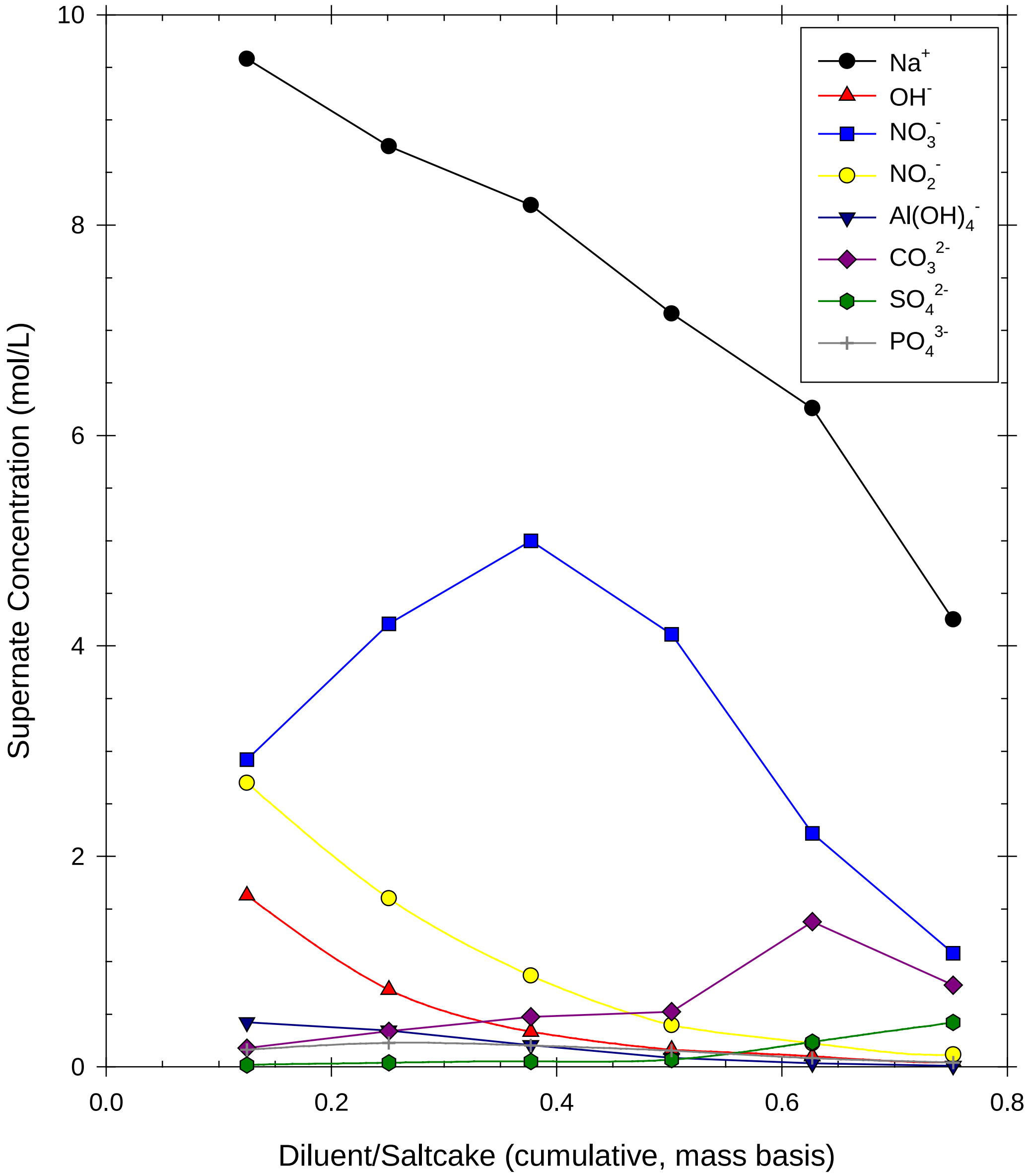


Figure 13: Component concentrations of decanted liquor during multiple-wash dissolution of Hanford S-112 saltcake simulant at 50 °C.

Salt Column Test

This test was a scoping study, so the procedure was evolving throughout the test. The intent of the test was to drain quickly the dissolution fluid through the bed of saltcake, but adjustments to the plan were made when the fluid did not readily drain. A 170 mL (6.5 inch tall by 1.5 inch in diameter) portion of saltcake was formed in a graduated cylinder from the cooling of 320 mL of evaporated salt slurry. Figure 14 shows the column of Average SRS saltcake and supernatant liquid. The test was performed at ambient laboratory temperature, which was nominally 20 °C.

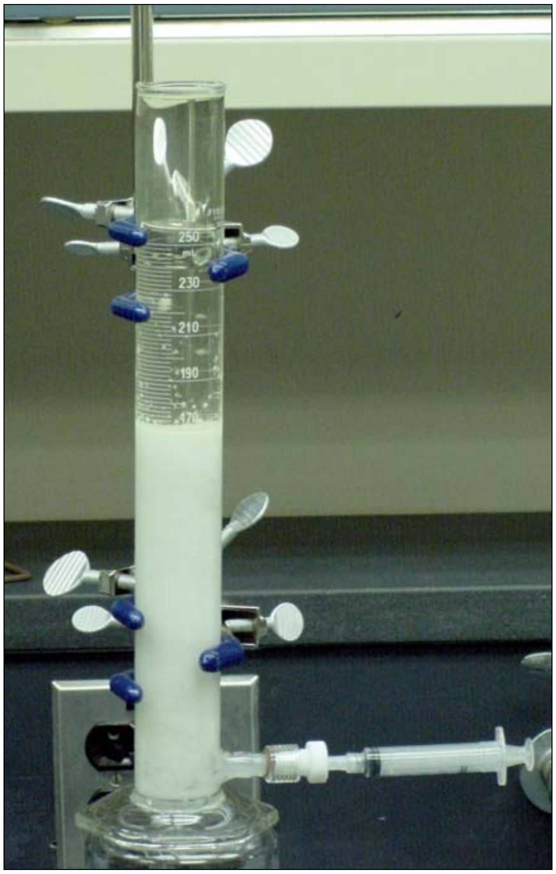


Figure 14: Salt Column Dissolution Scoping Test Apparatus

The first step is to remove the supernatant liquid by draining through the saltcake. A ¼ inch port was available near the bottom of the column to which a 60-mL syringe could be attached to supply suction. The supernate did not drain as well as expected. Initially, 5 to 10 mL of supernate was removed from the sampling port, but removal of additional liquid was too slow for this scoping test, which was designed to be performed within 1 to 2 shifts. The remaining supernatant fluid was removed via syringe from the top of the column.

The test was to dissolve the column of saltcake with a series of 50 mL inhibited water (IW) strikes. For each strike, the dissolution fluid was only to have contact with the saltcake for the amount of time required for the fluid to drain through the saltcake. When the first 50 mL IW strike was added to the top of the saltcake, it did not drain readily through the saltcake. In order to still drain the liquid “through” the saltcake, an attempt was made to short-circuit the column of salt. A direct path between the supernate and the port at the bottom of the column was created by pressing a ¼ inch diameter rod through the saltcake. When the rod was removed, a few milliliters of liquid trickled out of the port at the bottom of the column. Because the saltcake was not firm, salt rushed in to fill the well cutting off the flow of supernate. After repeating the rod insertion several times, the hole in the saltcake finally had enough integrity to allow for the supernate, along with a small amount (~10 mL) of saltcake, to be drained from the bottom of the column. The supernate was retained and the entrained saltcake was returned to the top of the column. This first contact of inhibited water with the saltcake column took place over approximately 30 minutes.

A series of six additional 50 mL inhibited water strikes were added to the column of salt. After each addition had sat on top of the salt column for 5 minutes, the ¼ inch diameter rod was inserted to allow for the liquid to be drained quickly from the port in the bottom of the column. The slurry collected was quickly separated, with the liquid being retained and any entrained salt being returned to the column.

Even though the inhibited water sat over the salt for a very short time (5 minutes) and the intentionally short-circuited drainage through the column did not provide intimate contact with the saltcake, the dissolution of salt was still significant. Figure 15 displays the density of each supernate solution as measured after draining from the column. The supernate densities from the Average SRS multiple wash tests are provided for reference. Both of these are plotted versus the diluent to saltcake ratio, this time provided on a volume basis. This shows that, although salt was dissolved in this limited-contact test, the efficiency of water usage was low. While the specific gravities of saturated Average SRS simulant was greater than 1.4 during initial stages of multiple-wash dissolution, the non-saturated supernates produced from the column test were in the range of less than 1.2 to just above 1.3.

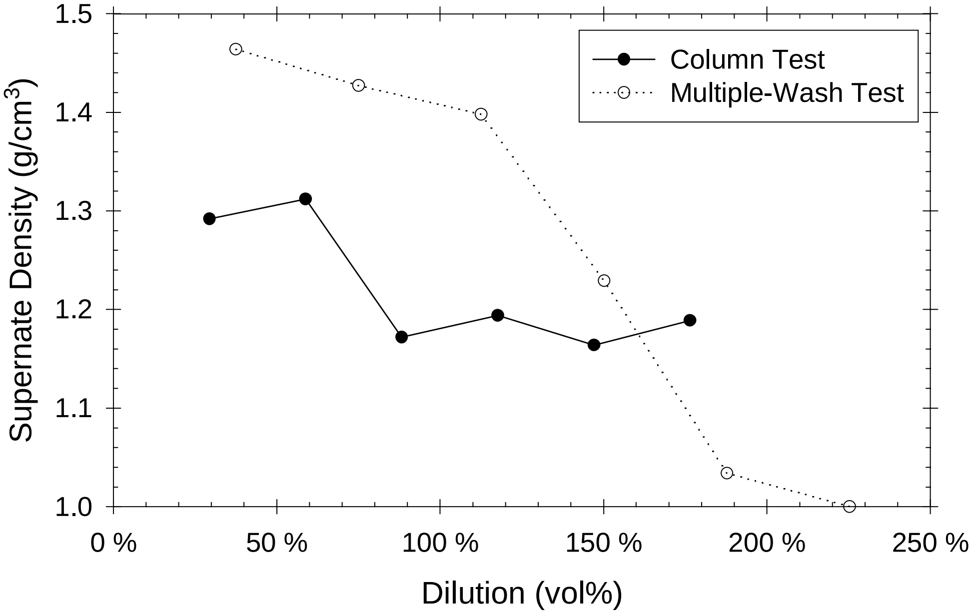


Figure 15: Density of Solutions Obtained from Short-Contact Saltcake Column Dissolution Scoping Test

Summary

Single-wash and multiple-wash dissolution with inhibited water was performed for Average SRS and Hanford S-112 saltcake simulants at 25 °C and 50 °C. The compositions of the supernatant fluids were analyzed, resulting in dissolution profiles for each salt component. The profiles for the relative elution of anions from saltcake during dissolution exhibit distinctions that are dependent upon the dissolution temperature and the initial saltcake composition. Phosphate shows a strong temperature dependence.

For both salt waste surrogates, dissolution of the soluble components was achieved at less than a 2:1 mass ratio of inhibited water to saltcake during multiple-wash tests. Dissolution of the Hanford S-112 simulant resulted in 4.2 g of residual dry $Al(OH)_3$ per 100 g of original wet saltcake. A scoping column test was performed to aid in the design of potential saltcake dissolution kinetics tests.

Quality Assurance

This work satisfies the requirements of the original task technical and quality assurance plan.[15] Laboratory Notebooks WSRC-NB-2001-00181, WSRC-NB-2002-00087, and WSRC-NB-2002-00147 contain the experimental data and procedures for the project documented in this report. Additional notebooks maintained by ADS contain additional analytical information.

Acknowledgements

The authors would like to acknowledge the Tanks Focus Area for their support of this work. The ideas of Dan Herting of Fluor Hanford were important in the design and interpretation of these tests. We also thank Fernando Fondeur for his assistance with the residual solids analysis by FTIR. We thank John Young for coordinating this work within ADS, and the various ADS researchers and technicians for their timely delivery of analytical results.

References

[1] D. T. Hobbs, “Final Report: Analysis of Tank 41H Saltcake Sample #2 and Comparison to Sample #1,” WSRC-TR-94-057, January 26, 1994.

[2] D. T. Hobbs, “Final Report on the Analytical Results for Tank Farm Samples in Support of Salt Dissolution Evaluations,” WSRC-TR-96-0410, Revision 0, December 12, 1996.

[3] R. F. Swingle, “Characterization of the Tank 38H Variable Depth and Core Samples,” WSRC-RP-2001-00574, Revision 0, May 2, 2001.

[4] L. N. Oji, “Characterization of Tank 37H Salt Core Samples,” WSRC-TR-22001-00517, Revision 0, November 12, 2001.

[5] C. J.Martino, “Tank 41H Salt-Well Sample Analysis,” WSRC-TR-2002-00343, Revision 0, August 15, 2002.

[6] B. J. Wiersma, “Recommendations for the Use of Inhibited Water During Phase I Salt Dissolution in Tank 41,” WSRC-TR-96-0085, January, 1996.

[7] B. J. Wiersma, “An Investigation of Density Driven Salt Dissolution Techniques,” WSRC-TR-96-0160, August 1996.

[8] G. S. Barney, “Vapor-Liquid-Solid Phase Equilibria of Radioactive Sodium Salt Wastes at Hanford,” ARH-ST-133, January 1976.

[9] D. L. Herting and R. L. Cleavenger, “Solubility Phase Diagram – Final Report,” (Rockwell Hanford Operations) SD-WM-TI-078, May 20, 1983.

[10] D. A. Reynolds and D. L. Herting, “Solubilities of Sodium Nitrate, Sodium Nitrite, and Sodium Aluminate in Simulated Nuclear Waste,” RHO-RE-ST-14 P, September 1984.

[11] D. L. Herting, D. W. Edmonson, J. R. Smith, T. A. Hill, and C. H. Delegard, “Saltcake Dissolution FY 1999 Status Report,” HNF-5193, Rev. 0, September 1999.

[12] D. L. Herting, “Saltcake Dissolution FY 2000 Status Report,” HNF-7031, Rev. 0, September 2000.

[13] D. L. Herting, “Saltcake Dissolution FY 2001 Status Report,” HNF-8849, Rev. 0, September 2001.

[14] D. D. Walker, “Preparation of Simulated Waste Solutions,” WSRC-TR-99-00116, Revision 0, April 15, 1999.

[15] C. J. Martino and M. R. Poirier, “Task Technical and Quality Assurance Plan for FY02 Salt Dissolution Simulant Studies,” WSRC-RP-2001-01111, Revision 0, January 24, 2002.

Appendix

Table 7: 25 °C single-wash test for the Average SRS saltcake simulant.

Diluent/Saltcake (mass basis)	0.2507	0.5027	0.7452	0.9961	1.496	2.712
Solid in Tube (vol. %)	60.5	22.9	5.2	1.0	*< 0.9*	*< 0.8*
Undissolved Saltcake (vol. %)	86	43	12	3	*< 3*	*< 5*
Undissolved Saltcake (wt. %)	84.0	57.2	19.9	6.9	4.5	4.1
Supernate Density (g/cm^3)	1.484	1.440	1.414	1.388	1.298	1.196
Est. Solid Density (g/cm^3)	1.9	2.6	3.2	4.8	*> 2.7*	*> 1.7*
Supernate Total Solids (wt. %)	n.d.	45.7	61.1	54.5	42.9	29.4
Solid Total Solids (wt. %)	78.8	75.9	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]
Supernate Composition (mol/L)						
Na^+	9.16	7.80	7.48	6.72	5.26	3.50
K^+	0.0625	0.0421	0.0318	0.0256	0.0202	0.0127
Cs^+	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]	n.d.[b]
OH^-	4.35	3.10	2.26	1.75	1.33	0.885
NO_3^-	1.57	2.12	2.64	2.13	1.79	1.45
NO_2^-	1.86	1.21	0.886	0.600	0.424	0.352
$Al(OH)_4^-$	1.14	0.738	0.533	0.418	0.334	0.214
CO_3^{2-}	0.0631	0.334	0.351	0.343	0.177[c]	0.203
SO_4^{2-}	0.0213	0.0516	0.114	0.171	0.140	0.107
PO_4^{3-}	9.12E-3	9.42E-3	0.0122	0.0120	8.95E-3	6.35E-3
Cl^-	0.0806	0.0470	0.0329	0.0212	0.0151	0.0121
F^-	*< 3.32E-3*	*< 3.14E-3*	*< 3.15E-3*	4.27E-3	0.0148	0.0183
$C_2O_4^{2-}$	6.10E-4	1.08E-3	1.74E-3	1.95E-3	3.38E-3	4.79E-3
SiO_3^{2-}	2.10E-3	1.32E-3	1.04E-3	7.38E-4	5.95E-4	3.68E-4
MoO_4^{2-}	6.68E-4	4.37E-4	3.26E-4	2.55E-4	2.06E-4	1.31E-4
Charge Balance (%)	100	102	97	89	87	102

a. not determined due to lack of residual solids
b. cesium concentration not measured
c. reported value likely low

Table 8: 50 °C single-wash test for the Average SRS saltcake simulant.

Diluent/Saltcake (mass basis)	0.2481	0.4999	1.0036	1.4864	1.999	2.978
Solid in Tube (vol. %)	51.4	25.6	2.1	*< 0.9*	n.d.[a]	*< 0.8*
Undissolved Saltcake (vol. %)	73	49	6	*< 3*	n.d.[a]	*< 5*
Undissolved Saltcake (wt. %)	70.7	46.7	14.0	9.2	n.d.[a]	3.1
Supernate Density (g/cm^3)	1.501	1.436	1.298	1.292	1.334	1.161
Est. Solid Density (g/cm^3)	2.1	1.7	1.4	*> 1.4*	n.d.[a]	*> 1.2*
Supernate Total Solids (wt. %)	49.6	46.2	42.9	37.5	29.7	24.9
Solid Total Solids (wt. %)	78.8	76.4	57.4	n.d.[b]	n.d.[b]	n.d.[b]
Supernate Composition (mol/L)						
Na^+	9.3	8.39	6.70	5.57	4.67	3.44
K^+	0.0487	0.0337	0.0232	0.0183	0.0150	0.0109
Cs^+	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]	n.d.[c]
OH^-	2.74	1.67	1.02	0.730	0.537	0.767[d]
NO_3^-	2.68	3.71	2.92	2.20	1.83	1.410
NO_2^-	1.75	1.04	0.715	0.569	0.473	0.359
$Al(OH)_4^-$	0.974	0.619	0.405	0.345	0.271	0.198
CO_3^{2-}	*< 0.118*	*< 0.119*	0.239	0.132	*< 0.122*	*< 0.127*
SO_4^{2-}	0.0163	0.0260	0.145	0.136	0.129	0.103
PO_4^{3-}	0.0299	0.0183	0.0129	9.90E-3	8.09E-3	6.07E-3
Cl^-	0.0672	0.0389	0.0261	0.0204	0.0167	0.0129
F^-	*< 6.19E-3*	*< 6.26E-3*	5.75E-3	0.0212	0.0244	0.0183
$C_2O_4^{2-}$	*< 6.68E-3*	*< 6.76E-3*	*< 5.91E-3*	6.72E-3	6.10E-3	4.39E-3
SiO_3^{2-}	1.81E-3	9.72E-4	5.46E-4	1.24E-3	4.08E-4	3.12E-4
MoO_4^{2-}	5.95E-4	3.50E-4	2.43E-4	1.82E-4	1.55E-4	1.16E-4
Charge Balance (%)	89	85	88	80	74	87

a. not determined due to leakage
b. not determined due to lack of residual solids
c. cesium concentration not measured
d. reported value likely high

Table 9: 25 °C single-wash test for the Hanford S-112 saltcake simulant.

Diluent/Saltcake (mass basis)	0.4978	0.9936	1.4967	1.9948	2.465	3.020
Solid in Tube (vol. %)	40.6	13.9	8.7	8.3	2.6 [b]	3.7
Undissolved Saltcake (vol. %)	76	38	32	29	14 [b]	24
Undissolved Saltcake (wt. %)	70.4	32.1	27.6	18.3	20.8	18.0
Supernate Density (g/cm^3)	1.437	1.362	1.273	1.218	1.182	1.164
Est. Solid Density (g/cm^3)	1.8	1.6	1.7	1.2	2.8 [b]	1.4
Supernate Total Solids (wt. %)	47.4	40.9	32.4	26.9	23.0	20.3
Solid Total Solids (wt. %)	69.2	48.1	44.5	n.d.[a]	n.d.[a]	n.d.[a]
Supernate Composition (mol/L)						
Na^+	7.30	6.31	5.10	3.94	3.59	3.04
OH^-	0.834	0.573	0.544	0.493	0.458	0.338
NO_3^-	2.59	2.64	2.17	1.93	1.60	1.35
NO_2^-	1.38	0.828	0.590	0.533	0.461	0.381
$Al(OH)_4^-$	0.353	0.193	0.130	0.113	0.103	0.0747
CO_3^{2-}	0.757	0.516	0.405	0.317	0.287	0.245
SO_4^{2-}	0.108	0.125	0.0953	0.0672	0.0642	0.0747
PO_4^{3-}	0.0318	0.0466	0.0613	0.0856	0.0811	0.0631
Charge Balance (%)	96	90	91	104	99	98

a. not determined due to lack of residual solids
b. suspected error in measurement

Table 10: 50 °C single-wash test for the Hanford S-112 saltcake simulant.

Diluent/Saltcake (mass basis)	0.2551	0.5000	0.9935	1.5026	2.003	2.919
Solid in Tube (vol. %)	52.9	25.0	13.0	n.d.[a]	n.d.[a]	3.6
Undissolved Saltcake (vol. %)	71	47	24	n.d.[a]	n.d.[a]	23
Undissolved Saltcake (wt. %)	73.3	43.7	24.4	n.d.[a]	n.d.[a]	23.9
Supernate Density (g/cm^3)	1.539	1.472	1.345	1.263	n.d.[a]	1.147
Est. Solid Density (g/cm^3)	2.0	1.8	2.0	n.d.[a]	n.d.[a]	2.0
Supernate Total Solids (wt. %)	54.1	48.6	41.0	32.6	n.d.[a]	20.2
Solid Total Solids (wt. %)	64.6	64.3	56.0	50.6	67.9	n.d.[b]
Supernate Composition (mol/L)						
Na^+	8.27	7.60	6.45	4.98	3.45	2.82
OH^-	0.579	0.743	0.333	0.288	0.226	0.212
NO_3^-	3.68	4.11	2.69	1.66[c]	1.64	1.33
NO_2^-	1.80	1.17	0.776	0.484[c]	0.472	0.414
$Al(OH)_4^-$	0.483	0.332	0.183	0.120	0.0966	0.0726
CO_3^{2-}	< *0.0965*	0.321	0.430	0.270	0.116	0.267
SO_4^{2-}	0.0290	0.0416	0.116	0.0751	0.0526	0.0518
PO_4^{3-}	0.228	0.188	0.142	0.0992	0.0744	0.0677
Charge Balance (%)	88	101	85	71	87	102

a. not determined due to leakage
b. not determined due to lack of residual solids
c. reported value likely low

Table 11: 25 °C multiple-wash test for the Average SRS saltcake simulant.

Wash #	1	2	3	4	5	6	7	8
Diluent/Saltcake (cumulative mass basis)	0.250	0.500	0.750	1.001	1.252	1.502	2.003	2.504
Supernate (mL)	18.0	27.0	23.0	18.5	15.0	15.0	31.0	30.5
Solid in Tube (vol. %)	59.1	34.1	20.7	11.9	*< 6.3*	*< 6.3*	*< 1.6*	*< 1.6*
Undissolved Saltcake (vol. %)	86	46	20	7	*< 3*	*< 3*	*< 2*	*< 2*
Undissolved Saltcake (wt. %)	82.3	44.3	16.5	1.9	0.5	0.6	0.7	0.7
Supernate Density (g/cm^3)	1.464	1.427	1.398	1.229	1.034	1.000	1.001	1.001
Est. Solid Density (g/cm^3)	n.d.[e]	n.d.[e]	1.6	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]
Supernate Total Solids (wt. %)	48.4	45.0	45.7	28.7	4.20	0.127	0.111	0.056
Supernate Composition (mol/L)								
Na^+	9.3	7.88	7.05	4.15	0.759	0.0930	n.d.[b]	n.d.[b]
K^+	0.0663	0.0289	9.14E-3	1.98E-3	1.36E-4	1.67E-4	n.d.[b]	n.d.[b]
Cs^+	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[b]	n.d.[b]
OH^-	4.17	1.97	0.511	0.0900	5.95E-3	6.00E-3	n.d.[b]	n.d.[b]
NO_3^-	1.54	2.03	2.82	2.12	0.0739	0.0157	n.d.[b]	n.d.[b]
NO_2^-	1.95	0.737	0.249	0.0483	0.0145	0.0114	n.d.[b]	n.d.[b]
$Al(OH)_4^-$	1.19	0.488	0.123	0.0201	1.34E-3	8.63E-4	n.d.[b]	n.d.[b]
CO_3^{2-}	0.0663	0.591	0.457	0.0741	*< 0.0595*	*< 0.0600*	n.d.[b]	n.d.[b]
SO_4^{2-}	0.0199	0.0944	0.200	0.376	0.155	5.64E-3	n.d.[b]	n.d.[b]
PO_4^{3-}	8.14E-3	9.57E-3	0.0143	0.0151	6.51E-4	*< 1.32E-4*	n.d.[b]	n.d.[b]
Cl^-	0.0914	0.0252	5.73E-3	*< 1.69E-3*	*< 1.68E-3*	*< 1.69E-3*	n.d.[b]	n.d.[b]
F^-	*< 3.16E-3*	*< 3.16E-3*	0.0126	0.0749	0.160	*< 3.16E-3*	n.d.[b]	n.d.[b]
$C_2O_4^{2-}$	6.13E-4	1.70E-3	2.95E-3	0.0101	0.0422	*< 3.41E-3*	n.d.[b]	n.d.[b]
SiO_3^{2-}	2.34E-3	1.04E-3	2.09E-4	1.04E-4	3.34E-4	5.17E-4	n.d.[b]	n.d.[b]
MoO_4^{2-}	6.81E-4	2.92E-4	7.45E-5	1.52E-5	*< 6.20E-6*	*< 6.26E-6*	n.d.[b]	n.d.[b]
Charge Balance (%)	98	84	72	80	86	50[c]	n.d.[b]	n.d.[b]

Notes for Table 11

a. cesium concentration not measured
b. low solids content, not analyzed
c. poor charge balance due to dilute solution detection limits
d. not determined from small amount of solids
e. not determined due to data recording error

Table 12: 50 °C multiple-wash test for the Average SRS saltcake simulant.

Wash #	1	2	3	4[a]	5	6[b]		6[c]
Diluent/Saltcake (cumulative mass basis)	0.125	0.250	0.375	0.499	0.634	0.768		
Supernate (mL)	15.0	12.0	12.5	12.5	9.5	5.0		
Solid in Tube (vol. %)	60.0	60.0	50.0	32.4	26.9	23.1		
Undissolved Saltcake (vol. %)	76	59	41	19	11	5		
Undissolved Saltcake (wt. %)	74.6	59.6	40.5	19.7	7.1	2.2		
Supernate Density (g/cm^3)	1.554	1.473	1.452	1.450	1.337	1.248	Solid Density (g/cm^3)	n.d.
Est. Solid Density (g/cm^3)	2.0	2.0	2.0	2.0	1.3	*> 0.8*		
Supernate Total Solids (wt. %)	60.7	47.9	45.4	46.3	40.8	25.7	Solid Total Solids (wt.%)	77.2
Supernate Composition (mol/L)							*Solid Composition (wt. %)*	
Na^+	10.4	8.89	7.73	7.81	6.12	4.20	Na^+	28.8
K^+	0.0766	0.0452	0.0213	8.72E-3	3.39E-3	1.10E-3	K^+	0.0123
Cs^+	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]	n.d.[d]	Cs^+	n.d.
OH^-	4.18	2.21	0.803	0.342	0.0822	0.0780	OH^-	*< 1.36*
NO_3^-	1.82	3.31	3.45	5.41	2.91	0.448	NO_3^-	1.03
NO_2^-	2.18	1.32	0.483	0.237	0.0687	0.0224	NO_2^-	*< 0.399*
$Al(OH)_4^-$	1.36	0.758	0.329	0.107	0.0278	4.92E-3	$Al(OH)_4^-$	3.01
CO_3^{2-}	0.0614	0.0902	0.279	0.463	0.819	0.554	CO_3^{2-}	*< 4.79*
SO_4^{2-}	4.94E-3	0.0232	0.0422	0.0983	0.471	1.08	SO_4^{2-}	31.9
PO_4^{3-}	0.0385	0.0263	0.0110	4.31E-3	1.38E-3	9.03E-4	PO_4^{3-}	0.229
Cl^-	0.105	0.0540	0.0168	5.70E-3	1.43E-3	*< 2.10E-3*	Cl^-	*< 0.0799*
F^-	*< 3.23E-3*	*< 3.17E-3*	4.06E-3	0.0118	0.0105	0.0532	F^-	*< 6.15*
$C_2O_4^{2-}$	*< 3.49E-3*	*< 3.42E-3*	2.15E-3	6.95E-3	8.80E-3	0.0197	$C_2O_4^{2-}$	3.30
SiO_3^{2-}	2.54E-3	1.06E-3	2.56E-4	2.46E-3	7.54E-4	3.20E-4	SiO_3^{2-}	2.00
MoO_4^{2-}	7.78E-4	4.42E-4	2.02E-4	6.77E-5	2.13E-5	7.83E-6	MoO_4^{2-}	*< 0.0013*
Charge Balance (%)	94	89	74	93	93	93	Total (wt. %)	≥ 70.2[e]

Notes for Table 12

a. leakage/loss of 7.1 wt. % of the slurry forced a re-baselining of the dissolution test
b. leakage of material, brought to equilibrium at ambient conditions (25 °C)
c. the soluble portion of the residual solids at 25 °C
d. cesium concentration not measured
e. the total weight percent was determined to be less than the total solids content likely due to the relatively large detection limits of F^- and CO_3^{2-}.

Table 13: 25 °C multiple-wash test for the Hanford S-112 saltcake simulant.

Wash #	1	2	3	4	5	6	7	8
Diluent/Saltcake (cumulative mass basis)	0.250	0.502	0.752	1.002	1.252	1.503	2.003	2.503
Supernate (mL)	12.0	27.0	24.0	17.0	17.0	16.0	30.0	28.0
Solid in Tube (vol. %)	72.7	41.3	29.4	32.0	29.2	27.3	16.7	17.6
Undissolved Saltcake (vol. %)	102	60	32	25	22	19	19	19
Undissolved Saltcake (wt. %)	90.7	53.8	27.0	20.5	14.9	13.1	12.5	12.8
Supernate Density (g/cm^3)	1.448	1.431	1.380	1.143	1.087	1.046	1.006	0.999
Est. Solid Density (g/cm^3)	n.d.[c]	n.d.[c]	1.6	1.5	1.3	1.3	1.3	1.3
Supernate Total Solids (wt. %)	49.2	46.7	44.5	18.1	9.84	4.77	0.753	0.139
	Solids Total Solids (wt. %)							32.8
Supernate Composition (mol/L)								
Na^+	7.65	7.71	6.59	2.79	1.75	0.763	0.156	n.d.[a]
OH^-	1.82	0.780	0.348	0.101	0.0866	0.0449	6.01E-3	n.d.[a]
NO_3^-	2.34	2.16	3.25	1.31	0.323	0.0913	0.0119	n.d.[a]
NO_2^-	2.07	0.789	0.340	0.157	0.0588	0.0253	0.0144	n.d.[a]
$Al(OH)_4^-$	0.331	0.300	0.0672	0.0211	0.0106	7.52E-3	2.88E-3	n.d.[a]
CO_3^{2-}	0.375	0.873	0.476	0.248	0.221	0.132	*< 0.0601*	n.d.[a]
SO_4^{2-}	0.0587	0.121	0.171	0.0588	0.0152	3.71E-3	7.88E-4	n.d.[a]
PO_4^{3-}	0.0251	0.0353	0.0474	0.151	0.316	0.188	0.0281	n.d.[a]
Charge Balance (%)	98	79	82	95	108	132[b]	78[b]	n.d.[a]

a. low solids content, not analyzed
b. poor charge balance due to dilute solution detection limits
c. not determined due to data recording error

Table 14: 50 °C multiple-wash test for the Hanford S-112 saltcake simulant.

Wash #	1	2	3	4	5	6[a]		6[b]
Diluent/Saltcake (cumulative mass basis)	0.125	0.251	0.377	0.502	0.627	0.752		
Supernate (mL)	12.5	12.5	13.0	12.0	9.5	7.5		
Solid in Tube (vol. %)	66.7	61.5	53.6	45.5	44.1	48.3		
Undissolved Saltcake (vol. %)	79	64	48	32	24	22		
Undissolved Saltcake (wt. %)	82.9	66.1	45.7	28.7	19.4	16.3		
Supernate Density (g/cm^3)	1.533	1.500	1.489	1.434	1.350	1.226		
Est. Solid Density (g/cm^3)	2.0	2.0	1.8	1.7	1.6	1.4		
Supernate Total Solids (wt. %)	55.4	51.9	53.0	46.7	38.8	25.4	Solid Total Solids (wt.%)	40.9
Supernate Composition (mol/L)							*Solid Composition (wt. %)*	
Na^+	9.58	8.75	8.19	7.16	6.26	4.25	Na^+	8.23
OH^-	1.63	0.733	0.334	0.162	0.100	0.0460	OH^-	0.052
NO_3^-	2.92	4.21	5.00	4.11	2.22	1.08	NO_3^-	5.07
NO_2^-	2.70	1.60	0.866	0.396	0.223	0.115	NO_2^-	0.343
$Al(OH)_4^-$	0.422	0.346	0.207	0.0854	0.0357	8.62E-3	$Al(OH)_4^-$	0.0547[d]
CO_3^{2-}	0.179	0.338	0.475	0.523	1.38	0.775	CO_3^{2-}	*< 1.84*
SO_4^{2-}	0.0188	0.0388	0.0510	0.0680	0.236	0.421	SO_4^{2-}	3.12
PO_4^{3-}	0.162	0.228	0.203	0.154	0.0823	0.0411	PO_4^{3-}	0.275
Charge Balance (%)	89	95	98	89	97	89	Total (wt. %)	≥ 17.1

a. leakage of material, brought to equilibrium at ambient conditions (25 °C)
b. the soluble portion of the residual solids at 25 °C
c. the total weight percent was determined to be less than the total solids content likely due to insoluble $Al(OH)_3$ not accounted for by $Al(OH)_4^-$

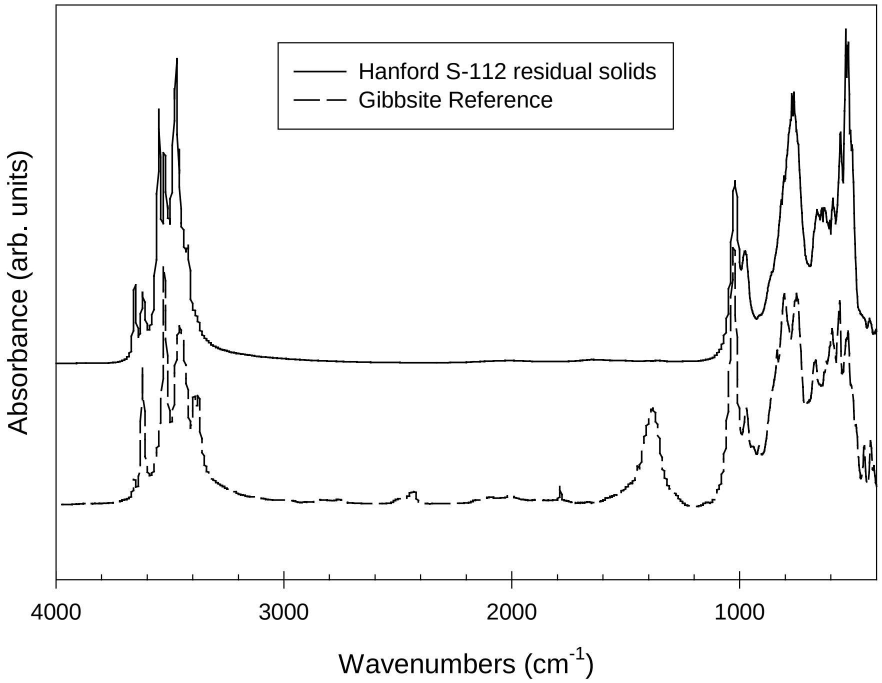


Figure 16: FTIR spectra for the washed residual solid material from the Hanford S-112 simulant 25 °C multiple-wash test (FTIR of gibbsite provided as a reference)

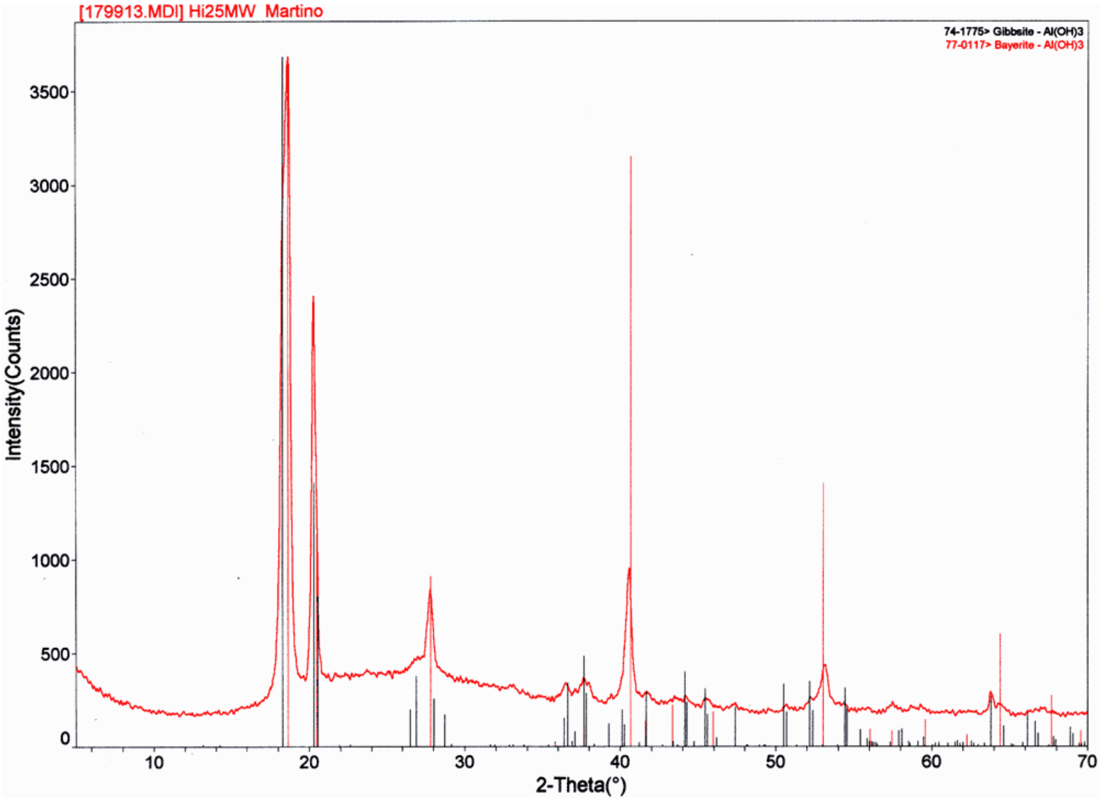


Figure 17: XRD of washed residual solid material from the Hanford S-112 simulant 25 °C multiple-wash test