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Abstract: A laboratory study was completed on the dissolution characteristics of Hanford waste from three single-shell waste tanks: BY-102, A-101, and S-102. Gross dissolution behavior is explained in terms of characteristics of individual salts in the waste. The percentage of the sodium inventory retrievable from the tanks by dissolving saltcake at reasonable dilution levels is estimated at 86% of the total sodium for tank BY-102, 90% for A-101, and 95% for S-102.

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ACRONYMS AND ABBREVIATIONS

A-101	single-shell tank 241-A-101
B-106	single-shell tank 241-B-106
BY-102	single-shell tank 241-BY-102
BY-106	single-shell tank 241-BY-106
BYSltCk	saltcake deposited during in-tank solidification evaporator campaigns
CSol	centrifuged solids
EDS	energy-dispersive x-ray spectrometer
ESP	Environmental Simulation Program
FY	fiscal year
GEA	gamma energy analysis
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
kgal	kilogallon (1,000 gallons)
kL	kiloliter (1,000 liters)
ML	megaliter (1,000,000 liters)
PLM	polarized light microscope (or microscopy)
RPP	River Protection Project
S-102	single-shell tank 241-S-102
SEM	scanning electron microscope
TCR	Tank Characterization Report
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
Vol	volume
Wt	weight
XRD	x-ray diffraction

1.0 INTRODUCTION AND EXECUTIVE SUMMARY

A laboratory study was completed on the dissolution characteristics of Hanford saltcake waste from three single-shell waste tanks: 241-BY-102, 241-A-101, and 241-S-102 (henceforth referred to as BY-102, A-101, and S-102, respectively). This work was funded by the Tanks Focus Area (EM-50) under Technical Task Plan Number RL0-8-WT-41, "PHMC Pretreatment – Saltcake Dissolution".

The tests performed on saltcake from tanks A-101 and S-102 were similar in scope to those completed in fiscal year (FY) 1998 on waste from tanks BY-102, BY-106, and B-106 (Herting 1998a). The BY-102 tests were expanded in FY 1999 to include column dissolution testing and solid phase characterization.

The River Protection Project (RPP) is tasked with retrieving waste from double-shell and single-shell tanks to provide feed for vitrification. The RPP organization needs chemical and physical data to evaluate technologies for retrieving the waste. No significant laboratory studies have been done to evaluate in-tank dissolution parameters for the various types of saltcake wastes that exist in single-shell tanks.

A computer modeling program known as the Environmental Simulation Program (ESP), produced by OLI Systems, Inc. of Morris Plains, New Jersey, is being used by the RPP organization to predict solubilities during dilution and retrieval of all tank waste types. Data from this task is provided to ESP users to support evaluation, refinement, and validation of the ESP model.

1.1 RESULTS SUMMARY

1.1.1 Dissolution Tests, Tanks A-101 and S-102

Weight percent dilution is defined in this report as 100 times the weight of diluent (water for these tests) divided by the weight of undiluted sample. A 50% dilution, for example, would be 50 g of H_2O added to 100 g of undiluted sample.

Some of the dissolution data for tanks A-101 and S-102 are plotted in Figures 4-1 and 4-2 as "Percent Undissolved" vs. weight percent dilution at two temperatures. The Percent Undissolved is defined as 100 times the weight of centrifuged solids after dissolution divided by the initial sample weight before diluent was added. This measurement provides a gross view of the extent of saltcake dissolution at various conditions, and provides a rough measure of the fraction of waste that could be retrieved from the tank by pumping the supernatant liquid.

Tank A-101 saltcake contained enough moisture to form a liquid layer when centrifuged at zero dilution; S-102 did not. For both tanks, most of the major salts were dissolved at 100% dilution, and only slightly more solids dissolved at 300% dilution.

Under almost all dilution conditions, dissolution was more extensive at 50 °C than at 25 °C, but not dramatically so.

Data are presented in Section 5 that explain the gross dissolution behavior in terms of solubilities of individual components in the waste. Evidence is provided there of the importance of double salts (sodium fluoride phosphate and others) in controlling the equilibrium concentrations of phosphate, fluoride, sulfate, and carbonate in the dissolved waste solutions. Identification of solid phases in equilibrium with the ions in solution is important for computer modeling of the thermodynamics of the system.

The percentage of sodium in each tank that could be retrieved at reasonable dilution levels by pumping liquid from the tank (i.e., the percentage of total sodium that is in the supernatant liquid) is estimated at >90% for tank A-101 and >95% for the saltcake layer in tank S-102.

Computer simulations of the saltcake **series** dissolution tests on tanks A-101 and S-102 were conducted by investigators at Mississippi State University, using ESP. Data from the **sequential** dissolution tests were used as input to the program. (See Sections 2.2 and 2.3 for definitions of sequential and series dissolution tests.) The major trends in the experimental data were also seen in the simulation results. Quantitative predictions were obtained for concentrations of all major anions at all levels of dilution for tank S-102. For tank A-101, ESP predictions for all major anions with the exceptions of fluoride and phosphate were in agreement with experimental data.

1.1.2 Tank BY-102 Solids Characterization Tests

One 50 g sample of BY-102 saltcake was divided into several fractions through a series of dissolution and evaporation steps. (See Section 2.4 for details.) Eight fractions of solid samples were analyzed by polarized light microscopy (PLM), scanning electron microscopy with an energy-dispersive x-ray spectrometer (SEM/EDS), and x-ray powder diffraction (XRD). Through this combination of techniques, the following solid phases were identified: $NaNO_3$, $Na_2CO_3 \cdot H_2O$, $Na_7F(PO_4)_2 \cdot 19H_2O$, Na_3FSO_4, $Al(OH)_3$, and $Na_2C_2O_4$. Some other phases, still unidentified, were also present.

1.1.3 Tank BY-102 Column/Stepwise Dissolution Tests

In-tank dissolution and subsequent retrieval of saltcake is envisioned, in one scenario, to occur by sprinkling of inhibited water (0.01 M NaOH / 0.01 M $NaNO_2$) over the saltcake, allowing the water to course through the salt, and retrieving the salt-saturated solution from the tank bottom. Laboratory tests were planned to model the dissolution of BY-102 saltcake by slow addition of inhibited water to duplicate columns

of saltcake, collection of the solution emerging from the column bottoms, and chemical/radiochemical analyses of the solutions to determine the solution compositions and saltcake dissolution rates. Unfortunately, the planned column BY-102 saltcake dissolution tests could not be performed because both test columns plugged. Efforts to loosen the plugs likewise were not successful.

Rather than abandon this study, an alternative experimental approach was designed and implemented. In the alternative approach, samples of BY-102 saltcake were contacted with multiple aliquots of inhibited water. In each contact, the inhibited water and saltcake were thoroughly agitated, the solid and solution phases separated by centrifugation, and the solutions analyzed. This dissolution approach (called Stepwise Dissolution) therefore simulated, in a stepwise manner, the continuous dissolution to be achieved during saltcake retrieval.

Eight dissolution steps were performed for duplicate BY-102 saltcake aliquots. The duplicate test data showed excellent experimental agreement. The saltcake in the initial dissolution step was below saturation (i.e., the component fully dissolved) for sodium nitrite, sodium chloride, and sodium hydroxide. The initial dissolution contacts evidently were at saturation in sodium carbonate, sodium fluoride sulfate, sodium fluoride phosphate, and sodium oxalate as shown by dissolution curves and by fluoride:sulfate and fluoride:phosphate mole ratios for the double salts. Sodium nitrate also may have been at saturation in the initial contact. Dissolution of the sodium salts proceeded in the order $NO_2^- \sim Cl^- > NO_3^- \sim OH^- > CO_3^{2-} > SO_4^{2-} > F^- > C_2O_4^{2-} > PO_4^{3-}$, with fractional dissolution of the saltcake solid phases occurring to some degree from sodium carbonate (CO_3^{2-}) onward. Within analytical capabilities, all these salts were fully dissolved by the final contact.

In contrast, Na, Al, Cr, Si, and ^{137}Cs had appreciable soluble and insoluble fractions, and Ca, Fe, Mn, Ni, and U were largely insoluble. In all, about 8% of the BY-102 saltcake remained undissolved after the eight stepwise dissolution contacts. By the eighth contact, significant peptization occurred, manifest by solid suspensions which resisted settling even after two hours of centrifugation. Because of this, a planned ninth contact was not attempted.

The presence of partially soluble constituents is evidence of the constituent's existence in both a solution and one or more solid phases or in two or more solid phases in the saltcake. Clearly, sodium is party to many soluble salt phases (sodium nitrate, sodium carbonate, sodium fluoride sulfate, sodium fluoride phosphate, sodium oxalate). However, about 1.6% of the sodium is not soluble. This insoluble sodium, and the presence of aluminum, silicon, and ^{137}Cs in the solid phase residue, indicates the presence of cancrinite, a sodium aluminosilicate. Some aluminum also is present in the solid phase as gibbsite, $Al(OH)_3$. Gibbsite was positively identified and cancrinite tentatively identified in separate XRD analyses. Cancrinite and gibbsite each comprise about 44% by weight of the insoluble residue. Soluble aluminum evidently is from sodium aluminate [$NaAl(OH)_4$]. Soluble chromium apparently is present as Na_2CrO_4 as shown by the bright yellow solution color, which diminishes with succeeding stepwise

dissolution. The chromium remaining in the solid phase likely is a chromium(III) (hydr)oxide but was not specifically identified. Solid phases containing Ca, Fe, Mn, Ni, and U also were not identified, but apatite [$Ca_5(PO_4)_3OH$], FeOOH and mixed transition metal oxyhydroxides, and sodium diuranate ($Na_2U_2O_7$) are likely. Confirmation of the identities of the solid phases requires additional study by techniques such as XRD, SEM/EDS, and PLM.

1.1.4 Feed Stability Tests

Various solutions derived from saltcake dissolution or tank waste supernatants were blended to determine if salts were stable to precipitation. Six different 1:1 mixtures from each of two tanks were prepared from solutions from five tanks. Solid phases were examined by polarized light microscopy.

In each case, salt precipitation was observed and all tests produced the sodium fluoride phosphate double salt, $Na_7F(PO_4)_2 \cdot 19H_2O$. Other phases observed included $NaNO_3$ and some unknown crystalline compounds.

1.2 COMPOSITION OF TANK WASTES

1.2.1 Tank BY-102

Tank BY-102 is predicted by historical model (Agnew 1997) to contain 29 kgal (109 kL) of sludge and 312 kgal (1.2 ML) of saltcake, the saltcake having been deposited during the in-tank solidification campaign of 1965-74. The saltcake waste type is identified by Agnew as type "BYSltCk". The current actual total waste volume (Sasaki 1997) in the tank is 277 kgal (1.05 kL).

One eight-segment core sample (core 157) was taken from the tank in June 1996. The first seven segments, plus a duplicate segment 5 (designated segment 5A) contained waste described as saltcake. Segment 1 was a partial segment. The bottom segment was approximately one-third full with liquid, and the remainder of the sampler was empty. Thus, none of the sludge layer was recovered.

Portions of segments 2 through 7 and 5A were used to make the composite sample for this study. This is the same composite sample used for the FY 1998 tests. The chemical compositions of the core sample and composite sample are shown in Table 8-1. The major components of the sample used for this study include (approximate weight percent): Na^+ (28%), CO_3^{2-} (21%), NO_3^- (11%), $Al(OH)_4^-$ (6%), SO_4^{2-} (5%), PO_4^{3-} (3%), $C_2O_4^{2-}$ (2%), H_2O (26.5%).

1.2.2 Tank A-101

Tank A-101 currently contains a small amount (3 kgal/11 kL) of sludge and 950 kgal (3.6 ML) of waste classified as saltcake (Field 1997). The saltcake is classified by the historical model (Agnew, 1997) as type SMMA1.

Two 19-segment core samples (cores 154 and 156) were taken from the tank in July, 1996. In both cores, segments 1-9 contained "moist salt" with no drainable liquid, and segments 11-19 contained mainly drainable liquid with some white solids, which presumably formed upon cooling from tank temperature to laboratory temperature. Segment 10 was mainly solid in core 154 and mainly liquid in core 156. Thus, the "saltcake" is made up of two distinct layers nearly equal in volume. The top (non-convective) layer contains a mixture of solid salts, interstitial liquid, and gas bubbles. The bottom (convective) layer is mainly liquid. This is Hanford's only "upside down" tank – liquid on the bottom, solids on top.

The composite sample for the current study was made by combining fractions of material from segments 2-9 of cores 154 and 156. The chemical compositions of the core sample solid segments (Field 1997) and the current composite sample are shown in Table 8-2. The major components of the sample used for this study include (approximate weight percent): Na^+ (21%), NO_3^- (13%), CO_3^{2-} (9%), $Al(OH)_4^-$ (8%), NO_2^- (7%), SO_4^{2-} (2%), $C_2O_4^{2-}$ (1%), H_2O (31%). The waste is clearly a mixture of several sodium salts, not dominated by any one salt.

1.2.3 Tank S-102

Tank S-102 currently contains a small amount (4 kgal/15 kL) of sludge and 545 kgal (2.1 ML) of waste classified as saltcake (Anantatmula 1999). Based on the historical model (Agnew 1997), the saltcake is made up of 204 kgal (780 kL) of saltcake type SMMS1 and 341 kgal (1.3 ML) of saltcake type SMMS2, both of which are products of the 242-S Evaporator operations.

Two core samples (cores 125 and 130), eleven segments each, were taken from the tank in January – March 1996. A third core (core 232) was taken in March – April 1998, mainly for retained gas sample analysis. In both of the 1996 cores, segment 1 was empty, segments 2-8 appeared to contain mainly saltcake (light gray with grainy texture), and segments 9-11 contained mainly sludge (black with pudding-like texture). Portions of segments 3, 4, and 6 were used to make the composite sample for this study.

The chemical compositions of the core sample and composite sample are shown in Table 8-3. Based on this comparison, the composite sample contained less liquid than the core samples, and thus had lower concentrations of most of the analytes but a higher concentration of sodium nitrate than the core samples. The major components of the composite sample used in this study include (approximate weight percent): NO_3^- (54%),

Na^+ (23%), CO_3^{2-} (3%), NO_2^- (2%), $Al(OH)_4^-$ (2%), H_2O (5 to 11%). The sample was obviously dominated by sodium nitrate.

Note that the composite sample represents only the saltcake layer in the tank. The apparent sludge layer is much larger than predicted by the historical model. The value given in the Results Summary (Section 1.1.1) for the percentage of sodium that could be retrieved by dilution applies only to the saltcake layer.

2.0 DESCRIPTION OF LABORATORY STUDIES

Composite samples of tank waste were prepared in a hotcell. Smaller samples were handled in fume hoods. The procedures, data, and observations are recorded in controlled laboratory notebook HNF-N-70-2. The procedures are described in this section, and the raw data are shown in the following section (3.0).

All dissolution tests were done on composite samples made by combining representative core segment samples from each tank. Two types of dissolution tests were done on saltcake from tanks A-101 and S-102. The **sequential dissolution tests** were done to establish an overall saltcake waste composition for each tank, as well as to define basic dissolution behavior. The **series dissolution tests** were done to establish dissolution characteristics of individual salts as a function of the amount of diluent added. These tests are described in detail in sections 2.2 and 2.3.

Solids characterization tests were done on saltcake from tank BY-102 using a combination of methods. **Column dissolution tests** were also done on BY-102 saltcake to model the in-situ retrieval process, though the test method had to be modified from the original plan. The revised tests are referred to as **stepwise dissolution tests**. The BY-102 tests are described in detail in sections 2.4 and 2.5.

Feed stability tests were done to evaluate whether solids might form if various retrieved liquid waste streams were mixed together, say in a staging tank. These tests are described in section 2.6.

2.1 PREPARATION OF COMPOSITE SAMPLES

Composite samples were made by combining archived fractions of individual core segment samples into a single composite jar for each tank. The entire contents of each archive jar were transferred to the composite jar. The waste in the completed composite jar was mixed thoroughly before transferring an aliquot from the hotcell to the fume hood. Weights of individual core segment samples used for each composite sample are shown in Table 2-1. Aliquots of each composite sample were analyzed for percent water by oven-drying at 120 °C and by thermogravimetric analysis (TGA).

Comparisons between analytical data for the composite samples and the tank core samples as reported in the Tank Characterization Report (TCR) for each tank are discussed in Section 8.

Table 2-1. Segment Samples Used to Create Core Composite Samples

Tank	Core	Segment[a]	Jar #	Weight, g
BY-102	157	2	10668	80.93
	157	3	10669	57.18
	157	4	10845	62.64
	157	5	10961	58.85
	157	5A	10846	35.17
	157	6	10670	81.99
	157	6	10671	34.14
	157	7	10780	33.05
	157	7	10781	42.78
	157	7	10782	12.96
	157	7	10847	62.06
		Composite	Total Wt =	561.75
A-101	154	2 U	11137	40.20
	156	3 U	11129	41.97
	154	4 U	11247	40.93
	156	5 U	11134	41.95
	156	6 U	10884	37.29
	154	7 U	10836	37.16
	156	8 U	11260	37.17
	154	9 L	11250	31.93
		Composite	Total Wt =	308.60
S-102	130	3 U	9202	72.03
	130	4 U	9203	79.14
	130	6 BU	9198	66.31
		Composite	Total Wt =	217.48

[a] Segment 1 is at top of waste; U = upper half of segment; L = lower half of segment; A, B = alternate (backup) segment.

2.2 SEQUENTIAL DISSOLUTION TESTS

The following tests were performed on composite samples from tanks A-101 and S-102. Results for BY-102 were reported previously (Herting 1998a).

Approximately 30 g of tank composite sample were transferred into each of two 50 mL centrifuge cones, and an equal weight of water was added. The cones were mixed with a vortex mixer, then placed on a rocker and tumbled end-over-end for at least 24 hours at ambient temperature (approximately 23 °C). The cones were then centrifuged for one hour at roughly 400 G.

The supernatant liquids from both cones were combined into a sample bottle. The liquid was analyzed by inductively coupled plasma spectroscopy (ICP), ion chromatography (IC), total inorganic carbon (TIC), total organic carbon (TOC), free hydroxide (OH^-), density, percent water by oven drying at 120 °C, and radionuclides by gamma energy analysis (GEA).

The weight and volume of centrifuged solids in each cone were recorded. Then 30 g of water were added to each cone. The cones were mixed again with a vortex mixer, then tumbled end-over-end for at least 24 hours at ambient temperature. The cones were centrifuged again, and the supernatant liquids combined as before in a new sample bottle. The second wash solution was analyzed for the same components as the first wash solution.

The volume and weight of undissolved centrifuged solids were recorded. Then the solids were transferred from the cones into a sample vial, combining the solids from both cones into a single sample vial. The solids were analyzed for TIC, TOC, and $\%H_2O$ by TGA. The solids were also subjected to acid digestion, and the resulting solution was analyzed for metals by ICP.

The analytical results from the sequential dissolution tests were used to determine the overall composition of the composite samples. This overall composition was used as input to the ESP modeling done at Mississippi State University.

2.3 SERIES DISSOLUTION TESTS

The following tests were performed on composite samples from tanks A-101 and S-102. Results for BY-102 were reported previously (Herting 1998a).

Four to six grams of composite sample were placed into each of six 15 mL centrifuge cones. An amount of water was added to each cone representing 0% to 300% by weight of the composite sample in the cone. Each cone was mixed with a vortex mixer, then tumbled end-over-end for at least 24 hours at ambient temperature. The cones were centrifuged for 30 minutes at roughly 400 G. The total volume and centrifuged solids volume in each cone were recorded. The liquid from each cone was decanted into a sample vial to be analyzed for density, TIC/TOC, IC, and ICP. The cones were re-weighed to determine the weight of undissolved centrifuged solids.

The series dissolution test just described was repeated, except that the 24-hour tumbling was done in an oven maintained at 50 °C, and the centrifuge was heated to approximately the same temperature. The decanted supernatant liquid samples were held at ambient temperature for 24 hours to watch for signs of precipitation that might be caused by cooling. If solids formed, the samples were diluted 1:1 by weight with water to re-dissolve the crystals before the samples were analyzed. This dilution was required for the A-101 sample at 0% dilution and the S-102 samples at 51% and 77% dilution.

2.4 SOLIDS CHARACTERIZATION TESTS

A "roadmap" of the BY-102 sample breakdown for the solids characterization test is shown in Figure 2-1. Details of the procedure are as follows.

In the 1E-1 hotcell, approximately one gram of the BY-102 composite sample was transferred to a sample vial labeled "**BY-102 Original Solids**" to be analyzed by PLM, SEM/EDS, and XRD. A much larger aliquot of the composite sample (56.0 g) was transferred to a jar with a magnetic stirbar.

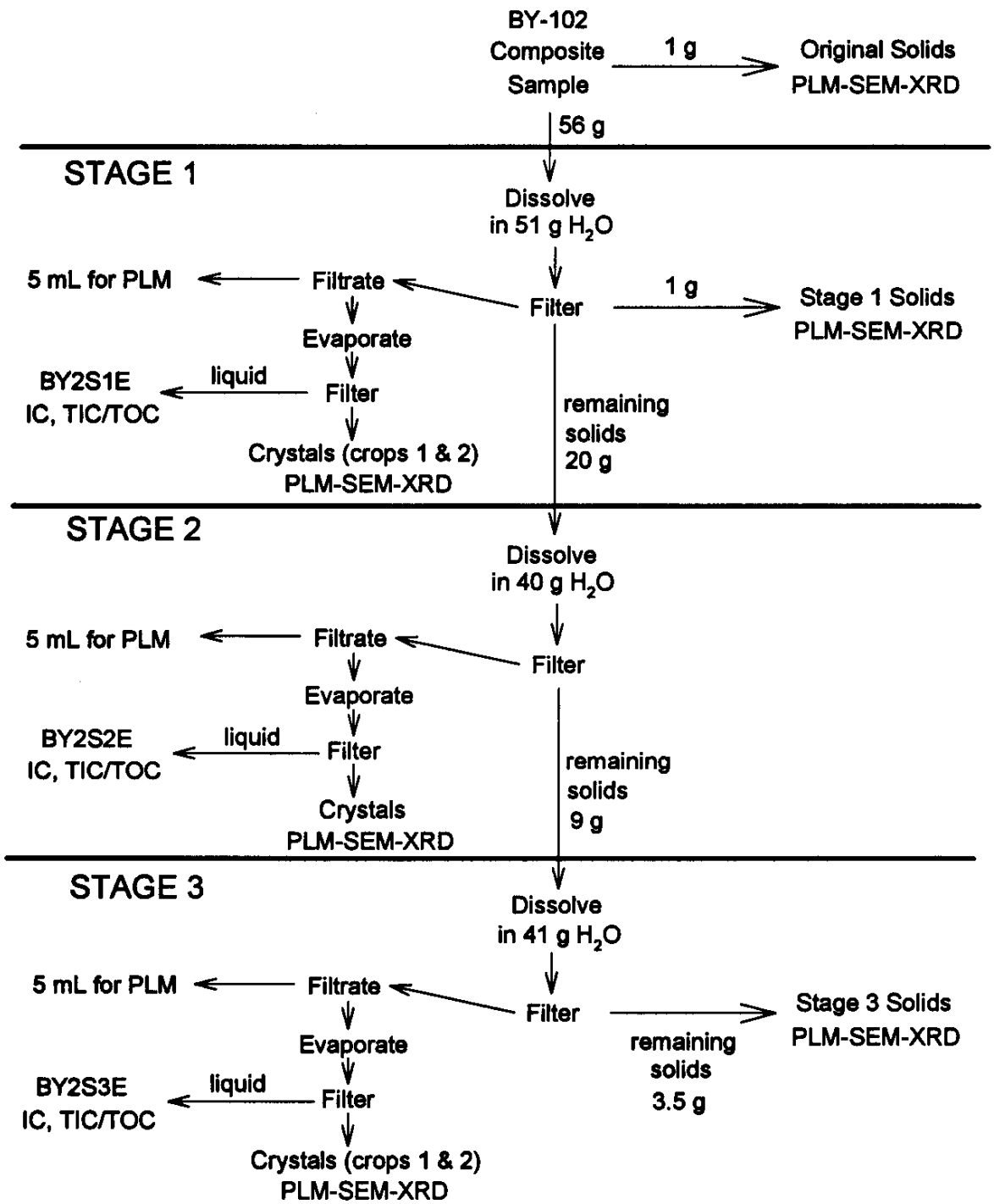
2.4.1 Stage 1

Water (51.0 g) was added to the jar containing the BY-102 composite sample. The slurry was stirred for two hours at 24 °C, then transferred from the hotcell to a fume hood. The diluted, mixed sample was chocolate brown, and resembled thin mud.

The sample was vacuum filtered. The dark brown filtered solids (19.9 g) were transferred to a 50 mL beaker for the Stage 2 dissolution. A small sample (0.2 g) of the filtered solids was transferred from the 50 mL beaker to a sample vial labeled "**Stage 1 Solids**" to be analyzed by PLM, SEM/EDS, and XRD. The bright yellow filtrate (liquid) was split into two fractions: 5 mL into a vial labeled "**BY-102 Stage 2 Filtrate**" and the remainder (~50 mL) into a 50 mL beaker for evaporation. The 5 mL sample was used as a mounting fluid for PLM analysis of some of the solid samples.

The filtrate in the 50 mL beaker was evaporated while stirring at ambient or slightly elevated temperature. At ~30 mL remaining volume, crystals were observed to be present in the solution. The crystals were examined by PLM, and then the slurry was filtered to collect the crystals, which were transferred to a sample vial labeled "**BY-102 Stage 1 Crop 1 Crystals**" for analysis by SEM/EDS and XRD. The filtrate was returned to the 50 mL beaker for further evaporation. At ~18 mL remaining volume, the solution contained new crystals, which were collected by filtration and transferred to a sample vial labeled "**BY-102 Stage 1 Crop 2 Crystals**" for analysis by PLM, SEM/EDS, and XRD. The filtrate was transferred to a sample vial labeled "**BY2S1E**" (Labcore #S99R000013) to be analyzed for IC and TIC/TOC. (Labcore is the laboratory information and management system used at the 222-S Laboratory.)

Figure 2-1. BY-102 Test Procedure Flowchart



2.4.2 Stage 2

Water (40 mL) was added to the 50 mL beaker containing 19.7 g of Stage 1 undissolved solids. The slurry was stirred for 2 hours at ambient temperature, then filtered. The solids (9.0 g) were transferred to a 50 mL beaker for dissolution in Stage 3. No aliquot was taken of the solids for analysis because the radiation dose rate was rather high. The liquid (50 mL) was transferred to a 50 mL beaker for evaporation. At ~15 mL remaining volume the filtrate had formed a fairly thick slurry of crystals. An aliquot of the slurry (~1 mL) was transferred to a sample vial labeled "**BY-102 Stage 2 Crystals**" for analysis by PLM, SEM/EDS, and XRD. The remainder of the slurry was filtered, and the filtrate was transferred to a sample vial labeled "BY2S2E" (Labcore #S99R000014) to be analyzed for IC and TIC/TOC.

2.4.3 Stage 3

Water (41 mL) was added to the 50 mL beaker containing 9.0 g of Stage 2 undissolved solids. The slurry was stirred for 2 hours at ambient temperature, then filtered. The solids (3.5 g) were transferred to a sample vial labeled "**BY-102 Stage 3 Solids**" and a small amount of the filtrate was added as a PLM slide mounting fluid. These solids were not quite as high in dose rate as the Stage 2 solids because they retained slightly more liquid, which provided some shielding from the radiation. The remaining pale yellow filtrate (41 mL) was transferred to a 50 mL beaker for evaporation. At ~23 mL remaining volume, crystals were observed to be present in the solution. The crystals were examined by PLM, and then the slurry was filtered to collect the crystals, which were transferred to a sample vial labeled "**BY-102 Stage 3 Crop 1 Crystals**" for analysis by SEM/EDS and XRD. The filtrate was returned to the 50 mL beaker for further evaporation. At ~5 mL remaining volume, the slurry had become a rather thick paste, a portion of which was transferred to a sample vial labeled "**BY-102 Stage 3 Crop 2 Crystals**" for PLM, SEM/EDS, and XRD. The remainder of the slurry was filtered, and the filtrate was transferred to a sample vial labeled "**BY2S3E**" (Labcore #S99R000015) for IC and TIC/TOC analyses.

2.5 COLUMN AND STEPWISE DISSOLUTION TESTS

One technique that has been proposed to retrieve saltcake from the Hanford waste tanks is to sprinkle water on the saltcake surface. The water then will percolate through the saltcake and the resulting salt-laden solution will be retrieved from the tank bottom with a recirculating saltwell jet pump. The goal of the present testing is to emulate the in-tank dissolution process using a composite saltcake sample from tank BY-102.

The in-tank saltcake dissolution process initially was modeled using a small column test bed, and a simulated saltcake was used to develop the test procedure. The simulated saltcake, prepared by evaporation of a clear solution, contained the usual major

sodium salts (nitrate, nitrite, carbonate, hydroxide, aluminate). The primary solid phases that crystallized were sodium carbonate and sodium nitrate.

The test column was a 50 mL graduated cylinder (~2-cm diameter) modified by adding a sidearm port at the bottom of the cylinder and a wire mesh screen at the bottom to prevent solids from draining out the sidearm. Simulated saltcake was added to the cylinder to a depth of approximately 5 cm. Inhibited water (0.01 M NaOH and 0.01 M $NaNO_2$) was added dropwise to the top of the salt bed by peristaltic pump at a rate of approximately 0.15 mL/min (roughly one drop every 20 seconds). The liquid was allowed to drain by gravity flow through the salt bed and out the sidearm at the bottom of the cylinder. Samples of the effluent could be collected periodically for analysis but no samples were taken during the simulant testing. With the actual BY-102 samples, the plan was to collect a series of nine effluent samples from each of two (duplicate) tests. The interval spacing of the sampling would be short during the first part of the run, where a large fraction of the salts would dissolve, and would increase near the end of the run, where little salt would be dissolving.

Several runs with simulated saltcake were performed to test the apparatus and improve the design. Video records of selected runs were shown at the annual Saltcake Dissolution Workshop held in Knoxville, Tennessee, on May 18-19, 1999. The apparatus worked well with the simulated saltcake, though occasional plugging of the drain line occurred followed by rapid draining once the plugs cleared.

With the actual BY-102 saltcake samples, the desired continuous slow percolation of solution through the saltcake did not occur and both columns plugged. In the first three hours of the test, no liquid drained out of either sidearm by the force imposed by the hydrostatic head of inhibited water that ultimately reached a depth of about 10 cm. Subsequent thorough mechanical stirring of the test bed with a metal rod or air bubbling through the sidearm and upward through the salt bed (in an attempt to loosen the packed saltcake) failed to increase flow. Application of a vacuum to the sidearm after complete mixing of the test bed produced less than 1 mL of opaque sludge through the exit screen of one test apparatus and nothing through the second. After two days, less than 1 mL of additional bright yellow clear liquid was observed. No noticeable increase in the throughput volume was found several days later.

Rather than abandon the test entirely, the procedure was changed. Instead of a continuous slow addition of inhibited water to the saltcake with continuous removal of the saturated stream, a series of stepwise batch dissolutions was conducted. The diluent volumes were smaller for the initial contacts where greater salt dissolution was expected and larger in the final contacts to dissolve the less soluble salts such as $Na_7F(PO_4)_2 \cdot 19H_2O$ and $Na_2C_2O_4$, whose solubilities are more susceptible to ionic strength. Thus the process was like the Sequential Dissolution tests, but with more contacts and shorter contact times.

In duplicate tests, 30-gram aliquots of BY-102 composite sample were placed into each of two tare-weighed 50-mL graduated centrifuge cones (labeled A and B). The

cones plus saltcake were weighed, portions of inhibited water were added to each cone, the cones plus contents re-weighed, and the cones with contents vortex-mixed or agitated manually for 5 minutes. The cones then were centrifuged for 30 minutes. Total volumes and centrifuged solids volumes were recorded, and the liquids were decanted into sample vials for analysis. The cones with residual solids were weighed to determine the weights of centrifuged solids and the quantities of solution decanted. Then fresh portions of inhibited water were added and the cycle of mixing/centrifuging/decanting was repeated.

A series of nine contacts was planned, with nominal inhibited water contact volumes of, in order, 10, 10, 10, 10, 20, 20, 40, 40, and 40 mL. The 30-g saltcake weight, 200-mL total volume, number of samples, and emphasis on sampling early in the overall dissolution matched that planned for the column test. On the eighth contact, however, peptization of the undissolved solids occurred with poor solids settling observed even with 2-hours' centrifugation. Because of the peptization, the ninth contact was not attempted.

The liquid samples were analyzed by ICP, IC, TIC/TOC, OH^-, $\%H_2O$ by oven drying at 120°C, GEA, and density. Residual solids from one of the tests were measured for $\%H_2O$ by TGA. Sample sizes were insufficient to analyze the water concentration in the second residual solid nor analyze either solid for TIC/TOC. Portions of the solids were analyzed by ICP and GEA following fusion digest. Percent water of the original BY-102 composite saltcake was also determined so that quantities of analytes present in the two ~30-gram starting aliquots could be estimated for material balance purposes.

2.6 FEED STABILITY TESTS

The objective of this test series was to determine if salt precipitation occurs by mixing clear tank waste solutions (most of which were generated by dissolution of salt cake) with each other. Five tank waste solutions were used; their nominal initial concentrations are presented in Table 2-2.

Selected pairs of the solutions, without accompanying solids, were added to 15 mL centrifuge cones in approximately equal volume of 5 mL each and the solutions mixed. The mixtures were allowed to stand in the hot cell at ambient temperature (~23°C), and visual observations made and noted over the next several days. After 5 days of standing, the cones with contents were centrifuged and the centrifuged solids volumes recorded. The solids with a few milliliters of supernatant solution were removed from the hot cell for examination by PLM. The physical observations of the solution blends are noted in Table 2-3.

The sodium fluoride phosphate double salt, $Na_7F(PO_4)_2 \cdot 19H_2O$, was found in each test, though its crystal habit (shape), quantity, and fraction of total solids varied from test to test. The only other crystal phase identified by PLM was sodium nitrate, $NaNO_3$, and that was for the mixture of the solutions having, respectively, the highest sodium (AN-104) and nitrate (BY-106-1) concentrations. A third unidentified phase

consisting of anisotropic, low-birefringence crystals was found in the blend of the BY-102-2 and BY-106-1 solutions and the BY-102-2 and AN-104 blend.

Table 2-2. Solution Compositions (in mg/L) for Feed Stability Tests

Component	AN-104	BY-102-1[a]	BY-102-2	BY-106-1[a]	C-104
	4AN-0[b]	S98R000204	S98R000206	S98R000024	S99T001099
Al	37200	1280	8710	10300	184
Na	244000	156000	70000	157000	23700
F^-	494	2690	7940	2090	11700
NO_2^-	107000	14800	2870	18200	5650
NO_3^-	176000	92300	12300	293000	3350
PO_4^{3-}	3390	1680	3810	1500	1250
SO_4^{2-}	3800	10500	36000	1710	762
TIC	2390	16200	5890	9590	1320
OH^-	66000	9020	1400	7660	896
Appearance	Heavy colorless solution; fine dark settled solids	Large crystals ~2-3 mm thick (~10% settled vol) on bottom	Colorless, clear, low viscosity	Fine white easy to suspend crystals (~5% settled vol) on bottom	Amber solution

[a] Some solids crystallized from the BY-102-1 and BY-106-1 solutions upon standing in the hot cell for ~1 year. Because the solutions were not reanalyzed, the effects of crystallization on the stated compositions are indeterminate.

[b] Analysis taken from Table 3-9 of Herting (1998b)

Table 2-3. Physical Observations of Solution Blends

Mixture	Observations		
	10 minutes	18 hours	5 days CSol volume; PLM
BY-102-2 BY-102-1	No reaction	No reaction; no crystals	< 0.1 mL, mostly white with some dark brown solids; only $Na_7F(PO_4)_2 \cdot 19H_2O$ found, but in an unusual habit
BY-102-2 BY-106-1	No reaction	~0.1 mm square crystals on wall	0.3 mL; $Na_7F(PO_4)_2 \cdot 19H_2O$ found, but in an unusual habit, with unknown anisotropic, low birefringence "rock candy" agglomerates
AN-104 BY-102-1	No reaction	Smaller crystals than above, some settled	< 0.1 mL; mostly $Na_7F(PO_4)_2 \cdot 19H_2O$ with traces of anisotropic crystals
BY-102-2 AN-104-sup	Froth/foam on mixing	~0.1 mL white crystals in bottom; some on wall	0.6 mL, some very large crystals (~0.2 mm); mostly "rock candy" agglomerates with a few $Na_7F(PO_4)_2 \cdot 19H_2O$
AN-104-sup BY-106-1	No reaction	Colorless crystals plated on one side	0.2 mL; mainly $NaNO_3$ with some $Na_7F(PO_4)_2 \cdot 19H_2O$ in the usual habit
AN-104-sup C-104-sup	Seems to have bubbles	Amber/orange clear solution and floating waxy lens	< 0.1 mL, mixed white and brown solids; almost exclusively $Na_7F(PO_4)_2 \cdot 19H_2O$ in an irregular but very consistent habit

3.0 RESULTS – RAW DATA

"Raw data" include values of net weight, volume, and chemical and physical analyses of the samples. Visual observations of the test materials are also presented in this section. The raw data provide a reference record of the tests. However, sample-to-sample comparisons of raw data generally should not be made because of variations in initial sample weights and volumes. Comparisons based on normalized data, accounting for initial volume and weight differences, are presented in later sections of the report.

3.1 TANK A-101

The aliquot of the composite sample taken for %H_2O analysis was labeled A101CMPAL1, and was assigned Labcore number S99R000037. Analytical results were 31.2% H_2O by TGA and 30.1% by oven-drying.

3.1.1 A-101 Sequential Dissolution Test

Two 50 mL centrifuge cones were labeled SEQA and SEQB. The procedure was described in Section 2.2. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-1. Sample analytical results are shown in Table 3-2.

3.1.2 A-101 Series Dissolution Test, Ambient Temperature

Six 15 mL centrifuge cones were labeled A through F. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-3. Sample analytical results are shown in Table 3-4.

3.1.3 A-101 Series Dissolution Test, 50 °C

Six 15 mL centrifuge cones were labeled G through L. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-5. The supernatant liquid from sample H (0% dilution) was diluted to dissolve crystals that formed when the samples cooled from 50 °C to ambient temperature. Sample analytical results for the liquid samples, including the dilution-corrected results for sample H, are shown in Table 3-6.

Table 3-1. Raw Data, Tank A-101 Sequential Dissolution Test.
(weights in grams, volumes in mL)

	SEQA	SEQB
Sample Wt	30.92	29.95
Wt H_2O Added (1st wash)	30.98	30.02
Total Vol	47	46
1st Water Wash Sample ID[a]	A101SEQAB1 / S99R000038	
CSol[b] Vol[c]	~4	~4
CSol Wt	4.39	4.31
Wt H_2O Added (2nd wash)	31.03	30.02
Total Vol	35	33
2nd Water Wash Sample ID	A101SEQAB2 / S99R000082	
CSol Vol[c]	~2	~2
CSol Wt	1.39	1.33
CSol Sample ID	A101SEQABS / S99R000039 and 040	

[a] decanted supernatant liquid; customer ID number / Labcore ID number
[b] CSol = centrifuged solids
[c] volumes below 5 mL are estimates only.

Table 3-2. Analytical Results, Tank A-101 Sequential Dissolution Test.

Analyte	1st Water Wash A101SEQAB1 S99R000038 (µg/mL)	2nd Water Wash A101SEQAB2 S99R000082 (µg/mL)	CSol A101SEQABS S99R000039-40 (µg/g)
Al	15900	1150	11400
Ca	< 40	5	2940
Cr	92	10	35300
Fe	< 20	< 2	3910
K	2230	173	251
Mn	< 4	< 1	610
Na	139000	16100	21900
Ni	< 8	2	893
P	948	69	665
Pb	< 40	< 4	707
S	5420	426	371
Si	99	11	2670
U	< 200	< 20	7670
F^-	467	37	na
Cl^-	2780	210	na
NO_2^-	50200	3980	na
NO_3^-	85400	6450	na
PO_4^{3-}	2800	< 133	na
SO_4^{2-}	16500	1270	na
$C_2O_4^{2-}$	< 541	12100	na
TIC	12100	1050	1620
TOC	2040	2470	4580
OH^-	14200	1090	na
^{137}Cs (µCi/mL)	133	11	na
Density (g/mL)	1.303	1.054	na
$\%H_2O$	66.7	94.9	78.44

[a] na = not analyzed

Table 3-3. Raw Data, Tank A-101 Series Dissolution Test, Ambient Temperature
(weights in grams, volumes in mL)

Wt% Dilution:	0	50	99	113	193	302
Cone ID:	A	B	C	D	E	F
Sample Wt	17.002	11.290	8.247	8.228	5.642	3.803
Wt H2O Added	0.000	5.641	8.198	9.262	10.916	11.502
Total Vol	10.0	12.0	12.5	13.5	13.7	13.3
CSol Vol	7.6	2.4	1.2	1.1	0.8	0.3
CSol Wt	14.335	4.660	1.919	1.838	1.125	0.559
Supernate ID	A101AMA	A101AMB	A101AMC	A101AMD	A101AME	A101AMF
S99R000...	041	042	043	044	045	046

Table 3-4. Analytical Results, Tank A-101 Series Dissolution Test, Ambient Temp.
(μg/mL except as noted)

Wt% Dilution:	0	50	99	113	193	302
Supernate ID	A101AMA	A101AMB	A101AMC	A101AMD	A101AME	A101AMF
S99R000...	041	042	043	044	045	046
Density (g/mL)	1.552	1.452	1.348	1.319	1.246	1.158
Al	i.s.[1]	23200	15200	14000	9020	6550
Ca	i.s.	< 40	< 40	< 40	< 20	< 20
Cr	i.s.	96	65	59	38	27
Fe	i.s.	< 20	< 20	< 20	< 10	< 10
K	i.s.	3270	2180	2070	1350	956
Mn	i.s.	< 4	< 4	< 4	< 2	< 2
Na	i.s.	186000	131000	126000	83000	58200
Ni	i.s.	< 8	< 8	< 8	< 4	< 4
P	i.s.	785	866	887	591	406
Pb	i.s.	< 40	< 40	< 40	< 20	< 20
S	i.s.	6590	5630	5310	3380	2360
Si	i.s.	165	119	112	68	54
U	i.s.	< 200	< 200	< 200	< 100	< 100
F^-	401	222	495	378	290	193
Cl^-	i.s.	4390	2590	1830	1550	1360
NO_2^-	i.s.	81500	50600	35900	29700	23500
NO_3^-	i.s.	122500	70500	53300	52450	35200
PO_4^{3-}	2280	2200	2480	2010	1230	1340
SO_4^{2-}	2620	22200	16700	11900	10100	8440
$C_2O_4^{2-}$	< 541	< 223	335	361	968	2860
TIC	1240	13300	11500	10900	7520	5250
TOC	4340	3280	1520	1390	1320	1420

[1] i.s. = insufficient sample to complete analysis

Table 3-5. Raw Data, Tank A-101 Series Dissolution Test, 50 °C
(weights in grams, volumes in mL)

Wt% Dilution:	0	52	97	152	203	299
Cone ID:	H	L	G	J	I	K
Sample Wt	10.109	5.311	6.209	4.486	3.736	3.285
Wt H2O Added	0.000	2.744	5.995	6.841	7.597	9.811
Total Vol	5.8	5.5	9.4	9.0	9.4	11.5
CSol Vol	3.9	1.2	0.5	0.4	0.3	0.2
CSol Wt	7.147	2.198	0.951	0.642	0.488	0.290
Supernate ID	A101L50H	A101L50L	A101L50G	A101L50J	A101L50I	A101L50K
S99R000...	049	053	048	051	050	052
Sup Sample Wt	2.849	dilution not required				
Wt H_2O Added	2.849					
Density Diluted	1.239					
Vol Diluted	4.60					
Vol Undiluted	1.75					
Density Undil	1.63					
Diln Factor (v/v)	2.63					

Table 3-6. Analytical Results, Tank A-101 Series Dissolution Test, 50 °C
(µg/mL except as noted)

Wt% Dilution:	0[a]	52	97	152	203	299
Supernate ID	A101L50H	A101L50L	A101L50G	A101L50J	A101L50I	A101L50K
S99R000...	049	053	048	051	050	052
Density (g/mL)	1.63	1.372	1.321	1.245	1.208	1.141
Al	50700	22300	15400	11400	8920	6630
Ca	< 105	< 40	< 40	< 40	< 20	< 20
Cr	481	222	120	76	55	37
Fe	< 53	< 20	< 20	< 20	< 10	< 10
K	7100	3210	2200	1710	1290	937
Mn	< 11	< 4	< 4	< 4	< 2	< 2
Na	276000	169000	134000	103000	79600	60500
Ni	< 21	< 8	< 8	< 8	< 4	< 4
P	2760	1250	1000	698	563	419
Pb	< 105	< 40	< 40	< 40	< 20	< 20
S	657	5040	5600	4270	3200	2440
Si	376	151	106	81	60	48
U	< 526	< 200	< 200	< 200	< 100	< 100
F^-	597	319	493	356	292	200
Cl^-	9640	4540	2940	2060	1750	1200
NO_2^-	173000	82500	54500	37100	30900	21300
NO_3^-	256000	132000	84950	63900	50000	34200
PO_4^{3-}	8145	4600	2810	1900	1640	1180
SO_4^{2-}	1450	16500	18300	12900	10200	7540
$C_2O_4^{2-}$	1310	< 435	560	1510	2320	3740
TIC	2020	11900	12200	9090	7150	5280
TOC	4970	2280	1770	1520	1540	1700

[a] corrected for dilution of analytical sample to prevent precipitation on cooling

3.2 TANK S-102

One aliquot of the composite sample (S102CMPAL1 / Labcore ID S99R000055) was analyzed for %H_2O by oven-drying. The result was 5.0%. The sample was not analyzed by TGA. The oven-drying result is believed to be low. Based on mass balance measurements from the sample analyses, the %H_2O should be close to 11%.

3.2.1 S-102 Sequential Dissolution Test

Two 50 mL centrifuge cones were labeled SEQA and SEQB. The procedure was described in Section 2.2. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-7. Sample analytical results are shown in Table 3-8.

3.2.2 S-102 Series Dissolution Test, Ambient Temperature

Six 15 mL centrifuge cones were labeled S102AMA through S102AMF. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-9. Sample analytical results are shown in Table 3-10.

3.2.3 S-102 Series Dissolution Test, 50 °C

Six 15 mL centrifuge cones were labeled S102L50G through S102L50L. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-11. The liquid samples from cones S102L50L (51% dilution) and S102L50K (77% dilution) were diluted 1:1 with water to dissolve crystals that formed when the sample cooled from 50 °C to ambient temperature. Sample analytical results for the undiluted liquid sample (corrected for the 1:1 dilution) are shown in Table 3-12 with the results for the other four samples which were not diluted.

Table 3-7. Raw Data, Tank S-102 Sequential Dissolution Test.
(weights in grams, volumes in mL)

	SEQA	SEQB
Sample Wt	30.48	30.92
Wt H_2O Added (1st wash)	30.05	31.67
Total Vol	44	46
1st Water Wash Sample ID[a]	S102SEQAB1 / S99R000063	
CSol[b] Vol[c]	~4	~4
CSol Wt	2.83	2.45
Wt H_2O Added (2nd wash)	30.14	30.94
Total Vol	33	34
2nd Water Wash Sample ID	S102SEQAB2 / S99R000064	
CSol Vol[c]	~1	~1
CSol Wt	0.82	0.89
CSol Sample ID	S102SEQABS / S99R000065-66	

[a] decanted supernatant liquid; customer ID number / Labcore ID number
[b] CSol = centrifuged solids
[c] volumes below 5 mL are estimates only.

Table 3-8. Analytical Results, Tank S-102 Sequential Dissolution Test.

Analyte	1st Water Wash S102SEQAB1 S99R000063 (µg/mL)	2nd Water Wash S102SEQAB2 S99R000064 (µg/mL)	CSol S102SEQABS S99R000065-66 (µg/g)
Al	4350	237	23400
Ca	< 40	< 2	1440
Cr	547	30	16800
Fe	< 20	< 1	918
K	513	22	107
Mn	< 4	< 1	705
Na	164000	9930	14600
P	1320	55	480
S	904	55	66
Si	124	9	3090
F^-	< 122	< 5	na
Cl^-	1185	62	na
NO_2^-	14700	752	na
NO_3^-	387000	19200	na
PO_4^{3-}	3765	161	na
SO_4^{2-}	2285	145	na
$C_2O_4^{2-}$	< 1070	1595	na
TIC	4170	292	503
TOC	891	455	529
OH^-	3020	187	na
^{137}Cs (µCi/mL)	43.5	2.3	na
Density (g/mL)	1.393	1.010	na
$\%H_2O$	53.8	96.5	86.8

[a] na = not analyzed

Table 3-9. Raw Data, Tank S-102 Series Dissolution Test, Ambient Temperature
(weights in grams, volumes in mL)

Wt% Dilution:	51	101	147	200	251	297
Cone ID:	F	C	B	A	D	E
Sample Wt	6.727	4.959	5.444	5.575	4.152	2.542
Wt H2O Added	3.448	4.986	8.015	11.147	10.424	7.548
Total Vol	6.4	7.0	10.2	13.3	12.0	8.5
CSol Vol	2.0	0.2	0.2	0.2	0.2	0.1
CSol Wt	4.260	0.378	0.341	0.382	0.203	0.150
Supernate ID	S102AMF	S102AMC	S102AMB	S102AMA	S102AMD	S102AME
S99R000...	061	058	057	056	059	060

Table 3-10. Analytical Results, Tank S-102 Series Dissolution Test, Ambient Temp.
(μg/mL except as noted)

Wt% Dilution:	51	101	147	200	251	297
Supernate ID	S102AMF	S102AMC	S102AMB	S102AMA	102AMD	S102AME
S99R000...	061	058	057	056	059	060
Density (g/mL)	1.392	1.377	1.273	1.231	1.178	1.165
Al	7790	4110	3240	2670	1930	1880
Ca	< 40	< 40	< 40	< 40	< 40	< 40
Cr	956	526	386	320	225	237
Fe	< 20	< 20	< 20	< 20	< 20	< 20
K	959	514	500	307	279	289
Mn	< 4	< 4	< 4	< 4	< 4	< 4
Na	157000	163000	116000	99500	79000	65600
Ni	< 8	< 8	< 8	< 8	< 8	< 8
P	1540	1350	741	1010	566	508
Pb	< 40	< 40	< 40	< 40	< 40	< 40
S	1630	996	885	604	356	405
Si	229	123	101	85	58	62
U	< 200	< 200	< 200	< 200	< 200	< 200
F^-	< 50	< 62	< 62	< 62	< 62	< 62
Cl^-	1990	1170	1080	835	603	758
NO_2^-	27900	15000	12300	9460	7390	6870
NO_3^-	359000	411000	304000	237000	200000	173000
PO_4^{3-}	4320	4510	2750	3630	1890	1800
SO_4^{2-}	4360	3230	3040	1940	1180	1460
$C_2O_4^{2-}$	< 435	< 541	659	998	566	652
TIC	6710	3550	3510	2470	1640	1590
TOC	1260	479	746	751	470	471

Table 3-11. Raw Data, Tank S-102 Series Dissolution Test, 50 °C
(weights in grams, volumes in mL)

Wt% Dilution:	51	77	100	152	200	304
Cone ID:	L	K	I	J	H	G
Sample Wt	5.837	5.801	6.703	4.884	4.355	3.177
Wt H2O Added	2.952	4.444	6.728	7.446	8.722	9.658
Total Vol	5.5	7.1	9.7	9.5	10.5	10.9
CSol Vol	1.5	0.2	0.2	0.2	0.2	0.2
CSol Wt	2.452	0.380	0.403	0.184	0.157	0.161
Supernate ID	S102L50L	S102L50K	S102L50I	S102L50J	S102L50H	S102L50G
S99R000...	072	071	069	070	068	067
Sup Sample Wt	6.245	9.802	not diluted			
Wt H_2O Added	6.337	9.827				
Density Diluted	1.196	1.153				
Vol Diluted	10.52	17.02				
Vol Undiluted	4.00	6.90				
Density Undil	1.56	1.42				
Diln Factor (v/v)	2.63	2.47				

Table 3-12. Analytical Results, Tank S-102 Series Dissolution Test, 50 °C
(samples L and K are dilution-corrected; all results µg/mL except as noted)

Wt% Dilution:	51	77	100	152	200	304
Supernate ID	S102L50L	S102L50K	S102L50I	S102L50J	S102L50H	S102L50G
S99R000...	072	071	069	070	068	067
Density (g/mL)	1.561	1.421	1.381	1.285	1.232	1.154
Al	8420	5580	4250	3650	2220	1820
Ca	< 53	< 49	< 20			
Cr	913	612	495	387	265	226
Fe	< 26	< 25	< 10			
K	821	331	409	243	290	204
Mn	< 5	< 5	< 2			
Na	220000	203000	165000	121000	92100	68600
Ni	< 11	< 10	< 4			
P	2280	1520	1370	875	624	537
Pb	< 53	< 49	< 20			
S	926	772	684	649	423	547
Si	203	141	114	98	65	52
U	< 260	< 250	< 100			
F^-	< 66	< 62				< 50
Cl^-	2840	1660	1520	1150	736	547
NO_2^-	31700	20461	17630	12200	8900	5900
NO_3^-	402000	374000	431000	283000	260000	168000
PO_4^{3-}	7810	4370	4840	2710	2420	1790
SO_4^{2-}	3200	2500	2520	1940	1410	1640
$C_2O_4^{2-}$	< 586	< 550	756	1120	1030	894
TIC	7630	7080	3110	2970	1670	1750
TOC	744	1480	617	658	458	426

3.3 TANK BY-102

3.3.1 Batch Dissolution Tests

Sequential dissolution and series dissolution tests were performed on the BY-102 composite sample previously (Herting 1998a). See Table 8-1 for a summary of the composition data.

3.3.2 Solids Characterization

Data for weights of solids and volumes of solutions were included in the procedure narrative in Section 2.4. At the conclusion of each stage of evaporation, the concentrated liquid which was in equilibrium with the final crop of crystals was analyzed for IC and TIC/TOC. The results of these analyses are shown in Table 3-13.

Table 3-13. Analytical Results, Filtrate Samples, Tank BY-102
Solids Characterization Test (μg/mL)

Analyte	BY2S1E	BY2S2E	BY2S3E
	S99R000013	S99R000014	S99R000015
F^-	1060	4590	13100
Cl^-	2730	281	100
NO_2^-	44900	4520	467
NO_3^-	243000	24000	3290
PO_4^{3-}	< 620	3700	8750
SO_4^{2-}	1240	40000	19600
$C_2O_4^{2-}$	< 540	2580	4700
TIC	7960	11900	4120
TOC	2150	1370	1860

3.3.3 Stepwise Dissolution Tests

An aliquot of BY-102 composite sample, labeled 102-BY and assigned Labcore number S99R000168, was taken for %H_2O analysis. The sample was 21.5% H_2O compared with 26.5% reported for prior studies of this composite waste (Table 7-2 of Herting 1998a). Drying of the material evidently occurred during one-year's storage in

the hot cell. The concentrations of the non-water components of BY-102 saltcake reported by Herting (1998) were adjusted by the gravimetric factor

$$(100-21.5)/(100-26.5) = 1.068$$

to account for the loss of water. The adjusted concentrations then were used to compare with concentrations found in prior studies (see Table 8-1).

The stepwise dissolution test procedure conducted in centrifuge cones labeled A and B was described in Section 2.5. Weights, volumes, and sample identification numbers for the duplicate tests are shown in Table 3-14. Sample analytical results for the A and B series are presented in Tables 3-15 and 3-16, respectively.

Qualitatively, the solutions showed a gradation in properties with increase in contact number. However, within a given contact number, solutions from series A and series B had similar properties. Thus, the solution from the initial contact was bright yellow, almost oily in viscosity, and contained some fine dark suspended solids that did not settle even with overnight standing and one hour of centrifugation. The intensity of the yellow color, the apparent solution viscosity, and the prevalence of solids decreased continuously in subsequent contacts such that the solutions from the 7th contact appeared as colorless and free-flowing as water with no suspended solids. However, in the final (8th) contact, which marked the onset of peptization, sufficient solids were found suspended in the solution that the suspension displayed a pink-amber color. Radiological dose rates of the solutions also decreased with increase in contact number, but again the trend was reversed for the final contact that suffered peptization.

The centrifuged solids present with the dissolving solutions during the stepwise contacts decreased in volume with increasing contact number (see Table 3-14). Granular solids could be observed in the early contacts by slow sloshing of the suspension while the centrifuge tube was held horizontally. Upon centrifugation, layering of the solids occurred but the stratification decreased with contact number, finally becoming indistinguishable by the 5th contact. In the early contacts, a dark (brown-green?) layer was found at the bottom followed by a thin almost black layer and a top light gray layer. Some larger granules were still observed in the suspension in the 7th contact but the final residual solid after the 8th contact was dark brown, almost black, and smooth in consistency with no obvious granularity.

Table 3-14. Raw Data, Tank BY-102 Stepwise Dissolution Test.
(weights in grams, volumes in mL)

	Sample A: initial wt 30.942 g							
Contact # →	1	2	3	4	5	6	7	8
Wt Inh H2O Added	11.023	10.066	9.664	9.563	20.904	20.946	40.854	38.234
Total Vol	26.5	22.5	20.0	18.0	27.0	26.5	43.0	40.0
CSol[a] Vol	13.0	10.0	8.0	7.0	4.5	3.5	2.5	2.2
CSol Wt	23.828	18.296	14.511	11.400	7.587	4.215	2.873	2.612
Solution Vol	13.5	12.5	12.0	11.0	22.5	23.0	40.5	37.8
Solution Wt	18.137	15.598	13.449	12.674	24.717	24.318	42.196	38.495
Soln Customer ID[b]	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8
Labcore ID[c]	173	174	175	176	177	178	179	180
Residual Solids Customer ID[b]								A-SOL
Residual Solid Labcore ID: S99R000...								169/172
	Sample B: initial wt 30.404 g							
Contact # →	1	2	3	4	5	6	7	8
Wt Inh H2O Added	11.228	10.064	10.427	10.244	19.480	22.483	39.222	40.962
Total Vol	26.5	23.0	20.5	19.0	25.5	27.0	41.5	43.0
CSol[a] Vol	13.2	10.0	8.0	7.0	5.0	3.0	2.0	2.0
CSol Wt	24.772	18.097	14.197	10.625	6.595	3.215	2.542	2.325
Solution Vol	13.2	13.0	12.5	12.0	20.5	24.0	41.5	41.0
Solution Wt	16.860	16.739	14.327	13.816	23.510	25.863	39.895	41.179
Soln Customer ID[b]	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8
Labcore ID[c]	182	183	184	185	186	187	188	189
Residual Solids Customer ID[b]								B-SOL
Residual Solid Labcore ID: S99R000...								170/172

[a] CSol = centrifuged solids
[b] Customer IDs all begin with "BY2-"
[c] Labcore IDs all begin with "S99R000"

Table 3-15. Analytical Results, Tank BY-102 Stepwise Dissolution Test A.

Analyte	Concentrations								
	1st Contact, BY2-A-1 / -173	2nd Contact, BY2-A-2 / -174	3rd Contact, BY2-A-3 / -175	4th Contact, BY2-A-4 / -176	5th Contact, BY2-A-5 / -177	6th Contact, BY2-A-6 / -178	7th Contact, BY2-A-7 / -179	8th Contact, BY2-A-8 / -180	Residue, BY2-A-SOL / -169,-171
	(μg/mL)								(μg/g)
Al	10700	6300	2770	953	183	83.7	22.4	157	127000
Ca	<60	<60	<60	<60	<60	<10	<2	1.92	6860
Cr	1760	1050	458	162	33.6	7.82	1.23	5.30	13300
Fe	<30	<30	<30	<30	<30	<5	<1	4.35	12100
K	1700	1040	<300	<300	<300	<50	<10	<1	na[a]
Mn	<6	<6	<6	<6	<6	<1	<0.2	1.55	7550
Na	193000	164000	111000	78000	45700	25900	6070	867	50400
Ni	<12	<12	<12	<12	<12	<2	<0.4	0.53	1460[b]
P	467	636	868	1070	2130	6160	2010	87.5	<5320
S	2010	3220	8600	13200	11900	1290	55.1	11.4	<2660
Si	375	263	205	147	66.7	24.7	13.5	127	38500
U	<300	<300	<300	<300	<300	<50	<10	2.82	16500
F^-	1660	2600	6760	8940	8210	3620	728	29.6	na
Cl^-	1490	855	389	115	<36	<36	<7	<1	na
NO_2^-	22200	12600	5780	2200	654	435	453	463	na
NO_3^-	128000	84900	47300	16600	2210	386	57.6	77.5	na
PO_4^{3-}	1820	1960	4110	3450	5980	19200	6230	273	na
PO_4^{3-}(ICP)[c]	1430	1950	2660	3280	6530	18900	6160	268	<16300
SO_4^{2-}	6760	11600	30700	44100	34200	3790	164	30.6	na
SO_4^{2-}(ICP)[c]	6020	9650	25800	39600	35600	3860	165	34.2	<8000
$C_2O_4^{2-}$	646	939	3520	4530	6880	12300	950	80.6	na
TIC	20200	21400	17400	10700	2920	294	24.0	20.1	na
TOC	1085	664	776	1450	1930	2850	240	58.2	na
"Acetate"[d]	2230	1000	--	527	131	--	--	89.0	na
OH^-	10700	5830	2600	1120	889	512	170[d]	170[d]	na
^{137}Cs (μCi/mL)	46.9	28.1	12.4	5.02	1.22	1.29	0.27	1.01	216 μCi/g
%H_2O	61.0	66.4	75.8	81.5	89.2	93.4	98.4	99.7	na
Density (g/mL)	1.370	1.337	1.249	1.175	1.095	1.063	1.010	1.000	na

[a] na denotes not analyzed
[b] nickel concentration in residue derived from Ni/Fe ratio in 8th contact and Fe concentration in residue
[c] the PO_4^{3-} and SO_4^{2-} data in these rows were derived from ICP P and S data, respectively
[d] "Acetate" calculated as difference between TOC and carbon found in oxalate, adjusted to acetate speciation

Table 3-16. Analytical Results, Tank BY-102 Stepwise Dissolution Test B.

Analyte	Concentrations								
	1st Contact, BY2-B-1 / -182	2nd Contact, BY2-B-2 / -183	3rd Contact, BY2-B-3 / -184	4th Contact, BY2-B-4 / -185	5th Contact, BY2-B-5 / -186	6th Contact, BY2-B-6 / -187	7th Contact, BY2-B-7 / -188	8th Contact, BY2-B-8 / -189	Residue, BY2-B-SOL / -170,-172
	(µg/mL)								(µg/g)[a]
Al	12200	4480	1880	689	139	67.6	37.3	157	127000
Ca	<60	68.90	<20	<20	<20	<10	<1	2.30	9110
Cr	2020	745	316	121	24.0	6.02	0.95	7.73	11000
Fe	<30	<30	<10	<10	<10	<5	0.57	5.82	8160
K	2030	670	272	<100	<100	<50	<5	<1	na
Mn	<6	<6	<2	<2	<2	<1	<0.10	2.36	6920
Na	193000	120000	96100	82300	43600	24900	2890	721	48300
Ni	<12	<12	<4	<4	<4	<2	<0.2	0.80	1120[b]
P	505	962	936	1120	2100	6490	859	54.1	<9600
S	1770	2990	11000	13700	10500	1040	34.2	7.44	<4770
Si	453	214	314	243	65.7	26.1	27.4	123	41300
U	<300	<300	<100	<100	<100	<50	<5	3.98	5580[b]
F^-	1620	2470	7390	9100	7840	3350	325	17.5	na
Cl^-	1660	692	271	80.2	<19	8.71	<2	<0.4	na
NO_2^-	23800	10100	4200	1620	615	421	428	471	na
NO_3^-	142000	71300	25300	8870	1550	248	50.8	72.6	na
PO_4^{3-}	2030	2360	3680	3080	6250	20800	2710	167	na
PO_4^{3-}(ICP)	1550	2950	2870	3430	6440	19900	2630	166	<29200
SO_4^{2-}	6520	10400	33700	40000	32400	3040	99.9	20.0	na
SO_4^{2-}(ICP)	5300	8960	33000	41000	31500	3120	102	22.3	<14300
$C_2O_4^{2-}$	1080	996	3420	3630	6990	10080	466	16.3	na
TIC	24400	24400	15700	12400	3310	407	26.5	20.2	na
TOC	1180	819	792	1100	1785	2390	143	40.0	na
"Acetate"	2180	1340	--	271	--	--	38.8	87.4	na
OH^-	12000	5830	2070	970	788	441	161	148	na
^{137}Cs-137 (µCi/mL)	52.1	24.3	8.46	3.56	0.94	1.09	0.34	0.35	215 µCi/g
%H_2O	60.5	68.3	78.4	81.4	89.2	93.6	99.2	99.7	na
Density (g/mL)	1.383	1.344	1.207	1.190	1.103	1.069	0.989	0.998	na

[a] accurate weight of residue for fusion analysis not possible; concentrations of analytes normalized to that of aluminum based on aluminum concentrations in Test A

[b] nickel and uranium concentrations in residue derived from Ni/Fe and U/Fe ratios in 8th contact and Fe concentration in residue

4.0 DILUTION RESULTS, VOLUME AND WEIGHT MEASUREMENTS

All results quoted in this section have been "normalized" to a common basis for comparison. The common basis is defined in each sub-section as appropriate.

4.1 TANK A-101

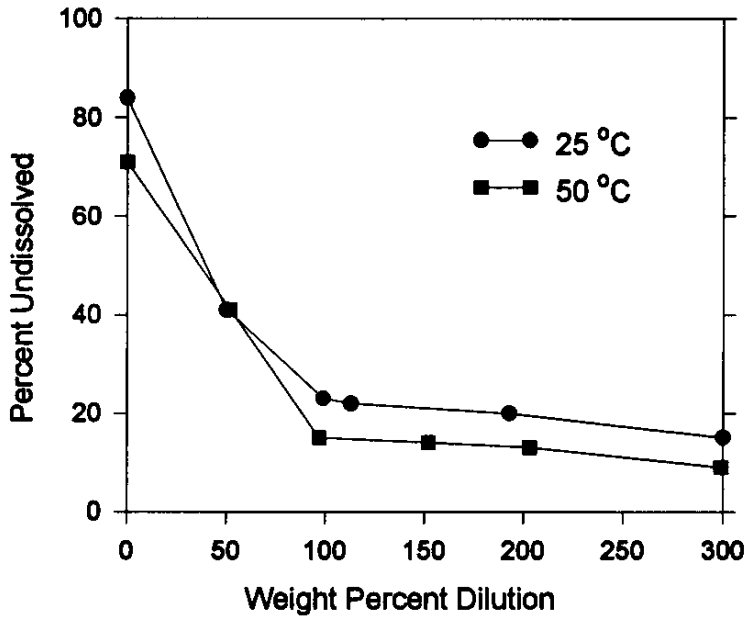
The obvious, direct way to determine how much saltcake dissolved upon dilution is to measure the volume percent and/or weight percent centrifuged solids remaining after the dissolution. These values as measured during the series dilution tests are shown in Table 4-1. Entries for volume percent centrifuged solids (Vol% CSol) and weight percent centrifuged solids (Wt% CSol) are measured relative to the total volume and weight, respectively, of the diluted samples. Entries for "Wt% CSol relative to undiluted sample" are self-explanatory, and provide a more consistent way of visualizing the amount of sample remaining undissolved. The latter data are plotted in Figure 4-1, where the same values are expressed as "percent undissolved".

Table 4-1. Percent Centrifuged Solids as a Function of Dilution, Tank A-101

at 25 °C						
Wt% Dilution→	0	50	99	113	193	302
Vol% CSol	76	20	10	8	6	2
Wt% CSol	84	28	12	11	7	4
Wt% CSol relative to undiluted sample	84	41	23	22	20	15
50 °C						
Wt% Dilution→	0	52	97	152	203	299
Vol% CSol	67	22	5	4	3	2
Wt% CSol	71	27	8	6	4	2
Wt% CSol relative to undiluted sample	71	41	15	14	13	9

It is clear from the data that most of dissolution occurred between 0% and 100% dilution, and only a small amount of dissolution took place at higher dilution. It is also clear that raising the temperature from 25 °C to 50 °C had a small impact on the overall solubility of the saltcake.

Figure 4-1. Tank A-101 Saltcake Dissolution



4.2 TANK S-102

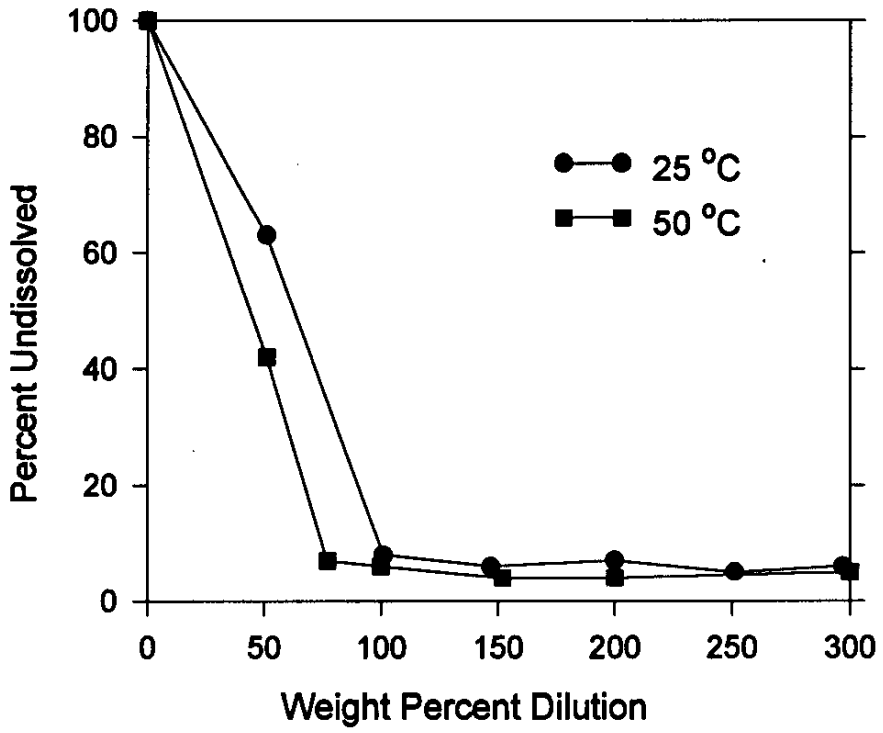
The percent centrifuged solids values for the tank S-102 series dilution tests are shown in Table 4-2. The undiluted composite sample was never centrifuged. Given the very low weight percent water and the general appearance of the saltcake, centrifugation would be unlikely to produce any separation of a liquid phase. The Vol% CSol and Wt% CSol can be assumed to be 100%. The "percent undissolved" values, or Wt% CSol relative to undiluted sample, are plotted in Figure 4-2.

Even more of the saltcake sample is soluble in water than for the A-101 saltcake. Over 95% of the sample dissolved at 200% dilution by weight and 50 °C. That indicates that, ideally, over 95% of the saltcake could be retrieved from the tank as supernatant liquid under similar dissolution conditions. As with A-101, raising the temperature from 25 °C to 50 °C had a small impact on the overall solubility of the saltcake.

Table 4-2. Percent Centrifuged Solids as a Function of Dilution, Tank S-102

at 25 °C						
Wt% Dilution→	51	101	147	200	251	297
Vol% CSol	31	3	2	2	2	1
Wt% CSol	42	4	3	2	1	1
Wt% CSol relative to undiluted sample	63	8	6	7	5	6
at 50 °C						
Wt% Dilution→	51	77	100	152	200	304
Vol% CSol	27	3	2	2	2	2
Wt% CSol	28	4	3	1	1	1
Wt% CSol relative to undiluted sample	42	7	6	4	4	5

Figure 4-2. Tank S-102 Saltcake Dissolution



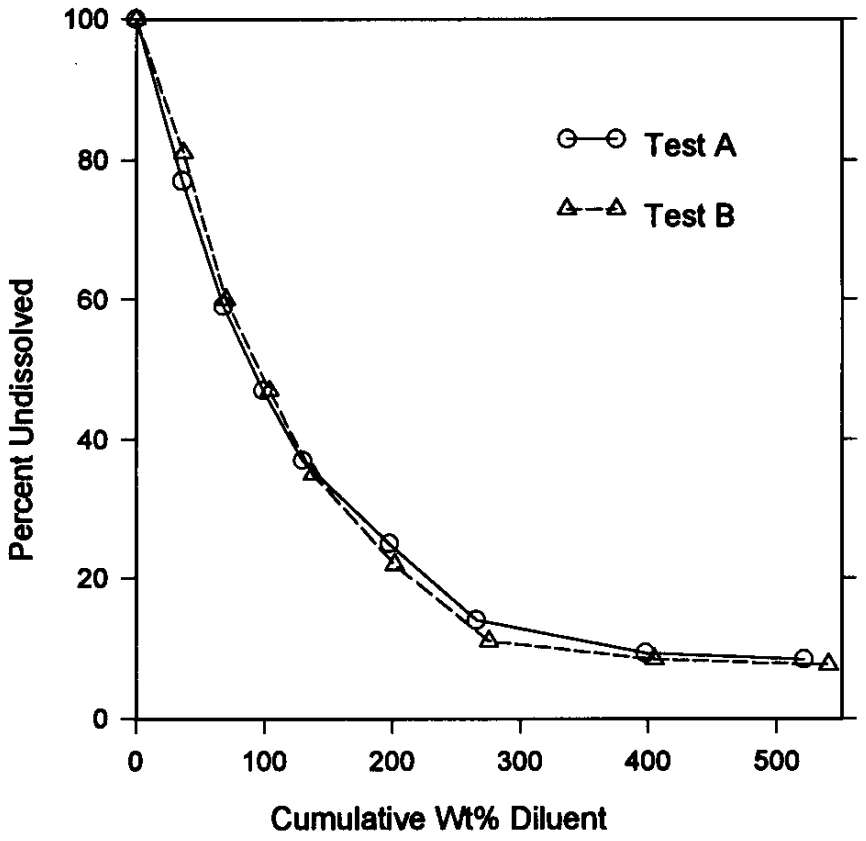
4.3 TANK BY-102 STEPWISE DISSOLUTION TEST

One way to measure the effectiveness of the dissolution brought about by stepwise addition of inhibited water is to measure the volume and weight percent of centrifuged solids remaining after each dissolution contact. The volume percent centrifuged solids (Vol% CSol) and weight percent centrifuged solids (Wt% CSol) are measured relative to the total volume and weight, respectively, of the diluted samples including the volumes and weights arising from all prior contacts. The "Wt% CSol relative to undiluted sample" provides a more consistent way of visualizing the amount of sample remaining undissolved. Values for the respective series A and B tests are presented in Table 4-3. The "Wt% CSol relative to undiluted sample" data, shown in Figure 4-3 as "Percent Undissolved", indicate the reproducibility of tests A and B, and show the weight of residual solids approaches about 8% of the initial saltcake weight as the cumulative quantity of inhibited water diluent increases to about 530%. The undiluted composite BY-102 material was not centrifuged. Because of the low water concentration (21.5%) and tarry consistency of the saltcake, centrifugation likely would not have produced a separate liquid layer. Therefore, both the Vol% CSol and Wt% CSol of the starting material are assumed to be 100%; the bulk density of the starting saltcake is assumed to be 2.0 g/mL.

Table 4-3. Percent Centrifuged Solids as a Function of Contact and Dilution with Inhibited Water, Tank BY-102

Contact →	1st	2nd	3rd	4th	5th	6th	7th	8th
Test A								
Cumulative Inh. Water Added, Wt%	36	68	99	130	198	266	398	521
Vol% CSol	49	29	18	13	5.3	3.3	1.5	1.1
Wt% CSol	57	35	24	16	8.2	3.7	1.9	1.4
Wt% CSol relative to undiluted sample	77	59	47	37	25	14	9.3	8.4
Test B								
Cumulative Inh. Water Added, Wt%	37	70	104	138	202	276	405	540
Vol% CSol	50	28	17	12	6.0	2.8	1.2	1.0
Wt% CSol	60	35	23	15	7.2	2.8	1.7	1.2
Wt% CSol relative to undiluted sample	81	60	47	35	22	11	8.4	7.6

Figure 4-3. Tank BY-102 Stepwise Dissolution



As shown previously (Herting 1998a), most of the BY-102 saltcake is soluble. However, the amount of salt dissolved for a given quantity of diluent is greater in the present tests that use multiple diluent contacts. For example, in the prior studies, a single dilution at 25°C using 300% diluent left 27% CSol relative to the starting saltcake. In the present studies, 270% diluent added in six portions left about 11-14% CSol. Two further contacts, virtually doubling the diluent quantity to about 530%, decreased the residual solids to about 8% CSol.

5.0 CHEMICAL COMPOSITION TRENDS

Sequential and series dissolution tests have now been performed on saltcake samples from four single-shell tanks: BY-102 and BY-106 in FY 1998 (Herting 1998a), and A-101 and S-102 in FY 1999. It is helpful to examine how the dilution trends for individual components compare among the tanks and different types of saltcake. In addition, the gross sample behavior explored in the previous section (i.e., volume and weight of centrifuged solids as a function of dilution) can be understood in terms of what happens to individual saltcake components.

The overall composition of the composite sample from each tank was determined by the sequential dissolution tests. The results are summarized in Table 5-1. Saltcakes from BY-106 and S-102 are similar in that they are both relatively high in $NaNO_3$. Saltcake from BY-102 is much higher than the others in carbonate, phosphate, sulfate, and fluoride. Tank A-101 saltcake is higher in moisture than the others, and is higher in all of the components that are normally not saturated in waste liquors, including nitrite, aluminate, hydroxide, acetate, chloride, potassium, and ^{137}Cs.

The stepwise dissolution tests, described in Section 5.9, illustrate the varied solubilities of the component salts in the BY-102 saltcake. The salts dissolve from the saltcake in an overlapping sequential manner and leave about 8% insoluble residue.

5.1 NITRITE

Liquid phase concentration data for nitrite are shown in Figure 5-1. Values are compiled from Tables 3-4, 3-6, 3-10, 3-12, and corresponding tables in the FY 1998 report (Herting 1998a) for tanks BY-102 and BY-106. The nitrite data are typical of the trends expected for a component that is fully soluble at all dilution levels tested. The concentration in solution falls with increasing dilution in a predictable pattern. The 50 °C nitrite data for tank BY-102 are plotted in Figure 5-2 as the ratio (C_o/C) of the concentration at 50% dilution to the concentration at the relevant dilution level. The line in Figure 5-2 is a first-order regression fit to the data. Points should follow this linear pattern if the only effect from one dilution level to another is, in fact, simple dilution of the liquid. Any dissolution of nitrite-containing solids occurring with dilution would cause the points to deviate from the linear relationship. The nitrite data from all four tanks follow this straight-line dilution pattern.

Table 5-1. Overall Composition (in wt%) of Composite Saltcake Samples

	BY-102	BY-106	A-101	S-102
Al	1.65	1.59	2.39	0.67
Cr	0.20	0.11	0.17	0.12
Fe	0.05	0.02	0.02	0.03
K	0.10	0.24	0.31	0.07
Na	27.8	25.0	21.2	23.0
P	1.00	0.08	0.14	0.18
S	2.04	0.45	0.80	0.13
Si	0.07	0.02	0.03	0.03
U	0.06	0.02	0.03	< 0.01
F^-	1.17	0.62	0.07	< 0.02
Cl^-	0.11	0.16	0.41	0.16
NO_2^-	1.85	2.71	7.43	2.04
NO_3^-	10.9	40.5	12.6	53.7
PO_4^{3-} by IC	0.60	0.34	0.39	0.52
PO_4^{3-} by ICP	3.06	0.24	0.44	0.56
SO_4^{2-} by IC	5.12	1.16	2.44	0.32
SO_4^{2-} by ICP	6.11	1.34	2.41	0.38
$C_2O_4^{2-}$	1.99	1.26	1.35	0.17
CO_3^{2-}	20.6[a]	7.15	9.04	2.95
"acetate"[c]	0.21	0.16	0.75	0.39
OH^-	1.09	1.14	2.10	0.42
^{137}Cs (μCi/g)	44	78	197	61
H_2O	26.5	14.7	31.2	5.0[b]
Mass Bal[c]	105.5	98.9	94.8	90.5
Chg Bal (+/-)[c]	0.89	0.92	0.93	0.91

[a] probably erroneously high due to analytical error; should be closer to 15% (Table 8-1)
[b] probably erroneously low due to analytical error; should be closer to 11%
[c] see Section 7.1.2 for definitions of "acetate", Mass Bal, and Chg Bal (+/-)

Figure 5-1. Nitrite Concentration in Supernatant Liquid
(open symbols 25 °C, filled symbols 50 °C)

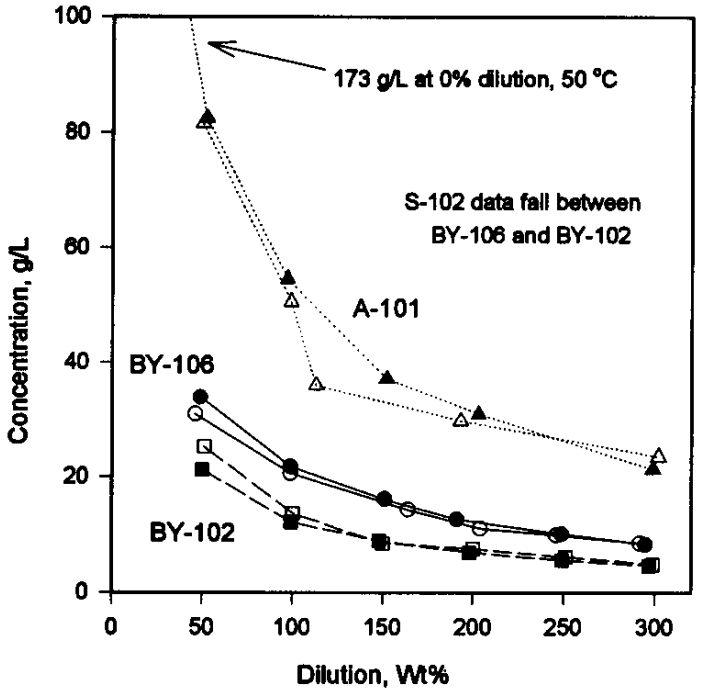
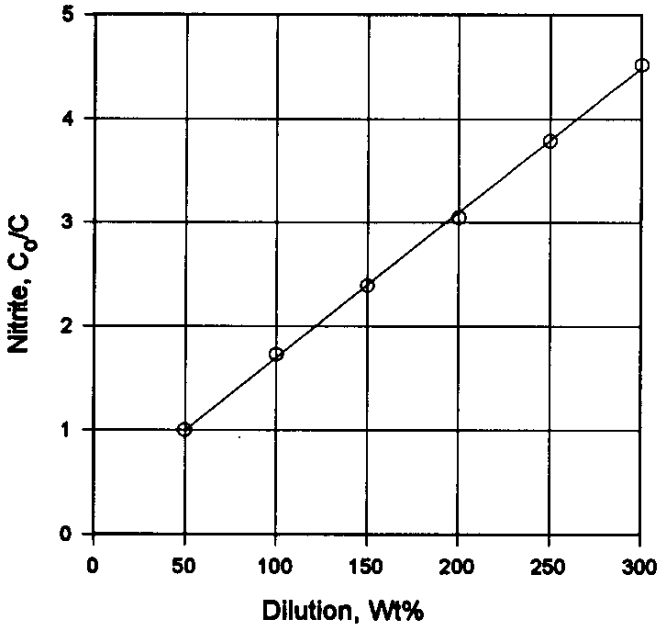


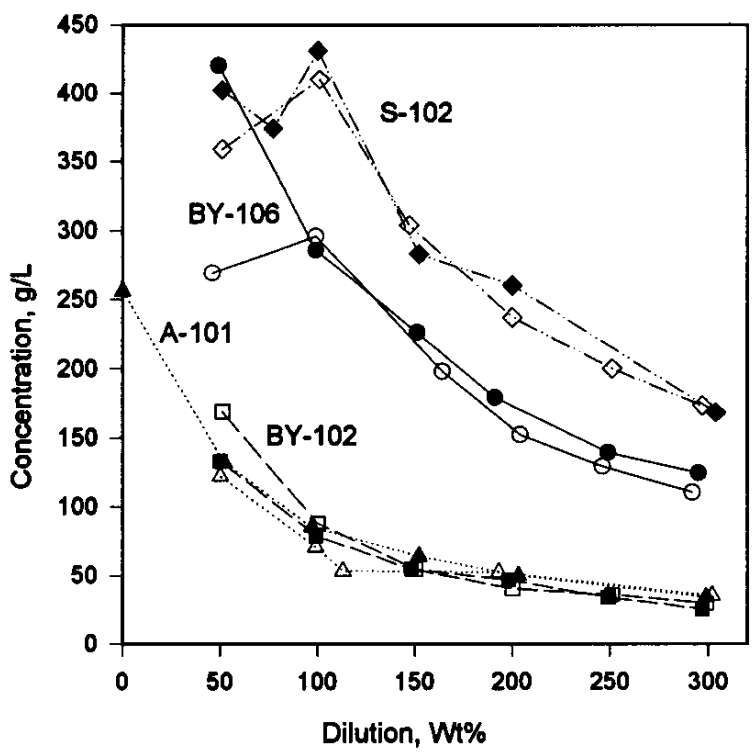
Figure 5-2. Tank BY-102 Nitrite Ratio Plot, 50 °C



5.2 NITRATE

Figure 5-3 shows the nitrate dilution data for all four tanks. The pattern for tanks A-101 and BY-102 is typical of an unsaturated component, like the nitrite just discussed. The pattern for BY-106 at 25 °C is a classic example of a component that is present in the solid phase at 0% and 50% dilution, but is unsaturated at all dilutions beyond 100%. Figure 5-4 shows a ratio plot (C_o/C) of this BY-106 data with the 100% dilution data point assigned as C_o. The deviation from the regression line at 50% dilution is obvious.

The concentration of nitrate in solution is higher at 100% than at 50% dilution (still looking at BY-106, 25 °C, Figure 5-3) because sodium concentration and the ionic strength of the solution are lower at 100% dilution, thus increasing the solubility of the sodium nitrate. The same dilution trend is observed in tank S-102 at 25 °C, but at a higher solubility level. The reason for the higher level is again the lower ionic strength – tank S-102 saltcake has lower concentrations of the other major sodium salts (carbonate, nitrite, hydroxide, aluminate) than tank BY-106, as seen in Table 5-1.

Figure 5-3. Nitrate Concentration in Supernatant Liquid

(open symbols 25 °C, filled symbols 50 °C)