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D. L. Herting
D. W. Edmonson
Numatec Hanford Corporation

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Saltcake Dissolution FY 1998 Status Report

D. L. Herting
D. W. Edmonson
Numatec Hanford Corporation, Richland, WA 99352
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Abstract: A laboratory scouting study was completed on the dissolution characteristics of Hanford waste from three single-shell waste tanks: 241-BY-102, 241-BY-106, and 241-B-106. Gross dissolution behavior (percent undissolved solids as a function of dilution) 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, 98% for BY-106, and 79% for B-106.

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CONTENTS

TABLES

FIGURES

ACRONYMS AND ABBREVIATIONS

B-106	Single-shell tank 241-B-106
BSltCk	Saltcake deposited during 242-B Evaporator operation, 1951 to 1953
BY-102	Single-shell tank 241-BY-102
BY-106	Single-shell tank 241-BY-106
BYSltCk	Saltcake deposited during ITS evaporator campaigns
ESP	Environmental Simulation Program
GEA	gamma energy analysis
IC	ion chromatography
ICP	inductively coupled plasma spectroscopy
ITS	in-tank solidification
kgal	kilogallon (1,000 gallons)
kL	kiloliter (1,000 liters)
ML	megaliter (1,000,000 liters)
PLM	polarized light microscope (or microscopy)
rpm	revolutions per minute
TCR	Tank Characterization Report
TIC	total inorganic carbon
TOC	total organic carbon
TWRS	Tank Waste Remediation System

1.0 INTRODUCTION AND EXECUTIVE SUMMARY

A laboratory study was completed on the dissolution characteristics of Hanford waste from three single-shell waste tanks: 241-BY-102, 241-BY-106, and 241-B-106 (henceforth referred to as BY-102, BY-106, and B-106). The first two tanks contain saltcake waste; the third tank was predicted to contain saltcake, based on historical process information (Agnew 1997), but the waste behaved more like a sludge. For this report, saltcake is defined as tank waste composed mainly of water-soluble sodium salts and is relatively dry; sludge is defined as tank waste that contains a high proportion of water-insoluble metal hydroxides and other water-insoluble compounds, and has a relatively high moisture content.

The Tank Waste Remediation System (TWRS) is tasked with retrieving waste from double-shell and single-shell tanks to provide feed for vitrification. The TWRS 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) is being used by the TWRS organization to predict dilution/retrieval behavior of all tank waste types. Data from this task is provided to ESP users to support evaluation, refinement, and validation of the ESP model.

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 work will continue into fiscal year 1999.

1.1 RESULTS SUMMARY

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

Some of the dissolution data 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 is a rough measure of the fraction of waste that could be retrieved from the tank by pumping the supernatant liquid.

The percent undissolved solids for tanks BY-102, BY-106, and B-106 at 25 °C and 100% dilution with water were 75%, 27%, and 50%, respectively. At 100% dilution and 50 °C, the dissolution improved to 48% and 19% for BY-102 and BY-106 (B-106 was not measured). At 300% dilution and 50 °C, the dissolution improved further to 13%

and 5% undissolved solids for BY-102 and BY-106, which were the respective maximum dissolution levels observed during the current study. Dilution beyond 100% did not improve the dissolution of the B-106 waste.

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 sodium fluoride sulfate) in controlling the equilibrium concentrations of phosphate, fluoride, and sulfate 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 liquid phase or can be dissolved) is estimated at 86% for BY-102, 98% for BY-106, and 79% for B-106.

For tanks BY-102 and BY-106, the solids that remain undissolved after two successive wash steps are mainly sodium salts, most of which have not been identified yet. Sodium oxalate is certainly a large component of these sparingly-soluble salts, but other unknown fluoride, phosphate, and sulfate salts are also major contributors. For tank B-106, the sludge components already discussed make up a large proportion of the undissolved solids. However, an unknown salt containing sodium and phosphate appears to be the largest single component of these solids.

Computer simulations of the saltcake series dissolution tests on tanks BY-102 and BY-106 were conducted by investigators at Mississippi State University, using ESP. Analytical results from the sequential dissolution tests were used as input to the program. 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 dilutions of 100% and higher. Fluoride, phosphate, and sulfate concentrations showed marked discrepancies between the ESP predictions and the experimental data at dilutions below 100%. Additional laboratory work is needed to determine the solid-liquid equilibria for the double salt systems, to provide better thermodynamic data for ESP to use in the predictions.

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 (ITS) 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. The chemical composition 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%). Sodium nitrate is a major salt in this waste, but it does not have the dominance that it does in other saltcakes, including BY-106.

1.2.2 Tank BY-106

Tank BY-106 is predicted by historical model to contain 44 kgal (166 kL) of sludge and 544 kgal (2.05 ML) of BYSltCk. The current actual total waste volume (Bell 1996) in the tank is 642 kgal (2.43 ML).

One ten-segment core sample (core 121) was taken from the tank between December, 1995 and January, 1996. All ten segments contained waste described as saltcake. Segment 1 was a partial segment. Portions of segments 3 through 8 were used to make the composite sample for this study. The chemical composition of the core sample and composite sample are shown in Table 8-2. The major components of the sample used for this study include (approximate weight percent): NO_3^- (41%), Na^+ (25%), $Al(OH)_4^-$ (8%), CO_3^{2-} (7%), NO_2^- (3%), SO_4^{2-} (1%), $C_2O_4^{2-}$ (1%), H_2O (15%). Sodium nitrate is definitely the dominant salt in this waste.

1.2.3 Tank B-106

Tank B-106 is predicted by historical model to contain 116 kgal (438 kL) of saltcake derived from the 1951-53 operation of the 242-B evaporator. This waste type is defined by Agnew as type "BSltCk". The current actual total waste volume (McCain 1996) in the tank is 117 kgal (443 kL).

Two core samples (cores 93 and 94), two segments each, were taken from the tank in July, 1995. In both cores, the upper segment and the top half of the lower segment were said to contain light-to-dark brown sludge. The bottom half of the bottom segment contained light green sludge. Portions of segments 1U (upper half of segment 1), 1L (lower half of segment 1), and 2U were used to make the composite sample for this study.

The chemical composition of the core sample and composite sample are shown in Table 8-3. The major components of the composite sample used in this study include (approximate weight percent): NO_3^- (16%), Na^+ (9.5%), NO_2^- (1%), SO_4^{2-} (1%), Fe (1%), U (1%), H_2O (58%). This waste had a much higher percentage of water and of water-insoluble components (Al, Bi, Ca, Fe, U) than the other two tank waste samples.

2.0 DESCRIPTION OF LABORATORY STUDIES

Composite samples of actual 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. 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. Both types of tests are described in detail in sections 2.2 and 2.3.

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.

2.2 SEQUENTIAL DISSOLUTION TESTS

The following tests were performed on composite samples from all three tanks – BY-102, BY-106, and B-106.

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. [For tank B-106, two additional cones were treated with 3 M NaOH instead of water.] 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 approximately 2000 rpm.

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
BY-106	121	3	8531	46.31
	121	4	8533	61.11
	121	5	8536	83.17
	121	6	8541	129.35
	121	7	8544	64.15
	121	8	8552	68.55
		Composite	Total Wt =	449.94
B-106	93	2 U	7416	31.64
	93	1 L	7420	55.52
	94	1 U	7423	46.22
	94	2 U	7425	52.09
	94	1 L	8454	22.05
	94	1 U	9687	50.64
	94	2 U	9688	4.98
		Composite	Total Wt =	263.14

[a] Segment 1 is at top of waste; U = upper half of segment; L = lower half of segment.

The supernatant liquids from both cones were combined into a sample bottle. The liquid was analyzed for metals by inductively coupled plasma spectroscopy (ICP), anions by 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 (or 3 M NaOH for the appropriate B-106 cones) 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, again 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.

2.3 SERIES DISSOLUTION TESTS

The following tests were performed on composite samples from two of the three tanks – BY-102 and BY-106.

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 50, 100, 150, 200, 250, or 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 approximately 2000 rpm. 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, and IC. 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. 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 all of the BY-102 samples and the 50% sample from BY-106.

3.0 RESULTS – RAW DATA

"Raw data" are values obtained for net weight and volume measurements and chemical analyses. They are reproduced here for documentation purposes. Sample-to-sample comparisons should not be made on raw data measurements because of differences in initial sample weights and volumes. Comparisons must be based on normalized data, accounting for initial volume and weight differences. The normalized data are presented in Section 4.

3.1 Tank BY-102

The aliquot of the composite sample taken for %H_2O analysis was labeled 2BYTC, and was assigned Labcore number S98R000195. (Labcore is the laboratory information and management system used at the 222-S Laboratory.) Analytical results were 26.53% H_2O by TGA and 26.0% by oven-drying.

3.1.1 BY-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 3-1. Sample analytical results are shown in Table 3-2.

3.1.2 BY-102 Series Dissolution Test, Ambient Temperature

Six 15 mL centrifuge cones were labeled BY2-A through BY2-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 BY-102 Series Dissolution Test, 50 °C

Six 15 mL centrifuge cones were labeled BY2H-A through BY2H-F. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-5. Liquid samples were diluted to dissolve crystals that formed when the samples cooled from 50 °C to ambient temperature. Sample analytical results for the diluted liquid samples are shown in Table 3-6a. The corresponding undiluted sample results are shown in Table 3-6b.

Table 3-1. Raw Data, Tank BY-102 Sequential Dissolution Test.
(weights in grams, volumes in mL)

	SEQA	SEQB
Sample Wt	30.670	32.183
Wt H_2O Added (1st wash)	29.310	30.278
Total Vol	44.0	45.0
1st Water Wash Sample ID[a]	2BYSEQAB1 / S98R000204	
CSol[b] Vol	15.0	4.0
CSol Wt	22.995	16.222
Wt H_2O Added (2nd wash)	30.171	29.160
Total Vol	44.5	38.0
2nd Water Wash Sample ID	2BYSEQAB2 / S98R000206	
CSol Vol	6.0	6.0
CSol Wt	8.628	8.868
CSol Sample ID	2BYSEQABS / S98R000207 and 208	

[a] decanted supernatant liquid; customer ID number / Labcore ID number
[b] CSol = centrifuged solids

Table 3-2. Analytical Results, Tank BY-102 Sequential Dissolution Test.

Analyte	1st Water Wash 2BYSEQAB1 S98R000204 (µg/mL)	2nd Water Wash 2BYSEQAB2 S98R000206 (µg/mL)	CSol 2BYSEQABS S98R000207-8 (µg/g)
Al	8710	1280	21700
Ca			1540
Cr	1110	168	2350
Fe			1910
K	1320	< 300	< 970
Mg			366
Mn			876
Na	156000	70000	136000
Ni			951
P	604	1150	29000
Pb			254
S	3590	13500	5390
Si	257	140	1080
U			2290
F^-	2690	7940	na[a]
Cl^-	1060	< 173	na
NO_2^-	14800	2870	na
NO_3^-	92300	12300	na
PO_4^{3-}	1680	3810	na
SO_4^{2-}	10500	36000	na
$C_2O_4^{2-}$	930	3860	na
TIC	(32700)[b]	5890	3140
TOC	1020	1110	14300
OH^-	9020	1400	na
^{137}Cs (µCi/mL)	36.1	6.3	na
Density (g/mL)	1.232	1.125	na
%H_2O	69.0	84.0	56.97

[a] na = not analyzed

[b] parentheses denote unrealistic analytical result

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

Wt% Dilution:	51%	100%	150%	200%	251%	299%
Cone ID:	BY2-E	BY2-B	BY2-C	BY2-D	BY2-F	BY2-A
Sample Wt	4.785	4.338	4.685	4.662	4.538	3.600
Wt H2O Added	2.447	4.345	7.040	9.325	11.382	10.767
Total Vol	4.6	6.3	9.2	11.5	13.5	12.2
CSol Vol	3.1	2.0	1.5	1.0	0.8	0.6
CSol Wt	5.123	3.274	2.008	1.548	1.344	0.962
Supernate ID	2BYE1	2BYB1	2BYC1	2BYD1	2BYF1	2BYA1
S98R000...	201	197	198	200	202	196

Table 3-4. Analytical Results, Tank BY-102 Series Dissolution Test, Ambient Temp. (µg/mL except as noted)

Wt% Dilution:	51%	100%	150%	200%	251%	299%
Supernate ID	2BYE1	2BYB1	2BYC1	2BYD1	2BYF1	2BYA1
S98R000...	201	197	198	200	202	196
Density (g/mL)	1.368	1.267	1.230	1.203	1.190	1.166
TIC	17600	16200	16300	13000	11000	9210
F^-	999	2780	4150	5530	5060	4460
Cl^-	1840	1010	583	464	398	390
NO_2^-	25200	13700	8520	7550	6180	4880
NO_3^-	169000	87700	54500	40300	35800	29500
PO_4^{3-}	1310	1980	2430	2410	3130	3700
SO_4^{2-}	5520	12600	19300	22700	20000	17200
$C_2O_4^{2-}$	< 541	1080	1560	2230	2520	2840

Table 3-5. Raw Data, Tank BY-102 Series Dissolution Test, 50 °C
(weights in grams, volumes in mL)

Wt% Dilution:	50%	99%	148%	198%	249%	297%
Cone ID:	BY2H-A	BY2H-B	BY2H-D	BY2H-E	BY2H-F	BY2H-C
Sample Wt	6.010	6.160	6.348	4.276	4.386	3.782
Wt H2O Added	3.000	6.112	9.422	8.462	10.903	11.232
Total Vol	5.8	8.2	11.8	7.5[a]	7.0[a]	12.5
CSol Vol	2.2	1.8	1.2	0.4[a]	0.3[a]	0.2
CSol Wt	4.250	2.937	2.083	0.939[a]	0.583[a]	0.502
Supernate ID	BY2HAL	BY2HBL	BY2HDL	BY2HEL	BY2HFL	BY2HCL
S98R000...	210	211	214	215	216	212
Sup Sample Wt	2.574	7.008	11.754	6.467	6.508	12.893
Sup H_2O Added	2.559	6.907	11.597	6.619	6.535	11.670
Density Diluted	1.172	1.138	1.112	1.086	1.062	1.069
Vol Diluted	4.38	12.23	21.00	12.05	12.28	22.98
Vol Undiluted	1.82	5.32	9.40	5.43	5.75	11.31
Density Undil	1.41	1.32	1.25	1.19	1.13	1.14
Diln Factor (v/v)	2.41	2.30	2.23	2.22	2.14	2.03

[a] Cones E and F broke during heating, and some sample was lost.

Table 3-6a. Analytical Results, Tank BY-102 Series Dissolution Test, 50 °C
(diluted samples; μg/mL except as noted)

Wt% Dilution:	50%	99%	148%	198%	249%	297%
Supernate ID	BY2HAL	BY2HBL	BY2HDL	BY2HEL	BY2HFL	BY2HCL
S98R000...	210	211	214	215	216	212
Density (g/mL)	1.172	1.138	1.112	1.086	1.062	1.069
TIC	10400	10100	7650	6040	5010	4250
F^-	880	1270	1740	2540	2570	1820
Cl^-	518	276	214	222	186	< 88
NO_2^-	8800	5330	3970	3130	2610	2300
NO_3^-	55200	34300	24500	21100	15900	12500
PO_4^{3-}	3450	4320	3620	5320	5120	(1980)
SO_4^{2-}	1600	3920	6150	8980	9250	(5850)
$C_2O_4^{2-}$	< 541	766	1020	1240	1500	1600

Table 3-6b. Analytical Results, Tank BY-102 Series Dissolution Test, 50 °C
(undiluted samples; µg/mL except as noted)

Wt% Dilution:	50%	99%	148%	198%	249%	297%
Supernate ID	BY2HAL	BY2HBL	BY2HDL	BY2HEL	BY2HFL	BY2HCL
S98R000...	210	211	214	215	216	212
Density (g/mL)	1.41	1.32	1.25	1.19	1.13	1.14
TIC	25000	23200	17100	13400	10700	8640
F^-	2120	2920	3890	5640	5490	3700
Cl^-	1250	634	478	493	398	< 176
NO_2^-	21200	12200	8870	6940	5580	4670
NO_3^-	133000	78800	54700	46800	34000	25400
PO_4^{3-}	8300	9930	8080	11800	10900	(4020)
SO_4^{2-}	3850	9010	13700	19900	19800	(11900)
$C_2O_4^{2-}$	< 1200	1760	2280	2750	3210	3250

3.2 Tank BY-106

Two aliquots of the composite sample taken for %H_2O analysis were labeled BY106CMPD (Labcore S98R000001) and BY6COMPRR2 (Labcore S98R000029). The analytical result for the first sample was 14.05% H_2O by TGA. Results for the second aliquot were 14.68% H_2O by TGA and 14.7% H_2O by oven-drying. The results from the second sample are used in the calculations in Section 4.

3.2.1 BY-106 Sequential Dissolution Test

Two 50 mL centrifuge cones were labeled BY6-SEQA and BY6-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 BY-106 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 3-9. Sample analytical results are shown in Table 3-10.

3.2.3 BY-106 Series Dissolution Test, 50 °C

Six 15 mL centrifuge cones were labeled BY6H-A through BY6H-F. The procedure was described in Section 2.3. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-11. The liquid sample from cone BY6H-A was diluted to dissolve crystals that formed when the sample cooled from 50 °C to ambient temperature. Sample analytical results for the undiluted liquid sample (dilution-corrected) are shown in Table 3-12 with the results for the other five samples which were not diluted.

Table 3-7. Raw Data, Tank BY-106 Sequential Dissolution Test.
(weights in grams, volumes in mL)

	BY6-SEQA	BY6-SEQB
Sample Wt	30.017	30.091
Wt H_2O Added (1st wash)	30.026	30.139
Total Vol	45.2	46.7
1st Water Wash Sample ID[a]	BY6SEQAB1 / S98R000024	
CSol[b] Vol	4.9	4.8
CSol Wt	6.702	6.225
Wt H_2O Added (2nd wash)	29.440	31.020
Total Vol	34.0	35.5
2nd Water Wash Sample ID	BY6SEQAB2 / S98R000025	
CSol Vol	3	3
CSol Wt	1.570	1.253
CSol Sample ID	BY6SEQABCS / S98R00027 and 28	

[a] decanted supernatant liquid; customer ID number / Labcore ID number
[b] CSol = centrifuged solids

Table 3-8. Analytical Results, Tank BY-106 Sequential Dissolution Test.

Analyte	1st Water Wash BY6SEQAB1 S98R000024 (µg/mL)	2nd Water Wash BY6SEQAB2 S98R000025 (µg/mL)	CSol BY6SEQABCD S98R000027-28 (µg/g)
Al	10300	1110	13000
Ca	< 40	< 10	2770
Cr	245	34	16200
Fe	< 20	< 5	4780
K	1660	158	< 200
Mg			214
Mn			248
Na	157000	29400	85100
Ni	< 8	< 2	1230
P	239	396	742
Pb	< 40	< 10	753
S	938	2910	2330
Si	85	34	340
Sr	< 40	< 1	1330
U	< 200	< 50	4120
F^-	2085	3130	na[a]
Cl^-	1100	118	na
NO_2^-	18200	2090	na
NO_3^-	273000	30450	na
PO_4^{3-}	1500	1290	na
SO_4^{2-}	1710	8800	na
$C_2O_4^{2-}$	475	7400	na
TIC	9590	1060	1340
TOC	952	1970	29200
OH^-	7660	881	na
^{137}Cs (µCi/mL)	52.4	6.3	na
Density (g/mL)	1.336	1.087	na
%H_2O	58.2	91.4	69.91

[a] na = not analyzed

Table 3-9. Raw Data, Tank BY-106 Series Dissolution Test, Ambient Temperature (weights in grams, volumes in mL)

Wt% Dilution:	46%	99%	164%	204%	246%	292%
Cone ID:	A	B	C	D	E	F
Sample Wt	4.637	6.352	4.030	3.961	4.446	4.187
Wt H2O Added	2.143	6.313	6.599	8.078	10.928	12.224
Total Vol	4.6	8.9	8.5	9.7	12.9	13.9
CSol Vol	1.9	1.0	0.4	0.4	0.3	0.2
CSol Wt	3.245	1.716	0.828	0.767	0.694	0.666
Supernate ID	AX1DH	BX1DH	CX1DH	DX2DH	EX2DH	FX2DH
S98R000...	002	004	005	006	008	009

Table 3-10. Analytical Results, Tank BY-106 Series Dissolution Test, Ambient Temp. (μg/mL except as noted)

Wt% Dilution:	46%	99%	164%	204%	246%	292%
Supernate ID	AX1DH	BX1DH	CX1DH	DX2DH	EX2DH	FX2DH
S98R000...	002	004	005	006	008	009
Density (g/mL)	1.400	1.353	1.260	1.233	1.198	1.191
TIC	14200	8180	5850	5480	4310	3930
F^-	1250	2085	3020	2650	2245	1850
Cl^-	1490	1154	774	626	580	470
NO_2^-	30900	20600	14300	11100	9940	8550
NO_3^-	269000	296000	198000	152000	129000	110000
PO_4^{3-}	778	791	870	900	1130	554
SO_4^{2-}	1230	2220	5345	4620	3960	3430
$C_2O_4^{2-}$	< 541	475	1010	1400	1785	2210

Table 3-11. Raw Data, Tank BY-106 Series Dissolution Test, 50 °C
(weights in grams, volumes in mL)

Wt% Dilution:	49%	99%	151%	191%	249%	295%
Cone ID:	BY6H-A	BY6H-B	BY6H-C	BY6H-D	BY6H-E	BY6H-F
Sample Wt	7.773	7.260	4.272	4.775	3.900	4.119
Wt H2O Added	3.779	7.181	6.445	9.119	9.706	12.167
Initial Total Wt	11.552	14.441	10.717	13.894	13.606	16.286
Final Total Wt[a]	11.182	10.454	10.511	8.838	11.629	15.800
Final Total Vol	7.1	7.8	8.3	7.1	9.6	13.5
CSol Vol	1.9	0.9	0.25	0.2	0.2	0.15
CSol Wt	3.849	1.387	0.484	0.473	0.253	0.228
Supernate ID	AHL	BHL	CHL	DHL	EHL	FHL
S98R000...	061	062	063	066	065	067
Sup Sample Wt	4.421	not diluted				
Sup H_2O Added	4.393					
Density Diluted	1.210					
Density Undil	1.40[b]					
Diln Factor (v/v)	2.4					

[a] Cones fractured during heating, and some sample was lost. Weights before and after heating indicate extent of sample loss. See text (Section 3.1.3) for more details.
[b] estimated

Table 3-12. Analytical Results, Tank BY-106 Series Dissolution Test, 50 °C
(sample A is dilution-corrected; all results μg/mL except as noted)

Wt% Dilution:	49%	99%	151%	191%	249%	295%
Supernate ID	BY6H-A	BY6H-B	BY6H-C	BY6H-D	BY6H-E	BY6H-F
S98R000...	061	062	063	066	065	067
Density (g/mL)	1.40	1.352	1.300	1.247	1.192	1.189
TIC	6530	9370	6330	5120	4720	4030
F^-	1370	2850	3730	2920	2490	1940
Cl^-	2470	1500	1070	886	727	527
NO_2^-	33800	21800	16100	12700	10100	8360
NO_3^-	420000	286000	226000	179000	139000	124000
PO_4^{3-}	3100	2330	1740	1410	1400	717
SO_4^{2-}	2090	3050	6640	5780	4980	4010
$C_2O_4^{2-}$	< 1300	1100	1490	1920	2700	3080

3.3 Tank B-106

The aliquot of the composite sample taken for %H_2O analysis was labeled B6COMP, and was assigned Labcore number S98R000195. Analytical results were 58.0% by TGA and 44.2% by oven-drying. The difference between the two results is a bit disturbing. The oven-drying analysis was done two weeks after the TGA analysis, and the sample may have dried out during the intervening time if the sample vial was not tightly capped. The TGA result is in good agreement with the core sample analytical results as reported in the Tank Characterization Report (McCain 1996). The oven-drying result is not used in any of the mass balance calculations in this report.

3.3.1 B-106 Sequential Dissolution Test

Four 50 mL centrifuge cones were labeled B6-SEQA through B6-SEQD. The procedure was described in Section 2.2. Cones A and B were used for dilution with inhibited water (0.01 M NaOH and 0.01 M $NaNO_2$). Cones C and D were used for dilution with 3 M NaOH solution. Weights, volumes, and analytical sample identification numbers of the various fractions are shown in Table 3-13. Sample analytical results are shown in Tables 3-14 and 3-15 for inhibited water diluent and 3 M NaOH diluent, respectively.

It became clear from the results of the sequential dissolution test that the B-106 composite sample behaved more like a sludge than a saltcake. Relatively little of the sample dissolved in either water or 3 M NaOH at ambient temperature. Therefore, the series dilution tests performed for the other two tanks were not performed for tank B-106.

Table 3-13. Raw Data, Tank B-106 Sequential Dissolution Test
(weights in grams, volumes in mL)

	B6-SEQA	B6-SEQB	B6-SEQC	B6-SEQD
Sample Wt	25.712	25.999	26.363	26.196
Diluent	inhibited H_2O	inhibited H_2O	3 M NaOH	3 M NaOH
Wt Diluent Added	25.012	24.981	27.070	26.983
Vol Diluent Added	25.01	24.98	24.17	24.09
Total Vol	43.8	44.5	43.8	44.0
Slurry Density	1.16	1.15	1.22	1.21
Slurry Color	caramel		red "BBQ sauce"	
1st Wash Sample ID	B6QAB1 / S98R000225		B6QCD1 / S98R000226	
CSol Vol	9.9	10.0	12.6	12.8
CSol Wt	12.932	13.077	17.430	18.226
Wt Dil (2nd Wash)	24.974	25.061	27.110	27.138
Total Vol	35.0	35.0	37.0	37.5
2nd Wash Sample ID	B6QAB2 / S98R000228		B6QCD2 / S98R000229	
CSol Vol	9.9	10.0	12.4	12.5
CSol Wt	12.273	12.397	15.586	16.732
CSol Sample ID	B6QABS / S98R000231, 3		B6QCDS / S98R000232, 4	

Table 3-14. Analytical Results, Tank B-106 Sequential Dissolution Test, Inhibited Water Diluent

Analyte	1st Water Wash B6QAB1 S98R000225 (μg/mL)	2nd Water Wash B6QAB2 S98R000228 (μg/mL)	CSol B6QABS S98R000231, 3 (μg/g)
Al	< 5	2	4740
Bi	< 10	< 4	5160
Ca	< 10	< 4	5060
Cr	16	4	371
Fe	< 5	< 2	27400
K	103	25	< 300
Mg	< 10	< 4	1190
Mn	< 1	< 1	215
Na	46400	13700	42500
P	3400	1180	28000
Pb	< 10	< 4	667
S	2880	787	745
Si	7	3	355
Sr	< 1	< 1	716
U	< 50	< 20	19000
F^-	524	534	na[a]
Cl^-	701	174	na
NO_2^-	5730	1600	na
NO_3^-	103000	26700	na
PO_4^{3-}	11300	3500	na
SO_4^{2-}	7240	2020	na
$C_2O_4^{2-}$	< 1070	< 117	na
TIC	162	64	112
TOC	204	60	376
OH^-	< 2500	< 63	na
^{137}Cs (μCi/mL)	2.2	0.5	na
Density (g/mL)	1.107	1.023	na
$\%H_2O$	84.1	95.7	76.7

[a] na = not analyzed

Table 3-15. Analytical Results, Tank B-106 Sequential Dissolution Test, 3 M NaOH Diluent

Analyte	1st Wash B6QCD1 S98R000226 (μg/mL)	2nd Wash B6QCD2 S98R000229 (μg/mL)	CSol B6QCDS S98R000232, 4 (μg/g)
Al	1340	519	741
Bi	< 20	< 20	3490
Ca	< 20	< 20	3150
Cr	30	16	216
Fe	< 10	< 10	18500
K	144	< 100	< 300
Mg	< 20	< 20	790
Mn	< 2	< 2	145
Na	69600	70800	101000
P	1660	1470	24400
Pb	< 20	< 20	449
S	3110	920	685
Si	118	176	216
Sr	< 2	< 2	475
U	< 100	< 100	12400
F^-	656	612	na[a]
Cl^-	822	307	na
NO_2^-	5710	1340	na
NO_3^-	111000	30500	na
PO_4^{3-}	5880	4270	na
SO_4^{2-}	8480	2250	na
$C_2O_4^{2-}$	< 1070	< 117	na
TIC	205	159	301
TOC	215	53	322
OH^-	16700	39500	na
^{137}Cs (μCi/mL)	10.3	3.3	na
Density (g/mL)	1.140	1.127	na
%H_2O	79.5	86.0	83.6

[a] na = not analyzed

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 BY-102

The obvious, direct way to determine how much salt 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".

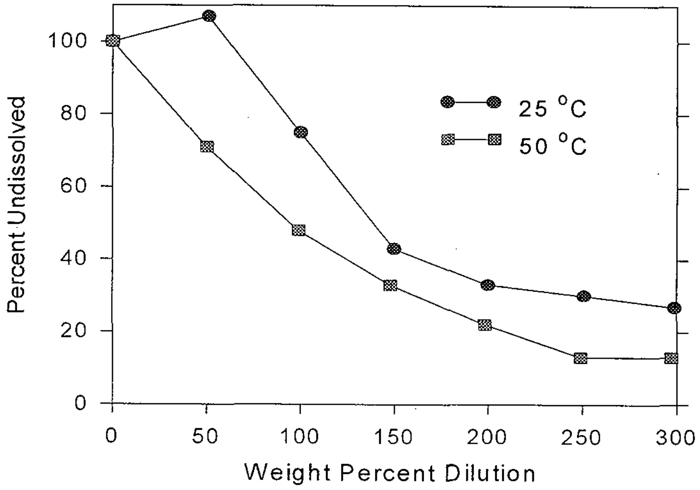
The undiluted composite sample was not centrifuged. Given the low weight percent water (approximately 26% – see Section 3.1) and the general appearance of the saltcake, centrifugation would be unlikely to produce any separation of a liquid phase. The Vol% CSol and Wt% CSol can be assumed to be 100%.

Table 4-1. Percent Centrifuged Solids as a Function of Dilution, Tank BY-102

at 25 °C						
Wt% Dilution→	51	100	150	200	251	299
Vol% CSol	67	32	16	9	6	5
Wt% CSol	72	38	17	11	8	7
Wt% CSol relative to undiluted sample	107	75	43	33	30	27
at 50 °C						
Wt% Dilution→	50	99	148	198	249	297
Vol% CSol	38	22	10	5	4	2
Wt% CSol	48	25	13	10	7	3
Wt% CSol relative to undiluted sample	71	48	33	na[1]	na[1]	13

[1] not available because unknown amount of sample was lost during heating.

Figure 4-1. Tank BY-102 Saltcake Dissolution



It is clear from the data that most of the saltcake sample is soluble in water. As much as 87% of the sample dissolved at 300% dilution by weight and 50 °C. It is also clear that raising the temperature from 25 °C to 50 °C had a dramatic impact on the overall solubility of the saltcake. The fact that the weight percent centrifuged solids was 107% relative to the undiluted sample at 50% dilution, 25 °C, is not surprising. The centrifuged solids from the diluted sample retained more interstitial liquid than the initial composite sample had.

4.1 Tank BY-106

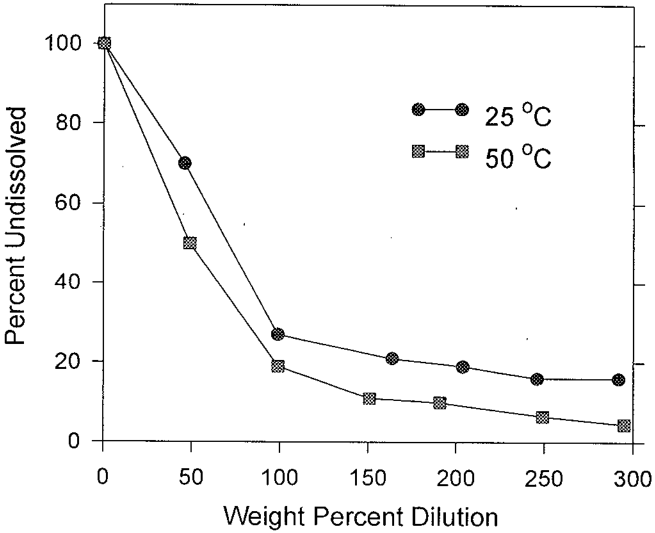
The percent centrifuged solids values for the tank BY-106 series dilution tests are shown in Table 4-2. Again, the undiluted composite sample was never centrifuged. Given the very low weight percent water (14.7% – see Section 3.2) and the general appearance of the saltcake, centrifugation would be unlikely 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.

Table 4-2. Percent Centrifuged Solids as a Function of Dilution, Tank BY-106

at 25 °C						
Wt% Dilution→	46	99	164	204	246	292
Vol% CSol	41	11	5	4	2	1
Wt% CSol	47	13	7.7	6.4	4.5	4.1
Wt% CSol relative to undiluted sample	70	27	21	19	16	16
at 50 °C						
Wt% Dilution→	49	99	151	191	249	295
Vol% CSol	27	12	3	3	2	1
Wt% CSol	34	13	5	5	2.2	1.4
Wt% CSol relative to undiluted sample	50	19	11	10	6.5	4.5

Even more of the saltcake sample is soluble in water than for the BY-102 saltcake. Over 95% of the sample dissolved at 300% 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 BY-102, raising the temperature from 25 °C to 50 °C had a dramatic impact on the overall solubility of the saltcake.

Figure 4-2. Tank BY-106 Saltcake Dissolution



5.0 CHEMICAL COMPOSITION TRENDS

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. Most of the trends described in the following sections can be observed in the "Analytical Results" tables in Section 3.

Certain components can be assumed, based on prior solubility studies on Hanford waste samples (Person 1996, Herting 1997, 1998), to be completely soluble under all dilution conditions. These components include chloride, potassium, and – for the current cases – nitrite. Solubilities of other components can often be evaluated by comparing concentration trends with these completely soluble components.

5.1 Tank BY-102

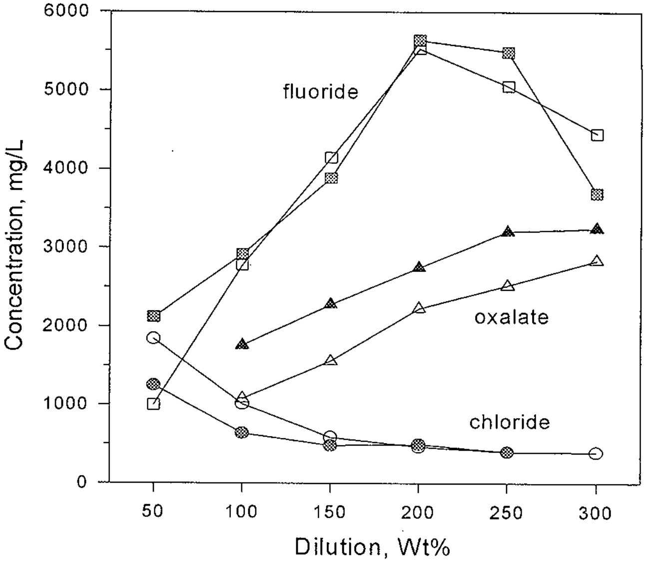
Liquid phase concentration data for chloride, fluoride and oxalate are shown in Figure 5-1.

The **chloride** data are typical of the trends expected for a component that is fully soluble at all dilution levels. The concentration in solution falls with increasing dilution in a predictable pattern (see discussion of nitrite below). Presumably, all of the chloride is in solution at 50% dilution for both temperatures. The total liquid volume, though, is smaller at 25 °C because there are fewer total salts dissolved, as evidenced by the volume of centrifuged solids (67% at 25 °C vs. 38% at 50 °C, cf. Table 4-1). Therefore, the chloride concentration is significantly higher at 25 °C than at 50 °C. The concentration curves for the two temperatures converge at higher dilution because the liquid volumes are less different after the major salts have dissolved.

The **fluoride** data, in contrast, show the behavior of a sparingly soluble component that becomes increasingly soluble as the ionic strength of the solution drops with dilution. Fluoride concentration rises with dilution from 50 to 200% dilution, then begins to fall with further dilution. The shape of the curve in Figure 1 implies that there are fluoride-containing solids present until approximately 200-250% dilution. The solid phase responsible for controlling the behavior of the fluoride ion is open to speculation at this point. Candidates include NaF, Na3FSO4, and $Na_7F(PO_4)_2 \cdot 19H_2O$, and indeed a mixture of the candidates is possible. The solubility of the fluoride-phosphate double salt is known to be very temperature dependent (Beahm 1998), and may be responsible for the large difference between the two temperature points at 50% dilution. To further the same argument, at 100-200% dilution all of the fluoride-phosphate double salt would be dissolved, and the solubility of the remaining solid phase(s) would have little or no dependence on temperature. Solubility dependence on ionic strength remains high, though, implicating the fluoride-sulfate double salt. The presence of this salt is further implied by the sulfate data (*vide infra*).

Figure 5-1. Tank BY-102 Chloride, Fluoride, Oxalate

(open symbols 25 °C; closed symbols 50 °C)

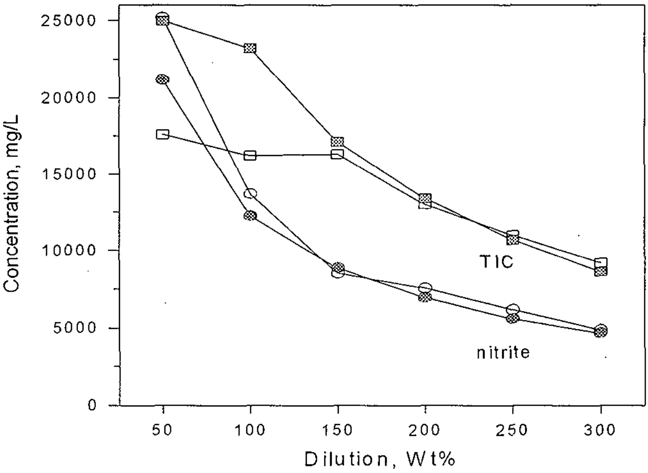


The **oxalate** data show a continual increase in liquid phase concentration with dilution throughout the dilution range. The undissolved solids at 250% dilution still include sodium oxalate, and probably at 300% dilution as well. The effect of temperature on solubility of sodium oxalate has been studied with simulated waste solutions over the temperature range of 25 to 50 °C (Barney 1997). The observed solubility was lowest at 25 °C and highest at 30 °C. Under conditions of pH and ionic strength roughly matching the current conditions, the Barney data show sodium oxalate solubility approximately 20% higher at 50 °C than at 25 °C. On an absolute scale, however, the agreement between the current data and the Barney data is not good – the current data are approximately one order of magnitude higher in oxalate concentration than the Barney data.

Figure 5-2 shows dilution trends for nitrite and carbonate (measured as TIC). The **nitrite** data are typical of a component (sodium nitrite) that is fully soluble at all dilution levels. At 50% dilution, nitrate concentration is higher at 25 °C than at 50 °C because of the smaller solution volume at 25 °C, as discussed above for chloride. The temperature curves converge at higher dilution. The 50 °C data are plotted in Figure 5-3 as the ratio of the concentration at 50% dilution (C_o) to the concentration at each higher dilution level (C). The line in Figure 5-3 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 solids occurring with dilution would cause the points to deviate from the linear relationship. **Nitrate** data are not plotted. They follow the same pattern as the nitrite data, but at a higher concentration level.

Figure 5-2. Tank BY-102 Nitrite, TIC

(open symbols 25 °C; closed symbols 50 °C)



The **carbonate (TIC)** data follow the same simple dilution behavior above 150% dilution. At lower dilutions, there is evidence of the presence of solid-phase sodium carbonate. The fact that the solubility is significantly higher at 50 °C than at 25 °C implies that the carbonate salt is hydrated, since the solubility of the anhydrous form of sodium carbonate exhibits inverse temperature dependence.

Figure 5-3. Tank BY-102 Nitrite Ratio Plot, 50 °C

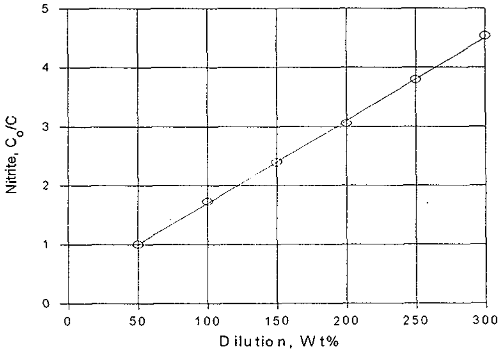
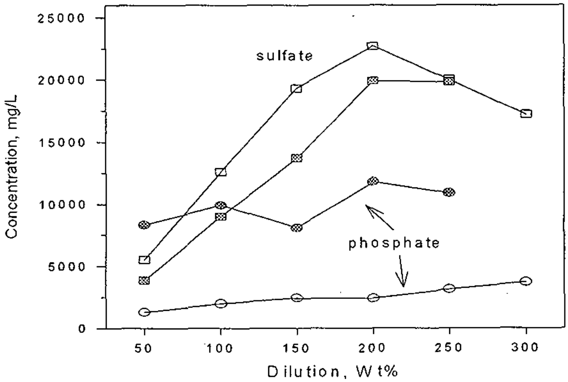


Figure 5-4 shows the dilution trends for phosphate and sulfate. The **phosphate** solubility is more temperature-dependent than any of the other salts. It is surprising, though, that the solubility doesn't increase more than it does with increasing dilution. The large temperature effect points to the double salt $Na_7F(PO_4)_2 \cdot 19H_2O$ as the solid phase, but the lack of dilution effect suggests that this is not the right species.

Figure 5-4. Tank BY-102 Phosphate, Sulfate

(open symbols 25 °C; closed symbols 50 °C)



The **sulfate** data parallel the fluoride data quite well. Concentration peaks at 200% dilution in both cases, and the sulfate:fluoride ratio is approximately 4, compared to 5.05 for the ideal ratio if the salt Na_3FSO_4 contributed all of the sulfate and fluoride. The assumption that the fluoride-phosphate double salt would also add to the fluoride level is consistent with the observed ratio being slightly lower than the ideal.

The assumption that all fluoride comes from fluoride-phosphate and fluoride-sulfate double salts provides a remarkably good fit to the observed fluoride data. At 25 °C and 50% dilution, the 1310 mg/L phosphate would account for 130 mg/L fluoride; 5520 mg/L sulfate would add 1090 mg/L fluoride; total fluoride predicted would be 1220 mg/L; observed fluoride was 1000 mg/L. Similar calculations at the other dilution/temperature levels result in the data presented in Table 5-1. The agreement between predicted and observed fluoride concentrations is compelling evidence for the presence of both fluoride double salts. The fact that the observed values are consistently slightly higher than the predicted values is evidence of a third salt, probably NaF.

Table 5-1. Fluoride Concentrations Predicted from Phosphate and Sulfate Data, Tank BY-102

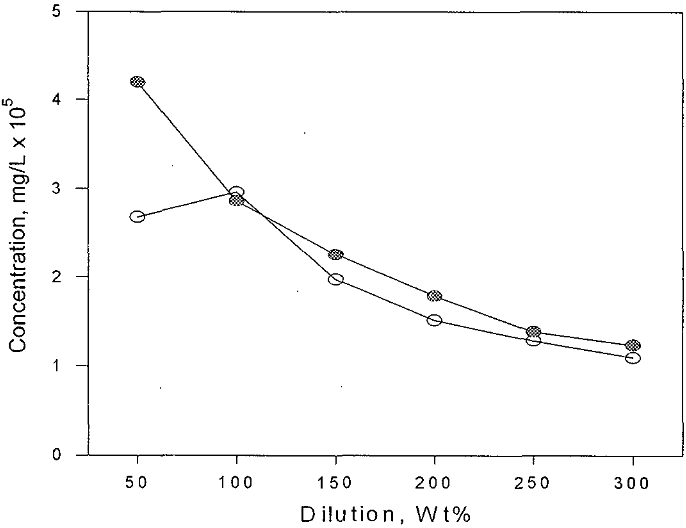
Dilution, Wt%	25 °C		50 °C	
	Predicted	Observed	Predicted	Observed
50	1220	999	1590	2120
100	2690	2780	2780	2920
150	4060	4150	3530	3890
200	4740	5530	5130	5640
250	4270	5060	5010	5490
300	3780	4460	--	--

5.2 Tank BY-106

Saltcake from tank BY-106 contains approximately ten times as much sodium nitrate as any other salt. The $NaNO_3$ dissolves readily in water. Figure 5-5 shows the concentration of **nitrate** in the liquid phase as a function of dilution. At 25 °C, there are clearly undissolved $NaNO_3$ solids at 50% dilution, but no solids remain beyond 100% dilution. At 50 °C, there is probably a trace of solid $NaNO_3$ remaining at 50% dilution. The data from 100% to 300% dilution can be plotted as the concentration ratio C_o/C, similar to Figure 5-3. (The nitrate plot is not shown.) In this case, the concentration at 100% dilution is defined as C_o. The resulting regression line can be used to predict the concentration at 50% dilution. The predicted concentration, based on the 50 °C data, is 477,000 mg/L, which is only a little higher than the 420,000 mg/L observed (Table 3-12).

Figure 5-5. Tank BY-106 Nitrate Concentrations

(open symbols 25 °C; closed symbols 50 °C)



Other components follow dilution patterns similar or analogous to those in waste from tank BY-102. Figure 5-6 shows the nitrite and TIC data. **Nitrite** is unsaturated at all dilution levels. **Carbonate** appears to be unsaturated at all levels at 25 °C, but there are undissolved solids at 50% dilution and 50 °C. If the anhydrous sodium carbonate exists under the latter conditions, then it is likely that its solubility would be lower than the solubility of the hydrated salt was at 25 °C, so the observed data are not inconsistent. However, the possibility of an analytical error in either the 25 or 50 °C data at 50% dilution can't be ruled out.

Figure 5-6. Tank BY-106 Nitrite, TIC

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

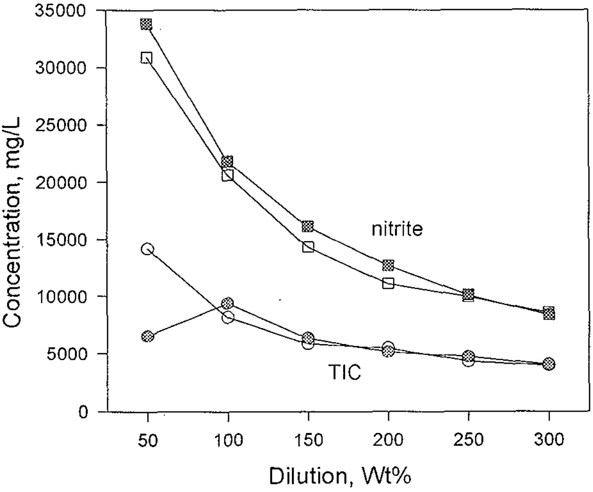
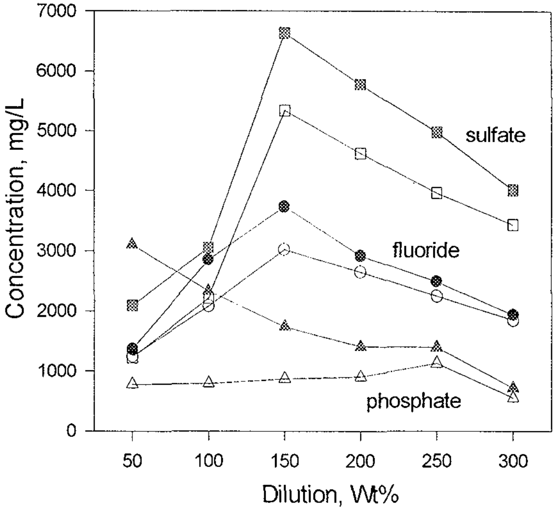


Figure 5-7 shows the concentration data for **fluoride, phosphate and sulfate**. Trends for fluoride and sulfate are parallel, but the fluoride concentration is two to four times higher than what would be predicted from the contributions from fluoride-sulfate and fluoride-phosphate double salts. Apparently, much or most of the fluoride in BY-106 waste comes from the simple NaF salt.

Figure 5-7. Tank BY-106 Fluoride, Phosphate, Sulfate

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

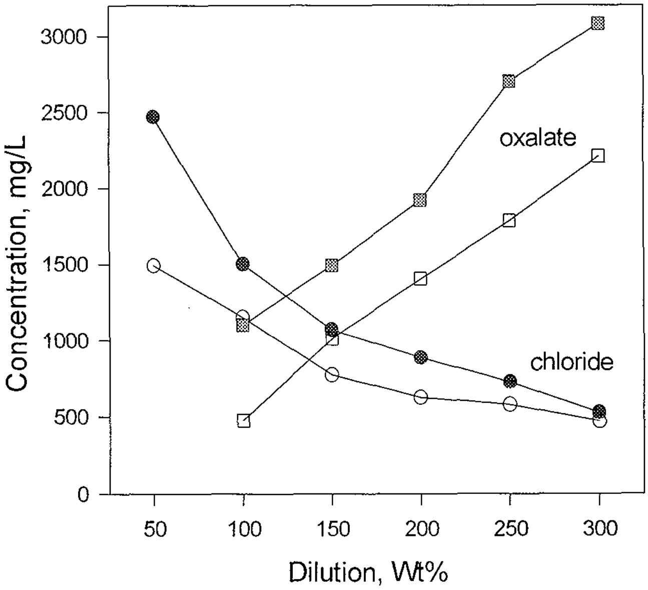


The temperature dependence of the **sulfate** concentration is rather perplexing, especially when comparing the results for BY-102 and BY-106. In BY-102 waste (see Figure 5-4), the sulfate was more soluble at 25 °C, and in BY-106 waste the sulfate is more soluble at 50 °C. Furthermore, for BY-106, the two curves for the different temperatures should converge at high dilution where [presumably] all of the sulfate is dissolved, but they do not.

Sodium oxalate solubility (Figure 5-8) increases steadily with dilution and falling ionic strength, as expected. The concentrations are approximately the same at all dilutions as those found for the tank BY-102 study. The **chloride** data (also Figure 5-8) show the same perplexing temperature differences noted above for sulfate. With all of the chloride in solution at all dilution levels, the temperature curves should nearly coincide, except for differences in solution volumes which should be relatively small. There is no apparent reason for the chloride concentration to be higher at 50 °C than at 25 °C.

Figure 5-8. Tank BY-106 Chloride, Oxalate

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



6.0 POLARIZED LIGHT MICROSCOPY

The polarized light microscope (PLM) provides a convenient tool for identifying solid crystalline phases in waste samples. Crystal size and shape (morphology) and optical properties (number of unique refractive indexes, approximate birefringence, extinction position) can be determined by simple microscopic observation of the crystals with polarized light. Each crystalline phase has a "fingerprint" set of physical and optical properties that make it identifiable virtually at a glance. Several types of crystalline phases common to Hanford waste have been fingerprinted this way and catalogued (Herting 1992).

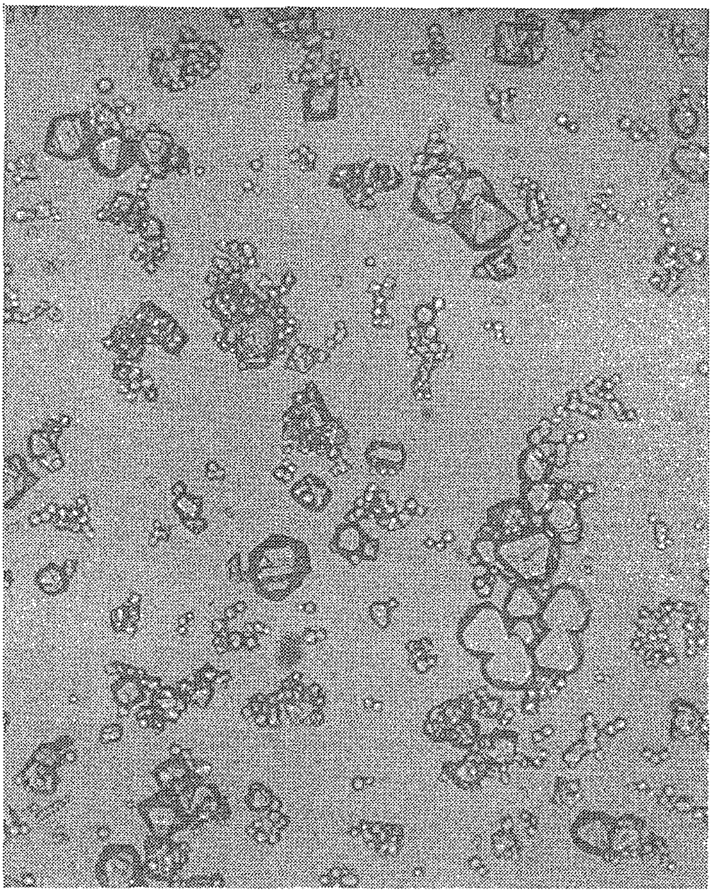
6.1 Tank BY-102

As noted previously, all of the 50 °C liquid samples from the tank BY-102 series dilution test formed crystals when the liquids cooled to ambient temperature. One drop of slurry from each of these samples was examined by PLM. In all cases, the crystals were isotropic (only one refractive index) and octahedral (belonging to the cubic crystal system). The size varied from sample to sample (see Figures 6-1 and 6-2). Crystals matching these properties have previously been identified as the fluoride-phosphate double salt $Na_7F(PO_4)_2 \cdot 19H_2O$. Sodium fluoride (NaF) crystals have similar properties, but have not been observed to precipitate in such quantity from cooled solutions, as the double salt crystals have been (Herting 1996).

6.2 Tank BY-106

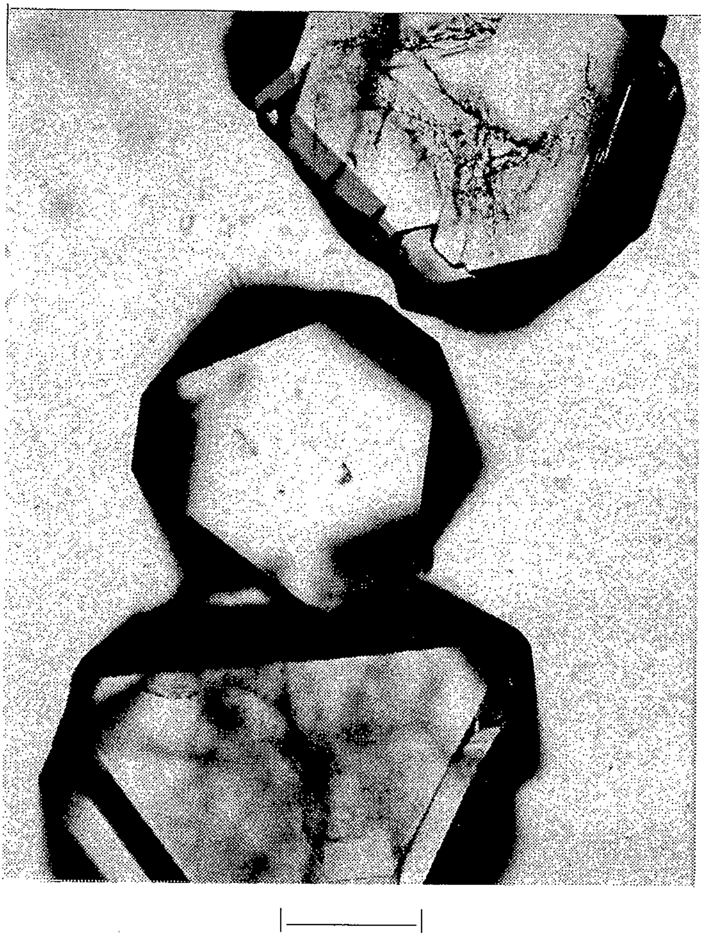
The liquid from the second wash step in the sequential dissolution test on BY-106 waste was expected to be saturated in sodium oxalate, but not in any other sodium salts. A portion of the wash liquid was evaporated in an open beaker on a magnetic stirplate until crystals began to form. A drop of the slurry was examined by PLM. The crystals (Figure 6-3) were elongated rods with moderate birefringence. They were positively identified as sodium oxalate by precipitating known sodium oxalate crystals under similar conditions in a simulated waste matrix. Further evaporation of the wash liquid produced a mixture of several types of crystals including $NaNO_3$, $Na_2CO_3 \cdot H_2O$, and some unidentified crystals. Further development work on identification of crystalline phases by a combination of PLM and x-ray analysis is planned for next fiscal year.

Figure 6-1. Crystals Formed when BY-102 Liquid Cooled from 50 °C to Ambient Temperature; Examples of Smaller Crystals



crystals identified as sodium fluoride diphosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$

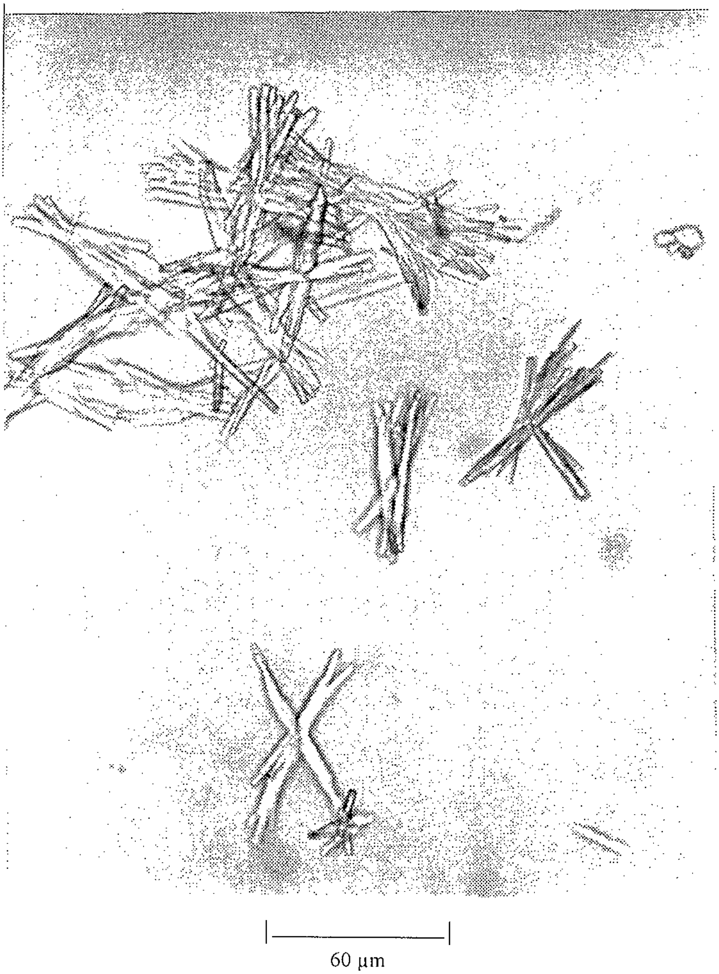
Figure 6-2. Crystals Formed when BY-102 Liquid Cooled from 50 °C to Ambient Temperature; Examples of Larger Crystals



200 µm

crystals identified as sodium fluoride diphosphate, $Na_7F(PO_4)_2 \cdot 19H_2O$

Figure 6-3. Crystals Formed by Evaporation of BY-106 Liquid from 2nd Water Wash



crystals identified as sodium oxalate, $Na_2C_2O_4$

7.0 PHASE DISTRIBUTION ANALYSIS

The analytical data from the sequential dissolution tests can be used to calculate bulk waste compositions and solid/liquid phase distributions at 100% dilution and ambient temperature.

7.1 Tank BY-102

7.1.1 Physical Sample Data

Table 7-1 contains a summary of the physical measurement data used to calculate the bulk composition and phase distributions. Columns labeled "SEQA" and "SEQB" contain data recorded for each individual [duplicate] centrifuge cone. The column labeled "Total" represents either the sum of the individual cone entries or the analysis of the sample created by combining the contents of the two cones (see Section 2.2).

Table 7-1. Summary of Measurements from BY-102 Sequential Dissolution Test (weights in grams, volumes in mL)

Measurement	SEQA	SEQB	Total
Sample Weight	30.670	32.183	62.853
Wt H_2O Added	29.310	30.278	59.588
Wt 1st H_2O Wash	36.985	46.239	83.224
Vol 1st H_2O Wash	29.0	36.0	65.0
Density 1st H_2O Wash			1.232
%H_2O 1st H_2O Wash			69.0[a]
Wt Centrifuged Solids	22.995	16.222	39.127
Wt H_2O Added	30.171	29.160	59.331
Wt 2nd H_2O Wash	44.538	36.514	81.052
Vol 2nd H_2O Wash	38.5	32.0	70.5
Density 2nd H_2O Wash			1.125
%H_2O 2nd H_2O Wash			84.0
Final Wt Centrifuged Solids	8.628	8.868	17.496
%H_2O Centrifuged Solids			56.97

[a] corresponds to 48% H_2O in centrifuged solids after 1st wash (which wasn't measured)

7.1.2 Composition by Fractions

Table 7-2 shows the weight in grams of each component in the 1st water wash, 2nd water wash, centrifuged solids, and total sample (sum of the three fractions). The column labeled "Wt%" is the total sample value for each component divided by the total sample weight from Table 7-1. The weights in each wash solution are found by multiplying the analytical result (Table 3-2) by the wash solution volume (Table 7-1). Similarly, the CSol weight come from the analytical result (again Table 3-2) times the final weight of centrifuged solids (Table 7-1).

Table 7-2. Tank BY-102 Analysis by Fractions[1]
(all values in grams)

Analyte	1st Wash	2nd Wash	CSol	Total	Wt%
Al	0.57	0.09	0.38	1.04	1.65
Ca			0.027	0.027	0.04
Cr	0.072	0.012	0.041	0.125	0.20
Fe			0.033	0.033	0.05
K	0.086			0.086	0.14
Mn			0.015	0.015	0.02
Na	10.14	4.94	2.38	17.45	27.8
Ni			0.017	0.017	0.03
P	0.039	0.081	0.51	0.63	1.00
S	0.23	0.95	0.094	1.28	2.04
Si	0.017	0.010	0.019	0.045	0.07
U			0.040	0.040	0.06
F^-	0.18	0.56	na	0.74	1.17
Cl^-	0.069		na	0.069	0.11
NO_2^-	0.96	0.20	na	1.16	1.85
NO_3^-	6.00	0.87	na	6.87	10.9
PO_4^{2-}	0.11	0.27	na	0.38	0.60
SO_4^{2-}	0.68	2.54	na	3.22	5.12
$C_2O_4^{2-}$	0.06	0.27	0.20[4]	1.20	1.99
TIC	2.13	0.42	0.06	2.60	4.13
TOC	0.066	0.078	0.25	0.40	0.63
OH^-	0.59	0.10	na	0.69	1.09
^{137}Cs (mCi)	2.35	0.44	na	2.79	--
H_2O	57.42	68.08	9.97	16.68	26.5
Total Mass Calculated[2]	88.4	80.1	16.3	65.8	104.6
Total Mass Measured[3]	83.2	81.1	17.5	62.9	100.0

[1] Blank entries indicate analytical result was below detection limit.

[2] Sum of individual components (see text for details).

[3] Actual weights of wash solutions, centrifuged solids, and total sample.

[4] Calculated assuming TOC is 100% oxalate in the centrifuged solids.

The "Total Mass Calculated" in Table 7-2 and following tables represents the sum of the individual components in each fraction. The basic formula is:

$$\text{Total Mass Calc} = \sum_i M_i + 3M_{TOC} + 5M_{TIC} + (59/27)M_{Al}$$

where M_i is the mass in grams of each metal ion (Al through U but not P or S) and anion (F^- through SO_4^{2-} plus OH^-) and H_2O. Masses of TOC, TIC, and Al are adjusted to account for the weight of oxygen and other elements associated with the aluminum and carbon. The TOC multiplier is based on the molecular weight to carbon weight ratio of "typical" organic compounds likely to be present in the waste, such as acetate and chelating agents. The TIC multiplier converts carbon to carbonate. The Al multiplier converts Al to AlO_2^-, the anhydrous form of the aluminate ion, $Al(OH)_4^-$. The anhydrous form is used because the hydration water is included in the H_2O mass as determined by TGA or oven-drying. No attempt was made to account for speciation of the more minor components.

In some cases, modifications to the basic formula are necessary. Where oxalate values are higher than the TOC would account for, the mass of oxalate is used instead of the adjusted mass of TOC. Where P values are higher than one-third of the corresponding phosphate values, the P mass is used and adjusted by the multiplier (95/31) to convert mass of P to mass of PO_4^{3-}.

The "Total Mass Measured" in Table 7-2 and following tables is based on actual weights of fractions (initial sample, wash solutions, and centrifuged solids) recorded during the centrifuge cone phase separations. These values are taken from Table 7-1.

The agreement between Total Mass Calculated and Total Mass Measured provides an estimate of the degree of reliability of the analytical results and the calculations performed. Agreement within ±5% is considered good.

7.1.3 Solid/Liquid Phase Distribution

Table 7-3 (next page) is similar to Table 7-2. In Table 7-3, all results are "normalized" to 100 grams of composite sample. This table shows breakdown by solid/liquid phase distribution.

The first data column ("Total Sample") shows the amount of each analyte present in 100 g saltcake, regardless of whether it is present in the solid or liquid phase. The value is the same as that found in the "Wt%" column in Table 7-2. The H_2O entry in this column includes the 100 g dilution water added per 100 g saltcake.

The second data column ("Supernate") shows the weight of each component present in the supernatant liquid decanted from the sample at 100% by weight dilution. This is calculated by normalizing (dividing by total sample weight and multiplying by 100) the values from Table 7-2 "1st Wash". Comparing this column with the previous one provides an estimate of how much of each component in the saltcake waste would be retrievable by pumping the liquid from the tank after a 1:1 dilution (by weight) with water at 25 °C.

Table 7-3. Tank BY-102 Solid/Liquid Phase Distribution at 100% Dilution[1]
(all values in grams per 100 grams of saltcake sample)

Analyte	Total Sample	Supernate	Interstitial Liquid	Total Liquid	Undissolved Solids	% Undissolved
Al	1.65	0.90	0.28	1.18	0.46	28
Ca	0.043				0.043	100
Cr	0.199	0.115	0.036	0.151	0.048	24
Fe	0.053				0.053	100
K	0.136	0.136	0.043	0.179	-0.043	0
Mn	0.024				0.024	100
Na	27.75	16.12	5.09	21.21	6.54	24
Ni	0.026				0.026	100
P	0.998	0.062	0.020	0.082	0.916	92
S	2.03	0.37	0.12	0.49	1.55	76
Si	0.072	0.027	0.008	0.035	0.037	51
U	0.064				0.064	100
F^-	1.17	0.28	0.09	0.37	0.80	69
Cl^-	0.11	0.11	0.035	0.14	-0.035	0
NO_2^-	1.85	1.53	0.48	2.01	-0.16	0
NO_3^-	10.92	9.54	3.01	12.55	-1.63	0
PO_4^{3-}	(0.60)	0.17	0.06	0.23	(0.37)	see P
SO_4^{2-}	5.12	1.08	0.34	1.43	3.69	72
$C_2O_4^{2-}$	1.99	0.10	0.03	0.13	1.86	94
TIC	4.13	3.38	1.07	4.45	-0.32	0
TOC	0.63	0.105	0.033	0.14	0.49	78
OH^-	1.09	0.93	0.29	1.23	-0.14	0
^{137}Cs (mCi)	4.44	3.73	1.18	4.91	-0.47	0
H_2O	126.51	91.30	35.21	126.51	0.00	0 (assumed)
Total Mass Calculated[2]	204.3	140.5	50.8	190.1	18.9	--
Total Mass Measured[3]	200.0	132.4	51.0	183.4	16.6	--

[1] Blank entries indicate analytical result was below detection limit.
[2] Sum of individual components (see text for details).
[3] Actual weights of wash solutions, centrifuged solids, and total sample.
[4] Calculated assuming TOC is 100% oxalate in the centrifuged solids.

The next column shows how much of each component remains in the interstitial liquid of the centrifuged solids after the 1st water wash. This is calculated by assuming that all of the water in the centrifuged solids is associated with interstitial liquid. This assumption is in error to the extent that some of the undissolved salts may contain waters of hydration. The values in this column represent a fraction of the corresponding Supernate column values, where the fraction is determined by the %H_2O analyses.

The "Total Liquid" column represents the sum of the two previous columns. "Undissolved Solids" is the Total Sample minus the Total Liquid. Negative numbers in this column point out obvious (but small) errors in the data, which are probably related to the assumption used to assign the amount of interstitial liquid present.

The last column ("%Undissolved) represents the fraction of each component that remains in the solid phase relative to the total amount of that component present in the sample.

7.2 Tank BY-106

Tables 7-4 through 7-6 have the same explanations as the corresponding tables for tank BY-102. Tank BY-106 saltcake contains a much higher percentage of $NaNO_3$ than tank BY-102 saltcake, and is much more soluble at 100% dilution. As shown in Tables 7-3 and 7-6, the total amount of undissolved solids is approximately 3% of the initial sample weight for BY-106, compared to 17% for BY-102.

Table 7-4. Summary of Measurements from BY-106 Sequential Dissolution Test (weights in grams, volumes in mL)

Measurement	SEQA	SEQB	Total
Sample Weight	30.017	30.091	60.108
Wt H_2O Added	30.026	30.139	60.165
Wt 1st H_2O Wash	53.341	54.005	107.346
Vol 1st H_2O Wash	40.3	41.9	82.2
Density 1st H_2O Wash			1.336
%H_2O 1st H_2O Wash			58.2[a]
Wt Centrifuged Solids	6.702	6.225	12.927
Wt H_2O Added	29.440	31.020	60.460
Wt 2nd H_2O Wash	34.572	35.992	70.564
Vol 2nd H_2O Wash	31.0	32.5	63.5
Density 2nd H_2O Wash			1.087
%H_2O 2nd H_2O Wash			91.4
Final Wt Centrifuged Solids	1.570	1.253	2.823
%H_2O Centrifuged Solids			69.91

[a] corresponds to 50% H_2O in centrifuged solids after 1st wash (which wasn't measured)

Table 7-5. Tank BY-106 Analysis by Fractions[1]
(all values in grams)

Analyte	1st Wash	2nd Wash	CSol	Total	Wt%
Al	0.85	0.07	0.04	0.95	1.59
Ca			0.008	0.008	0.01
Cr	0.020	0.002	0.046	0.068	0.11
Fe			0.013	0.013	0.02
K	0.136	0.010		0.146	0.24
Mn			0.001	0.001	0.00
Na	12.90	1.87	0.24	15.01	25.0
Ni			0.003	0.003	0.01
P	0.020	0.025	0.002	0.047	0.08
S	0.077	0.185	0.007	0.268	0.45
Si	0.007	0.002	0.001	0.010	0.02
U	0.012			0.012	0.02
F^-	0.17	0.20	na	0.37	0.62
Cl^-	0.091	0.007	na	0.098	0.16
NO_2^-	1.50	0.13	na	1.63	2.71
NO_3^-	22.43	1.93	na	24.37	40.5
PO_4^{3-}	0.12	0.08	na	0.20	0.34
SO_4^{2-}	0.14	0.56	na	0.70	1.16
$C_2O_4^{2-}$	0.04	0.47	0.25[4]	0.76	1.26
TIC	0.79	0.07	0.004	0.86	1.43
TOC	0.08	0.12	0.08	0.29	0.48
OH^-	0.63	0.06	na	0.69	1.14
^{137}Cs (mCi)	4.31	0.40	na	4.71	--
H_2O	62.48	64.50	1.97	8.84	14.7
Total Mass Calculated[2]	106.7	70.3	3.0	59.6	99.1
Total Mass Measured[3]	107.3	70.6	2.8	60.1	100.0

[1] Blank entries indicate analytical result was below detection limit.

[2] Sum of individual components (see text for details).

[3] Actual weights of wash solutions, centrifuged solids, and total sample.

[4] Calculated assuming TOC is 100% oxalate in the centrifuged solids.

Table 7-6. Tank BY-106 Solid/Liquid Phase Distribution at 100% Dilution[1]
(all values in grams per 100 grams of saltcake sample)

Analyte	Total Sample	Supernate	Interstitial Liquid	Total Liquid	Undissolved Solids	% Undissolved
Al	1.58	1.41	0.15	1.56	0.03	2
Ca	0.013				0.013	100
Cr	0.113	0.034	0.003	0.037	0.076	67
Fe	0.019				0.019	100
K	0.243	0.227	0.024	0.251	-0.008	0
Na	24.98	21.47	2.24	23.71	1.27	5
Ni	0.006				0.006	100
P	0.078	0.033	0.003	0.036	0.042	54
S	0.447	0.128	0.013	0.142	0.305	68
Si	0.017	0.012	0.001	0.013	0.004	24
U	0.019				0.019	100
F^-	0.62	0.28	0.03	0.32	0.30	49
Cl^-	0.16	0.15	0.02	0.17	-0.01	0
NO_2^-	2.71	2.49	0.26	2.75	-0.04	0
NO_3^-	40.54	37.32	3.89	41.22	-0.68	0
PO_4^{3-}	0.34	0.20	0.02	0.23	0.11	34
SO_4^{2-}	1.16	0.23	0.02	0.26	0.90	78
$C_2O_4^{2-}$	1.26	0.06	0.01	0.07	1.19	94
TIC	1.43	1.31	0.14	1.45	-0.02	0
TOC	0.48	0.13	0.01	0.14	0.33	70
OH^-	1.14	1.05	0.11	1.16	-0.02	0
^{137}Cs (mCi)	7.83	7.17	0.75	7.91	-0.08	0
H_2O	114.70	103.95	10.75	114.70	0.00	0 (assumed)
Total Mass Calculated[2]	199.2	177.6	18.4	196.1	4.0	--
Total Mass Measured[3]	200.0	178.6	18.5	197.1	2.9	--

[1] Blank entries indicate analytical result was below detection limit.

[2] Sum of individual components (see text for details).

[3] Actual weights of wash solutions, centrifuged solids, and total sample.

[4] Calculated assuming TOC is 100% oxalate in the centrifuged solids.

7.3 Tank B-106

Tables 7-7 through 7-9 have the same explanations as the corresponding tables for tank BY-102. Inhibited water (0.01 M NaOH and 0.01 M $NaNO_2$) was used for the dilution rather than pure H_2O because of the initial low pH (< 12) of the composite sample. Tank B-106 waste has many of the properties of a sludge, as well as some properties of a saltcake. The initial high water content (58% H_2O) and low pH are typical of a sludge. On the other hand, $NaNO_3$ makes up a very high percentage of the non-H_2O fraction of the waste, typical of a saltcake.

Table 7-7. Summary of Measurements from B-106 Sequential Dissolution Test with Inhibited Water Diluent (weights in grams, volumes in mL)

Measurement	SEQA	SEQB	Total
Sample Weight	25.712	25.999	51.711
Wt inh. H_2O Added	25.012	24.981	49.993
Wt 1st H_2O Wash	37.792	37.903	75.695
Vol 1st H_2O Wash	33.8	34.5	68.35
Density 1st H_2O Wash			1.107
%H_2O 1st H_2O Wash			84.1[a]
Wt Centrifuged Solids	12.932	13.077	26.009
Wt inh. H_2O Added	24.974	25.061	50.035
Wt 2nd H_2O Wash	25.633	25.741	51.374
Vol 2nd H_2O Wash	25.1	25.0	50.1
Density 2nd H_2O Wash			1.023
%H_2O 2nd H_2O Wash			95.7
Final Wt Centrifuged Solids	12.273	12.397	24.670
%H_2O Centrifuged Solids			76.7

[a] corresponds to 67% H_2O in centrifuged solids after 1st wash (which wasn't measured)

Corresponding data for the dissolution in 3 M NaOH are not shown. Refer to Tables 3-14 and 3-15 for the analytical results. The 3 M NaOH enhanced the solubility of aluminum, which is a minor component, and depressed the solubility of phosphate, which is only sparingly soluble in either diluent. It had little or no effect on the major components, relative to inhibited water as the diluent.

Table 7-8 Tank B-106 Analysis by Fractions, Inhibited Water Diluent[1]
(all values in grams)

Analyte	1st Wash	2nd Wash	CSol	Total	Wt%
Al			0.12	0.12	0.23
Bi			0.13	0.13	0.24
Ca			0.12	0.12	0.23
Cr	0.001		0.009	0.010	0.02
Fe			0.68	0.68	1.31
K	0.007	0.001		0.008	0.02
Mg			0.029	0.029	0.06
Na	3.17	0.69	1.05	4.91	9.49
Ni			0.002	0.002	0.01
P	0.23	0.06	0.69	0.98	1.90
S	0.20	0.04	0.02	0.26	0.49
Sr			0.018	0.018	0.04
U			0.47	0.47	0.90
F^-	0.036	0.027	na	0.063	0.12
Cl^-	0.048	0.009	na	0.057	0.11
NO_2^-	0.39	0.08	na	0.47	0.90
NO_3^-	7.04	1.34	na	8.38	16.20
PO_4^{3-}	0.77	0.18	na	0.95	1.83
SO_4^{2-}	0.50	0.10	na	0.60	1.15
$C_2O_4^{2-}$	not detected in any fractions				
TIC	0.011	0.003	0.003	0.017	0.03
TOC	0.014	0.003	0.009	0.026	0.05
OH^-	not detected in any fractions				
^{137}Cs (mCi)	0.15	0.025	na	0.175	--
H_2O	63.66	49.16	18.92	29.99	58.00
Total Mass Calculated[2]	75.7	51.6	23.9	49.4	97.1
Total Mass Measured[3]	75.7	51.4	24.7	51.7	100.0

[1] Blank entries indicate analytical result was below detection limit.

[2] Sum of individual components (see text for details).

[3] Actual weights of wash solutions, centrifuged solids, and total sample.

Table 7-9. Tank B-106 Solid/Liquid Phase Distribution at 100% Dilution[1]
with Inhibited Water Diluent
(all values in grams per 100 grams of saltcake sample)

Analyte	Total Sample	Supernate	Interstitial Liquid	Total Liquid	Undissolved Solids	% Undissolved
Al	0.23				0.23	100
Bi	0.25				0.25	100
Ca	0.24				0.24	100
Cr	0.020	0.002	0.001	0.003	0.018	87
Fe	1.31				1.31	100
K	0.016	0.014	0.004	0.017	-0.001	0
Mg	0.057				0.057	100
Na	9.49	6.13	1.64	7.78	1.71	18
Ni	0.004				0.004	100
P	1.90	0.45	0.12	0.57	1.33	70
S	0.49	0.38	0.10	0.48	0.01	2
Si	0.018	0.001		0.001	0.017	94
Sr	0.034				0.034	100
U	0.91				0.91	100
F^-	0.12	0.07	0.02	0.09	0.03	27
Cl^-	0.11	0.09	0.02	0.12	-0.01	0
NO_2^-	0.91	0.76	0.20	0.96	-0.05	0
NO_3^-	16.20	13.62	3.65	17.27	-1.06	0
PO_4^{3-}	(1.83)	1.49	0.40	1.90	see P	
SO_4^{2-}	1.15	0.96	0.26	1.21	-0.06	0
TIC	0.033	0.021	0.006	0.027	0.006	18
TOC	0.051	0.027	0.007	0.034	0.017	33
^{137}Cs (mCi)	0.34	0.29	0.08	0.37	-0.03	0
H_2O	158.01	123.12	34.88	158.01	0.00	0 (assumed)
Total Mass Calculated[2]	195.8	146.5	41.1	187.6	10.2	--
Total Mass Measured[3]	200.0	146.4	41.5	187.9	12.1	--

[1] Blank entries indicate analytical result was below detection limit.
[2] Sum of individual components (see text for details).
[3] Actual weights of wash solutions, centrifuged solids, and total sample.
[4] Calculated assuming TOC is 100% oxalate in the centrifuged solids.

8.0 COMPARISONS

This section is devoted to comparisons of the current data with computer modeling predictions, with Tank Characterization Report (TCR) characterization data, and with prior sludge washing studies.

8.1 COMPUTER MODELING

Computer simulations of the saltcake series dissolution tests for tanks BY-102 and BY-106 were conducted by investigators at Mississippi State University using the Environmental Simulation Program (ESP). The full results of the modeling will be published by them in the near future. A brief summary is provided here.

Analytical results from the sequential dissolution experiments were used as input to the ESP program. All anions from the analysis were included, and all cations present at concentrations > 150 ppm were included in the simulation for each tank waste studied. Limits imposed on the number of interphase and intraphase equilibrium relationships which can be considered by ESP necessitated the exclusion of cations present at low concentrations. The input data were reconciled for electroneutrality and for pH. The result of these reconciliation processes was a stream with the molecular composition which reproduced the measured analytical data.

Dilution ratios of 0% to 500 % by weight (100% dilution = 1 g saltcake/1 g diluent) were considered. For tanks BY-102 and BY-106, dilution with water at 25 °C and 50 °C were simulated. For both tanks, major trends in the experimental data were seen in the simulation results. At dilution ratios of 100% and higher, quantitative prediction was obtained for all major anions (Cl^-, NO_2^-, NO_3^-, $C_2O_4^{2-}$, F^-, PO_4^{3-}, SO_4^{2-}, TIC). At dilution ratios of less than 100%, quantitative prediction was obtained only for select anions (Cl^-, NO_2^-, $C_2O_4^{2-}$, TIC).

The major salt predicted in the solid phase at 0 % dilution is sodium nitrate. A maximum in the nitrate concentration is predicted at ca. 40% dilution by simulation. The nitrate concentration then exhibits classic exponential decay at higher dilution ratios. Other species predicted to be present in the solid phase at 0% dilution include $Na_7F(PO_4)_2 \cdot 19H_2O$ and Na_3FSO_4. The anions associate with these species showed marked discrepancies between the concentrations predicted by ESP and those measured experimentally at dilution ratios < 100%. This indicates a need to further examine the solid-liquid equilibrium behavior for these double salt systems through well-defined laboratory experiments. Also beneficial in this effort would be speciation data on the solid phase, verifying that these double salts are indeed present in the undissolved saltcake.

8.2 COMPARISONS WITH TCR DATA AND SLUDGE WASH DATA

Tank Characterization Reports (TCRs) have been published for all three tanks. The following tables provide comparisons of the current data with the core sample characterization data from the TCRs. For tank B-106, comparisons are also made with data from prior sludge washing tests.

In general, the agreement between the current data and TCR data is very good, but there are some differences. There are two reasons for these discrepancies – analytical errors and genuine sample differences.

The TCR data are typically averages of a large number of analytical determinations. Current data are single determinations or, at best, an average of two determinations. As a rule of thumb, analytical values are generally considered accurate to approximately ± 10%. Larger differences between current data and TCR data are likely due to genuine differences in sample composition. These differences may indicate the variations in composition likely to be encountered within the tank waste during retrieval operations.

Composite samples for the current study were derived from a limited number of archived core segment samples. There is no guarantee that these composite samples accurately represent the overall tank waste composition. However, the solubility studies are at least internally consistent, because all of the tests for each tank were done on a single homogenized composite sample.

8.2.1 Tank BY-102

Table 8-1 shows the comparison between the TCR data (Sasaki 1997) and the current data (Total Sample column in Table 7-3) derived from the sequential dissolution tests. The TCR data are taken from Table B3-4 of the TCR, and represent the mean concentrations for solid segment sample data from the 1996 core samples.

The TCR data for metal ions are derived from fusion digest sample preparations, while the current data are derived from acid digest preparations. That might explain why certain metals are significantly higher in the TCR data (Al, Si). In general, the agreement between the two sets of data is very good, especially for the major components.

Table 8-1. Tank BY-102 Comparison with TCR Data
(all values in grams per 100 grams of saltcake sample, i.e., weight percent)

Analyte	Current Study	TCR
Al	1.65	4.16
Ca	0.043	< 0.21
Cr	0.199	0.187
Fe	0.053	< 0.19
Mn	0.024	< 0.037
Na	27.75	26.7
Ni	0.026	0.48[1]
P	0.998	< 0.95
S	2.03	1.73
Si	0.072	0.435
U	0.064	< 1.01
F^-	1.17	1.80
Cl^-	0.11	0.12
NO_2^-	1.85	1.39
NO_3^-	10.92	9.50
PO_4^{3-}	(0.60)	2.70
SO_4^{2-}	5.12	5.77
$C_2O_4^{2-}$	1.99	1.93
TIC	4.13	2.78
TOC	0.63	0.44
H_2O	26.51	26.5

[1] fusion in nickel crucible?

8.2.2 Tank BY-106

Table 8-2 shows the comparison between the TCR data (Bell 1996) and the current data (Total Sample column in Table 7-6) derived from the sequential dissolution tests. The TCR data are taken from Table 4-2 of the TCR, and represent the mean concentrations for data from the 1994-6 core samples 64, 65, and 121. Core 121 provided all of the segment samples used to make the composite sample for the current tests (see Table 2-1).

The current data tend to be higher than the corresponding TCR data, with some exceptions. The %H_2O is significantly lower for the current study, which indicates that the segment samples may have dried out somewhat during storage in the hotcells. Such drying would tend to make the other analytes appear relatively high in concentration.

Table 8-2. Tank BY-106 Comparison with TCR Data
(all values in grams per 100 grams of saltcake sample, i.e., weight percent)

Analyte	Current Study	TCR
Al	1.58	2.04 (2.87)[1]
Ca	0.013	0.031
Cr	0.113	0.086 (0.13)
Fe	0.019	0.022
K	0.243	0.247
Na	24.98	20.3 (21.1)
Ni	0.006	0.005
P	0.078	0.103
S	0.447	0.328
Si	0.017	0.018
U	0.019	0.016
F^-	0.62	0.51
Cl^-	0.16	0.21
NO_2^-	2.71	3.21
NO_3^-	40.54	32.9
PO_4^{3-}	0.34	0.53
SO_4^{2-}	1.16	1.13
$C_2O_4^{2-}$	1.26	0.90
TIC	1.43	0.74
TOC	0.48	0.25
^{137}Cs (mCi)	7.83	10.6
H_2O	14.70	25.5

[1] fusion results in parentheses; others are from acid digest

8.2.3 Tank B-106

Table 8-3 shows the comparison between the current data (Total Sample column in Table 7-9) derived from the sequential dissolution tests in inhibited water, TCR data (McCain 1996), and the data from sludge washing tests done at Los Alamos National Laboratory (Temer 1997). The TCR data are taken from Table ES-2 of the TCR, and represent the mean concentrations for segment sample data from the 1995 core samples 93 and 94. The Temer data are taken from Table 4, page 74, in that report. The Temer data are reported as "concentration in initial solids", implying that the values might be adjusted to account for moisture content.

The waste contained two obvious layers that differed in physical appearance and in chemical composition. Each core sample contained two segments. The top segment (1) from each core and the top half of the bottom segment (2) were assigned to the "top layer", and the bottom half of the bottom segment was assigned to the "bottom layer". The composite sample for the current study contained portions of segment 1 upper and lower halves, and segment 2 upper half only. Therefore, the composite sample from the current study should represent only the "top layer" of waste in the tank. The data comparison indicates, however, that the composite sample may contain some of the bottom layer waste. The composite sample for the Temer study included samples from both waste layers.

Table 8-3. Tank B-106 Comparison with TCR Data
(all values in grams per 100 grams of saltcake sample, i.e., weight percent)

Analyte	Current Study	TCR		Temer (1997)[2]
		Top Layer	Bottom Layer	
Al	0.23	0.15	1.37	0.73
Bi	0.25	0.08	1.94	0.55
Ca	0.24	0.24	0.03	0.53
Cr	0.020	0.022	0.073	0.070
Fe	1.31	1.84	8.22	3.42
Na	9.49	10.7	12.1	19.7
Ni	0.004	0.007	0.002	0.013
Si	0.018	0.15	0.44	0.30
Sr	0.034	0.051	0.015	0.097
U	0.91	1.64	0.33	3.06
F^-	0.12	0.15	1.01	na
Cl^-	0.11	0.15	0.15	na
NO_2^-	0.91	0.78	0.66	na
NO_3^-	16.20	19.4	17.0	na
PO_4^{3-}	5.82[1]	7.56	6.71	na
SO_4^{2-}	1.15	1.48	1.40	na
TOC	0.051	0.24	0.021	na
^{137}Cs (mCi)	0.34	0.22	0.12	na
H_2O	58.01	62.4	56.8	na

[1] calculated from P result in Table 7-9.

[2] reported as "concentration in initial solids", rather than initial sludge.

The current data for the percentage of each analyte undissolved in the inhibited-water wash (Table 7-9, last column) can be compared with similar data from Temer. The first step in the sludge wash experiments was an inhibited-water wash at 200% dilution (2 g H_2O/g sludge) at 100 °C for 1 hour. The current study used 100% dilution at ambient temperature for 24 hours. The percentage of each analyte remaining in the solid phase under these conditions is shown in Table 8-4.

Table 8-4. Percentage of B-106 Analyte Undissolved in Inhibited Water.

Analyte	Current Study[1]	Temer (1997)[2]
Al	100	72
Bi	100	100
Ca	100	100
Cr	87	88
Fe	100	100
K	0	32
Mg	100	100
Na	18	5
Ni	100	99
P	70	40
Si	94	95
Sr	100	100
U	100	99

[1] 100% by weight dilution, ambient temperature, 24 hour mix time.

2 200% by weight dilution, 100 °C, 1 hour mix time.

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