INFORMATION CLEARANCE REVIEW AND RELEASE APPROVAL

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This document summarizes the caustic demand measurements and solid phase characterization tests on archive samples from tanks 241-AX-101 and 241-AX-103. The work results provide a baseline to support planned retrieval of AX-101 and AX-103.

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Revision 0

TEST RESULTS FOR CAUSTIC DEMAND MEASUREMENTS ON TANK 241-AX-101 AND TANK 241-AX-103 ARCHIVE SAMPLES

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Contractor for the U.S. Department of Energy
Office of River Protection under Contract DE-AC27-08RV14800

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WRPS-1602862
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TEST RESULTS FOR CAUSTIC DEMAND MEASUREMENTS ON TANK 241-AX-101 AND TANK 241-AX-103 ARCHIVE SAMPLES

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Date Published
July 2016

WRPS

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

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APPROVED
By Janis Aardal at 12:44 pm, Oct 04, 2016

Release Approval   Date

washington river protection solutions

INTEROFFICE MEMO

WRPS-1602862 Rev. 0

Date: July 14, 2016

To: W. J. Powell
Production Operations Process Engineering

From: S. R. Doll, Chemist
S. D. Bolling, Chemist
Process Chemistry

Subject: TEST RESULTS FOR CAUSTIC DEMAND MEASUREMENTS ON TANK 241-AX-101 AND TANK 241-AX-103 ARCHIVE SAMPLES

Reference: WRPS-1505529, 2016, "Test Plan and Procedure for Caustic Demand Testing on Tank 241-AX-101 and Tank 241-AX-103 Archive Samples," (internal letter from D. L. Herting to W. J. Powell, January 18), Washington River Protection Solutions LLC, Richland, Washington.

Results Summary:

Caustic demand testing has been completed on three archive samples: a single segment sample from tank 241-AX-101, a composite sample from tank 241-AX-101, and a composite sample from tank 241-AX-103. This fulfilled the requirement of the test plan (Reference). Test results showed a caustic demand of 0.05-0.08 moles of hydroxide per kg of tank waste for 241-AX-101 segment 1 and zero caustic demand for the 241-AX-101 and 241-AX-103 composite samples. The caustic demand for segment 1 can be attributed to the reaction of disodium phosphate with NaOH:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

Detailed results for the solid phase characterization tests are presented in the Enclosure to this memo.

If you have any questions or comments regarding the AX-101 and AX-103 caustic demand studies or the analyses results presented, please contact Stephanie Doll at 373-6381 or Stacey Bolling at 373-1990.

SRD:PLP

Enclosure: TEST RESULTS FOR CAUSTIC DEMAND MEASUREMENTS ON TANK 241-AX-101 AND TANK 241-AX-103 ARCHIVE SAMPLES (77 pages)

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ENCLOSURE

TEST RESULTS FOR CAUSTIC DEMAND MEASUREMENTS ON TANK 241-AX-101 AND TANK 241-AX-103 ARCHIVE SAMPLES

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Abbreviations and Acronyms

AX-101	tank 241-AX-101
AX-103	tank 241-AX-103
DL	detection limit
EDS	energy dispersive spectroscopy
EQL	estimated quantitation limit
IC	ion chromatography
ICP	inductively coupled plasma
ISL	interstitial liquid in solids (including dissolved salts)
MDL	method detection limit
PLM	polarized light microscopy
QAPP	Quality Assurance Project Plan
QC	Quality Control
RPD	relative percent difference
SEM	scanning electron microscopy
SPC	solid phase characterization
TC	total carbon
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TOC	total organic carbon
TWINS	Tank Waste Inventory Network System
WHL	WAI Hanford Laboratory
XRD	X-ray diffraction

Units

Å	Angstrom
ºC	degrees Celsius
g	gram
hr	hour
kg	killogram
L	liter
µg	micrograms
µm	micrometer
mEq	milliequivalents
mg	milligram
mL	milliliter
mmol	millimole
min	minute
M	molarity or moles per liter
mol	mole
pH	hydrogen ion concentration
pKa	acid dissociation constant
wt%	weight percent

1 INTRODUCTION

Caustic demand testing is used to determine the necessary amount of caustic required to neutralize species present in the Hanford tank waste and obtain a target molarity of free hydroxide for tank corrosion control. The presence and quantity of hydroxide-consuming analytes are just as important in determining the caustic demand as is the amount of free hydroxide present. No single data point can accurately predict whether a satisfactory hydroxide level is being met as it is dependent on multiple factors (e.g., free hydroxide, buffers, amphoteric metal hydroxides, bicarbonate, etc.).

This enclosure contains the caustic demand, scanning electron microscopy (SEM), polarized light microscopy (PLM), and X-ray diffraction (XRD) analysis for the tank 241-AX-101 (AX-101) and 241-AX-103 (AX-103) samples. The work was completed to fulfill a customer request outlined in the test plan, WRPS-1505529, “Test Plan and Procedure for Caustic Demand Testing on Tank 241-AX-101 and Tank 241-AX-103 Archive Samples.” The work results will provide a baseline to support planned retrieval of AX-101 and AX-103.

Note: The word “sample” has many uses in this report.

- Archive core sample: the solid or slurry contained in one of the hot cell archive jars, taken from a core sample and stored with no further alteration or amendment
- Test sample: one of three samples prepared specifically for this caustic demand test
    - AX-101 Core 226 Segment 1 archive sample, unaltered
    - AX-101 Core Composite (see Table 2-1)
    - AX-103 Core Composite (see Table 2-1)
- Analytical sample: an aliquot derived from a test sample and submitted for chemical analysis or solid phase characterization (SPC).

2 CAUSTIC DEMAND TEST SAMPLE PREPARATION

2.1 Archived Material

Archived core sample material was used to generate three caustic demand test samples, as shown in Table 2-1. The core samples were originally retrieved in 1997 and 1998. Since then, they have been stored in the hot cell archive located at the 222-S Laboratory. Upon retrieval from storage, the core samples were re-weighed prior to opening to determine the effect of evaporation over time. Very little weight loss was observed (see net weight difference in Table 2-1). Visual inspection found 9 of 11 AX-101 and 4 of 9 AX-103 archive samples contained a liquid layer on top of the slurry. (No effort was made to re-hydrate the samples.) With the exception of Jar Numbers 13689, 14198, and 14206, archive samples were grey in color. (Jar Numbers 13689, 14198, and 14206 were off-white in color. See photos in Appendix A.) Based on the lack of weight loss over the storage time period and the hydrated state of the core samples, the composite integrity was deemed representative of current tank waste. Before proceeding with the testing, each archive core sample was mixed to ensure homogeneity.

Table 2-1. Preparation of Caustic Demand Test Samples.

Test Sample	Jar	Core	Segment	Consistency	Color	Net Weight Difference* (%)
AX-101 Segment 1	13663	226	1	Dry Solid	Grey	-0.7
AX-101 Core Composite	13507	226	2	Slurry	Grey	-0.2
	13674	226	5	Slurry	Grey	-1.1
	13678	226	7	Slurry	Grey	-0.2
	13685	226	10	Slurry	Grey	-0.8
	13689	226	14	Wet Solid	Off-white	-4.8
	14014	228	3	Slurry	Grey	0.0
	13860	228	6	Slurry	Grey	-0.7
	14019	228	9	Slurry	Grey	-0.5
	14206	228	12	Slurry	Off-white	-1.0
	14198	228	15	Slurry	Off-white	-0.1
AX-103 Core Composite	13087	212	2	Slurry	Grey	0.1
	19053	212	2	Wet Solid	Grey	1.2
	13089	214	1	Wet Solid	Grey	-1.0
	13088	214	1	Wet Solid	Grey	-1.7
	19301	214	1	Wet Solid	Grey	-0.2
	12819	214	2	Wet Solid	Grey	-6.1
	19132	214	2	Slurry	Grey	-1.7
	13091	214	2	Slurry	Grey	-1.2
	13090	214	2	Slurry	Grey	-1.3

* Measure of weight loss by evaporation during storage (current net weight minus original net weight divided by original net weight).

2.2 Test Material Preparation

Three caustic demand test samples were prepared from archived sample material: AX-101 core 226 segment 1, AX-101 core 226/228 composite (excluding segment 1), and AX-103 core 212/214 composite. Core 226 segment 1 was treated separately because its composition (based on TWINS[1] data) was significantly different from that of the other AX-101 segments. With the exception of Jar Numbers 13087 and 19053, approximately 10 g of each respective archive sample was used to create the AX-101 and AX-103 composite samples, so that no individual archive sample was depleted. See Table 2-2. The weights of the composite samples and their respective jar identification numbers are located in Table 2-3. Concentrations of the major components in the three test samples, based on information from the TWINS database, are shown in Table 2-4.

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[1] Tank Waste Inventory Network System (TWINS) database, Queried 11/18/15 [Sample Analysis/Tank Results RPP 241/Tank Results (Hide QA records)], https://twins.labworks.org/twinsdata/Forms/About.aspx.

Table 2-2. Tank Archive Core Samples Used In Test Samples.

Test Sample	Jar	Core	Segment	Available Mass (g)	Mass Used (g)
AX-101 Segment 1	13663	226	1	34.3	34.3
AX-101 Core Composite	13507	226	2	93.0	10.0
	13674	226	5	102.2	10.0
	13678	226	7	104.3	10.1
	13685	226	10	99.7	10.1
	13689	226	14	76.9	10.2
	14014	228	3	109.7	10.4
	13860	228	6	110.9	10.1
	14019	228	9	104.3	10.3
	14206	228	12	79.3	10.3
	14198	228	15	76.7	10.2
AX-103 Core Composite	13087	212	2	69.1	15.4
	19053	212	2	10.3	5.0
	13089	214	1	74.5	10.2
	13088	214	1	66.5	10.1
	19301	214	1	44.6	10.7
	12819	214	2	35.5	10.2
	19132	214	2	46.7	10.0
	13091	214	2	63.6	10.0
	13090	214	2	83.9	10.1

Table 2-3. Laboratory Identification of Test Samples.

Test Sample	OmniLIMS Sample Number	Mass (g)
AX-101 Core Segment 1	S16R000001	35.5
AX-101 Core Composite	S16R000025	101.6
AX-103 Core Composite	S16R000058	91.8

Table 2-4. Projected Concentrations (Wt%) of Major Components in Test Samples.

Analyte	AX-101 Segment 1	AX-101 Composite[b]	AX-103 Composite
Cl	0.1	0.4	0.5
NO_3	40.2	19.1	10.8
NO_2	1.6	8.5	9.3
CO_3	4.0	6.3	6.0
C_2O_4	0.4	0.8	0.7
PO_4	0.7	0.6	0.5
SO_4	0.6	1.7	1.3
Al	0.9	2.3	2.4
Cr	0.02	0.2	0.4
Fe	2.8	0.02	0.1
Na	19.1	20.6	19.7
Total[a]	70.4	60.5	51.7

[a] Weight percent sum is less than 100% because of components not listed in table: H_2O and the O/OH associated with Al, Cr, Fe, and Na.
[b] Excluding segment 1.

2.3 Caustic Demand Cone Preparation

Twenty-two tare-weighed 50 mL centrifuge cones were labeled A through V. Test sample material was dispensed into the cones in the following way: ~4 g of AX-101 segment 1 test sample into cones A through F; ~10 g of AX-101 core composite test sample into cones G through N; and ~9 g of AX-103 core composite test sample into cones O through V. Deionized water was added to each cone in the ratio of 3:1 (w/w) water to test sample. Cones A, G, and O were designated as control cones. To the non-control cones, 9.261 M NaOH was added to reach a desired NaOH concentration (see Table 2-5).

The volume of NaOH added to each non-control cone was calculated from Equation 2-1:

$$[\mathrm{OH}]_{\mathrm{Desired}} = \frac{[\mathrm{OH}]_{\mathrm{NaOH}} \times \mathrm{V}_{\mathrm{NaOH}}}{\mathrm{V}_{\mathrm{H_2O}} + \mathrm{V}_{\mathrm{NaOH}}} \tag{2-1}$$

Where

$[OH]_{Desired}$ = desired free hydroxide concentration (mmol/mL)
V_{NaOH} = volume of caustic solution to be added (mL)
$[OH]_{NaOH}$ = concentration of the caustic solution (9.261 mmol/mL)
V_{H_2O} = volume of water added (mL)

Table 2-5. Preparation of Caustic Demand Cones A-V.

Test Sample	Cone	$[OH]_{Desired}$ (M)	Test Sample (g)	Water (g)	V_{H_2O}[a] (mL)	V_{NaOH} (mL)	NaOH[b] (g)
AX-101 Segment 1	A	0	3.98	11.85	11.89	0.00	0.00
	B	0.1	3.69	11.01	11.04	0.12	0.16
	C	0.4	3.55	11.03	11.06	0.48	0.63
	D	0.8	4.05	11.93	11.97	1.10	1.44
	E	1.2	3.98	11.98	12.02	1.78	2.32
	F	1.6	3.66	11.08	11.11	2.29	2.98
AX-101 Core Composite	G	0	8.97	26.65	26.73	0.00	0.00
	H	0.1	11.21	33.14	33.24	0.35	0.46
	I	0.4	9.80	29.99	30.08	1.28	1.67
	J	0.8	11.75	35.43	35.54	3.34	4.35
	K	1.2	9.96	29.55	29.64	4.39	5.73
	L	1.6	10.76	32.59	32.69	6.79	8.85
	M	2.0	9.20	27.86	27.94	7.63	9.95
	N	2.4	6.84	19.72	19.78	7.28	9.49
AX-103 Core Composite	O	0	8.66	25.86	25.94	0.00	0.00
	P	0.1	9.17	27.47	27.55	0.28	0.37
	Q	0.4	9.01	26.94	27.02	1.19	1.55
	R	0.8	9.15	27.41	27.49	2.64	3.44
	S	1.2	9.33	27.94	28.02	4.16	5.43
	T	1.6	8.94	26.83	26.91	5.56	7.25
	U	2.0	8.83	26.51	26.59	7.23	9.43
	V	2.4	9.23	27.67	27.75	9.91	12.92

[a] Based on the water density at 24 °C of 0.997 g/mL from the *CRC Handbook of Chemistry and Physics* (Lide 1978) book.

[b] Based on a density of 1.304 g/mL for 9.261 M NaOH.

3 PROCEDURES

After all additions were made to the cones, each was briefly mixed, then placed onto a tumbler and tumbled end-over-end for a minimum of 24 hr. Cones were then centrifuged for 15 min, re-weighed, and volumes of centrifuged solids and liquids were observed and recorded. From each cone, a liquid portion was decanted into a 20-mL vial, assigned a laboratory identification number, and submitted to WAI Hanford Laboratory (WHL) for chemical analysis with an emphasis on hydroxide concentration. (Excess liquids for cones H, M, P, U, G, N, O, and V were decanted into clean beakers for later use.)

After all liquids were decanted, the cones were reweighed to determine the weight of remaining centrifuged solids. Solids from select cones (H, M, P, and U) were transferred into separate 20-mL vials, assigned laboratory identification numbers, and submitted for SPC (PLM, SEM, XRD). Solids from other select cones (G, N, O, and V) were transferred into separate 20-mL vials, assigned laboratory identification numbers, and submitted to WHL for chemical analysis (inductively coupled plasma [ICP], thermogravimetric analysis [TGA]). (Solid transfer was achieved by reintroducing approximately 5 mL of the appropriate excess centrifuged liquid to the solid, shaking to suspend the solids, and pouring the slurry into the assigned 20-mL vial. The samples were gravity settled overnight, after which the liquid was decanted and discarded.)

Portions of the two untreated caustic demand composite test samples were also submitted for chemical analysis and SPC. A portion of the untreated segment 1 test sample was submitted for SPC only.

4 LABORATORY ANALYSIS

All centrifuged liquid was clear and showed no evidence of a floating organic liquid phase. The partitioned centrifuged liquids were analyzed for free hydroxide (OH), inorganic carbon by the persulfate oxidation method (TIC), total carbon by the furnace method (TC), metals by ICP spectroscopy, density, anions by ion chromatography (IC), and wt% H_2O by TGA. WHL procedure and revision-modification numbers are shown in Table 4-1. Analytical results for the liquid samples are shown in Tables 4-2, 4-3, and 4-4.

Table 4-1. Chemical Analysis Procedures.

Analytical Method	WHL Procedure Number	Revision -Mod	Procedure Title
Free Hydroxide	LA-211-102	K-1	"Determination of Free OH-/H+ Using Metrohm Titrando"
Inorganic Carbon by Persulfate Oxidation	LA-342-100	12-0	"Determination of Carbon By Hot Persulfate Oxidation and Coulometric Detection"
Total Carbon by Furnace	LA-344-105	L-1	"Determination of Carbon in Solutions by Combustion and Coulometry"
Inductively Coupled Plasma Spectroscopy	LA-505-174	1-5	"Inductively Coupled Plasma (ICP) Emission Spectrometric Method for the Thermo Scientific iCAP 6500"
Density	LA-510-112	10-3	"Determination of Density for Free Liquid Samples"
Anions by Ion Chromatography	LA-533-166	C-1	"Ion Chromatographic Analysis of Anions and Small Organic Acids on DIONEX Model ICS 3000"
Thermogravimetric Analysis	LA-514-115	7-2	"Thermal Stability and Percent Weight Loss Using the TA DSC and TGA"

All centrifuged solids were dark grey-brown in color. (Cone O appeared to contain a piece of white plastic, possibly from the archive sample jar lid.) The centrifuged solids in cones H, M, P, and U were analyzed by PLM, SEM, and XRD (see Appendix C). The centrifuged solids in cones G, N, O, and V were analyzed for wt% H_2O by TGA and metals by ICP (see Table 4-2).

Table 4-2. Analytical Results for AX-101 Segment 1 Analytical Sample Centrifuged Liquids.

(Concentrations in µg/mL, except where brackets [ ] indicate molarity, or otherwise noted.)

	Cone					
	A	B	C	D	E	F
S16R000…	003	004	005	006	007	008
Wt% H_2O	78.8	80.7	81.6	78.9	78.8	79.6
d_{Liquid} (g/mL)	1.143	1.137	1.136	1.158	1.136	1.170
Fluoride	193	193	192	168	171	180
Glycolate	<DL	<DL	<DL	<DL	<DL	<DL
Acetate	323	320	330	332	320	326
Formate	639	619	613	615	605	610
Chloride	210	197	211	187	178	191
Nitrite	4430	4100	4070	4010	3670	3820
Sulfate	2040	1870	1860	1810	1680	1780
Oxalate	1210	1220	1170	1090	1060	1120
Bromide	1530	1450	1410	1440	1350	1370
Nitrate	133000	127000	114000	126000	120000	109000
Phosphate	2870	2650	2420	2280	2320	2230
Aluminum	<DL	<DL	16.6	22.8	22.6	32.0
Boron	<DL	6.93	15.2	16.1	17.5	18.2
Chromium	38.8	33.3	34.1	32	28.3	30.2
Copper	<DL	<DL	<DL	<DL	<DL	<DL
Iron	<DL	<DL	<DL	<DL	<DL	<DL
Phosphorus	636	553	559	472	456	463
Potassium	186	173	180	157	145	150
Sodium	67600	60600	62200	72700	75000	78900
Sulfur	685	534	557	519	459	511
Uranium	<DL	<DL	<DL	<DL	<DL	<DL
TIC	2390	2090	2050	2050	1850	1950
TC	3060	2790	2600	2130	2380	2460
TOC*	670	700	550	80	530	510
OH	100	1300	5910	12200	18800	25200
$[OH]_{Found}$	0.01	0.08	0.35	0.72	1.11	1.48
$[OH]_{Calc}$	0.01	0.10	0.37	0.74	1.11	1.50

<DL = less than detection limit
TOC = total organic carbon
*TOC = TC - TIC

Table 4-3. Analytical Results for AX-101 Composite Analytical Sample Centrifuged Liquids.

(Concentrations in µg/mL, except where brackets [ ] indicate molarity, or otherwise noted.)

	Cone							
	G	**H**	**I**	**J**	**K**	**L**	**M**	**N**
S16R000…	029	030	031	032	033	034	035	036
Wt% H_2O	82.8	82.5	82.6	81.3	80.5	80.2	80.3	78
d_{Liquid} (g/mL)	1.130	1.129	1.132	1.147	1.162	1.168	1.178	1.190
Fluoride	186	299	183	173	186	175	160	149
Glycolate	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Acetate	566	957	526	495	472	466	458	430
Formate	856	1190	809	794	771	757	719	708
Chloride	1000	1810	886	825	771	687	615	571
Nitrite	22000	38800	20300	18900	20000	17100	17400	15700
Sulfate	4450	10300	4340	4220	4140	3810	3660	3200
Oxalate	2340	5090	2060	1770	1500	1360	1200	1020
Bromide	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Nitrate	46400	83300	46800	51600	52600	52900	52100	62900
Phosphate	2230	4960	2130	1900	2100	2060	1730	1780
Aluminum	7240	6490	5990	6000	5440	5040	4640	5130
Boron	5.87	4.61	4.84	5.33	7.01	7.66	7.47	11.9
Chromium	16	14.2	14.1	15.9	15.1	14.7	14.8	18.2
Copper	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Iron	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Phosphorus	696	632	613	594	599	582	472	366
Potassium	1150	1030	944	953	858	806	748	881
Sodium	69400	64100	69700	82500	87600	93000	100000	142000
Sulfur	1720	1630	1570	1640	1530	1400	1350	992
Uranium	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
TIC	3580	3600	3400	3310	3300	3080	2950	2590
TC	4560	4780	4540	4240	4150	3890	3530	3150
TOC*	980	1180	1140	930	850	810	580	560
OH	7040	8190	11800	17300	22600	29600	35700	42500
$[OH]_{Found}$	0.41	0.48	0.69	1.02	1.33	1.74	2.10	2.50
$[OH]_{Calc}$	0.41	0.49	0.72	1.06	1.40	1.74	2.09	2.54

<DL = less than detection limit
*TOC = TC - TIC

Table 4-4. Analytical Results for AX-103 Composite Analytical Sample Centrifuged Liquids.

(Concentrations in µg/mL, except where brackets [ ] indicate molarity, or otherwise noted.)

	Cone							
	O	**P**	**Q**	**R**	**S**	**T**	**U**	**V**
S16R000…	062	063	064	065	066	067	068	069
Wt% H_2O	83.2	79.4	82.4	83.5	81.6	81.3	81.3	80.2
d_{Liquid} (g/mL)	1.133	1.142	1.138	1.198	1.158	1.164	1.177	1.187
Fluoride	407	279	393	367	351	362	338	299
Glycolate	596	580	596	582	587	589	582	573
Acetate	520	459	494	475	486	474	474	468
Formate	1020	919	994	946	950	952	915	886
Chloride	1400	1140	1340	1280	1250	1240	1120	1070
Nitrite	26200	26900	22600	22400	21500	20800	20400	20200
Sulfate	4810	3760	4620	4610	4220	4310	3970	3830
Oxalate	2660	2230	2320	1810	1620	1480	1120	991
Bromide	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Nitrate	29400	65600	34700	35000	29800	23800	23300	23300
Phosphate	3190	2380	3050	2640	2750	2830	2540	2210
Aluminum	4110	3090	4280	3810	3160	3680	3850	3190
Boron	9.11	6.41	9.92	9.79	8.77	11.4	13.4	10.4
Chromium	199	148	203	183	150	178	187	157
Copper	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Iron	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Phosphorus	1120	639	1110	935	830	973	947	716
Potassium	918	666	928	792	683	799	826	684
Sodium	66300	66400	77700	82400	72500	88300	105000	98300
Sulfur	1810	1290	1810	1740	1360	1590	1650	1410
Uranium	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
TIC	5970	4530	5850	5990	5620	5450	5200	2830
TC	7610	5840	7220	7190	7420	7370	7060	6500
TOC*	1640	1310	1370	1200	1800	1920	1860	3670
OH	4200	4680	9600	15400	21700	27600	33500	39800
$[OH]_{Found}$	0.25	0.28	0.57	0.91	1.28	1.62	1.97	2.34
$[OH]_{Calc}$	0.25	0.33	0.59	0.90	1.29	1.64	2.00	2.42

<DL = less than detection limit
*TOC = TC - TIC

5 CAUSTIC DEMAND RESULTS

Caustic demand testing was performed in the 222-S Laboratory hot cells located in 11A. A calibrated balance was used to record the weight of each test sample, the weight of water, and the weight of caustic added to each cone. The lab visually estimated the volume of sample + water. This estimation was used in an attempt to calculate the density of the test samples. The test sample volume could not be accurately measured, therefore, the caustic demand is reported as mol/kg instead of mol/L.

Test results showed a caustic demand of 0.05-0.08 moles of hydroxide per kg of tank waste for AX-101 segment 1 test sample and zero caustic demand for the AX-101 and AX-103 composite test samples. The caustic demand for segment 1 can be attributed to the reaction of disodium phosphate with NaOH:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

The following sections describe how these conclusions were derived from the test results.

5.1 Caustic Demand Calculations

5.1.1 Calculation of the Mass of Centrifuged Liquid and Solid

To calculate the total liquid volume, V_{Total}, it is necessary to first determine the masses of the centrifuged liquid, C_{Liq}, and centrifuged solid, C_{Solids}. The mass of C_{Liq} represents the weight of the water added, NaOH added, interstitial liquid (ISL), and dissolved salts. The mass of C_{Solids} represents the weight of undissolved test sample remaining after decanting the centrifuge liquid.

$$C_{Liq} = m_{H_2O} + m_{NaOH} + m_{archrive} - C_{Solids} \tag{5-1}$$

Where

m_{H_2O} = weight of water added (g)
m_{NaOH} = weight of NaOH added (g)
$m_{archive}$ = weight of test sample (g)
$m_{archive} - C_{solids}$ = weight of ISL and dissolved salts (g)

C_{Liq} is then divided by the density of the liquid to determine the total liquid volume, V_{Total}. Density results are provided as part of the chemical analyses testing.

$$V_{Total} = C_{Liq}\,(g) / \text{density}\,(g/mL) \tag{5-2}$$

5.1.2 Interstitial Liquid Calculations

The liquid layer, V_{Total}, present after centrifugation represents the combination of the test sample ISL (including dissolved salts), the water added to each cone, and sodium hydroxide added to all cones except the control cones. In order to calculate the hydroxide contributed from the ISL, $[OH]_{ISL}$, the volume of ISL, V_{ISL}, is required and is calculated from the following equation:

$$V_{ISL} = V_{Total} - V_{H_2O} - V_{NaOH} \tag{5-3}$$

Where

V_{Total} = total centrifuged liquid volume (mL)
V_{H_2O} = volume of water added (mL)
V_{NaOH} = volume of the 9.261 M NaOH solution added (mL)

The control sample is used to calculate $[OH]_{ISL}$. All of the hydroxide in the control sample comes from the ISL. Therefore,

$$[OH]_{ISL} = [OH]_{Found} \times \frac{V_{Total}}{V_{ISL}} \tag{5-4}$$

The $[OH]_{ISL}$ calculated in Equation 5-4 is assumed to apply to all samples associated with that control sample.

5.1.3 Calculation of $[OH]_{Calc}$

Caustic demand is determined by plotting the reported free hydroxide concentration ($[OH]_{Found}$) as a function of the calculated hydroxide concentration based on dilution alone ($[OH]_{Calc}$) for the series of points tested. Both values are calculated in molarity and are included in Table 5-1. $[OH]_{Calc}$ is taken from Equation 5-5:

$$[OH]_{Calc} = \frac{([OH]_{NaOH} \times V_{NaOH}) + ([OH]_{ISL} \times V_{ISL})}{V_{H_2O} + V_{NaOH} + V_{ISL}} \tag{5-5}$$

Where

$[OH]_{NaOH}$ = concentration of the NaOH standard (9.261 mmol/mL)
V_{NaOH} = volume of the 9.261 M NaOH solution added (mL)
$[OH]_{ISL}$ = hydroxide concentration attributed to the ISL
V_{ISL} = volume of ISL (including dissolved salts)
V_{H_2O} = volume of water added (mL)

Within Equation 5-3, two assumptions are invoked. The first is that the volumes of ISL, water, and 9.261 M NaOH solution are additive. This assumption is not strictly correct but has generally proved to be adequate for this purpose. The second assumption is that the volume of ISL is defined as the volume of liquid present in the segment or composite test sample plus the volume occupied by any salts that dissolved in the water added. Thus, V_{ISL} is equal to the volume of centrifuged liquid minus the volume of water and NaOH added (Equation 5-3).

5.1.4 Calculation of Caustic Demand

There are two independent ways to calculate the caustic demand. In the graphical method, $[OH]_{Found}$ is plotted against $[OH]_{Calc}$. The $[OH]_{Found}$ is the reported analytical value in µg/mL divided by 17,000 µg/mmol. Based on reference FH-0300059[2], the slope (b) of the resulting regression line is related to the amount of buffering present (B) by Equation 5-6:

$$b = \frac{-B}{V_{Liq}} \qquad (5\text{-}6)$$

Where

b = y-intercept of the regression plot (mmol/mL)
B = buffer present in sample (mmol)
V_{Liq} = $V_{Total} - V_{NaOH}$ (mL)

Note: V_{Liq} represents the ISL + dissolved salts + water added

Caustic demand for the archive sample is the moles of buffer per kg of segment or composite test sample. Rearranging Equation 5-6 and dividing by the average test sample mass ($m_{Test\ sample}$) gives Equation 5-7:

$$\text{Graphical caustic demand } \left(\frac{\text{mmol}}{\text{g}}\right) = \frac{B}{m_{test\ sample}} = \frac{-b \times V_{Liq}}{m_{test\ sample}} \qquad (5\text{-}7)$$

In the difference method, the arithmetic difference, $[OH]_{Diff}$, between the $[OH]_{Calc}$ and $[OH]_{Found}$ for each analytical sample is calculated and then averaged. Averages are also calculated for V_{Liq} and $m_{test\ sample}$. Caustic demand is calculated by Equation 5-8.

$$\text{Difference caustic demand } \left(\frac{\text{mmol}}{\text{g}}\right) = [OH]_{Diff} \times \frac{V_{Liq}}{m_{test\ sample}} \qquad (5\text{-}8)$$

5.2 AX-101 Segment 1 Caustic Demand Results

The AX-101 segment 1 test sample exhibited a small caustic demand of 0.05-0.08 moles of hydroxide per kg archive tank waste sample. Experimental data is shown in Table 5-1, and the associated calculations follow the table.

Table 5-1. AX-101 Segment 1 Caustic Demand [OH] Results. (2 pages)

Cone	V_{Total} (mL)	V_{Liq} (mL)	$m_{Archive}$ (g)	$[OH]_{Calc}$ (M)	$[OH]_{Found}$ (M)	$[OH]_{Diff}$ (M)	$m_{Cent\ Liq}$ (g)	$m_{Cent\ Solids}$ (g)
A	12.76	12.76	3.98	0.006	0.006	0.000	14.59	1.24
B	12.01	11.88	3.69	0.101	0.076	0.025	13.65	1.21
C	12.28	11.80	3.55	0.369	0.348	0.021	13.95	1.26

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[2] FH-0300059, "Caustic Demand Test Results, Tank 241-AZ-102 Sludge."

Table 5-1. AX-101 Segment 1 Caustic Demand [OH] Results. (2 pages)

Cone	V_{Total} (mL)	V_{Liq} (mL)	$m_{Archive}$ (g)	$[OH]_{Calc}$ (M)	$[OH]_{Found}$ (M)	$[OH]_{Diff}$ (M)	$m_{Cent\ Liq}$ (g)	$m_{Cent\ Solids}$ (g)
D	13.97	12.87	4.05	0.737	0.718	0.019	16.18	1.24
E	15.00	13.22	3.98	1.105	1.106	-0.001	17.04	1.24
F	14.13	11.84	3.66	1.502	1.482	0.020	16.53	1.19

The $[OH]_{Found}$ vs. $[OH]_{Calc}$ plot for segment 1 is shown in Figure 5-1. The graph contains two lines. The dashed line represents the theoretical situation where there is no buffering. The solid line represents the first-order regression fit to the data points. The regression parameters are shown in Equation 5-7:

$$[OH]_{Found\ AX\text{-}101\ segment\ 1} = 1.0083[OH]_{Calc} - 0.0234 \tag{5-7}$$

From Equation 5-5, the graphical caustic demand for segment 1 is calculated as 0.076 mol/kg of test sample. And from Equation 5-6, the caustic demand by difference is calculated as 0.055 mol/kg of test sample.

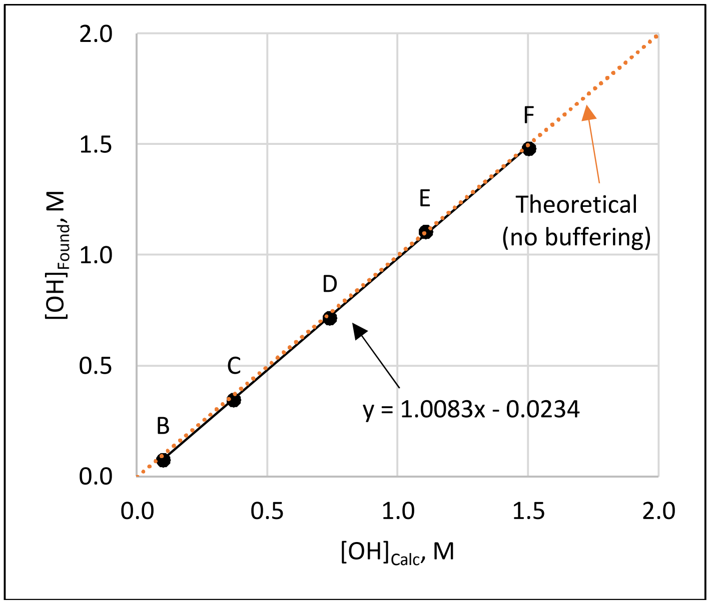

Figure 5-1. AX-101 Segment 1 Graphical Caustic Demand Plot.

5.3 AX-101 Composite Caustic Demand Results

The AX-101 composite test sample exhibited zero caustic demand. Experimental data is shown in Table 5-2, and the associated calculations follow the table.

Table 5-2. AX-101 Composite Caustic Demand [OH] Results.

Cone	V_{Total} (mL)	V_{Liq} (mL)	$m_{Archive}$ (g)	$[OH]_{Calc}$ (M)	$[OH]_{Found}$ (M)	$[OH]_{Diff}$ (M)	$m_{Cent\ Liq}$ (g)	$m_{Cent\ Solids}$ (g)
G	30.92	30.92	8.97	0.414	0.414	0.000	34.94	0.68
H	38.80	38.45	11.21	0.495	0.482	0.013	43.81	1.00
I	35.91	34.63	9.80	0.718	0.694	0.024	40.65	0.81
J	43.98	40.65	11.75	1.058	1.018	0.040	50.45	1.08
K	38.12	33.72	9.96	1.396	1.329	0.067	44.29	0.95
L	43.95	37.16	10.76	1.742	1.741	0.001	51.33	0.87
M	39.17	31.54	9.20	2.086	2.100	-0.014	46.14	0.87
N	29.67	22.39	6.84	2.542	2.500	0.042	35.31	0.74

The $[OH]_{Found}$ vs. $[OH]_{Calc}$ plot for the AX-101 composite is shown in Figure 5-2. The regression parameters are shown in Equation 5-8:

$$[OH]_{Found\ AX\text{-}101\ composite} = 1.003[OH]_{Calc} - 0.0285 \tag{5-8}$$

From Equation 5-5, the graphical caustic demand for the composite is calculated as 0.098 mol/kg of test sample. And from Equation 5-6, the caustic demand by difference is calculated as 0.084 mol/kg of test sample. However, based on the high level of $[OH]_{Found}$ in the control sample ($[OH]_{ISL}$ = 3.00 M) and the small scatter in the data (note that points L and M in Figure 5-2 fall on and above the theoretical line, respectively), these caustic demand numbers are judged not to be different from zero. With 3 M hydroxide in the ISL, there are no weak acids present to consume additional hydroxide ions.

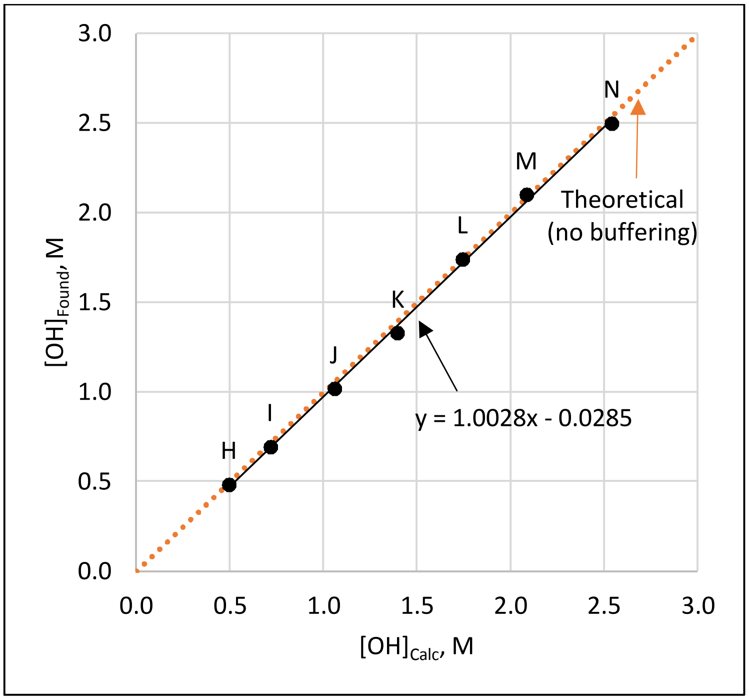

Figure 5-2. AX-101 Composite Graphical Caustic Demand Plot.

5.4 AX-103 Composite Caustic Demand Results

The AX-103 composite material exhibited zero caustic demand. Experimental data is shown in Table 5-3, and the associated calculations follow the table.

Table 5-3. AX-103 Composite Caustic Demand [OH] Results.

Cone	V_{Total} (mL)	V_{Liq} (mL)	$m_{Archive}$ (g)	$[OH]_{Calc}$ (M)	$[OH]_{Found}$ (M)	$[OH]_{Diff}$ (M)	$m_{Cent\ Liq}$ (g)	$m_{Cent\ Solids}$ (g)
O	29.14	29.14	8.66	0.247	0.247	0.000	33.01	1.5
P	31.33	31.05	9.17	0.334	0.275	0.059	35.78	1.23
Q	31.56	30.37	9.01	0.587	0.565	0.022	35.91	1.59
R	32.03	29.39	9.15	0.898	0.906	-0.008	38.37	1.63
S	35.28	31.12	9.33	1.290	1.276	0.014	40.86	1.84
T	35.40	29.84	8.94	1.641	1.624	0.017	41.2	1.82
U	36.57	29.34	8.83	2.001	1.971	0.030	43.04	1.73
V	40.40	30.49	9.23	2.424	2.341	0.083	47.95	1.87

The $[OH]_{Found}$ vs. $[OH]_{Calc}$ plot for the AX-103 composite is shown in Figure 5-3. The regression parameters are shown in Equation 5-9:

$$[OH]_{Found\ AX\text{-}103\ composite} = 0.99[OH]_{Calc} - 0.0128 \quad (5\text{-}9)$$

From Equation 5-5, the graphical caustic demand for the composite is calculated as 0.043 mol/kg of test sample. And from Equation 5-6, the caustic demand by difference is calculated as 0.103 mol/kg of test sample. However, based on the high level of $[OH]_{Found}$ in the control sample ($[OH]_{ISL} = 2.19$ M) and the small scatter in the data (note that point R in Figure 5-3 falls above the theoretical line), these caustic demand numbers are judged not to be different from zero. With 2.19 M hydroxide in the ISL, there are no weak acids present to consume additional hydroxide ions. The slope of the line in Equation 5-9 also supports the lack of buffering present in the AX-103 archive sample. (The slope would be greater than 1.00 if buffering were present.)

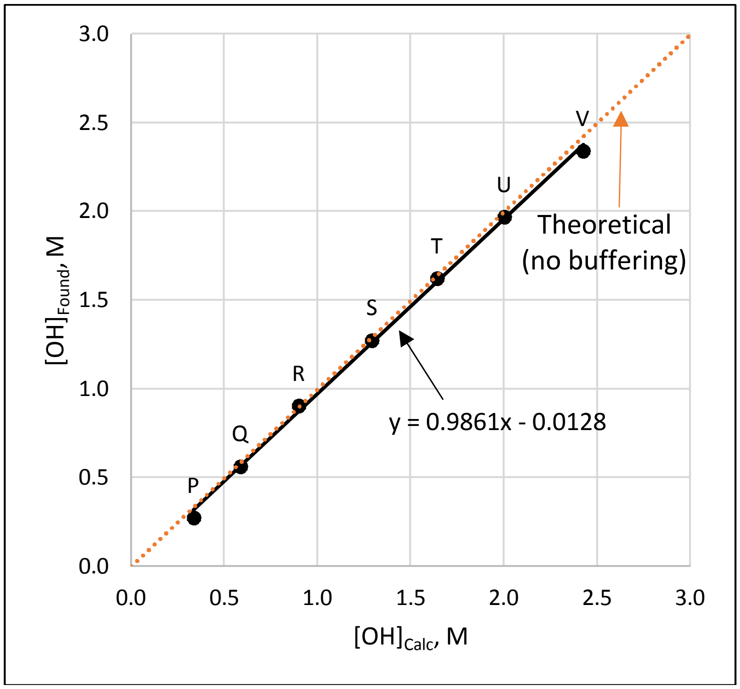

Figure 5-3. AX-103 Composite Graphical Caustic Demand Plot.

6 CHEMICAL ANALYSIS RESULTS

Analytical samples were submitted for chemical analysis (in addition to hydroxide analysis) for three reasons: identification of buffer species, characterization of archive samples, and quality control.

6.1 Buffer Species

6.1.1 AX-101 Segment 1 Buffer Species

The primary buffer species in AX-101 segment 1 is Na_2HPO_4.

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O \tag{6-1}$$

The phosphate concentration in the control sample (see cone A in Table 4-1) was 2870 µg/mL and the OH concentration was 0.006 M. Given the pKa of Na_2HPO_4 of 12.67, routine pH calculations show that 90% of the phosphate is present as Na_2HPO_4. Therefore, the concentration of biphosphate in the control sample was:

$$0.90 \times \frac{2870\ \mu g\ PO_4}{mL} \times \frac{1\ g}{10^6\ \mu g} \times \frac{10^3\ mL}{L} \times \frac{1\ mol\ PO_4}{95\ g} \times \frac{1\ mol\ Na_2HPO_4}{mol\ PO_4} = 0.027\ M\ Na_2HPO_4 \qquad (6\text{-}2)$$

This concentration of biphosphate buffer corresponds to a caustic demand of 0.088 mol/kg test sample, which is slightly higher than the overall caustic demand of 0.05-0.08 moles of hydroxide per kg test sample (see section 5.3).

$$\frac{0.027\ mol}{L} \times \frac{3.255\ L}{kg} = 0.088\ mol/kg \qquad (6\text{-}3)$$

Other common buffers present in tank waste include amphoteric metal hydroxides [$Al(OH)_3$ + NaOH → $NaAl(OH)_4$] and sodium bicarbonate [$NaHCO_3$ + NaOH → Na_2CO_3 + H_2O]. Neither of these is present in significant quantity in segment 1. A small amount of aluminum dissolved (see Figure 6-1), but the total moles of dissolved aluminum can account for only 5% of the buffer capacity observed. The 0.006 M OH in the control sample corresponds to a theoretical pH of 11.8, at which point only a trace of bicarbonate (pKa = 10.25) was present.

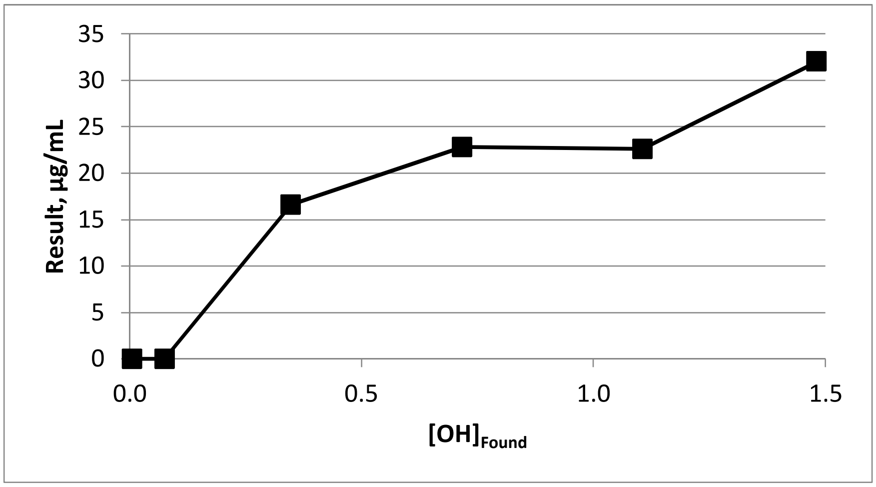

Figure 6-1. Aluminum Concentration as a Function of $[OH]_{Found}$.

The only other potential buffer present in the system based on the chemical analysis results was boron. Due to boron's complex chemistry, it is anticipated that several boron buffer reactions occur simultaneously [i.e., $Na_2B_4O_5(OH)_4$ + 2 NaOH + 5 H_2O → 4 $NaB(OH)_4$]. See Figure 6-2. Like the aluminum reaction though, the total moles of boron dissolved could account for only 5% of the buffer. No other metals showed any concentration increase with increasing OH concentration.

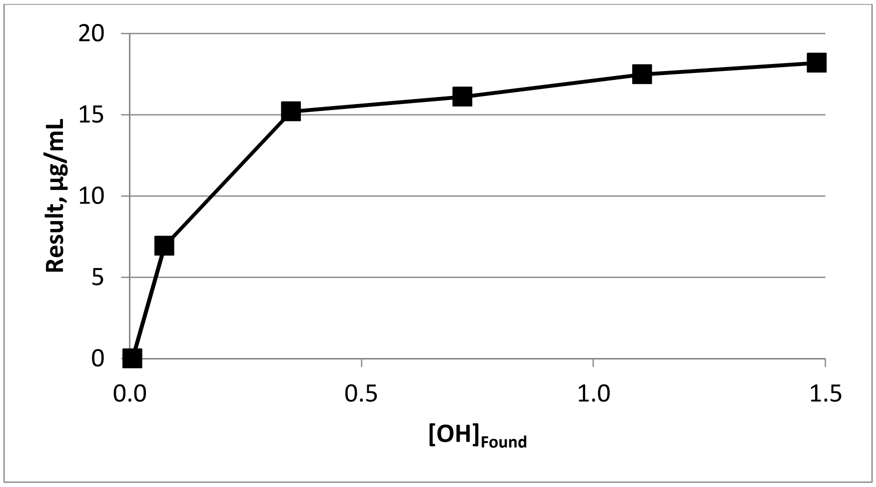

Figure 6-2. Boron Concentration as a Function of $[OH]_{Found}$.

6.1.2 AX-101 Composite and AX-103 Composite Buffer Species

The OH concentrations in the control analytical samples were 0.41 M and 0.25 M for AX-101 and AX-103, respectively (see Tables 4-2 ad 4-3). At these pH levels, the phosphate and carbonate are completely deprotonated. No metals showed any significant increase with increasing OH concentration. No buffer species were identified for either composite sample.

6.2 Quality Control

6.2.1 Analytical Instrumentation Quality Control Criteria

WHL calibrated analytical instrumentation and analyzed calibration check standards and blanks per applicable analytical procedures. Quality control (QC) analyses (duplicates, matrix spikes, blanks) were prepared and analyzed per analytical batch, as specified in the laboratory Quality Assurance Project Plan[3] (QAPP) and WHL analytical procedures. An analytical batch contains a maximum of 20 samples.

- Instrument standards are analyzed at the beginning of each batch, after every ten samples, and at the end of each batch. Acceptance criterion for instrument standards is 90-110% with the exception of TIC/TC. Acceptance criterion for TIC/TC instrument standards is 85-115%.
- Instrument blanks are analyzed after instrument standards for ICP, IC, OH, and TIC/TC. Acceptance criterion is <EQL (estimated quantitation limit).
- Acceptance criteria for preparation blanks are either <EQL or ≤5% of the measured concentration in the sample. If acceptance criteria are not met, samples are "B" flagged.
- A duplicate and matrix spike are analyzed per batch when applicable. (For example, matrix spikes are not applicable to density and TGA).
    - The relative percent difference (RPD) acceptance criterion is generally ≤20%. The exception is for ICP analysis on fusion digests. In this case, the ICP RPD

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[3] ATS-MP-1032, *222-S Laboratory Quality Assurance Project Plan.*

  - acceptance criterion for solids is ≤35%. If acceptance criterion is not met, samples are "c" flagged for the relevant analytes.
  - Acceptance criterion for matrix spikes is 75-125%. If acceptance criterion is not met, samples are "b" flagged for the relevant analytes.
- Serial dilutions only apply to ICP. A serial dilution is a 5-fold dilution prepared from the sample dilution and only applies to analytes detected at concentrations >50X the method detection limit (MDL). (The MDL is the minimum concentration of an analyte which can be detected above background.) The percent difference between the serial dilution and sample must be ≤10%. If this criterion is not met, relevant analytes are "e" flagged.

6.2.2 Quality Control Issues

None of the QC issues discussed below adversely impact conclusions reached in this study. As a result, re-analyses were not requested.

6.2.2.1 IC-Anions/Organic Acids

- Formate and oxalate were detected in the blank at a concentration level above the MDL, but below the EQL and above 5% of the sample results. A "B" flag was applied to the associated sample results.
- For AX-101 segment 1, the PO_4/P ratio is approximately 1.5 times higher than expected. In reviewing the data, it was noted that the phosphate concentrations were at or below the EQL. As a result, all of the samples, with the exception of cone A (S16R000003), were "J" flagged as estimates. These estimated phosphate results could result in the PO_4/P ratio being higher than anticipated.
- When the IC-anions/organic acids results are plotted against the $[OH]_{Found}$ results, the data for cone H (S16R000030) is twice as high as expected. This pattern is also seen in the SO_4/S and PO_4/P ratios for this sample. This anomaly is probably due to a dilution error.
- While viewing the plots of the IC analyte concentrations against $[OH]_{Found}$, it was noted that cone P (S16R000063) had lower results than expected for fluoride, acetate, formate, chloride, sulfate, phosphate, and oxalate. For this same sample, the nitrate result was approximately twice as high as expected. Interestingly, the SO_4/S ratio was equivalent to the expected value, but the PO_4/P ratio was ~20% higher.

6.2.2.2 ICP Metals

- Aluminum, cerium, silicon, and sodium were detected in the fusion preparation blank at concentrations above the MDL, but below the EQL and above 5% of the sample results. Therefore, a "B" flag was applied to the associated sample results.
- The thorium matrix spike recovery failed low and did not meet the specified range of 75-125% listed in the QAPP. As the thorium results were below the MDL, the associated results were reported with a "b" flag. This comment only applies to the fusion digested samples.

- An “e” flag was applied to the silicon result for cone A (S16R000003) because the percent difference between the sample and sample serial dilution (5-fold dilution) was >10%.
- The phosphorus concentration for cone N (S16R000036) did not follow the same trend as the other metals (Al, B, Cr, K, and Na) for this sample. The PO_4/P ratio is higher than anticipated, which could be due to the phosphorus concentration being slightly lower than expected.
- Similar to the IC results for cone P (S16R000063), the plots for the Al, B, Cr, P, K, and S concentrations against $[OH]_{Found}$ had lower results than expected.

6.2.2.3 TIC/TOC

- TIC/TOC is typically analyzed in sequence using a hot persulfate oxidation method. The TIC analysis was performed first and produced values that had a high degree of correlation between the sample, duplicate, and triplicate analyses. Additional reagents (H_2SO_4, $K_2S_2O_8$, and $AgNO_3$) were added to the sample vials in preparation of the TOC analysis; however, this addition resulted in the formation of a white precipitate. Due to this, the relative standard deviation between the sample, duplicate, and triplicate did not meet QC acceptance criteria. As the quality control did not pass, these results were not reported. WHL contacted the principal scientist regarding this issue and received permission to analyze the samples for total TC by the furnace method. The TOC was calculated by subtracting the TIC results from the TC results.
- When the TIC results for AX-103 composite are plotted against $[OH]_{Found}$, the result for cone P (S16R000063) is slightly lower than projected.

6.2.2.4 Density

- The density for cone E (S16R000007) appears to be low when the density data for AX-101 segment 1 is plotted against $[OH]_{Found}$.
- The density for cone R (S16R000065) is higher than projected when the density results for AX-103 composite are plotted against $[OH]_{Found}$.

6.2.2.5 Mass Charge Balance

A mass balance is the sum of all chemical species in a sample. The calculation shown below is used to convert an analyte concentration to weight percent:

$$\mathrm{Conc_{analyte}} \times \frac{\mathrm{FW_{compound}}}{\mathrm{FW_{analyte}}} \times \frac{\mathrm{V_{Liq}}}{(10^4 \times \mathrm{m_{archive}})} \qquad (6\text{-}1)$$

Where

$\mathrm{Conc_{analyte}}$ = concentration provided from the chemical analysis (µg/mL)
$\mathrm{FW_{compound}}$ = formula weight of the assumed compound (mg/mmol)
$\mathrm{FW_{analyte}}$ = formula weight of the analyte (mg/mmol)
$\mathrm{V_{Liq}}$ = $\mathrm{V_{Total} - V_{NaOH}}$ (mL)
$\mathrm{m_{archive}}$ = weight of test sample (g)

Note: 10^4 is a conversion factor that combines the µg to g and weight percent conversions

The following example, taken from AX-101 composite cone G, calculates the weight percent of sodium carbonate, which is based on the TIC result:

TIC analyte concentration = 3580 µg/mL
FW for carbon = 12 mg/mmol
FW for sodium carbonate = 106 mg/mmol
V_{Liq} = 30.92 mL
$m_{archive}$ = 8.97 g

$$3580\ \mu g/mL \times \frac{106\ mg/mmol}{12\ mg/mmol} \times \frac{30.92\ mL}{(10^4 \times 8.97\ g)} = 10.9\%\ \text{sodium carbonate}$$

Ideally, the mass balance for all constituents in a sample should be 100%. However, mass balance values from 95-102% are generally considered excellent while values from 90-105% are acceptable. If the values are below 90% or above 105%, the data should be reviewed for errors.

The charge balance calculation converts each analyte from mmol/g to mEq/g, sums the positive and negative equivalents, and then calculates the +/- ratio. Ideally, this ratio should be 1.00. However, charge balance values from 0.95 to 1.02 are generally considered excellent while values from 0.90 to 1.05 are acceptable. If the values are below 0.90 or above 1.05, the data should be reviewed for errors.

6.2.2.5.1 AX-101 Segment 1

The mass balances for cones A through F (S16R000003 - S16R000008) varied from 98.5-99.5% with an average of 99.2%. The charge balances for cones A through F varied from 0.9-1.04 with an average of 0.95. The charge balance data meets acceptance criteria while the mass balance results would be considered excellent.

6.2.2.5.2 AX-101 Composite

The mass balances for cones G through N (S16R000029 - S16R000036) varied from 99.4-104.8% with an average of 100.8%. This data would be considered acceptable. The charge balances for cones G through N had two outliers: Cone H at 0.68 and cone N at 1.33. The IC results for cone H were approximately twice as high as expected, which would result in the low charge balance. The charge balances for cones G, I, J, K, L, and M varied from a low of 1.04 to a high of 1.10 with an average of 1.06. The charge balances for these cones are higher than anticipated. The high charge balance results could be due to either a potential low bias in the anion/aluminum data and/or a possible high bias for sodium and/or potassium.

6.2.2.5.3 AX-103 Composite

The mass balances for cones O through V (S16R000062 - S16R000069) varied from 97.3-100.7% with an average of 99.1%. This data would be considered excellent. The charge balances had two outliers: Cone S at 0.89 and cone U at 1.13. The metal data indicates a decrease in concentration (low bias) for cone S and an increase in concentration (high bias) for cone U, which explains these outliers. Also cones Q, R, and V were higher than acceptance criteria at 1.10, 1.06, and 1.08, respectively. Only cones O, P, and T met acceptance criteria at 1.04, 0.95, and 1.02, respectively. There are interesting trends in the ICP data for sulfur, potassium, phosphorus, chromium, and aluminum. The variability in the metals data is probably the cause of the overall high bias seen in the charge balance results for this composite.

7 SOLID PHASE CHARACTERIZATION

Solid phase characterization, SPC, (i.e., identification of specific chemical and mineral phases present in the solids) was investigated using a combination of PLM, SEM, XRD, and chemical analysis. A summary of chemical analysis and SPC characterization results is presented here, and details are provided in Appendix C.

7.1 AX-101 Segment 1 Solid Phase Characterization

One analytical sample of the segment 1 test sample was submitted for SPC (PLM/SEM/XRD only). Due to a limited amount of available test sample, no analytical sample was provided for chemical characterization. No analytical samples of centrifuged solids were available for any SPC testing.

The phases identified (but not quantified) in the test sample, as identified by PLM/SEM/XRD, were $NaNO_3$, $Na_2CO_3{\bullet}H_2O$, and $NaAlSiO_4$ (generic cancrinite). Small amounts of phosphorus, chlorine, and iron were observed, but could not be tied to specific phases.

Some conclusions can be drawn about the solid phase composition of the water-soluble components of the test sample based on the analytical results for the centrifuged liquid analytical sample for control cone A. Based on those results, the AX-101 test sample contained (in wt%) approximately 58% $NaNO_3$, 8% $Na_2CO_3{\bullet}H_2O$, 3% $Na_2HPO_4{\bullet}xH_2O$ (x = 7 most probable), and less than 3% of all other common water-soluble salts. These results are consistent with the TWINS data for segment 1 shown in Table 2-4.

The total water-soluble components in control cone A (i.e., the sum of the wt%'s of the individual components) accounted for approximately 73 wt% of the test sample, based on the chemical analysis. This compares well with the direct measurement of centrifuge cone weights: 3.98 g of test sample, 1.24 g of centrifuged solids after water addition. The centrifuged solids contain all of the water-insoluble solids and a small amount (not determined) of ISL.

7.2 AX-101 Composite Solid Phase Characterization

Solid phase characterization was completed for three types of AX-101 composite samples using SPC (PLM, SEM, XRD) and chemical analysis techniques: untreated test sample, centrifuged solids from low-OH cones G and H, and centrifuged solids from high-OH cones M and N. Based on the results (see Appendix C for details):

The untreated composite test sample was composed of approximately (in wt%)

- 22% $NaNO_3$ (present in both solid and liquid phases, entirely water-soluble)
- 11% $NaNO_2$ (present in liquid phase only)
- 11% Na_2CO_3 (present in both solid and liquid phases, entirely water-soluble)
- 8% $NaAl(OH)_4$ (present in liquid phase only)
- 4-8% $NaAlSiO_4$ (present in solid phase only; not soluble in H_2O or NaOH)
- 6% NaOH (present in liquid phase only)
- 1-2% $Na_2C_2O_4$ (present in both solid and liquid phases; partially soluble in H_2O, less soluble at high hydroxide concentration; major phase in centrifuged solids, but quantity not established)
- 24% H_2O
- 8% other (Na/K salts of F, Cl, PO_4, SO_4, acetate, formate)

Water-insoluble solids (the centrifuged solids from cones G and H) accounted for only 5-10 wt% of the test sample. The dominant insoluble phase was cancrinite with varying composition, approximated by the formula $NaAlSiO_4$. Sodium oxalate was also a major contributor to the centrifuged solids. Other elements identified but not tied to specific phases were Cr, Ca, U, and Fe.

7.3 AX-103 Composite Solid Phase Characterization

Solid phase characterization was completed for three types of AX-103 composite samples using SPC (PLM, SEM, XRD) and chemical analysis techniques: untreated test sample, centrifuged solids from low-OH cones O and P, and centrifuged solids from high-OH cones U and V. Based on the results (see Appendix C for details):

The untreated composite test sample was composed of approximately (in wt%)

- 18% Na_2CO_3 (present in both solid and liquid phases, entirely water-soluble)
- 14% $NaNO_3$ (present in both solid and liquid phases, entirely water-soluble)
- 13% $NaNO_2$ (possibly present in solid as well as liquid phases, entirely water-soluble)
- 11% Al(O)OH (present in solid phase only; not soluble in H_2O or NaOH)
- 4% $NaAl(OH)_4$ (present in liquid phase only, entirely water-soluble)
- 3% NaOH (present in liquid phase only)
- 2% $Na_2C_2O_4$ (present in both solid and liquid phases; partially soluble in H_2O, less soluble at high hydroxide concentration; major phase in centrifuged solids, but quantity not established)
- 31% H_2O
- 4% other (Cr and Na/K salts of F, Cl, PO_4, SO_4, acetate, formate)

Water-insoluble solids (the centrifuged solids from cones O and P) accounted for approximately 10-15 wt% of the test sample. The dominant insoluble phase was probably boehmite [Al(O)OH], though the phase cannot be confirmed by XRD due to the amorphous nature of the solids. Other significant contributors to the centrifuged solids included cancrinite

($Na_6Ca_2Al_6Si_6O_{24}(NO_3)_2$), sodium oxalate ($Na_2C_2O_4$), and amorphous Cr-rich particles. Chromium was more prevalent in AX-103 than in AX-101. Although most of the Cr was apparently amorphous (associated in non-stoichiometric ratio to several other elements), some possible crystals of "hydrouvarovite" [$(Ca,Sr)_3(Cr,Al)_2(OH)_{12}$] were observed. Other elements identified but not tied to specific phases were Ca, Cl, U, and Fe.

8 CONCLUSIONS

Caustic demand testing has been completed on three archive samples: a single segment sample from AX-101, a composite sample from AX-101, and a composite sample from AX-103. This fulfilled the requirement of the test plan, WRPS-1505529. Test results showed a caustic demand of 0.05-0.08 moles of hydroxide per kg of tank waste for AX-101 segment 1 and zero caustic demand for the AX-101 and AX-103 composite samples. The caustic demand for segment 1 can be attributed to the reaction of disodium phosphate with NaOH.

9 REFERENCES

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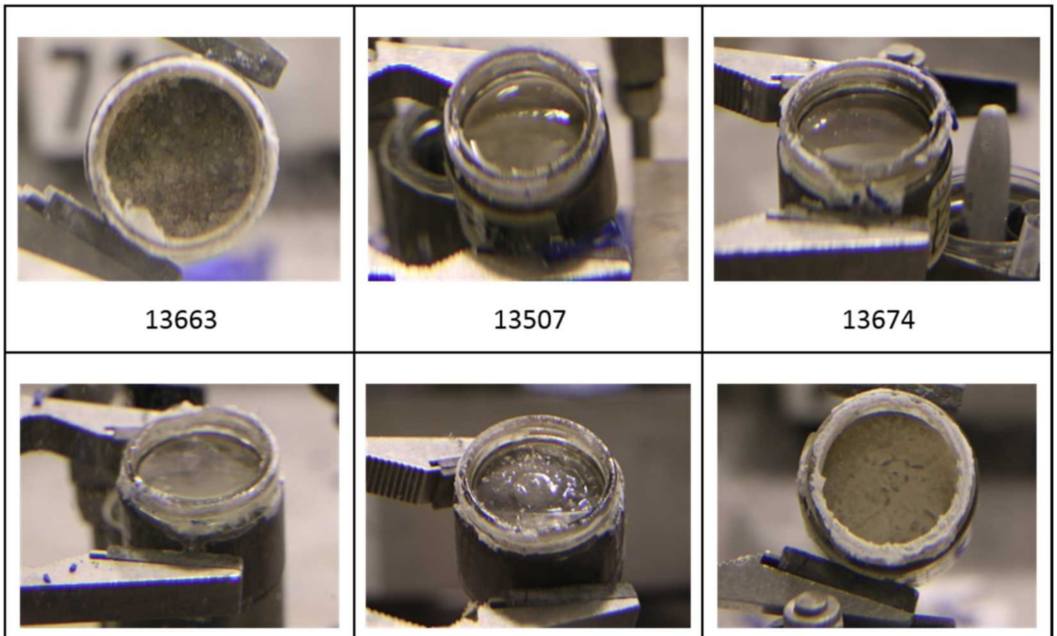
Tank Waste Inventory Network Systems (TWINS) database, Queried 11/18/15 [Sample Analysis/Tank Results RPP 241/Tank Results (Hide QA records)], https://twins.labworks.org/twinsdata/Forms/About.aspx.

WRPS-1505529, 2016, “Test Plan and Procedure for Caustic Demand Testing on Tank 241-AX-101 and Tank 241-AX-103 Archive Samples,” (internal letter from D. L. Herting to W. J. Powell, January 18), Washington River Protection Solutions LLC, Richland, Washington.

APPENDIX A

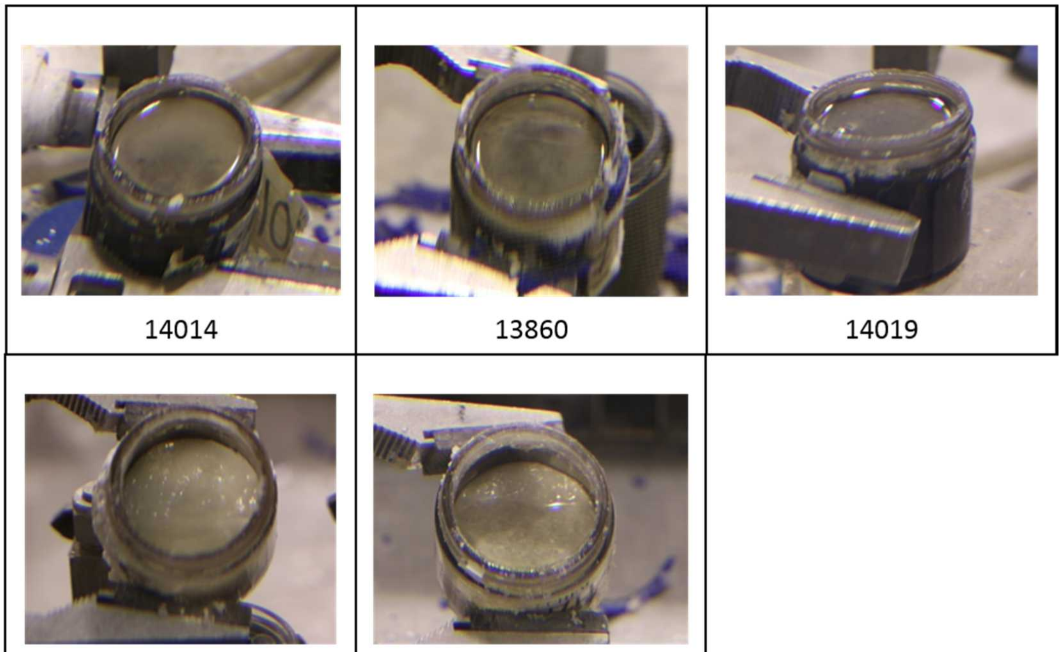
ARCHIVE SAMPLE PHOTOS



13663 13507 13674

13678 13685 13689

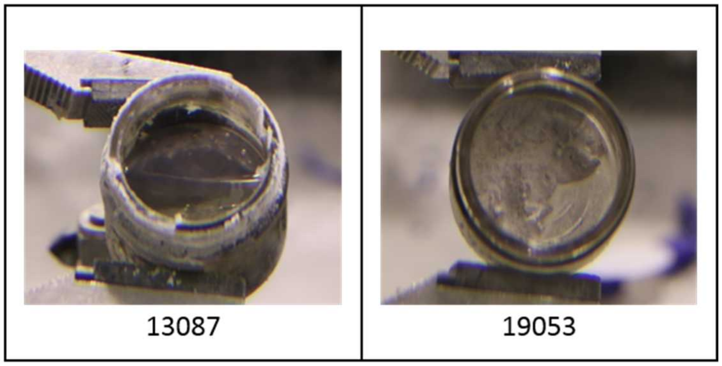
Figure A-1. Photographs of Core 226, 241-AX-101 Archive Samples Used.



14014 13860 14019

14206 14198

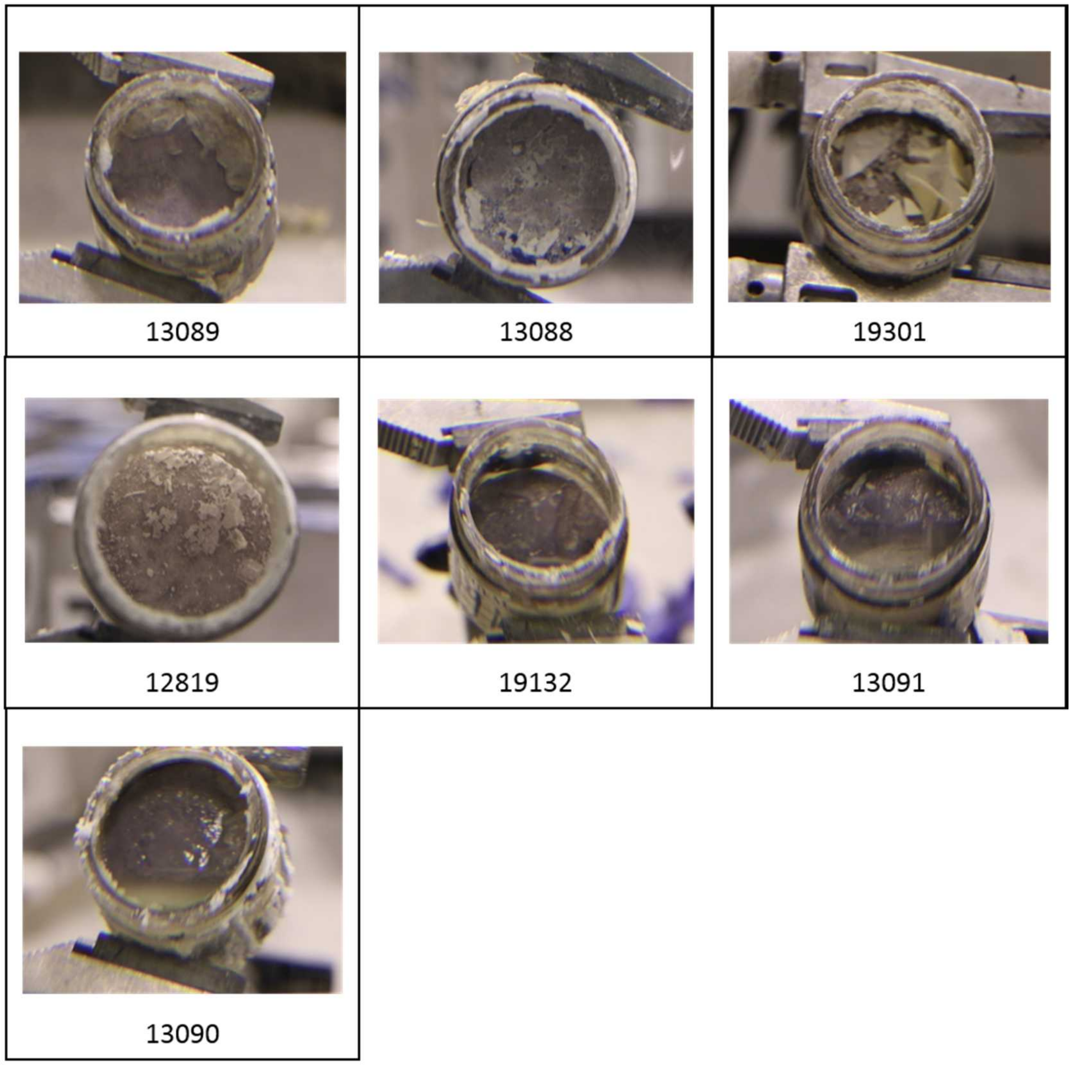
Figure A-2. Photographs of Core 228, 241-AX-101 Archive Samples Used.



13087

19053

Figure A-3. Photographs of Core 212, 241-AX-103 Archive Samples Used.



13089

13088

19301

12819

19132

13091

13090

Figure A-4. Photographs of Core 214, 241-AX-103 Archive Samples Used.

APPENDIX B

SAMPLE BREAKDOWN DIAGRAMS

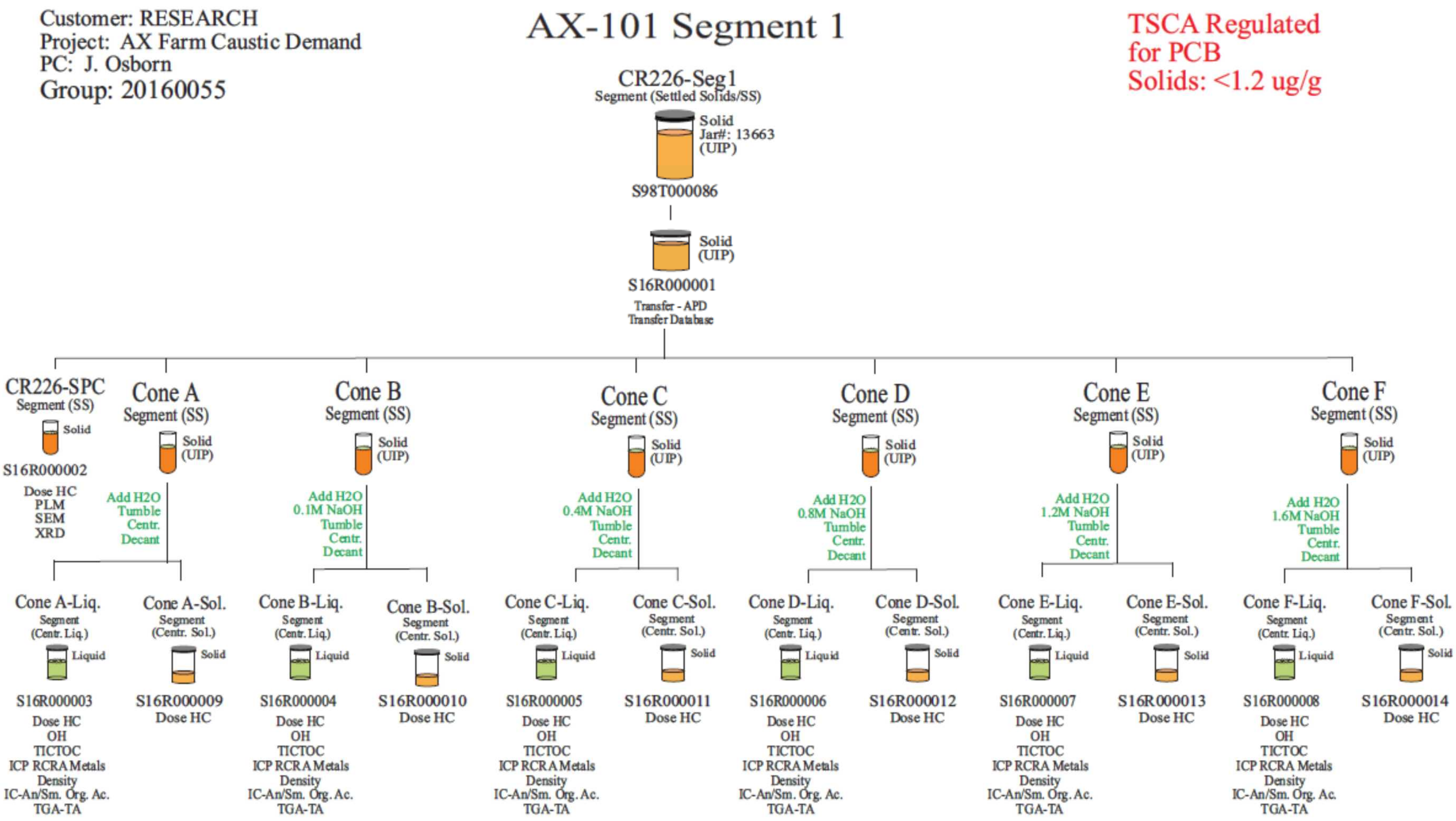


Figure B-1. Sample Breakdown Diagram for 241-AX-101 Segment 1.

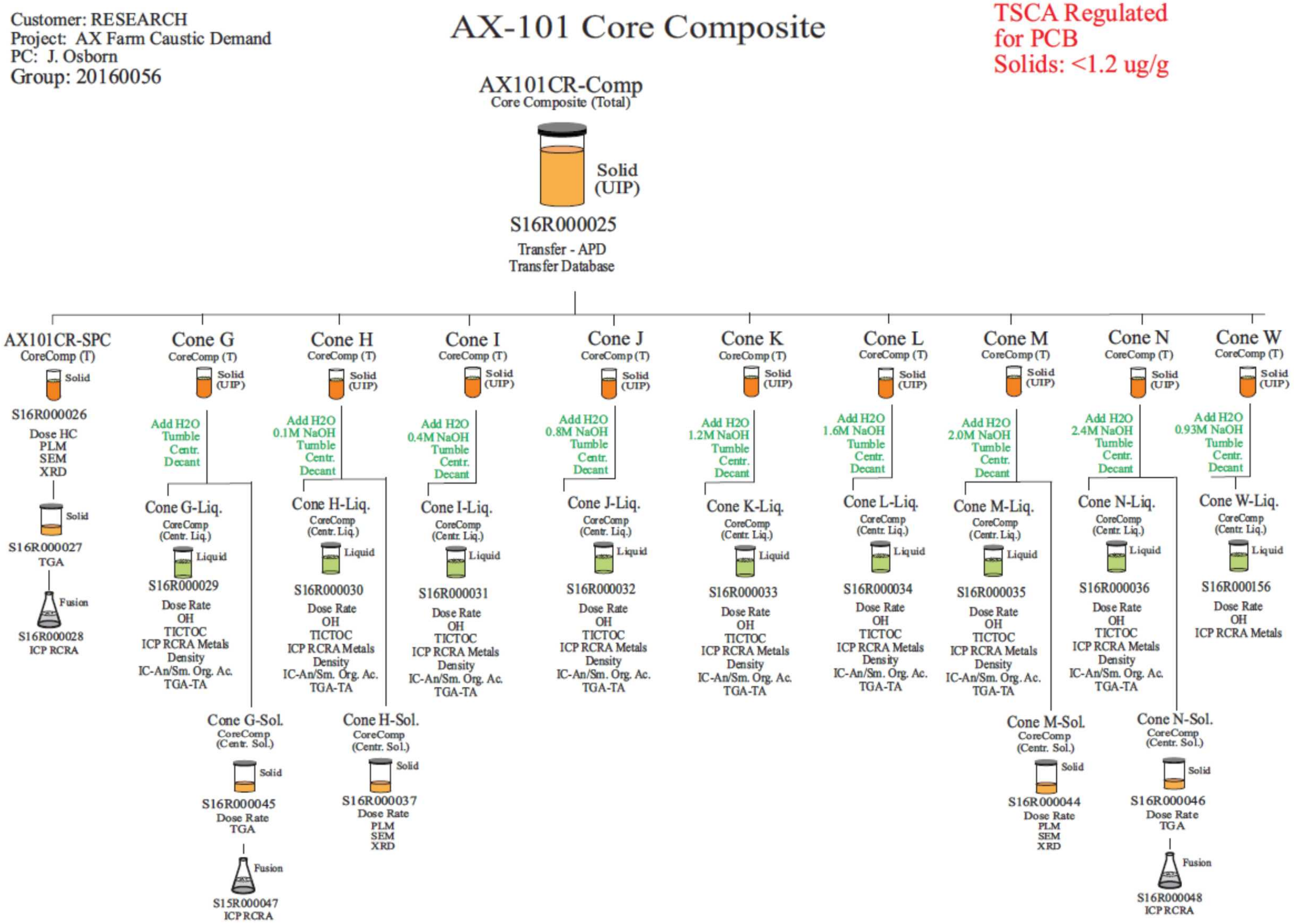


Figure B-2. Sample Breakdown Diagram for 241-AX-101 Core Composite.

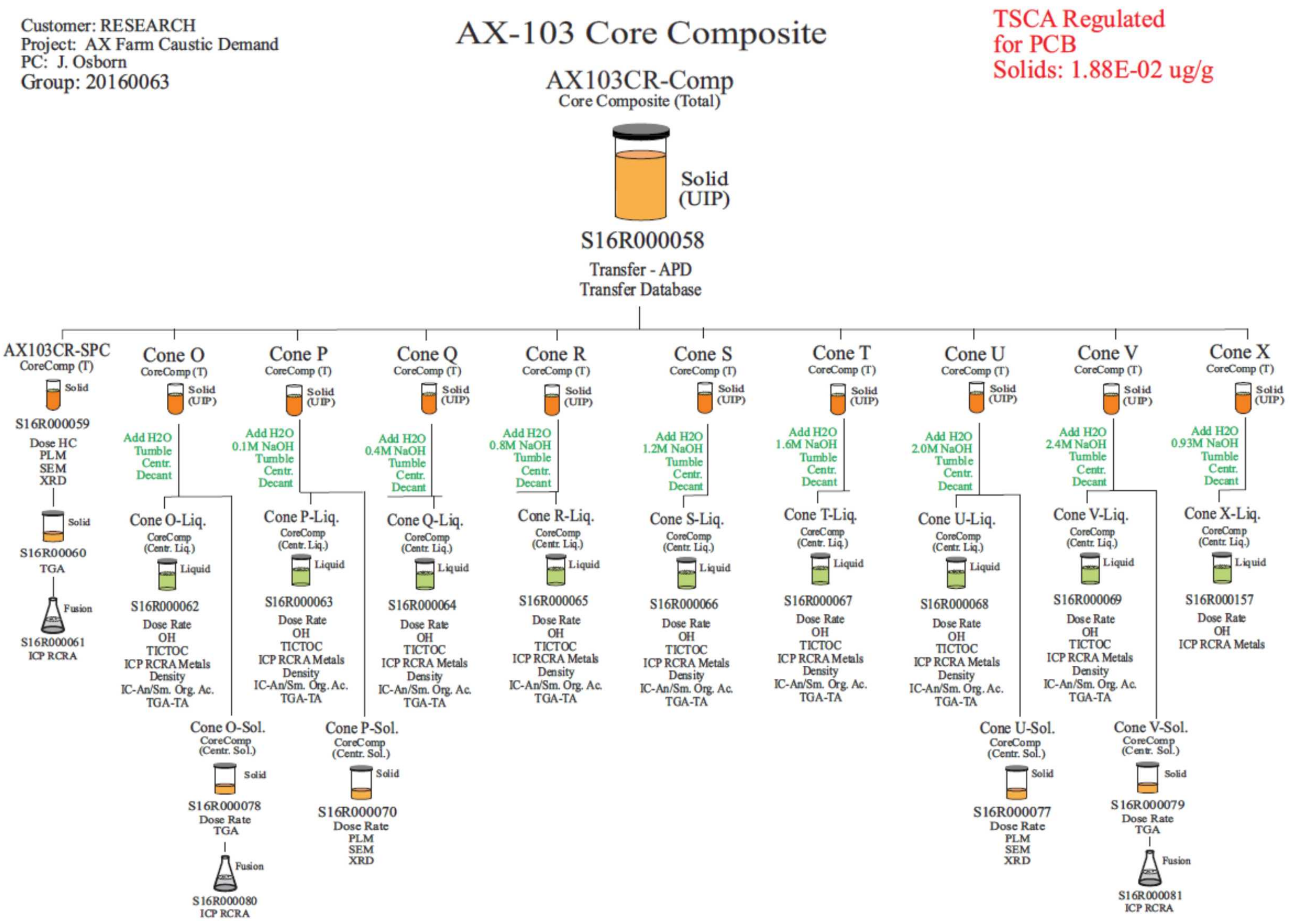


Figure B-3. Sample Breakdown Diagram for 241-AX-101 Core Composite.

APPENDIX C

SOLID PHASE CHARACTERIZATION

Solid phase characterization (SPC) is the process of identifying specific chemical (e.g., $NaNO_3$) and mineral (e.g., cancrinite) phases associated with tank waste samples. The purpose is to provide information about waste behavior that cannot be gleaned from traditional chemical analysis (i.e., concentrations of ions and elements). Chemical/mineral speciation is needed to better understand issues such as solubility (for waste retrieval), particle size distribution (for mixing and pumping issues), corrosion (for safe storage), and many others.

A trio of SPC analysis methods has been used at 222-S for a number of years to directly examine tank waste solids. The trio consists of polarized light microscopy (PLM), scanning electron microscopy (SEM), and x-ray diffraction (XRD). Each of the three methods has its distinct advantages and disadvantages, and SPC works best when the three methods are used in concert.

In addition to direct examination of solids, conclusions can be inferred from chemical analysis of both solid and liquid samples using the traditional techniques of ion chromatography (IC), inductively coupled plasma spectroscopy (ICP), total inorganic carbon/total organic carbon analysis (TIC/TOC), thermogravimetric analysis (TGA), and others.

All of these methods were applied to the following list of analytical samples from the tank 241-AX-101 (AX-101)/tank 241-AX-103 (AX-103) caustic demand test program. The results of the analyses are summarized in Section 7 of the report. Details are presented here.

- S16R000002 – AX-101 Segment 1 test sample PLM/SEM/XRD
- S16R000026 – AX-101 Composite test sample PLM/SEM/XRD
- S16R000027 – AX-101 Composite test sample TGA
- S16R000028 – AX-101 Composite test sample fusion digest/ICP
- S16R000037 – AX-101 Composite Cone H PLM/SEM/XRD
- S16R000044 – AX-101 Composite Cone M PLM/SEM/XRD
- S16R000045 – AX-101 Composite Control Cone G TGA
- S16R000046 – AX-101 Composite Cone N TGA
- S16R000047 – AX-101 Composite Control Cone G fusion digest/ICP
- S16R000048 – AX-101 Composite Cone N fusion digest/ICP
- S16R000059 – AX-103 Composite test sample PLM/SEM/XRD
- S16R000060 – AX-103 Composite test sample TGA
- S16R000061 – AX-103 Composite test sample fusion digest/ICP
- S16R000070 – AX-103 Composite Cone P PLM/SEM/XRD
- S16R000077 – AX-103 Composite Cone U PLM/SEM/XRD
- S16R000078 – AX-103 Composite Control Cone O TGA
- S16R000079 – AX-103 Composite Cone V TGA
- S16R000080 – AX-103 Composite Control Cone O fusion digest/ICP
- S16R000081 – AX-103 Composite Cone V fusion digest/ICP

Chemical Analyses

Chemical analysis of solids consisted of percent water analysis using TGA (LA-514-115, “Thermal Stability and Percent Weight Loss Using the TA DSC and TGA”) and metals by ICP (LA-505-174, “Inductively Coupled Plasma (ICP) Emission Spectrometric Method for the Thermo Scientific iCAP 6500”) following a fusion digest (LA-549-141, “Fusion by Alkali Metal Hydroxide”).

Polarized Light Microscopy

Polarized light microscopy analyses were performed at the 222-S Laboratory using procedure ATS-LT-519-107, “222-S Laboratory Polarized Light Microscopy.” The data can be found in controlled laboratory notebook HNF-N-395-2, “Polarized Light Microscopy” on pages 11–14 and pages 21–25. The samples analyzed were the result of the AX Farm Caustic Demand Study, which was performed under test plan WRPS-1505529, “Test Plan for Caustic Demand Testing on Tank 241-AX-101 and Tank 241-AX-103 Archive Samples.” All of the PLM photographs in this report were recorded with crossed polarizers and a Red I compensator.

Scanning Electron Microscopy

Scanning electron microscopy analysis was performed in accordance with ATS-LT-161-103, “222-S Laboratory Technology Procedure for the ASPEX Explorer Scanning Electron Microscope.” The analytical samples were prepared by transferring the dried solids from a small petri dish onto an aluminum SEM stub covered with an adhesive carbon tab. Samples were coated with a thin layer of carbon by evaporative disposition. The resulting SEM specimens were examined on the ASPEX®[4] PSEM located in Room 1-A at the 222-S Laboratory. Information pertaining to the preparation and analysis is contained in laboratory controlled notebook HNF-N-832-1, “PSEM Instrument,” on pages 221–223.

X-Ray Diffraction

Sample Preparation: For dry and wet sludge samples, solids were removed from the sample vial and deposited in a mortar and allowed to dry overnight as needed. Subsequently, the solids were wet ground in ethyl alcohol and allowed to dry. The powder-like specimen material was deposited on a masked and coated (thin layer of petroleum jelly) zero background substrate. The petroleum jelly layer was used as a compliant adhesive that helps to minimize crystallographic orientation of the sample materials. Sample material was evenly distributed across the petroleum jelly adherent, and excess sample was removed by tilting the sample on its side and tapping on the substrate. Once a uniform deposit was achieved, the masking material was removed revealing a centered, circular, thin deposit of finely ground sample material. The slurry samples were vacuum filtered in accord with the steps described in ATS-LT-161-104, “SEM Sample Preparation Procedure.” Subsequently, the filter cake solids were processed as described for the dry solid specimen material previously.

Data Acquisition: Diffraction patterns were acquired using measurement conditions as described in Table C-1, on the Rigaku™[5] MiniFlex II configured with an auto sample changer

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[4] ASPEX is a registered trademark of Aspex Corporation, Delmont, Pennsylvania.

[5] Rigaku is a trademark of Rigaku Americas Corporation, The Woodlands, Texas.

and graphite monochromator. All measurements were performed in accordance with the steps described in ATS-LT-507-103, “222-S Laboratory X-Ray Diffractometry (XRD) Using the Rigaku MiniFlex II.”

Table C-1. XRD Measurement Conditions.

S16R0000xx	02	26	37	44	59	70	77
Scan Range (deg)	5-85	5-85	5-85	5-85	5-85	5-85	5-85
Step Size (deg)	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Scan Speed (deg/min)	1	1	0.3	0.3	0.3	0.3	0.3
Sample Form	dry	wet sludge	slurry	wet sludge	slurry	slurry	slurry

Data Processing: Several processing strategies were evaluated during phase identification analyses performed on the data described in this report. The strategy that yielded the most complete results involved comparing the raw diffraction data with a background model to the powder diffraction file database using the whole pattern fitting algorithm in Jade®[6] analysis software. Typically the chemistry filter (including elements H, C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Pb, U) was included in the second and subsequent rounds of phase analysis. Individual data processing and interpretation details are presented in the following sections.

Initially the diffraction data were evaluated without phase chemistry information in hand and with the petroleum jelly contributions to the patterns manually subtracted prior to phase analysis being performed. In the final analysis, the chemistry filter was defined using energy dispersive spectroscopy (EDS) spectra collected from all seven samples, and a background model was specified prior to phase analysis. Manual subtraction was not performed in the interest of minimizing preprocessing numerical bias introduced in the data prior to the onset of phase analysis.

AX-101 Segment 1

Test Sample S16R000002

Sample S16R000002 represents untreated archive test sample from AX-101 core 226 segment 1. The sample was described as coarse, tan, “sand-like” granules.

PLM (AX-101 Segment 1 Test Sample): Two slides were mounted in 1.550 refractive index oil. Figure C-1 shows an overview of the sample, and includes several examples of the major phases (sodium carbonate and sodium nitrate) and an unidentified isotropic crystal as one of the

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[6] Jade is a trademark of Materials Data Incorporated, Livermore, California.

minor phases. Figure C-2 shows a single large sodium nitrate crystal. A third slide was mounted in one drop of deionized water. The water dissolved the majority of anisotropic material. The residue consisted of fine particulate (too small for identification by PLM) and a few interesting diamond-shaped crystals (Figure C-3).

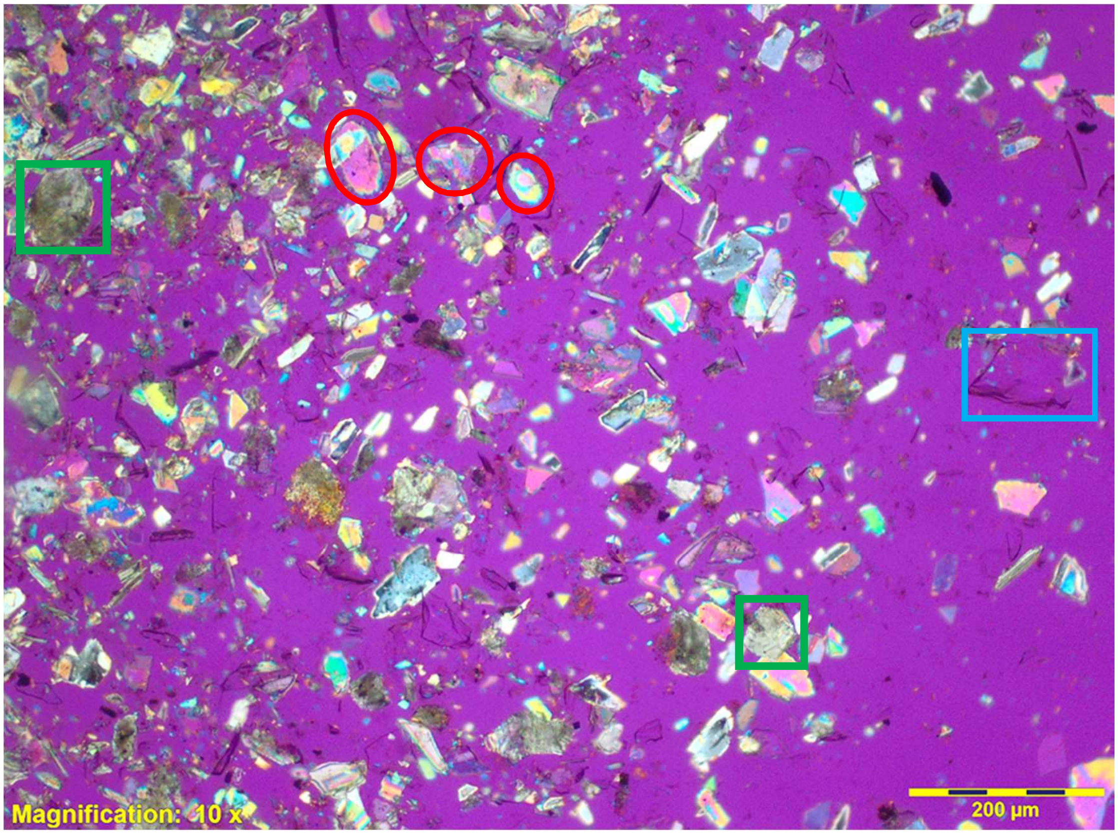


Figure C-1. AX-101 Segment 1 Test Sample PLM Photo S16R000002k Showing Sodium Carbonate (Red Circles), Sodium Nitrate (Green Squares), and an Unidentified Isotropic Crystal (Blue Rectangle).

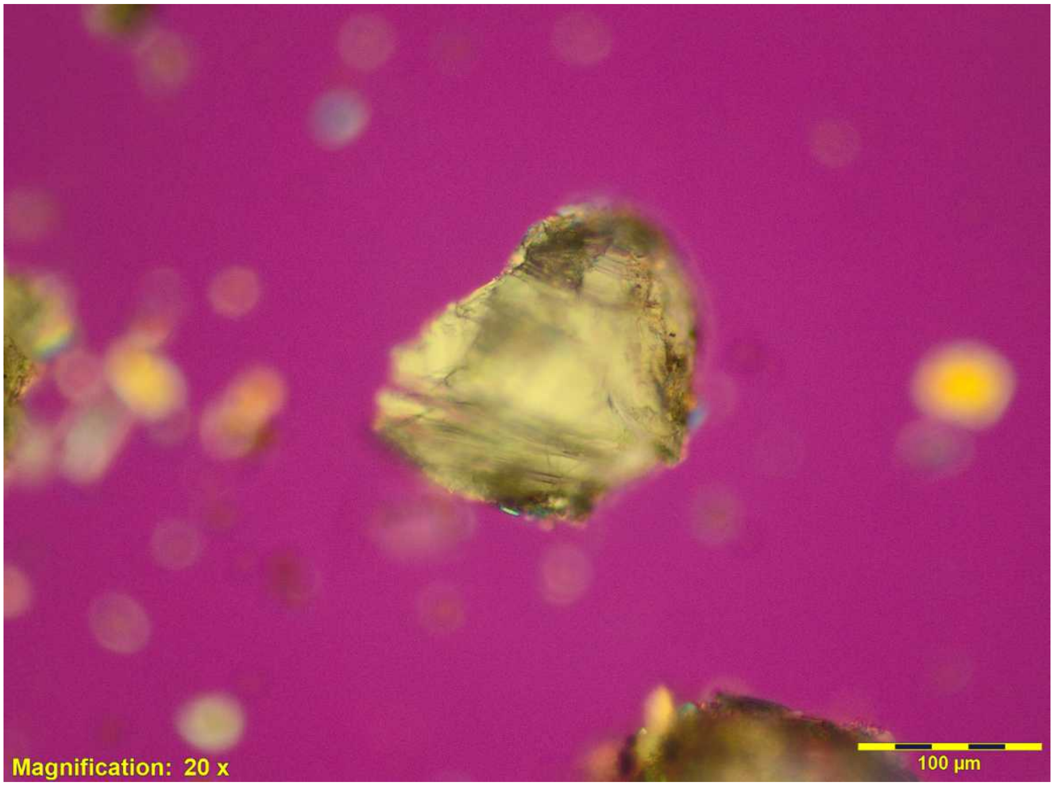


Figure C-2. AX-101 Segment 1 Test Sample PLM Photo S16R000002ee Showing Sodium Nitrate.

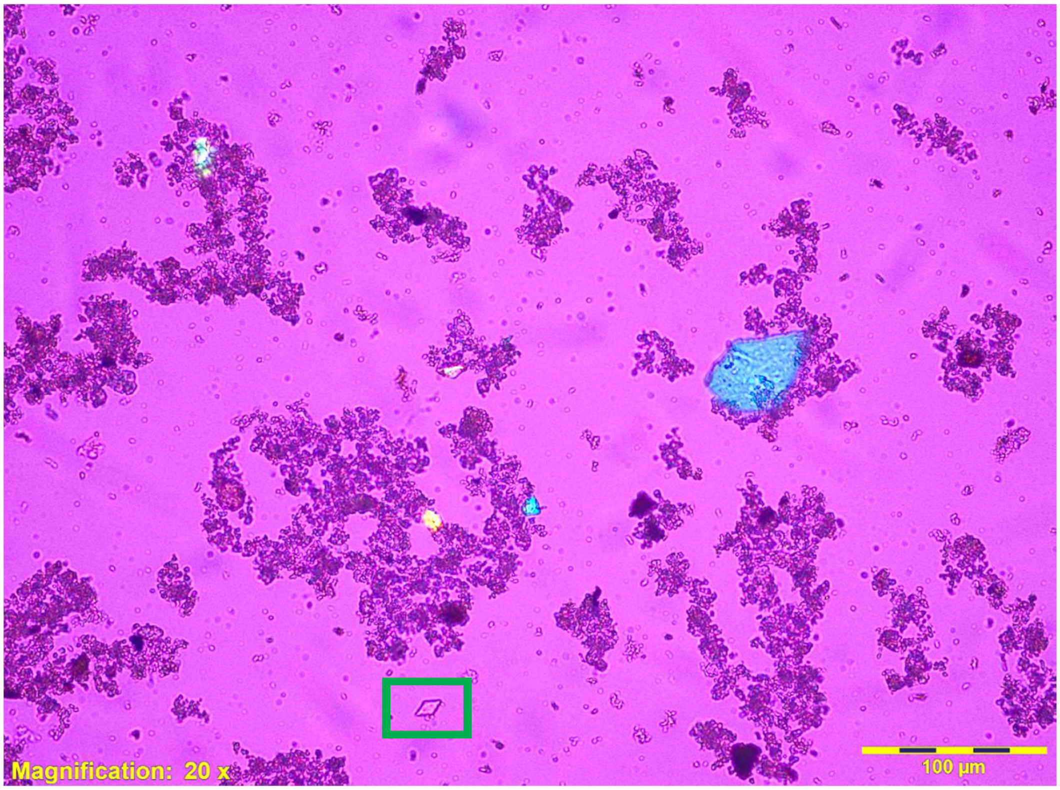


Figure C-3: AX-101 Segment 1 Test Sample PLM Photo S16R000002h Showing an Unknown Diamond-shaped Crystal (Green Rectangle).

<u>SEM (AX-101 Segment 1 Test Sample)</u>: No liquid was present so the sample was lightly crushed and lifted onto a double sticky carbon tab. SEM photos and EDS spectra were then taken. The sample consisted of Na-rich particles, with varying concentrations of O, C, Cl, Al, and Si, and had small concentrations of N, Ca, Fe, Ni, Cr, Mg, K, and S. The sample probably contained sodium nitrate ($NaNO_3$, Figure C-4), sodium carbonate ($Na_2CO_3 \cdot H_2O$, Figure C-5), and hematite (Fe_2O_3, Figure C-6).

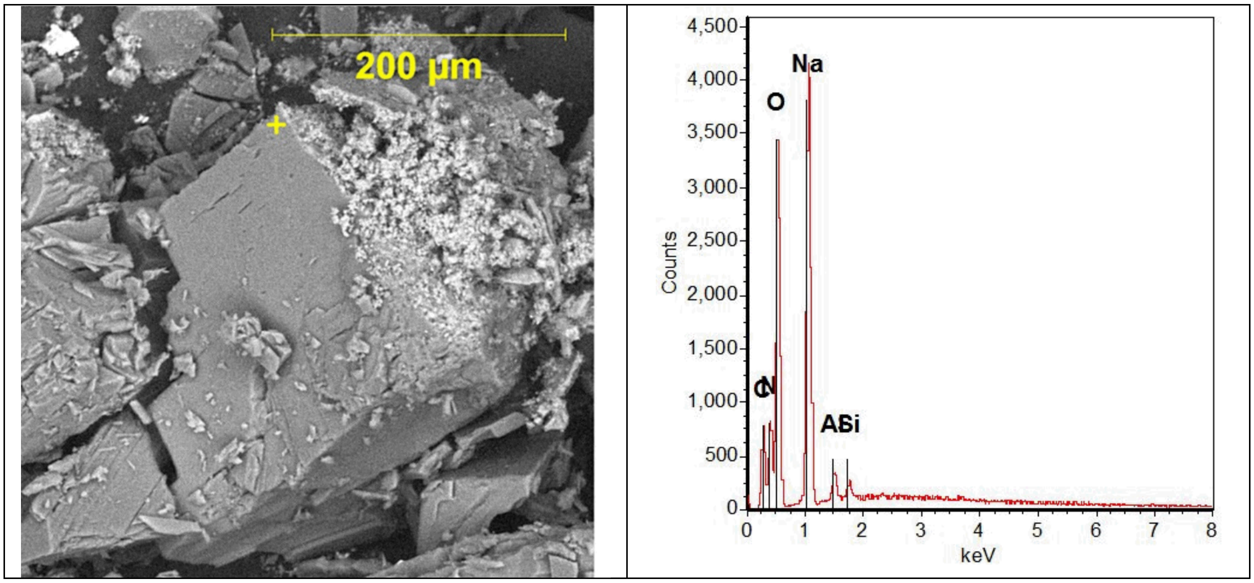


Figure C-4. AX-101 Segment 1 Test Sample SEM Photo and EDS Spectrum Showing $NaNO_3$.

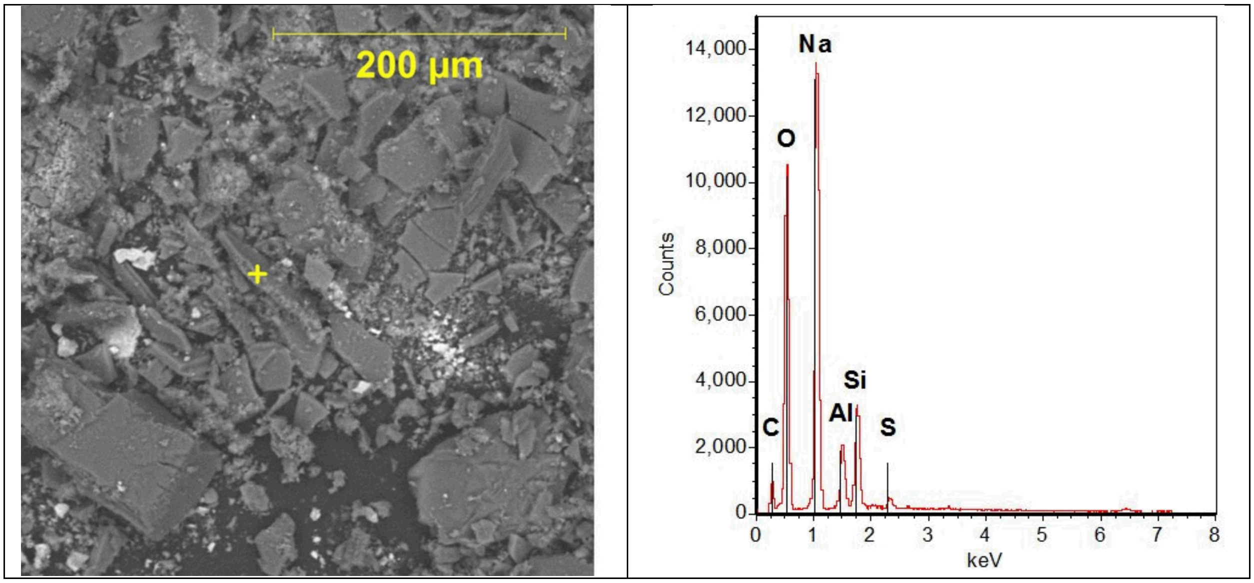


Figure C-5. AX-101 Segment 1 Test Sample SEM Photo and EDS Spectrum Showing [Mainly] $Na_2CO_3 \cdot H_2O$.

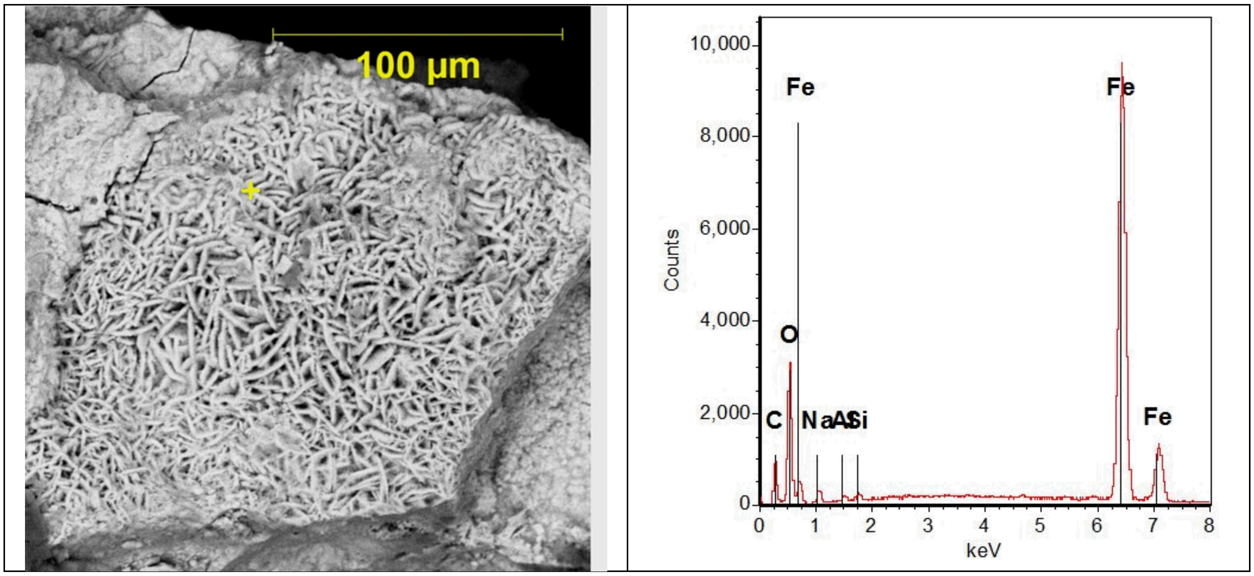


Figure C-6. AX-101 Segment 1 Test Sample SEM Photo and EDS Spectrum Showing Fe_2O_3.

<u>XRD (AX-101 Segment 1 Test Sample)</u>: A single piece of the sample was ground in a mortar and air-dried overnight. The sample was then ground in ethyl alcohol and allowed to dry. The resulting powder was deposited on a masked and coated (thin layer of petroleum jelly) zero background substrate. The petroleum jelly layer was used as a compliant adhesive that helps to minimize crystallographic orientation of the sample materials. The only phase identified (see Figure C-7) was nitratine ($NaNO_3$). Peak identification data are shown in Table C-2.

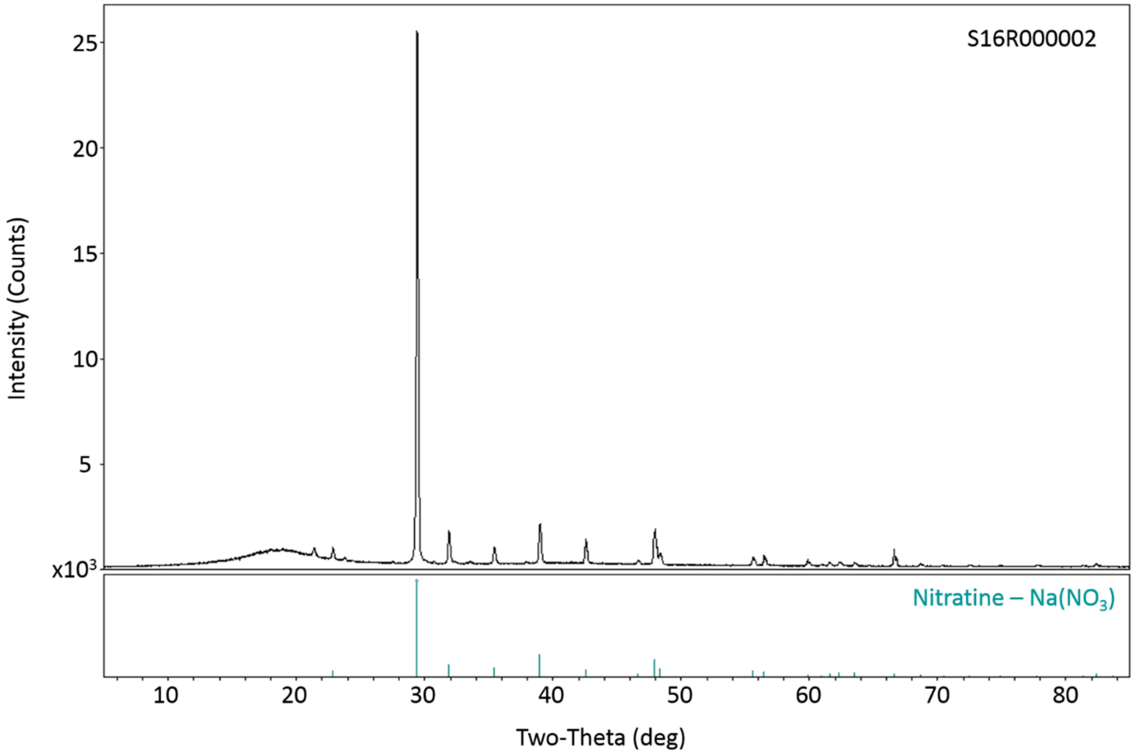


Figure C-7. AX-101 Segment 1 Test Sample S16R000002 XRD Phase Identification Data.

Table C-2. AX-101 Segment 1 Test Sample S16R000002 XRD Phase Identification Results.

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
21.461	4.1371	361	1.4	Unknown					
22.922	3.8767	532	2.1	Nitratine	3.8927	6.4	(0 1 2)	22.826	-0.095
29.481	3.0274	25241	100	Nitratine	3.0378	100	(1 0 4)	29.378	-0.103
31.979	2.7964	1531	6.1	Nitratine	2.8048	12.6	(0 0 6)	31.88	-0.099
35.500	2.5267	768	3	Nitratine	2.535	9.6	(1 1 0)	35.38	-0.121
39.061	2.3042	1850	7.3	Nitratine	2.3101	23	(1 1 3)	38.957	-0.104
42.621	2.1195	1140	4.5	Nitratine	2.1243	7.1	(2 0 2)	42.522	-0.099
48.020	1.8931	1695	6.7	Nitratine	1.8971	17.8	(0 1 8)	47.912	-0.108
48.422	1.8783	523	2.1	Nitratine	1.8807	8	(1 1 6)	48.357	-0.065
55.683	1.6494	371	1.5	Nitratine	1.6515	6.4	(2 1 1)	55.603	-0.08
56.542	1.6263	482	1.9	Nitratine	1.6282	5.6	(1 2 2)	56.472	-0.071
59.941	1.542	318	1.3	Nitratine	1.5438	2	(2 1 4)	59.863	-0.078
62.422	1.4865	186	0.7	Nitratine	1.4885	3.8	(1 2 5)	62.331	-0.091
66.680	1.4015	830	3.3	Nitratine	1.4024	3.2	(0,0,12)	66.633	-0.047

Chemical Analysis (AX-101 Segment 1 Test Sample): The chemical composition of the water-soluble fraction of solids in the test sample (which represents approximately 73 wt% of the sample) can be inferred from the analyses performed on the centrifuged liquid from the control cone A (sample S16R000003). The analytical results for this sample are shown in Table 4-1 in the body of the report. The key analytes and their reported concentrations are repeated here in the first two columns of Table C-3.

The total mass of centrifuged liquid in control cone A was 14.59 g (Table 2-5), and its density was 1.143 g/mL (Table 4-1), which gives a total volume of 12.76 mL. Multiplying the concentration of each analyte by the total volume and dividing by 1000 times the formula weight gives the molarity of each analyte in the centrifuged liquid (column 3 in Table C-3).

The fourth column in Table C-3 shows the most likely solid phase containing each analyte, with its molecular weight in the fifth column. Multiplying the molarity times the molecular weight times the volume (12.76 mL) gives the total mass of each compound present in the centrifuged liquid (column 6). Dividing the mass of each chemical by the total mass of the test sample in the cone (3.98 g) gives the wt% of each chemical in the test sample (column 7).

The sum of column 6 gives the total mass of the compounds in the centrifuged liquid. Dividing this sum (2.92 g) by the total test sample mass (3.98 g) gives the wt% of the test sample that dissolved in the water added to the cone and matches the sum of column 7 (73.4 wt%). By difference, 100 – 73.4 = 26.6 wt% of the test sample remained in the centrifuged solids.

In comparison, 3.98 g x 26.6 wt% = 1.06 g, which is the calculated mass of undissolved solids in control cone A. The actual mass of centrifuged solids was 1.24 g. Because the centrifuged solids include some [unmeasured] amount of interstitial liquid (ISL) in addition to the undissolved solids, the match is very good.

Table C-3. Calculation of Water-soluble Solids in AX-101 Segment 1 Test Sample.

Analyte	Result (µg/mL)	Molarity (mmol/mL)	Assumed Compound	Molecular Weight (mg/mmol)	Total Mass (mg)	Wt% of Test Sample
Fluoride	193	0.010	NaF ([a])	42	5	0.1
Chloride	210	0.006	NaCl	58.45	4	0.1
Nitrite	4430	0.096	$NaNO_2$	69	85	2.1
Nitrate	133000	2.145	$NaNO_3$	85	2327	58.5
Phosphate	2870	0.030	$Na_2HPO_4 \bullet 7H_2O$	268	103	2.6
Sulfate	2040	0.021	Na_2SO_4	142	39	1.0
Oxalate	1210	0.014	$Na_2C_2O_4$	134	24	0.6
Acetate	323	0.005	KCH_3COO ([b])	98.1	7	0.2
Formate	639	0.014	$NaHCO_2$	68	12	0.3
TIC	2390	0.199	$Na_2CO_3 \bullet H_2O$	124	315	7.9
Hydroxide	100	0.006	NaOH	40	3	0.1
Aluminum	< DL	< DL	Total		2924	73.4
Chromium	38.8	0.001				
Potassium	186	0.005				
Sodium	67600	2.939				

([a]) Fluoride is assumed to be present as either natrophosphate ($Na_7F(PO_4)_2 \bullet 19H_2O$) or kogarkoite ($Na_3FSO_4$) or both, but for the purposes of accounting for the mass, is shown separately.
([b]) Potassium is shown associated with acetate for accounting purposes because the number of moles of acetate and potassium happen (coincidentally) to match. Potassium is probably distributed more-or-less evenly among the sodium salts.

AX-101 Composite

Test Sample S16R000026

S16R000026 represents untreated AX-101 Core 226/228 composite archive test sample. The test sample was described as gray, moist, "sand-like" material.

PLM (AX-101 Composite Test Sample): An attempt was made to mount the original test sample both with and without refractive index oil, however an acceptable mount was not possible as the particles would not disperse. In these unacceptable mounts, a fair amount of $NaNO_3$ was observed. After verifying SEM and XRD analyses were complete, three drops of deionized water were added to the test sample vial and thoroughly mixed. The water dissolved the sodium nitrate allowing for acceptable subsequent PLM mounts. In Figure C-8, the PLM photo S16R000026f is representative of the phases observed in the diluted test sample, including $Na_2CO_3 \bullet H_2O$ as the primary phase, with $Na_2C_2O_4$ needles and isotropic crystals, suspected to be $Na_7F(PO_4)_2 \bullet 19H_2O$, also present.

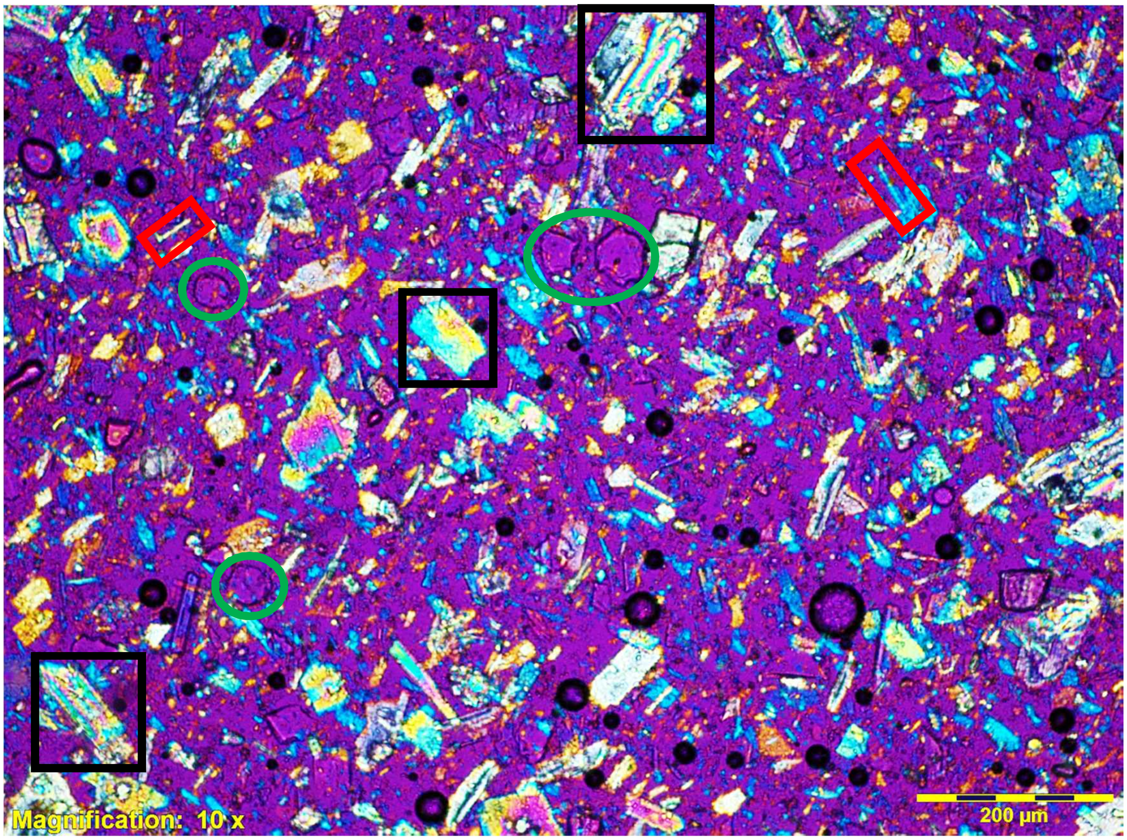


Figure C-8. Diluted AX-101 Composite Test Sample PLM Photo S16R000026f Showing Na_2CO_3 (Black Squares), $Na_2C_2O_4$ (Red Rectangles), and Suspected $Na_7F(PO_4)_2{\bullet}19H_2O$ (Green Circles).

<u>SEM (AX-101 Composite Test Sample)</u>: The test sample was mainly Na-rich with C and O in large concentrations. Other elements found were Al, N, Cl, K, P, S, U, Fe, Mn, Ca, Mg, and Si. The sample contained $NaNO_3$, $Na_2CO_3{\bullet}H_2O$ (Figure C-9), clarkeite ($Na(UO_2)O(OH){\bullet}0\text{-}1(H_2O)$) (Figure C-9), and $Na_6Ca_2Al_6Si_6O_{24}(NO_3)_2$. The brightness on top of some Na-rich particles was Cl. The U-rich and metal-rich particles were very small (<5 µm) and were detectable as bright spots within the sample (Figure C-9).

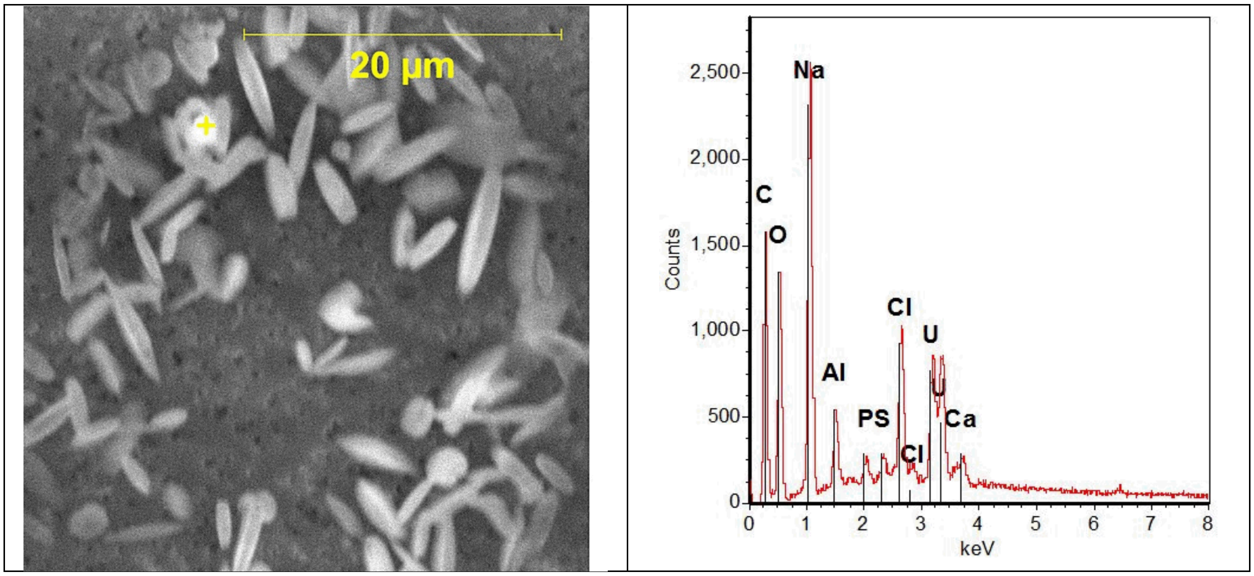


Figure C-9. AX-101 Composite Test Sample SEM Photo and EDS Spectrum Showing a $Na(UO_2)O(OH){\bullet}0\text{-}1(H_2O)$ Particle and (Likely) $Na_2CO_3{\bullet}H_2O$ Crystals.

<u>XRD (AX-101 Composite Test Sample)</u>: Two major phases were identified in the data ($NaNO_3$ and $Na_2CO_3{\bullet}H_2O$) with two unidentified peaks (see Figure C-10 and Table C-4).

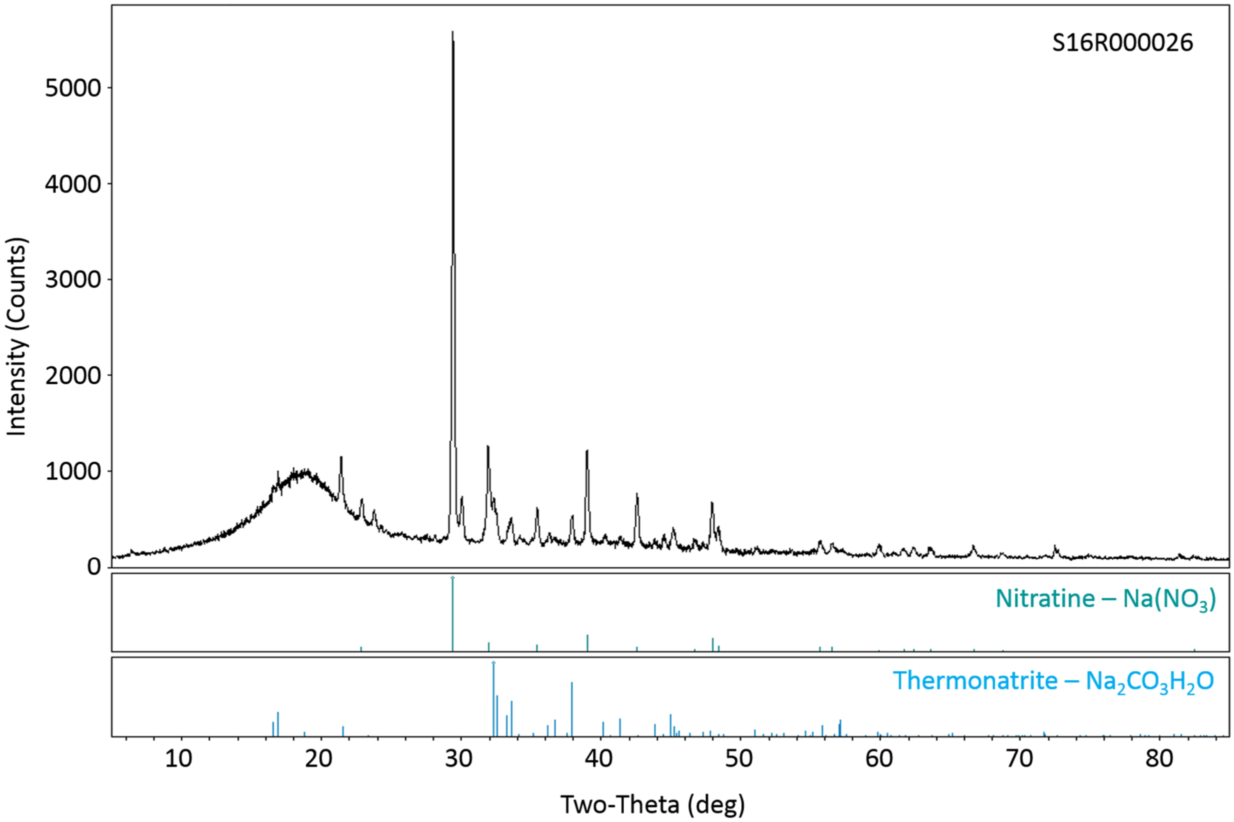


Figure C-10. AX-101 Composite Test Sample S16R000026 XRD Phase Identification Data.

Table C-4. AX-101 Composite Test Sample S16R000026 XRD Phase Identification Results.

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
6.442	13.7087	60	1.1	Unknown					
21.479	4.1338	483	9.1	Thermonatrite	4.1284	13.1	(2 0 1)	21.507	0.028
22.94	3.8737	227	4.3	Nitratine	3.8889	6.6	(0 1 2)	22.849	-0.091
23.803	3.7351	175	3.3	Thermonatrite	3.756	0.1	(2 1 0)	23.669	-0.135
27.596	3.2297	60	1.1	Thermonatrite	3.2265	0.5	(0 0 2)	27.624	0.028
28.164	3.1659	63	1.2	Unknown					
29.48	3.0275	5299	100	Nitratine	3.0345	100	(1 0 4)	29.41	-0.07
30.119	2.9647	445	8.4	Thermonatrite	2.9591	0.4	(3 1 0)	30.178	0.059
31.981	2.7962	1003	18.9	Nitratine	2.8013	12.5	(0 0 6)	31.921	-0.06
32.399	2.761	449	8.5	Thermonatrite	2.7659	100	(2 0 2)	32.341	-0.058
33.679	2.659	254	4.8	Thermonatrite	2.6636	46.4	(1 1 2)	33.619	-0.06
34.279	2.6138	77	1.5	Thermonatrite	2.627	3.3	(0 2 0)	34.102	-0.177
35.501	2.5266	391	7.4	Nitratine	2.5328	9.7	(1 1 0)	35.412	-0.088
36.339	2.4702	121	2.3	Thermonatrite	2.4796	14.4	(4 0 1)	36.198	-0.142
36.739	2.4443	73	1.4	Thermonatrite	2.4475	21.7	(2 1 2)	36.689	-0.049
38.019	2.3649	287	5.4	Thermonatrite	2.373	72.5	(1 2 1)	37.884	-0.135
39.061	2.3042	962	18.1	Nitratine	2.3079	22.4	(1 1 3)	38.995	-0.066
40.398	2.2309	88	1.7	Thermonatrite	2.2424	19.3	(4 1 1)	40.182	-0.215
41.459	2.1762	85	1.6	Thermonatrite	2.1808	22.9	(3 1 2)	41.368	-0.091
42.658	2.1178	542	10.2	Thermonatrite	2.1182	1.2	(3 2 0)	42.651	-0.007
44.582	2.0308	131	2.5	Thermonatrite	2.0372	3.5	(0 2 2)	44.435	-0.147
45.241	2.0027	203	3.8	Thermonatrite	2.0015	13.7	(1 2 2)	45.27	0.029
46.708	1.9432	98	1.8	Nitratine	1.9445	3.2	(0 2 4)	46.676	-0.032
48.001	1.8938	489	9.2	Nitratine	1.8949	17.7	(0 1 8)	47.972	-0.029
48.497	1.8756	236	4.5	Thermonatrite	1.878	2.3	(4 2 0)	48.431	-0.066
55.704	1.6488	130	2.4	Nitratine	1.6501	6.4	(2 1 1)	55.657	-0.047
56.639	1.6238	107	2	Thermonatrite	1.6231	3.2	(4 2 2)	56.665	0.026
59.96	1.5415	125	2.4	Thermonatrite	1.5422	3.3	(0 1 4)	59.931	-0.029
61.743	1.5012	71	1.3	Thermonatrite	1.5004	2.1	(6 1 2)	61.78	0.037
62.401	1.487	94	1.8	Nitratine	1.487	3.8	(1 2 5)	62.398	-0.003
63.66	1.4605	102	1.9	Thermonatrite	1.4603	0.8	(5 1 3)	63.675	0.014
66.701	1.4012	116	2.2	Nitratine	1.4007	3.1	(0,0,12)	66.727	0.026
72.562	1.3017	134	2.5	Nitratine	1.3016	0.9	(1 2 8)	72.573	0.011
75.139	1.2633	35	0.7	Nitratine	1.2664	0.4	(2 2 0)	74.928	-0.211
81.502	1.18	54	1	Thermonatrite	1.18	2.2	(1 3 4)	81.509	0.007
82.457	1.1688	52	1	Nitratine	1.1687	2.8	(1 3 4)	82.464	0.007

Chemical Analysis (AX-101 Composite Test Sample): One analytical sample of the AX-101 composite test sample was submitted for TGA (S16R000027) and fusion digest/ICP (S16R000028) analyses. Results are shown in Table C-5. (Results for other samples discussed later are also shown here.)

Table C-5. Analytical Results for AX-101 Composite Solids Samples.

Analyte[a]	Units	Result		
		S16R000027/28 Untreated Test Sample	S16R000045/47 Control Cone G Settled Solids	S16R000046/48 Cone N Settled Solids
%H_2O	wt%	24.3	79.3	74.0
Al	µg/g	20700	10800	7870
B	µg/g	<DL[1]	<DL	<DL
Cr	µg/g	1550	4,440	4050
Cu	µg/g	<DL	<DL	216
Fe	µg/g	<DL	497	<DL
P	µg/g	2260	604	371
Na	µg/g	257000	74600	107000
S	µg/g	4770	1340	807
Si[b]	µg/g	3220	3760	3880
U	µg/g	<DL	<DL	1060

[a] <DL = below detection limit

[b] Si reported in preparation blank sample at approximately the same concentration

As shown by the centrifuged liquid and centrifuged solids analyses that follow, much (but not all) of the Al was water-soluble, but very little of the Cr was water-soluble. At 1,550 µg/g, total Cr accounts for less than 0.2 wt% of the AX-101 composite test sample.

The chemical composition of the water-soluble fraction of solids in the test sample (which represents approximately 90-95 wt% of the sample) can be inferred from the analyses performed on the centrifuged liquid from the control cone G (sample S16R000029). The analytical results for this sample are shown in Table 4-2 in the body of the report. The key analytes and their reported concentrations are repeated here in the first two columns of Table C-6.

The total mass of centrifuged liquid in control cone G was 34.94 g (Table 2-5), and its density was 1.130 g/mL (Table 4-2), which gives a total volume of 30.92 mL. Multiplying the concentration of each analyte by the total volume and dividing by 1000 times the formula weight gives the molarity of each analyte in the centrifuged liquid (column 3 in Table C-6).

The fourth column in Table C-6 shows the most likely solid phase containing each analyte, with its molecular weight in the fifth column. Multiplying the molarity times the molecular weight times the volume (30.92 mL) gives the total mass of each compound present in the centrifuged liquid (column 6). Dividing the mass of each chemical by the total mass of the test sample in the cone (8.97 g) gives the wt% of each chemical in the test sample (column 7).

The sum of column 6 gives the total mass of the compounds in the centrifuged liquid. Dividing this sum (7.98 g) by the total test sample mass (8.97 g) gives the wt% of the test sample that dissolved in the water added to the cone and matches the sum of column 7 (88.9 wt%). By difference, 100 – 88.9 = 11.1 wt% of the test sample remained in the centrifuged solids.

In comparison, 8.97 g x 11.1 wt% = 1.00 g, which is the calculated mass of undissolved solids in control cone G. The actual mass of centrifuged solids was 0.68 g, indicating that even more than 89 wt% of the test sample dissolved.

Given that the test sample contained 24.3 wt% H_2O (Table C-5), several of the salts shown as "assumed compounds" in Table C-6 would have been present only as dissolved salts. This likely applies to the sodium/potassium salts of nitrite, acetate, formate, hydroxide, and aluminate.

Table C-6. Calculation of Water-soluble Solids in AX-101 Composite Test Sample.

Analyte	Result (ug/mL)	Molarity (mmol/mL)	Assumed Compound	Molecular Weight	Total Mass (mg)	Wt% of Test Sample
Fluoride	186	0.010	NaF (a)	--	--	--
Chloride	1000	0.028	NaCl	58.45	51	0.6
Nitrite	22000	0.478	$NaNO_2$	69	1020	11.4
Nitrate	46400	0.748	$NaNO_3$	85	1967	21.9
Phosphate	2230	0.023	$Na_7F(PO_4)_2$ (b)	268	195	2.2
Sulfate	4450	0.046	Na_2SO_4	142	204	2.3
Oxalate	2340	0.027	$Na_2C_2O_4$	134	110	1.2
Acetate	566	0.010	KCH_3COO (c)	98.1	29	0.3
Formate	856	0.019	KHCOO (c)	84.1	49	0.6
TIC	3580	0.298	Na_2CO_3 (b)	106	978	10.9
Hydroxide	7040	0.414	NaOH	40	512	5.7
Aluminum	7240	0.268	$NaAlO_2$ (b)	82	680	7.6
Chromium	16	0.000	H_2O	--	2180	24.3
Potassium	1150	0.029	Total		7975	88.9
Sodium	69400	3.017				

(a) Fluoride is assumed to be present as $Na_7F(PO_4)_2 \bullet 19H_2O$.

(b) Waters of hydration included in the H_2O entry, which is derived from the $\%H_2O$ analysis of S16R000027. The hydrated form of $NaAlO_2$ is $NaAl(OH)_4$.

(c) Potassium is shown associated with acetate and formate for accounting purposes because the number of moles of acetate+formate happened (coincidentally) to match the moles of potassium. Potassium is probably distributed more-or-less evenly among the sodium salts.

Centrifuged Solids Analytical Samples from AX-101 Composite Test Cone G (S16R000045/47) and Cone H (S16R000037)

The test plan, WRPS-1505529, called for PLM, SEM, XRD, and chemical analysis of the centrifuged solids from control cone G, but the volume of centrifuged solids was too small to perform all of the analyses required. Therefore, the cone G centrifuged solids were used for the TGA and ICP analyses, while the cone H centrifuged solids were used for the PLM, SEM, and XRD analyses.

Even with the cone substitution, the volume of centrifuged solids was too small to recover from the tip of the centrifuge cone, so excess centrifuged liquid was returned to the cone to slurry the solids. The slurry was transferred from cone H to the S16R000037 sample vial. The slurry was allowed to settle overnight, after which as much liquid as possible was decanted and discarded, and the settled solids were submitted for PLM, SEM, and XRD analyses. The same slurry/settle/decant process was used for transferring the control cone G solids into a sample vial, which was submitted for TGA (S16R000045) and fusion digest/ICP (S16R000047) analyses.

The analytical samples for cone G (S16R000045/47) and cone H (S16R000037) were described as dirty, gray, muddy water.

Chemical Analysis (Cone G): Analytical results for the settled solids from control cone G (S16R000045/47) are shown in Table C-5. The results are dominated by the Na and Al present in the large amount of ISL in the settled solids. The small amounts of Cr and Fe present in the sample are consistent with the SEM/EDS results for the corresponding sample from cone H (S16R000037).

PLM (Cone H): Three slide mounts were prepared in the mother liquor. In Figure C-11, the PLM photo S16R000037r is representative of the phases observed, including a fine-grained (mostly sub-micron) particulate being the primary phase and blue/yellow $Na_2C_2O_4$ needles (yellow with positive slope, blue with negative slope) being the secondary phase.

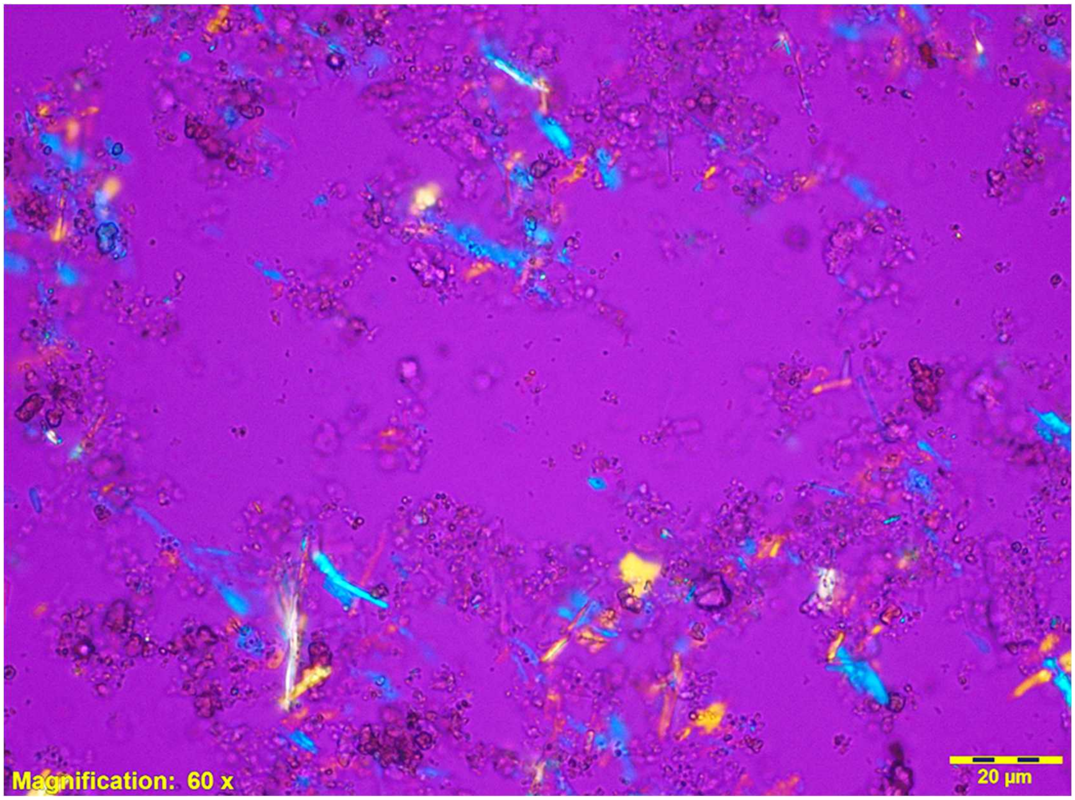


Figure C-11. Cone H PLM Photo S16R000037r Showing Sub-micron Particulate and $Na_2C_2O_4$ Needles.

SEM (Cone H): The analytical sample was mainly O-rich with Na, Al, Si, and C in large concentrations. Ca, Cr, and U were present in certain specimens. Other elements present were P, S, Cl, K, Fe, Ni, N, and Pb. The dominant phase was cancrinite (Figure C-12). Sodium oxalate needles were present, but not a major phase. Very small (<5 µm) metal-rich particles were present throughout the sample, and were detectable as bright spots within the sample. Tentatively identified phases included $Na(UO_2)O(OH)\bullet 0\text{-}1(H_2O)$, “hydrouvarovite” (Figure C-13), and Fe_2O_3.

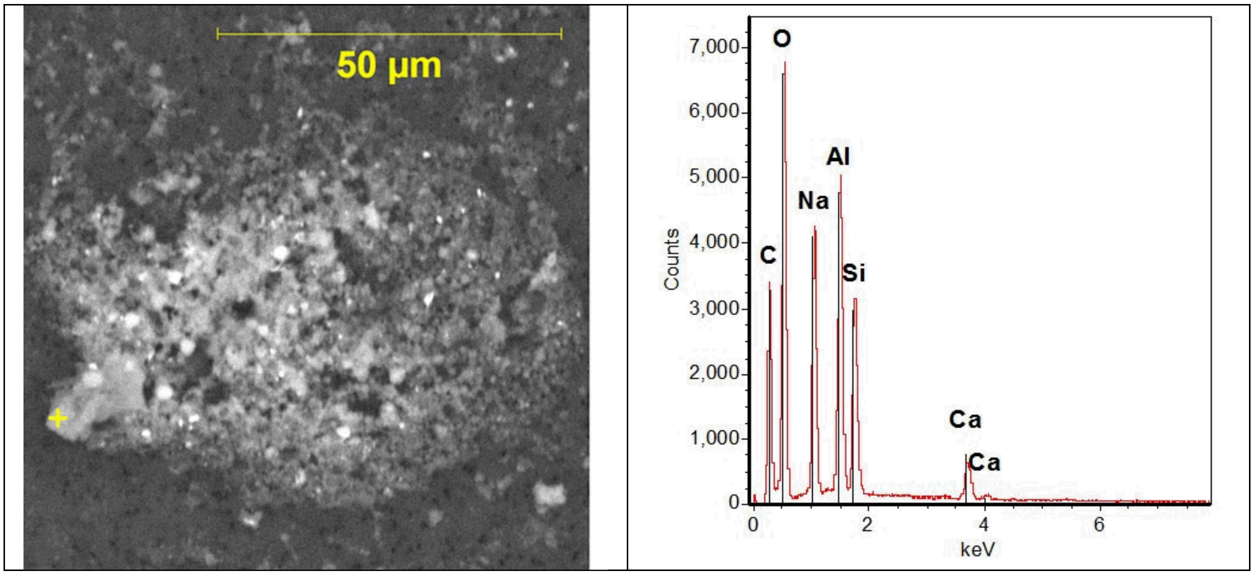


Figure C-12. Cone H Analytical Sample S16R000037 SEM Photo and EDS Spectrum Showing Cancrinite.

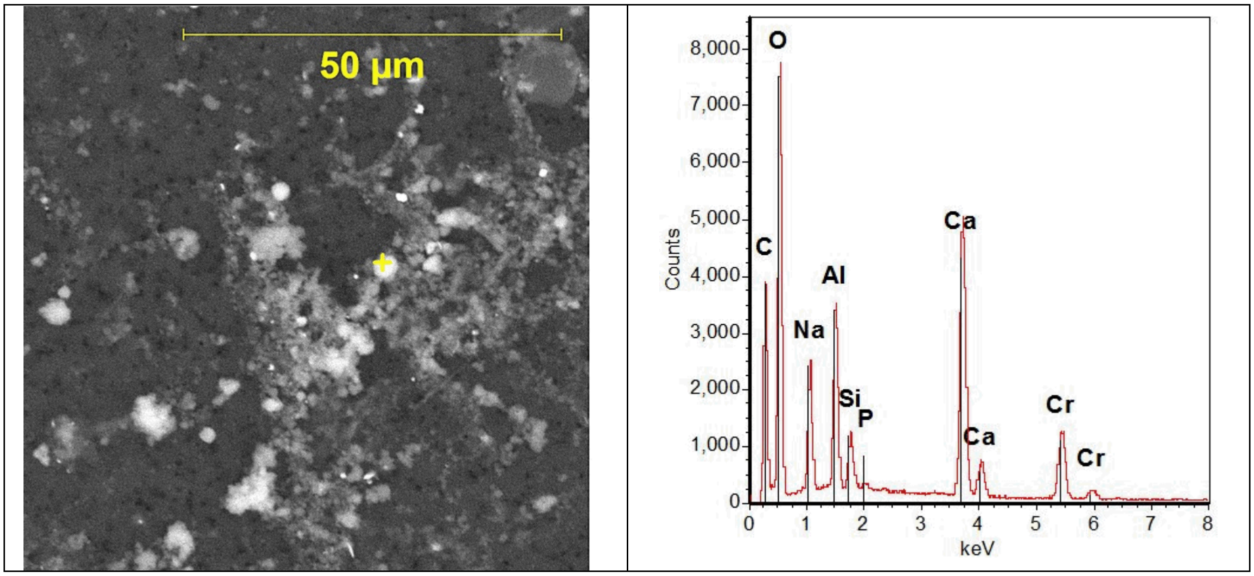


Figure C-13. Cone H Analytical Sample S16R000037 SEM Photo and EDS Spectrum Showing “Hydrouvarovite.”

<u>XRD (Cone H)</u>: Two major phases, vishnevite ($(Na, Ca, K)_6(Si, Al)_{12}O_{24}[(SO_4),(CO_3), Cl_2]_{2\text{-}4}\bullet nH_2O$) and natroxalate ($Na_2C_2O_4$), were identified in the data, with three unidentified peaks. (See Figure C-14 and Table C-7). Vishnevite is a close relative of cancrinite and may be thought of as “generic cancrinite.”

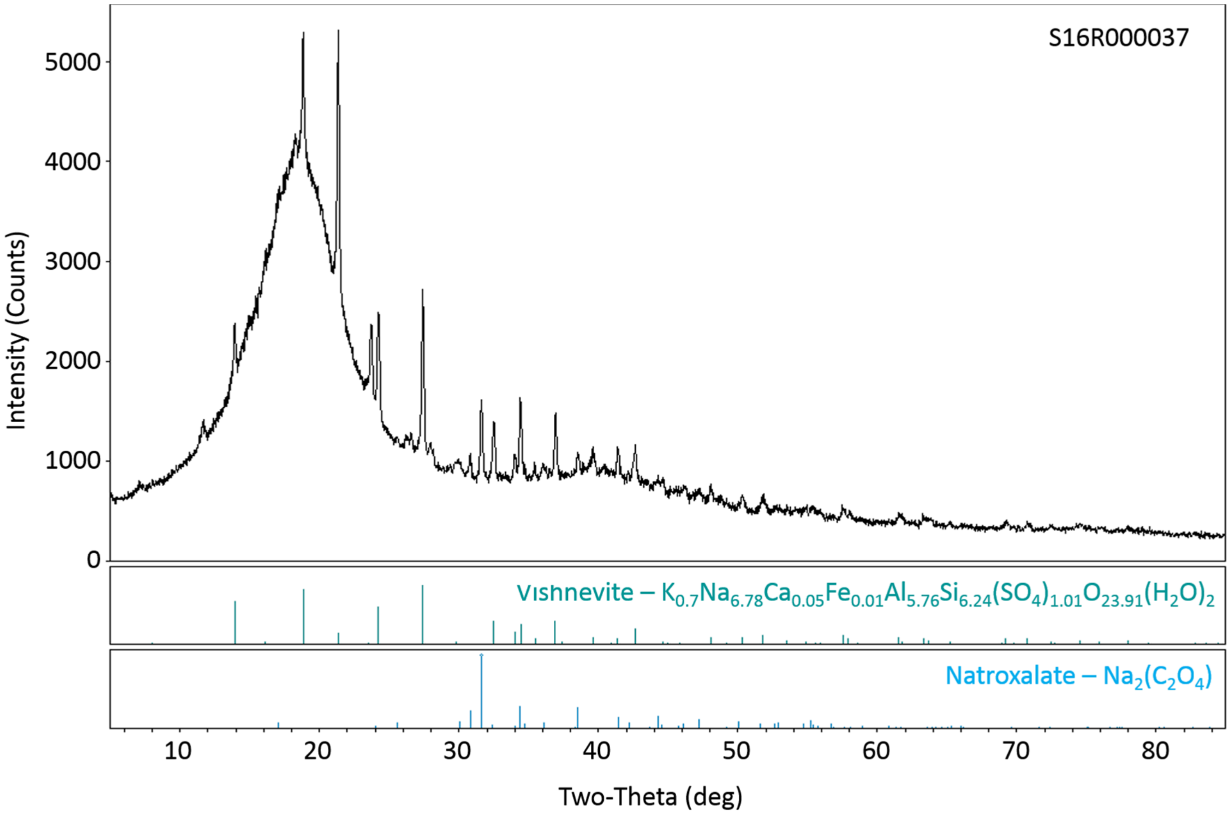


Figure C-14. Cone H Analytical Sample S16R000037 XRD Phase Identification Data.

Table C-7. Cone H Analytical Sample S16R000037 XRD Phase Identification Results.
(Page 1 of 2)

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
11.661	7.5826	212	8.1	Unknown					
13.979	6.3299	531	20.2	Vishnevite	6.3614	58.4	(1 1 0)	13.91	-0.07
18.898	4.692	1276	48.6	Natroxalate	4.6968	0.6	(0 1 1)	18.879	-0.02
21.419	4.1452	2623	100.0	Vishnevite	4.1645	15	(1 2 0)	21.318	-0.101
23.781	3.7386	817	31.1	Natroxalate	3.7017	2.4	(0 1 2)	24.021	0.241
24.299	3.66	1074	40.9	Vishnevite	3.6728	51	(3 0 0)	24.213	-0.086
26.622	3.3457	218	8.3	Unknown					
27.480	3.2431	1717	65.5	Vishnevite	3.2501	100	(2 1 1)	27.42	-0.06
28.018	3.182	225	8.6	Vishnevite	3.1807	0.4	(2 2 0)	28.03	0.012
30.080	2.9684	155	5.9	Natroxalate	2.9664	8.7	(-1 0 2)	30.102	0.021
30.880	2.8934	232	8.8	Natroxalate	2.9009	23	(0 1 3)	30.798	-0.082
31.661	2.8237	789	30.1	Natroxalate	2.8275	100	(1 0 2)	31.618	-0.043
32.562	2.7476	587	22.4	Vishnevite	2.7546	31.4	(4 0 0)	32.478	-0.084
34.061	2.63	263	10.0	Natroxalate	2.631	2.9	(0 2 0)	34.049	-0.013
34.463	2.6003	828	31.6	Vishnevite	2.599	27.3	(0 0 2)	34.481	0.018
35.459	2.5295	167	6.4	Vishnevite	2.5296	7.3	(1 0 2)	35.458	-0.001
36.120	2.4847	147	5.6	Natroxalate	2.4874	6.9	(1 1 2)	36.08	-0.04
36.999	2.4277	645	24.6	Vishnevite	2.4339	30.9	(4 0 1)	36.901	-0.099
38.620	2.3295	242	9.2	Natroxalate	2.334	27.3	(0 1 4)	38.541	-0.079
39.678	2.2697	308	11.8	Vishnevite	2.2732	8.9	(2 3 1)	39.614	-0.064
40.520	2.2245	151	5.8	Unknown					
40.982	2.2005	121	4.6	Vishnevite	2.2049	1.2	(5 0 0)	40.897	-0.085
41.460	2.1762	349	13.3	Natroxalate	2.1787	14.7	(1 1 3)	41.41	-0.05
42.182	2.1406	131	5.0	Natroxalate	2.1403	6.6	(-1 0 4)	42.188	0.006
42.719	2.1149	417	15.9	Vishnevite	2.1205	21.6	(3 3 0)	42.602	-0.117
43.257	2.0899	89	3.4	Vishnevite	2.0823	0.1	(4 2 0)	43.423	0.166
43.625	2.0731	90	3.4	Natroxalate	2.0698	0.8	(-1 2 1)	43.698	0.073
44.340	2.0413	158	6.0	Natroxalate	2.044	16.4	(1 2 1)	44.279	-0.06

Table C-7. Cone H Analytical Sample S16R000037 XRD Phase Identification Results.
(Page 2 of 2)

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
44.721	2.0248	160	6.1	Vishnevite	2.0289	3.6	(5 0 1)	44.626	-0.095
46.200	1.9634	128	4.9	Vishnevite	1.9634	0.1	(3 3 1)	46.199	0
47.379	1.9172	140	5.4	Natroxalate	1.9246	11.8	(1 2 2)	47.186	-0.193
48.160	1.8879	209	8.0	Vishnevite	1.8904	8.8	(4 0 2)	48.093	-0.066
49.258	1.8484	93	3.6	Vishnevite	1.8494	2	(5 1 1)	49.228	-0.03
50.121	1.8186	86	3.3	Natroxalate	1.822	8.9	(-1 2 3)	50.019	-0.102
50.418	1.8085	160	6.1	Vishnevite	1.8121	9.3	(2 3 2)	50.313	-0.105
51.900	1.7603	197	7.5	Vishnevite	1.765	12	(5 2 0)	51.754	-0.146
52.743	1.7342	93	3.5	Vishnevite	1.7315	0.5	(6 0 1)	52.83	0.088
53.098	1.7234	87	3.3	Natroxalate	1.7293	7.1	(-1 1 5)	52.902	-0.196
53.598	1.7085	112	4.3	Vishnevite	1.7105	4.9	(3 4 1)	53.53	-0.068
55.021	1.6676	116	4.4	Vishnevite	1.6707	3.9	(5 2 1)	54.911	-0.111
55.399	1.6572	125	4.7	Natroxalate	1.6574	4.3	(1 1 5)	55.391	-0.008
55.979	1.6413	94	3.6	Vishnevite	1.643	2.5	(3 3 2)	55.917	-0.062
57.564	1.5999	158	6.0	Vishnevite	1.5997	12.8	(1 6 1)	57.569	0.005
58.076	1.587	105	4.0	Natroxalate	1.5878	0.7	(-1 0 6)	58.044	-0.031
61.604	1.5043	117	4.5	Natroxalate	1.5029	1.1	(-1 2 5)	61.667	0.063
61.852	1.4988	87	3.3	Vishnevite	1.4998	3.6	(6 0 2)	61.809	-0.044
63.344	1.4671	132	5.0	Vishnevite	1.4667	7.1	(4 0 3)	63.364	0.021
63.921	1.4552	92	3.5	Natroxalate	1.4549	1.9	(1 2 5)	63.935	0.014
65.301	1.4278	67	2.6	Natroxalate	1.4276	2.9	(-2 1 4)	65.312	0.011
69.323	1.3544	105	4.0	Vishnevite	1.3565	8	(4 4 2)	69.199	-0.124
70.861	1.3288	99	3.8	Natroxalate	1.3272	0.4	(1 3 4)	70.955	0.095
74.360	1.2747	66	2.5	Natroxalate	1.2755	0.4	(0 4 2)	74.305	-0.054
74.639	1.2706	72	2.8	Vishnevite	1.2725	4.3	(7 1 2)	74.506	-0.133
78.022	1.2237	69	2.6	Vishnevite	1.2245	5	(6 3 2)	77.966	-0.057
79.058	1.2103	67	2.6	Natroxalate	1.2119	0.4	(-2 3 2)	78.933	-0.125
79.615	1.2032	70	2.7	Vishnevite	1.203	0.8	(2 2 4)	79.633	0.018

Centrifuged Solids Analytical Samples from AX-101 Composite Test Cones M (S16R000044) and N (S16R000046/48)

Cones M and N contained the largest amounts of NaOH added to the samples (relative to the size of the test samples), and they contained the largest fraction of centrifuged solids, suggesting that the highest OH concentrations suppressed the solubility of some salt(s) – likely $Na_2C_2O_4$. Still, the volumes of centrifuged solids were too small to accommodate the original test plan sampling, so the slurry/settle/decant procedure used for cones G and H was applied to cones M and N as well. The cone M settled solids were used for the PLM, SEM, and XRD analyses (S16R000044), and the cone N settled solids were used for the TGA (S16R000046) and ICP (S16R000048) analyses.

The analytical samples for cone M (S16R000044) and cone N (S16R000046/48) were described as an olive green watery consistency with olive green sediment.

PLM (Cone M): Three slide mounts were prepared in the mother liquor. In Figure C-15, the PLM photo S16R000044e is representative of the phases observed, including a fine-grained (mainly sub-micron) particulate with $Na_2CO_3 \cdot H_2O$/$Na_2C_2O_4$ needles being the major phases. (With small particles, it is very difficult to distinguish between $Na_2CO_3 \cdot H_2O$ and $Na_2C_2O_4$ by PLM because the optical and morphological properties of the two salts are very similar. Based on the XRD findings (below), the blue/yellow needles in Figure C-15 are likely $Na_2C_2O_4$.)

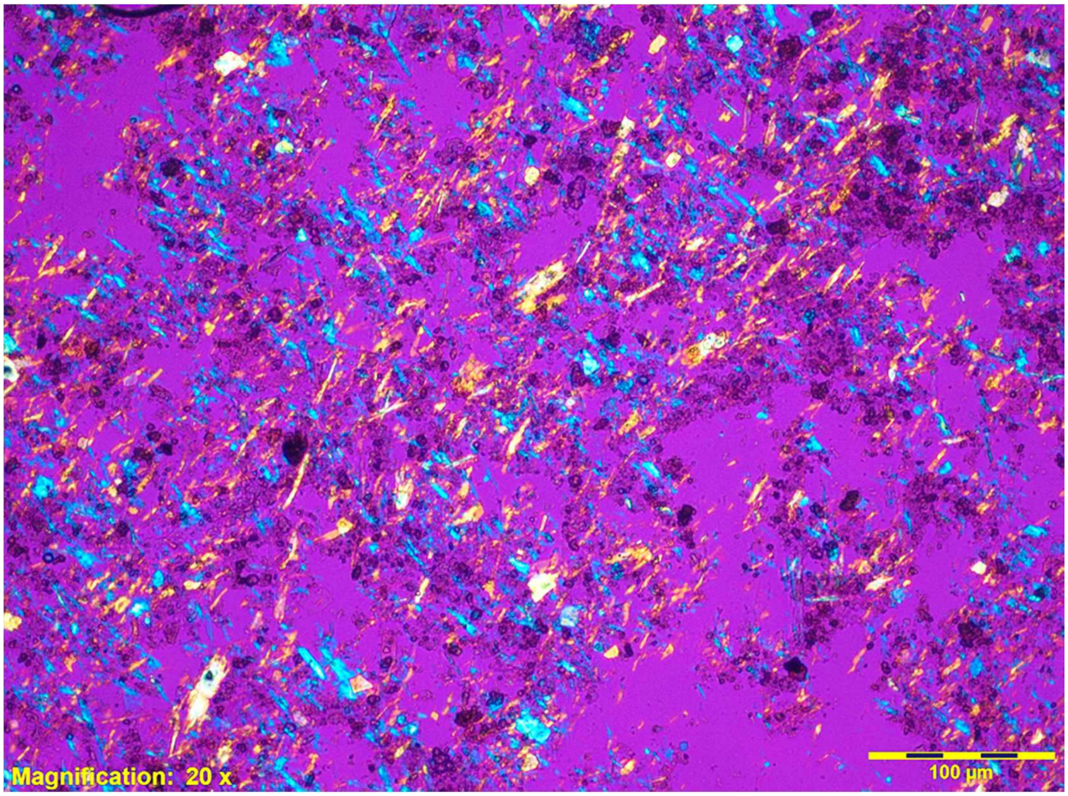


Figure C-15. Cone M PLM Photo S16R000044e Showing Unidentified Fine-Grained Particulate and Na_2CO_3/$Na_2C_2O_4$.

SEM (Cone M): The analytical sample was mainly C-rich with O, Na, and Al in large concentrations. Other elements present were N, Si, Sr, Ca, Fe, P, S, Cl, and K. Likely phases present include $Na_2CO_3 \cdot H_2O$ and/or $Na_2C_2O_4$ (likely $Na_2C_2O_4$, based on XRD results), "hydrouvarovite," and cancrinite.

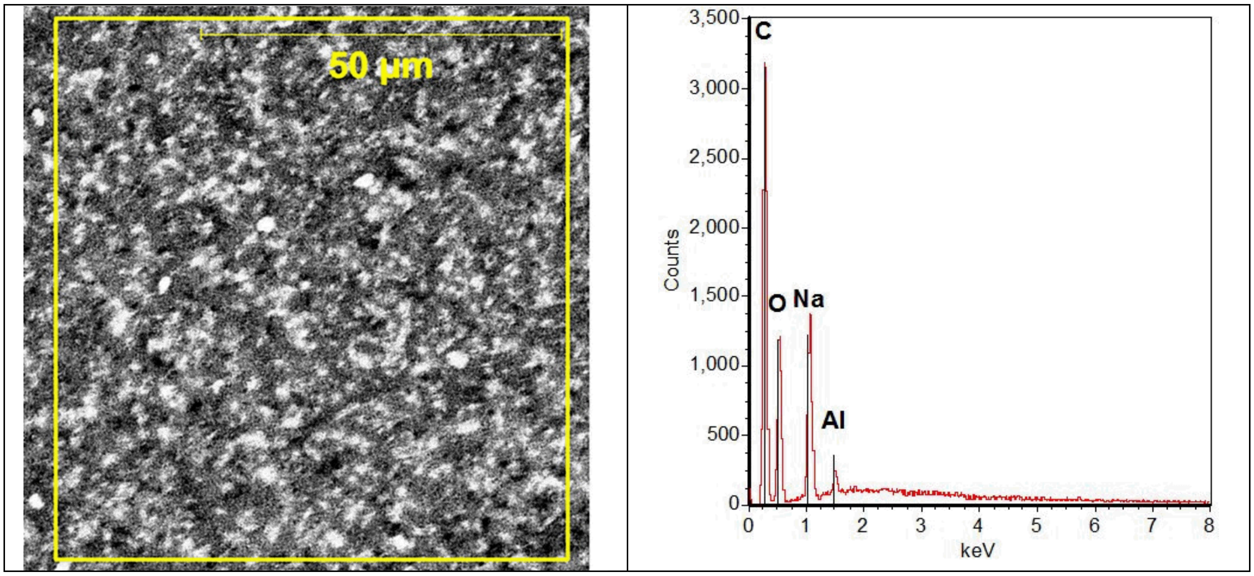


Figure C-16. Cone M Analytical Sample S16R000044 SEM Photo and EDS Spectrum Area Scan Showing Na-C-O Phase ($Na_2CO_3 \cdot H_2O$ and/or $Na_2C_2O_4$) Dominance.

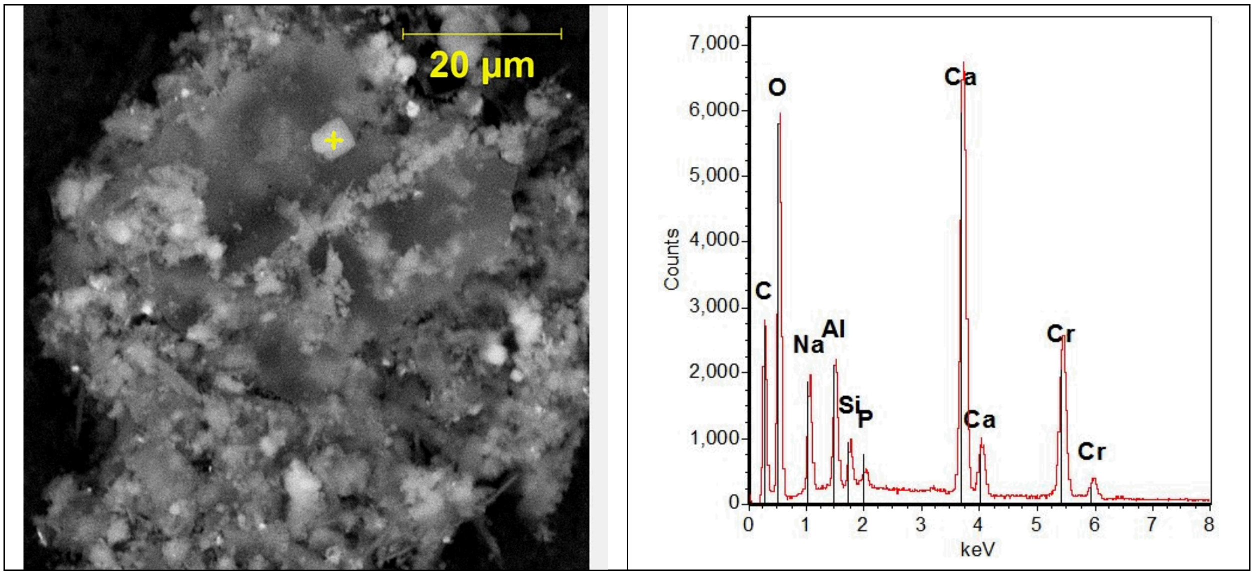


Figure C-17. Cone M Analytical Sample S16R000044 SEM Photo and EDS Spectrum of "Hydrouvarovite."

XRD (Cone M): Two major phases, vishnevite and natroxalate, were identified in analytical sample S16R000044, with two unidentified peaks (see Figure C-18 and Table C-8).

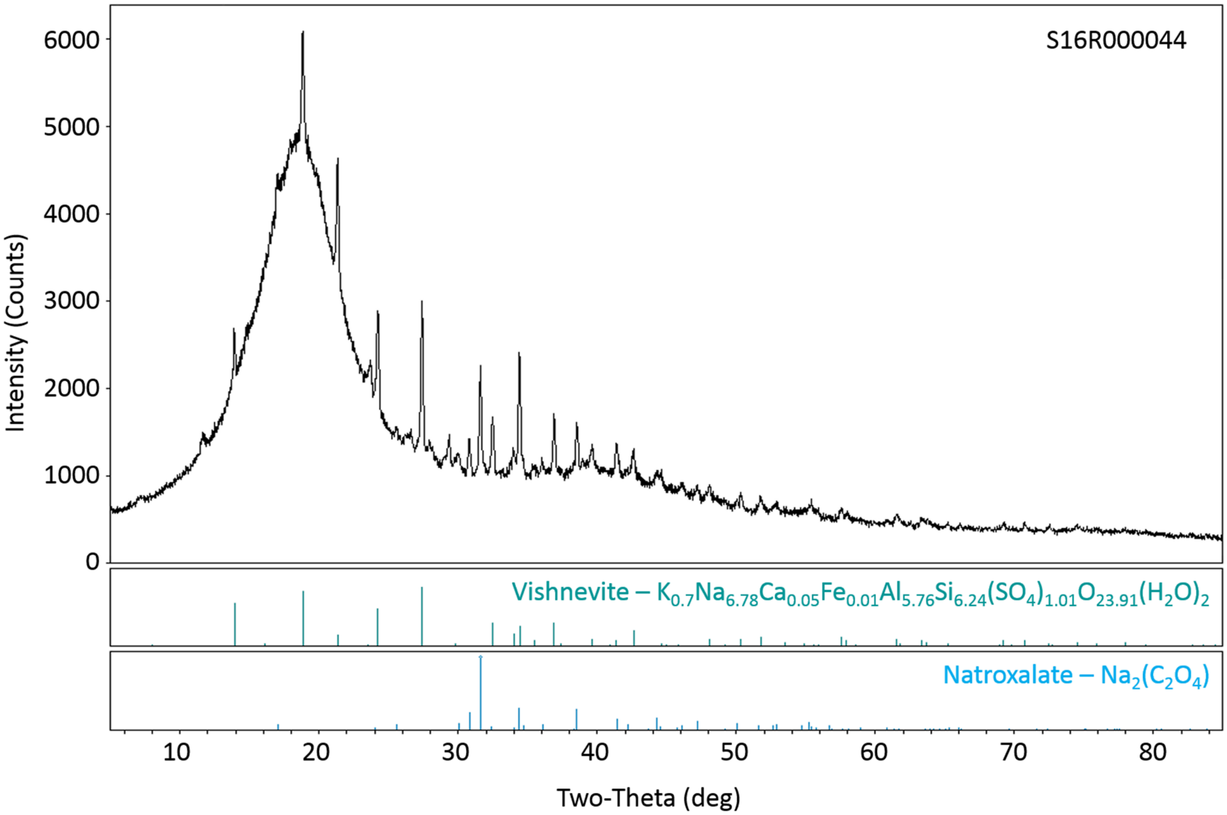
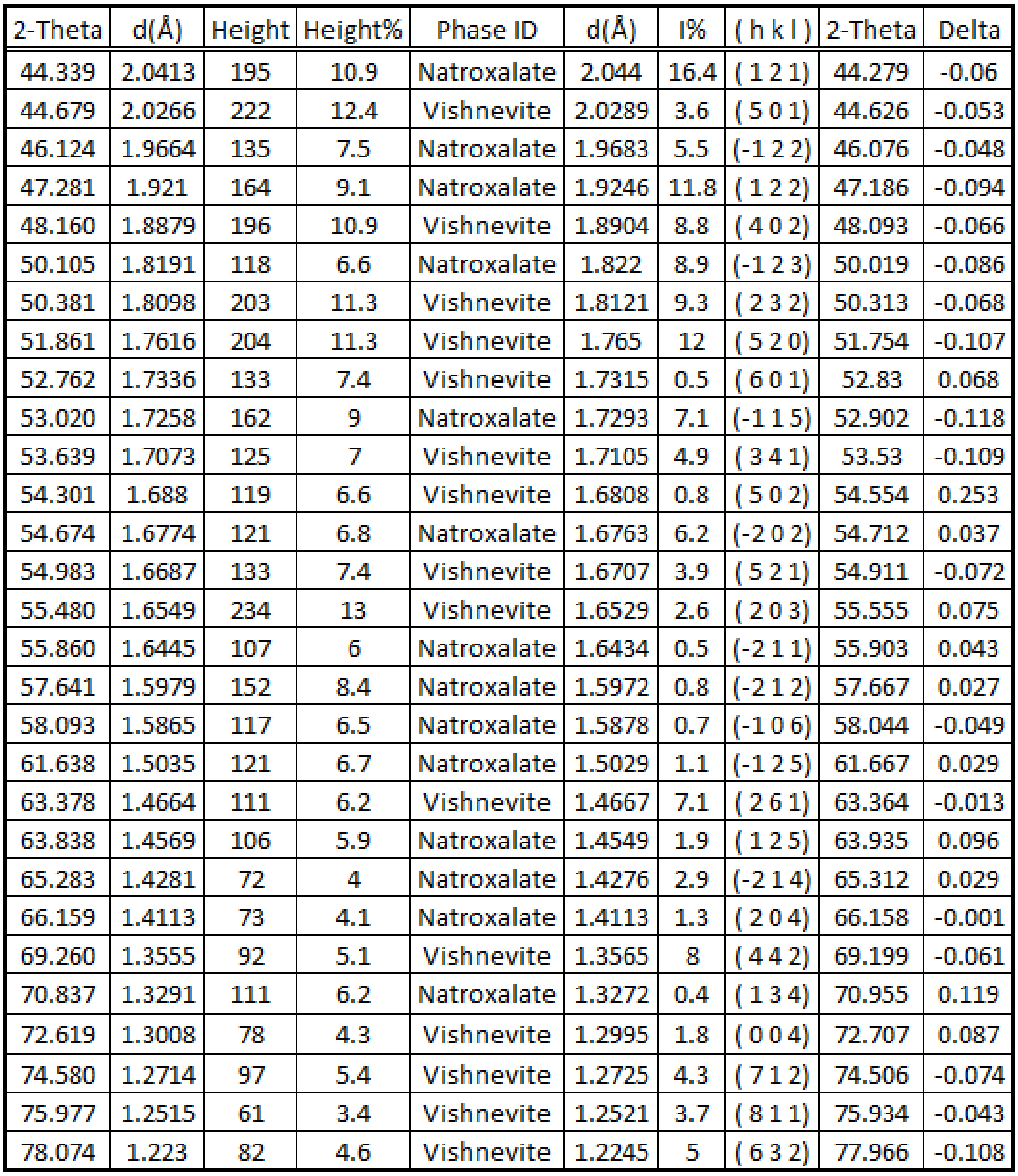


Figure C-18. Cone M Analytical Sample S16R000044 XRD Phase Identification Data.

Table C-8. Cone M Analytical Sample S16R000044 XRD Phase Identification Results.
(Page 1 of 2)

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
11.718	7.5458	214	11.9	Unknown					
13.961	6.338	632	35.2	Vishnevite	6.3614	58.4	(1 1 0)	13.91	-0.052
17.094	5.183	343	19.1	Natroxalate	5.2085	7.4	(0 0 2)	17.01	-0.084
18.898	4.6922	1221	67.9	Natroxalate	4.6968	0.6	(0 1 1)	18.879	-0.019
21.400	4.1489	1441	80.2	Vishnevite	4.1645	15	(1 2 0)	21.318	-0.081
23.744	3.7443	317	17.6	Vishnevite	3.7808	1.6	(2 0 1)	23.512	-0.232
24.299	3.66	1079	60	Vishnevite	3.6728	51	(3 0 0)	24.213	-0.086
25.640	3.4716	122	6.8	Natroxalate	3.477	7.2	(1 0 0)	25.599	-0.041
26.644	3.343	240	13.3	Unknown					
27.479	3.2433	1797	100	Vishnevite	3.2501	100	(2 1 1)	27.42	-0.059
27.981	3.1861	249	13.8	Vishnevite	3.1807	0.4	(2 2 0)	28.03	0.049
29.061	3.0702	121	6.7	Vishnevite	3.0559	0.7	(3 1 0)	29.2	0.138
29.421	3.0334	396	22	Unknown					
30.080	2.9684	205	11.4	Natroxalate	2.9664	8.7	(-1 0 2)	30.102	0.021
30.880	2.8933	398	22.1	Natroxalate	2.9009	23	(0 1 3)	30.798	-0.082
31.661	2.8237	1246	69.3	Natroxalate	2.8275	100	(1 0 2)	31.618	-0.044
32.559	2.7479	672	37.4	Vishnevite	2.7546	31.4	(4 0 0)	32.478	-0.081
34.041	2.6316	326	18.1	Natroxalate	2.631	2.9	(0 2 0)	34.049	0.007
34.479	2.5991	1418	78.9	Vishnevite	2.599	27.3	(0 0 2)	34.481	0.002
35.422	2.5321	129	7.2	Vishnevite	2.5296	7.3	(3 2 0)	35.458	0.036
36.098	2.4862	205	11.4	Natroxalate	2.4874	6.9	(1 1 2)	36.08	-0.018
36.961	2.4301	706	39.3	Vishnevite	2.4339	30.9	(4 0 1)	36.901	-0.061
38.600	2.3306	611	34	Natroxalate	2.334	27.3	(0 1 4)	38.541	-0.059
39.719	2.2675	366	20.3	Vishnevite	2.2732	8.9	(2 3 1)	39.614	-0.104
40.679	2.2161	111	6.2	Vishnevite	2.2049	1.2	(5 0 0)	40.897	0.217
41.024	2.1983	121	6.8	Vishnevite	2.2049	1.2	(1 2 2)	40.897	-0.127
41.461	2.1762	414	23.1	Natroxalate	2.1787	14.7	(1 1 3)	41.41	-0.05
42.182	2.1406	133	7.4	Natroxalate	2.1403	6.6	(-1 0 4)	42.188	0.007
42.698	2.1159	389	21.6	Vishnevite	2.1205	21.6	(3 3 0)	42.602	-0.097

Table C-8. Cone M Analytical Sample S16R000044 XRD Phase Identification Results.
(Page 2 of 2)



2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
44.339	2.0413	195	10.9	Natroxalate	2.044	16.4	(1 2 1)	44.279	-0.06
44.679	2.0266	222	12.4	Vishnevite	2.0289	3.6	(5 0 1)	44.626	-0.053
46.124	1.9664	135	7.5	Natroxalate	1.9683	5.5	(-1 2 2)	46.076	-0.048
47.281	1.921	164	9.1	Natroxalate	1.9246	11.8	(1 2 2)	47.186	-0.094
48.160	1.8879	196	10.9	Vishnevite	1.8904	8.8	(4 0 2)	48.093	-0.066
50.105	1.8191	118	6.6	Natroxalate	1.822	8.9	(-1 2 3)	50.019	-0.086
50.381	1.8098	203	11.3	Vishnevite	1.8121	9.3	(2 3 2)	50.313	-0.068
51.861	1.7616	204	11.3	Vishnevite	1.765	12	(5 2 0)	51.754	-0.107
52.762	1.7336	133	7.4	Vishnevite	1.7315	0.5	(6 0 1)	52.83	0.068
53.020	1.7258	162	9	Natroxalate	1.7293	7.1	(-1 1 5)	52.902	-0.118
53.639	1.7073	125	7	Vishnevite	1.7105	4.9	(3 4 1)	53.53	-0.109
54.301	1.688	119	6.6	Vishnevite	1.6808	0.8	(5 0 2)	54.554	0.253
54.674	1.6774	121	6.8	Natroxalate	1.6763	6.2	(-2 0 2)	54.712	0.037
54.983	1.6687	133	7.4	Vishnevite	1.6707	3.9	(5 2 1)	54.911	-0.072
55.480	1.6549	234	13	Vishnevite	1.6529	2.6	(2 0 3)	55.555	0.075
55.860	1.6445	107	6	Natroxalate	1.6434	0.5	(-2 1 1)	55.903	0.043
57.641	1.5979	152	8.4	Natroxalate	1.5972	0.8	(-2 1 2)	57.667	0.027
58.093	1.5865	117	6.5	Natroxalate	1.5878	0.7	(-1 0 6)	58.044	-0.049
61.638	1.5035	121	6.7	Natroxalate	1.5029	1.1	(-1 2 5)	61.667	0.029
63.378	1.4664	111	6.2	Vishnevite	1.4667	7.1	(2 6 1)	63.364	-0.013
63.838	1.4569	106	5.9	Natroxalate	1.4549	1.9	(1 2 5)	63.935	0.096
65.283	1.4281	72	4	Natroxalate	1.4276	2.9	(-2 1 4)	65.312	0.029
66.159	1.4113	73	4.1	Natroxalate	1.4113	1.3	(2 0 4)	66.158	-0.001
69.260	1.3555	92	5.1	Vishnevite	1.3565	8	(4 4 2)	69.199	-0.061
70.837	1.3291	111	6.2	Natroxalate	1.3272	0.4	(1 3 4)	70.955	0.119
72.619	1.3008	78	4.3	Vishnevite	1.2995	1.8	(0 0 4)	72.707	0.087
74.580	1.2714	97	5.4	Vishnevite	1.2725	4.3	(7 1 2)	74.506	-0.074
75.977	1.2515	61	3.4	Vishnevite	1.2521	3.7	(8 1 1)	75.934	-0.043
78.074	1.223	82	4.6	Vishnevite	1.2245	5	(6 3 2)	77.966	-0.108

Chemical Analysis (Cone N): Analytical results for the settled solids (S16R000046/48) from cone N ($[OH]_{Found}$ = 2.5 M) are shown in Table C-5. The results are dominated by the Na and Al present in the large amount of ISL in the settled solids. The small amount of Cr in the sample is consistent with the SEM/EDS results for the corresponding sample from cone M (S16R000044). The Cu and U reported in the ICP sample (Table C-5) are barely above their respective detection limits and were not observed in the SEM/EDS.

AX-103 Composite

AX-103 Composite Test Sample

Analytical sample S16R000059 represents untreated archive test sample from the AX-103 Core 212/214 composite. The sample was described as moist, small chunks of greenish solids.

PLM (AX-103 Composite Test Sample): Two slides were mounted in 1.550 refractive index oil. In Figure C-19, the PLM photo S16R000059l is representative of the phases observed, including (in approximate order of abundance) $Na_2CO_3•H_2O$ and/or $Na_2C_2O_4$, $NaNO_3$, and several unknowns. The isotropic crystals were difficult to identify due to the heavy amount of sample on the slides. A third slide was mounted in one drop of deionized water; the water dissolved all of the needles and most of the sodium carbonate, although a pocket of sodium carbonate was still present in the middle of the mount. Large, unknown, isotropic crystals were present in trace amounts in the water-mounted test sample.

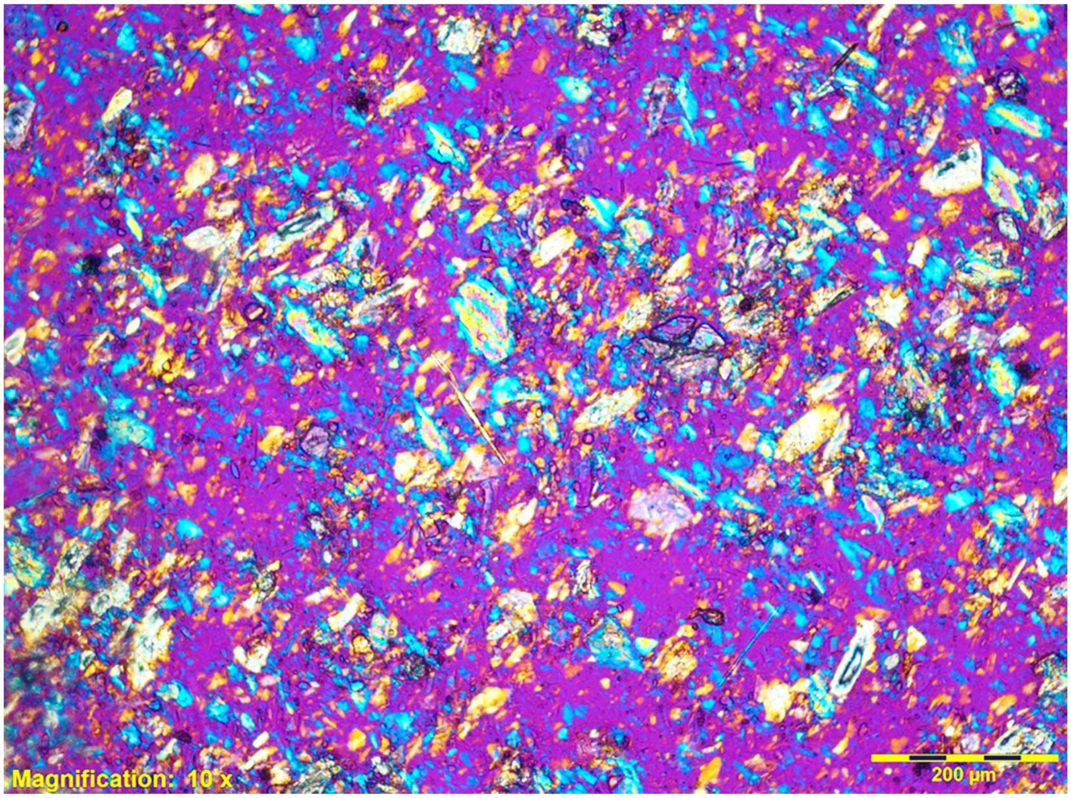


Figure C-19. AX-103 Composite Test Sample PLM Photo S16R000059l Showing $Na_2CO_3•H_2O$ and/or $Na_2C_2O_4$, $NaNO_3$, and Several Unknowns.

SEM (AX-103 Composite Test Sample): The test sample was mainly Na-rich with C and O in large concentrations. Other elements found were Al, N, Cl, K, S, Cr, Ca, Si, and F. Sodium carbonate/oxalate, nitrate, nitrite, aluminate, and chloride may be present. There were some very small (<5 µm) U-rich and metal-rich particles that were detectable as bright spots within the test sample.

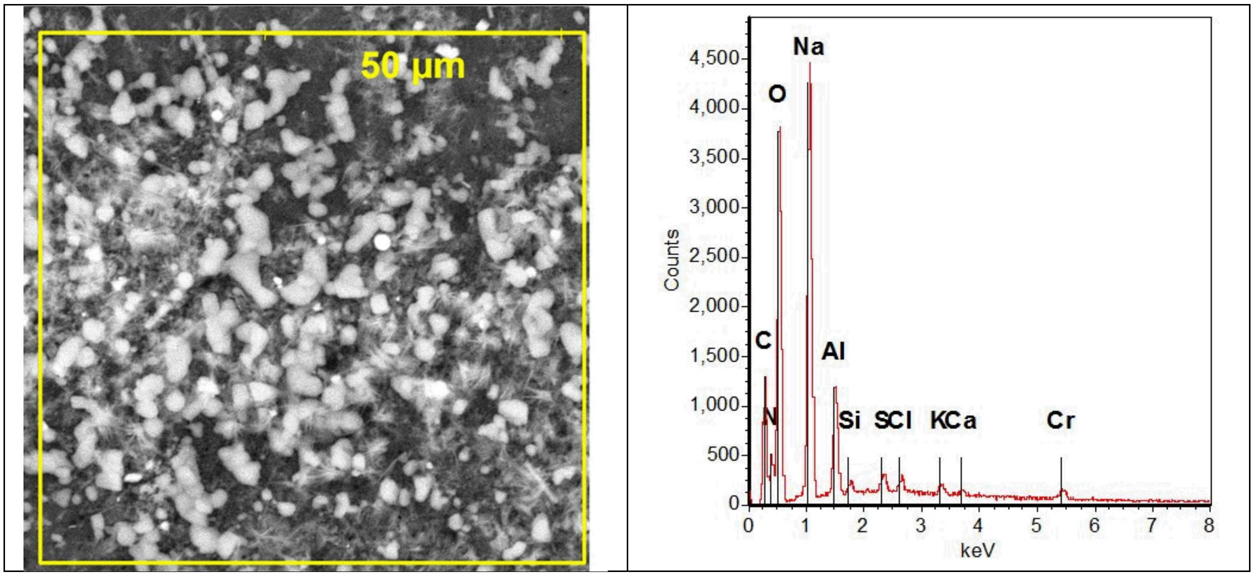


Figure C-20. AX-103 Composite Test Sample SEM Photo and EDS Spectrum Area Scan.

<u>XRD (AX-103 Composite Test Sample)</u>: Three major phases were identified in the test sample ($NaNO_3$, $Na_2CO_3•H_2O$, and $NaNO_2$) with five unidentified peaks (see Figure C-21 and Table C-9).

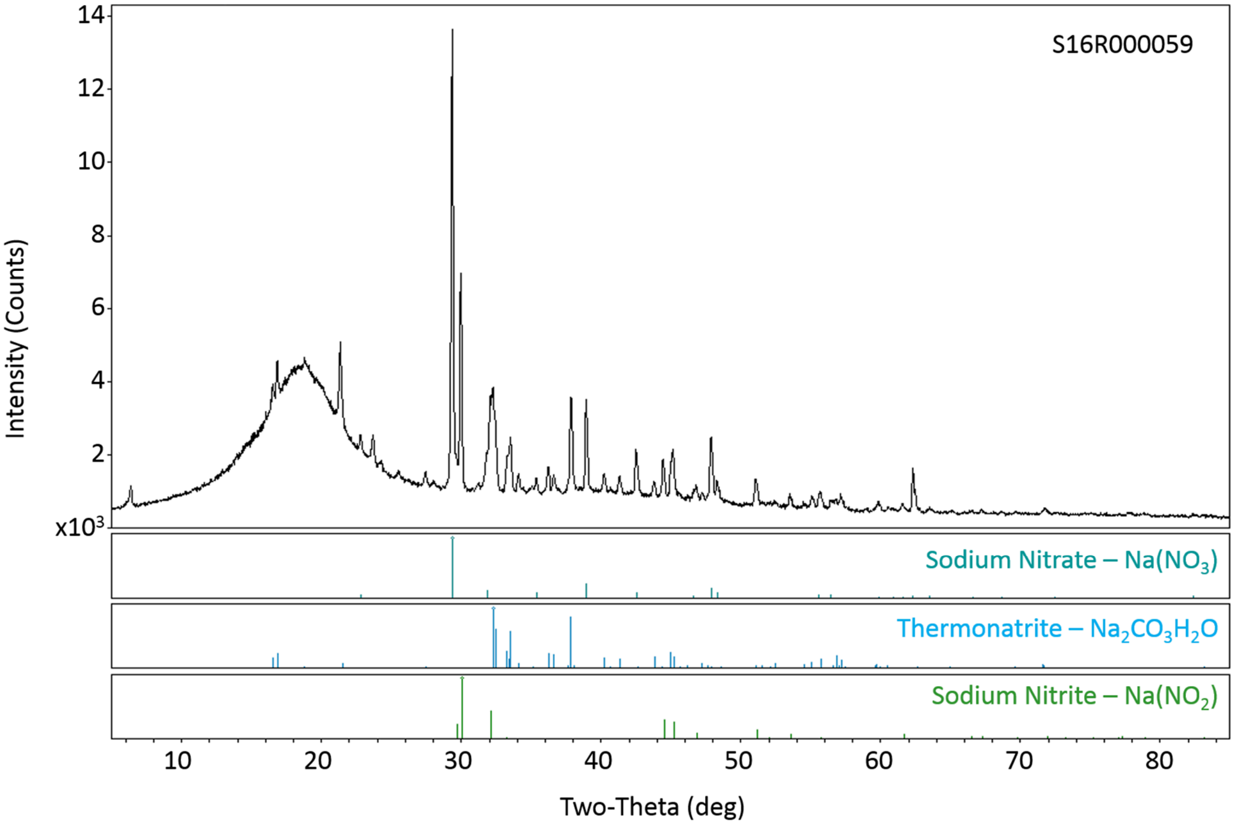


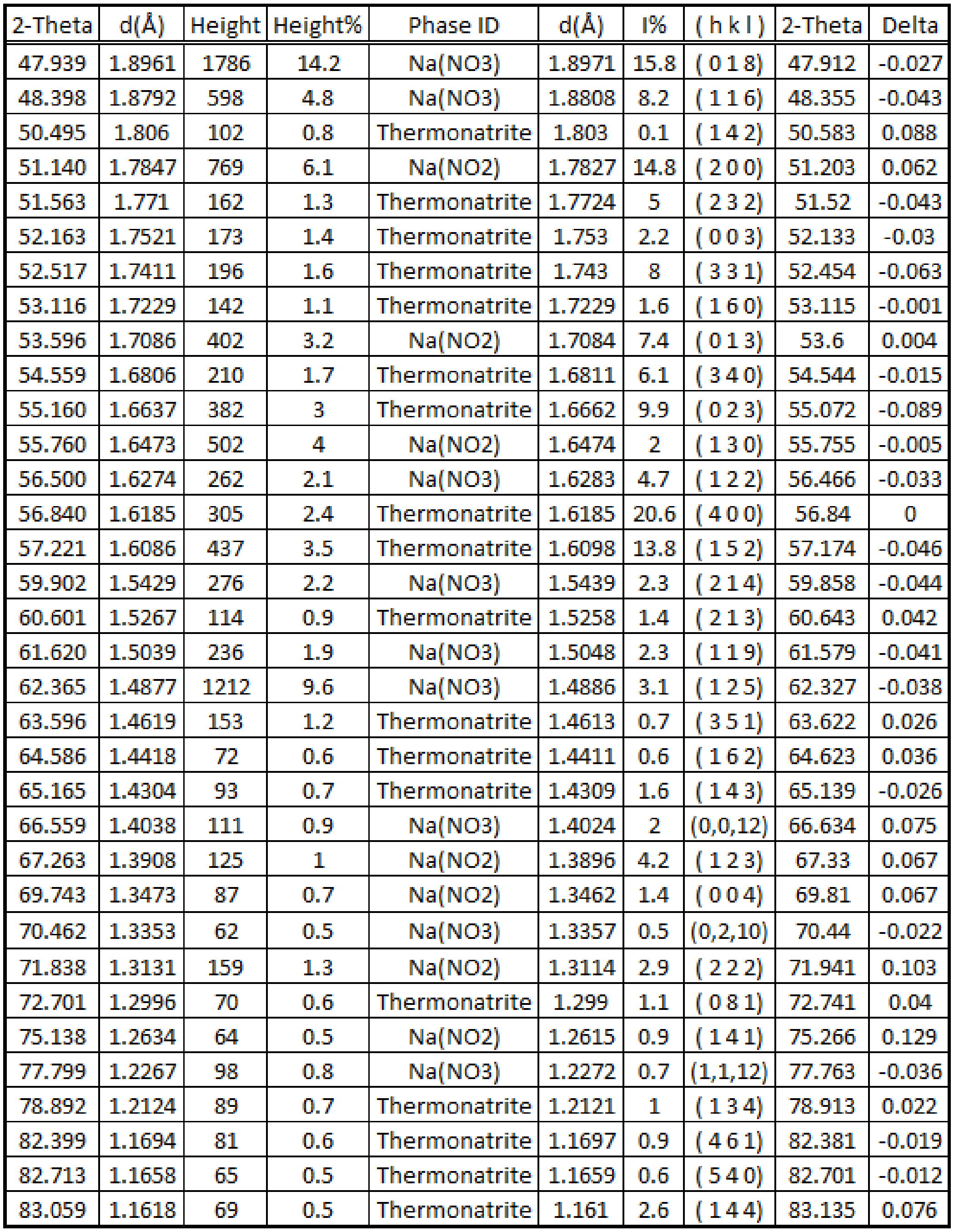
Figure C-21. AX-103 Composite Test Sample S16R000059 XRD Phase Identification Data.

Table C-9. AX-103 Composite Test Sample S16R000059 XRD Phase Identification Results.

(Page 1 of 2)

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
6.439	13.7168	580	4.6	Unknown					
16.595	5.3377	520	4.1	Thermonatrite	5.362	16.5	(0 2 0)	16.519	-0.076
16.901	5.2417	942	7.5	Thermonatrite	5.259	24.3	(0 0 1)	16.845	-0.056
18.861	4.7013	308	2.4	Thermonatrite	4.7218	2.5	(0 1 1)	18.778	-0.083
21.401	4.1486	2188	17.4	Thermonatrite	4.1295	7.9	(1 2 0)	21.501	0.1
22.879	3.8839	486	3.9	Na(NO3)	3.8929	5.3	(0 1 2)	22.825	-0.054
23.741	3.7447	800	6.4	Thermonatrite	3.7546	0.1	(0 2 1)	23.678	-0.063
24.321	3.6568	285	2.3	Unknown					
25.600	3.4768	245	1.9	Unknown					
27.520	3.2385	399	3.2	Thermonatrite	3.2479	2	(1 2 1)	27.439	-0.081
28.079	3.1752	212	1.7	Unknown					
29.420	3.0335	12586	100	Na(NO3)	3.0379	100	(1 0 4)	29.377	-0.043
30.040	2.9723	5934	47.1	Na(NO2)	2.9727	100	(1 0 1)	30.036	-0.004
31.260	2.859	214	1.7	Unknown					
31.862	2.8064	1015	8.1	Na(NO3)	2.8048	12	(0 0 6)	31.881	0.019
32.160	2.7811	2646	21	Na(NO2)	2.7864	44.3	(0 2 0)	32.097	-0.063
33.580	2.6666	1512	12	Thermonatrite	2.6699	60.9	(2 1 1)	33.538	-0.042
34.159	2.6227	513	4.1	Thermonatrite	2.6295	8.7	(0 0 2)	34.069	-0.091
35.139	2.5518	182	1.4	Thermonatrite	2.5539	2.6	(0 1 2)	35.11	-0.029
35.458	2.5296	405	3.2	Na(NO3)	2.5352	9.1	(1 1 0)	35.376	-0.081
36.317	2.4717	729	5.8	Thermonatrite	2.477	23.7	(1 4 0)	36.236	-0.081
36.698	2.4469	515	4.1	Thermonatrite	2.4516	22.8	(2 2 1)	36.625	-0.074
37.920	2.3708	2628	20.9	Thermonatrite	2.3757	83.1	(1 1 2)	37.839	-0.081
39.001	2.3076	2553	20.3	Na(NO3)	2.3102	23.8	(1 1 3)	38.954	-0.047
40.279	2.2372	539	4.3	Thermonatrite	2.2409	17.6	(1 4 1)	40.211	-0.069
40.718	2.2141	169	1.3	Thermonatrite	2.218	2.6	(1 2 2)	40.643	-0.075
41.380	2.1802	477	3.8	Thermonatrite	2.183	15.9	(2 3 1)	41.326	-0.055
42.580	2.1215	1240	9.8	Na(NO3)	2.1244	8.6	(2 0 2)	42.518	-0.062
43.860	2.0625	385	3.1	Thermonatrite	2.0648	18.7	(2 4 0)	43.81	-0.05
44.501	2.0343	1014	8.1	Na(NO2)	2.033	30.9	(1 2 1)	44.532	0.03
45.200	2.0044	1321	10.5	Na(NO2)	2.0047	26.2	(1 1 2)	45.194	-0.006
45.742	1.982	132	1	Thermonatrite	1.986	3.2	(0 5 1)	45.643	-0.098
46.900	1.9357	362	2.9	Na(NO2)	1.9362	9.5	(0 2 2)	46.887	-0.012
47.318	1.9195	254	2	Thermonatrite	1.9219	8.4	(2 4 1)	47.255	-0.063

Table C-9. AX-103 Composite Test Sample S16R000059 XRD Phase Identification Results.
(Page 2 of 2)



2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
47.939	1.8961	1786	14.2	Na(NO3)	1.8971	15.8	(0 1 8)	47.912	-0.027
48.398	1.8792	598	4.8	Na(NO3)	1.8808	8.2	(1 1 6)	48.355	-0.043
50.495	1.806	102	0.8	Thermonatrite	1.803	0.1	(1 4 2)	50.583	0.088
51.140	1.7847	769	6.1	Na(NO2)	1.7827	14.8	(2 0 0)	51.203	0.062
51.563	1.771	162	1.3	Thermonatrite	1.7724	5	(2 3 2)	51.52	-0.043
52.163	1.7521	173	1.4	Thermonatrite	1.753	2.2	(0 0 3)	52.133	-0.03
52.517	1.7411	196	1.6	Thermonatrite	1.743	8	(3 3 1)	52.454	-0.063
53.116	1.7229	142	1.1	Thermonatrite	1.7229	1.6	(1 6 0)	53.115	-0.001
53.596	1.7086	402	3.2	Na(NO2)	1.7084	7.4	(0 1 3)	53.6	0.004
54.559	1.6806	210	1.7	Thermonatrite	1.6811	6.1	(3 4 0)	54.544	-0.015
55.160	1.6637	382	3	Thermonatrite	1.6662	9.9	(0 2 3)	55.072	-0.089
55.760	1.6473	502	4	Na(NO2)	1.6474	2	(1 3 0)	55.755	-0.005
56.500	1.6274	262	2.1	Na(NO3)	1.6283	4.7	(1 2 2)	56.466	-0.033
56.840	1.6185	305	2.4	Thermonatrite	1.6185	20.6	(4 0 0)	56.84	0
57.221	1.6086	437	3.5	Thermonatrite	1.6098	13.8	(1 5 2)	57.174	-0.046
59.902	1.5429	276	2.2	Na(NO3)	1.5439	2.3	(2 1 4)	59.858	-0.044
60.601	1.5267	114	0.9	Thermonatrite	1.5258	1.4	(2 1 3)	60.643	0.042
61.620	1.5039	236	1.9	Na(NO3)	1.5048	2.3	(1 1 9)	61.579	-0.041
62.365	1.4877	1212	9.6	Na(NO3)	1.4886	3.1	(1 2 5)	62.327	-0.038
63.596	1.4619	153	1.2	Thermonatrite	1.4613	0.7	(3 5 1)	63.622	0.026
64.586	1.4418	72	0.6	Thermonatrite	1.4411	0.6	(1 6 2)	64.623	0.036
65.165	1.4304	93	0.7	Thermonatrite	1.4309	1.6	(1 4 3)	65.139	-0.026
66.559	1.4038	111	0.9	Na(NO3)	1.4024	2	(0,0,12)	66.634	0.075
67.263	1.3908	125	1	Na(NO2)	1.3896	4.2	(1 2 3)	67.33	0.067
69.743	1.3473	87	0.7	Na(NO2)	1.3462	1.4	(0 0 4)	69.81	0.067
70.462	1.3353	62	0.5	Na(NO3)	1.3357	0.5	(0,2,10)	70.44	-0.022
71.838	1.3131	159	1.3	Na(NO2)	1.3114	2.9	(2 2 2)	71.941	0.103
72.701	1.2996	70	0.6	Thermonatrite	1.299	1.1	(0 8 1)	72.741	0.04
75.138	1.2634	64	0.5	Na(NO2)	1.2615	0.9	(1 4 1)	75.266	0.129
77.799	1.2267	98	0.8	Na(NO3)	1.2272	0.7	(1,1,12)	77.763	-0.036
78.892	1.2124	89	0.7	Thermonatrite	1.2121	1	(1 3 4)	78.913	0.022
82.399	1.1694	81	0.6	Thermonatrite	1.1697	0.9	(4 6 1)	82.381	-0.019
82.713	1.1658	65	0.5	Thermonatrite	1.1659	0.6	(5 4 0)	82.701	-0.012
83.059	1.1618	69	0.5	Thermonatrite	1.161	2.6	(1 4 4)	83.135	0.076

Chemical Analysis (AX-103 Composite Test Sample): One analytical sample of the AX-103 composite test sample was submitted for TGA (S16R000060) and fusion digest/ICP (S16R000061) analyses. Results are shown in Table C-10. (Results for other samples discussed later are also shown here.)

Table C-10. Analytical Results for AX-103 Composite Solids Samples.

Analyte[a]	Units	Result		
		S16R000060/61 Untreated Test Sample	**S16R000078/80 Control Cone O Settled Solids**	**S16R000079/81 Cone V Settled Solids**
H_2O	wt%	31.0	73.0	71.9
Al	µg/g	23900	28300	22300
B	µg/g	<DL	<DL	<DL
Cr	µg/g	4370	9330	8080
Cu	µg/g	631	160	144
Fe	µg/g	<DL	633	578
P	µg/g	3630	1170	688
Na	µg/g	247000	70800	96100
S	µg/g	5830	1350	1010
Si[b]	µg/g	4260	6790	6510
U	µg/g	<DL	<DL	<DL

[a] <DL = below detection limit
[b] Si reported in preparation blank sample at approximately the same concentration.

The chemical composition of the water-soluble fraction of solids in the test sample (which represents approximately 90 wt% of the sample) can be inferred from the analyses performed on the centrifuged liquid from the control cone O (sample S16R000062). The analytical results for this sample are shown in Table 4-3 in the body of the report. The key analytes and their reported concentrations are repeated here in the first two columns of Table C-11.

The total mass of centrifuged liquid in control cone O was 33.01 g (Table 2-5), and its density was 1.133 g/mL (Table 4-3), which gives a total volume of 29.14 mL. Multiplying the concentration of each analyte by the total volume and dividing by 1000 times the formula weight gives the molarity of each analyte in the centrifuged liquid (column 3 in Table C-11).

The fourth column in Table C-11 shows the most likely solid phase containing each analyte, with its molecular weight in the fifth column. Multiplying the molarity times the molecular weight times the volume (29.14 mL) gives the total mass of each compound present in the centrifuged liquid (column 6). Dividing the mass of each chemical by the total mass of the test sample in the cone (8.66 g) gives the wt% of each chemical in the test sample (column 7).

The sum of column 6 gives the total mass of the compounds in the centrifuged liquid. Dividing this sum (7.85 g) by the total test sample mass (8.66 g) gives the wt% of the test sample that dissolved in the water added to the cone and matches the sum of column 7 (90.6 wt%). By difference, 100 – 90.6 = 9.4 wt% of the test sample remained in the centrifuged solids.

In comparison, 8.66 g x 9.4 wt% = 0.81 g, which is the calculated mass of undissolved solids for control cone O. The actual mass of centrifuged solids was 1.50 g, including the ISL associated with the centrifuged solids. This is a good match, which lends credibility to the analytical results.

Given that the test sample contained 31.0 wt% H_2O (Table C-10), several of the salts shown as “assumed compounds” in Table C-11 would have been present only as dissolved salts. This likely applies to the sodium/potassium salts of nitrite, acetate, formate, hydroxide, and aluminate.

Table C-11. Calculation of Water-Soluble Solids in AX-103 Composite Test Sample.

Analyte	Result (ug/mL)	Molarity (mmol/mL)	Assumed Compound	Molecular Weight	Total Mass (mg)	Wt% of Test Sample
Fluoride	407	0.021	NaF (a)	--	--	--
Chloride	1400	0.039	NaCl	58.45	67	0.8
Nitrite	26200	0.570	$NaNO_2$	69	1145	13.2
Nitrate	29400	0.474	$NaNO_3$	85	1174	13.6
Phosphate	3190	0.034	Na_3PO_4 (b)	268	160	1.9
Sulfate total (d)	4810	0.050	Na_3FSO_4	184	115	1.3
SO_4 minus F (d)	2754	0.029	Na_2SO_4	142	119	1.4
Oxalate	2660	0.030	$Na_2C_2O_4$	134	118	1.4
Acetate	520	0.009	$NaCH_3COO$ (c)	98.1	21	0.2
Formate	1020	0.023	KHCOO (c)	84.1	56	0.6
TIC	5970	0.498	Na_2CO_3 (b)	106	1536	17.7
Hydroxide	4200	0.247	NaOH	40	288	3.3
Aluminum	4110	0.152	$NaAlO_2$ (b)	82	364	4.2
Chromium	199	0.004	H_2O	--	2685	31.0
Potassium	918	0.023	Total		7848	90.6
Sodium	66300	2.883				

(a) Fluoride is assumed to be present as Na_3FSO_4.

(b) Waters of hydration included in the H_2O entry, which is derived from the %H_2O analysis of S16R000060. The hydrated form of $NaAlO_2$ is $NaAl(OH)_4$.

(c) Potassium is shown associated with formate for accounting purposes because the number of moles of formate happened (coincidentally) to match the moles of potassium. Potassium is probably distributed more-or-less evenly among the sodium salts.

(d) Fluoride is assigned to the double salt Na_3FSO_4, but there are significantly more moles of sulfate than of fluoride, so the excess sulfate is assigned (for accounting purposes) to Na_2SO_4. In the left half of the table, the entries for “Sulfate total” include all of the sulfate reported in the IC analysis, and the entry for “SO_4 minus F” is the molarity of total sulfate minus the molarity of fluoride. In the right half of the table, the mass of Na_3FSO_4 is based on the moles of fluoride from the left half of the table, and the mass of Na_2SO_4 is based on the row “SO_4 minus F.”

Centrifuged Solids Analytical Samples from AX-103 Composite Test Cone O (S16R000078/80) and Cone P (S16R000070)

The slurry/settle/decant process described for recovering the centrifuged solids from cones in the AX-101 test was carried out the same way for the AX-103 cones. The slurry from cone P was transferred to the S16R000070 sample vial, allowed to settle overnight, and the settled solids were submitted for PLM, SEM, and XRD analyses. The cone O settled solids were submitted for TGA (S16R000078) and fusion digest/ICP (S16R000080) analyses.

The analytical samples for cone O (S16R000078/80) and cone P (S16R000070) were described as a green sludge.

Chemical Analysis (Cone O): Analytical results for the settled solids from control cone O (S16R000078/80) are shown in Table C-10. The results are dominated by the Na and Al present in the large amount of ISL in the settled solids. The small amounts of Cr and Si present in the sample are consistent with the SEM/EDS results for the corresponding sample from cone P (S16R000070).

Note that the AX-103 composite settled solids sample (Table C-10, cone O) contained two to three times as much Al, Cr, and Si as the corresponding AX-101 sample (Table C-5, cone G). It is also noteworthy that the AX-101 control sample (cone G) had more than enough Al present in the centrifuged liquid to account for all of the Al in the untreated sample, but for the AX-103 control sample (cone O) only about half the Al in the untreated sample reported to the centrifuged liquid phase. The difference is likely the presence of insoluble Al(O)OH in the AX-103 composite sample.

PLM (Cone P): In Figure C-22, the PLM photo S16R000070h is representative of the phases observed, including a fine-grained (mostly sub-micron) particulate as the primary phase; larger (5 µm) isotropic agglomerates and blue/yellow $Na_2C_2O_4$ needles appear as minor phases.

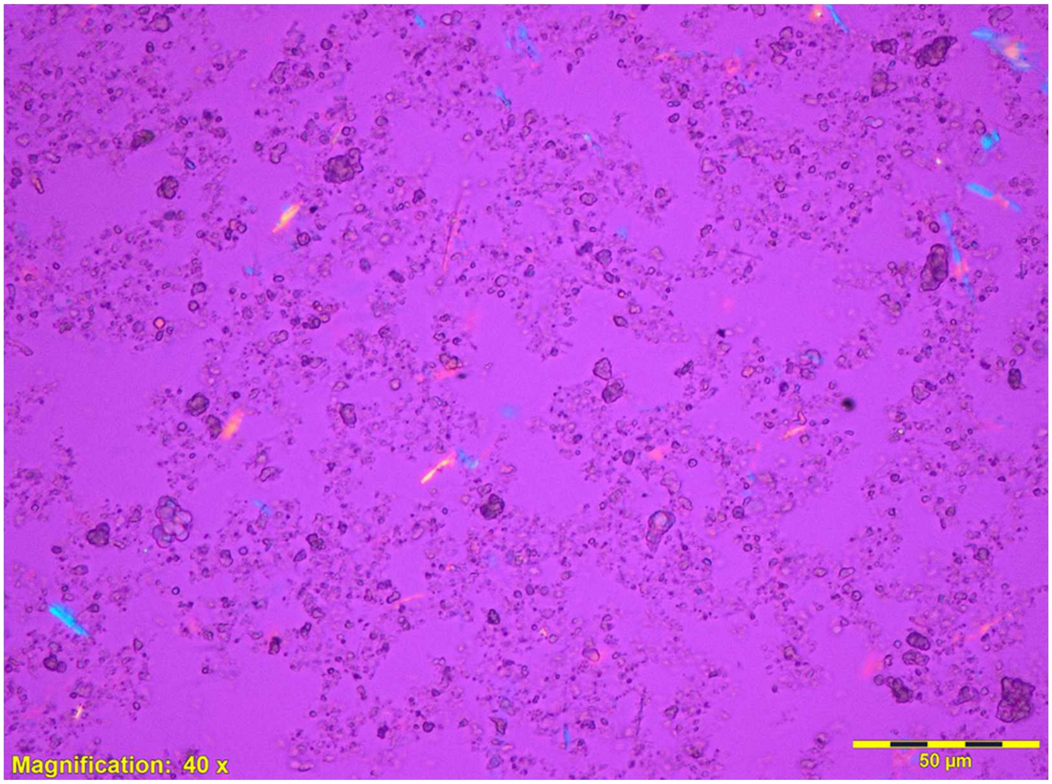


Figure C-22. Cone P PLM Photo S16R000070h Showing Fine-Grained Particulates, Isotropic Agglomerates, and $Na_2C_2O_4$.

SEM (Cone P): The analytical sample was mainly O-rich with Na and Al in large concentrations. Other elements present were C, Si, Ca, Cr, N, P, S, Cl, U, and Fe. Very small (<5 µm) metal-rich particles were present throughout the sample and were detectable as bright spots within the sample. Tentatively identified phases included cancrinite (Figure C-23), Al(O)OH (Figure C-24), $Na(UO_2)O(OH){\bullet}0\text{-}1(H_2O)$, "hydrouvarovite," and Fe_2O_3.

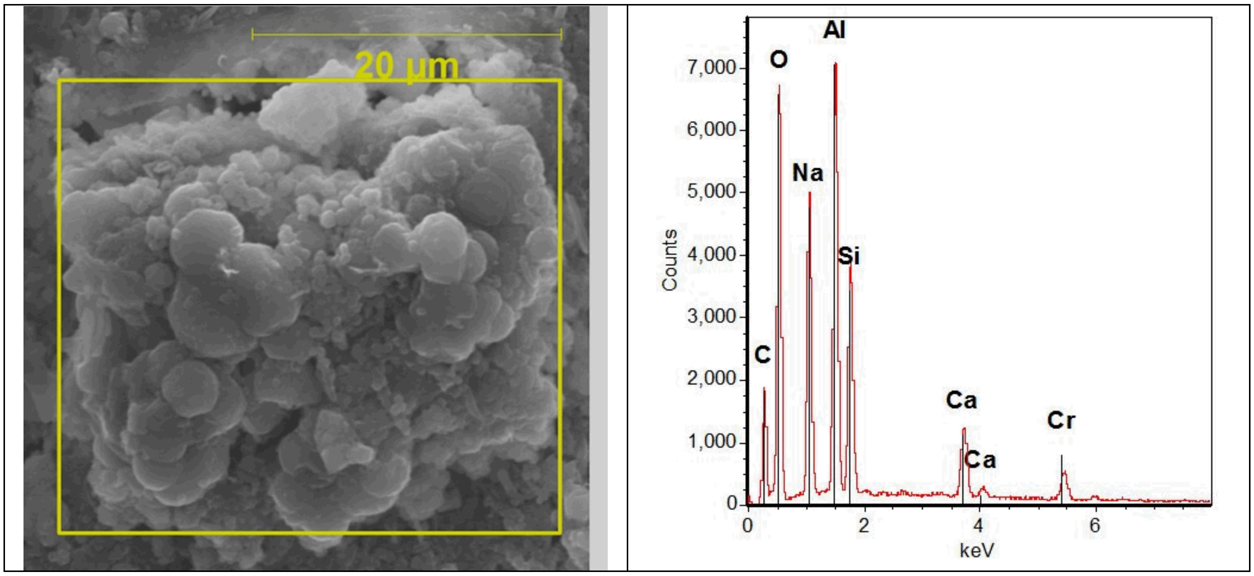


Figure C-23. Cone P Analytical Sample S16R000070 SEM Photo and EDS Spectrum Area Scan Showing Cancrinite.

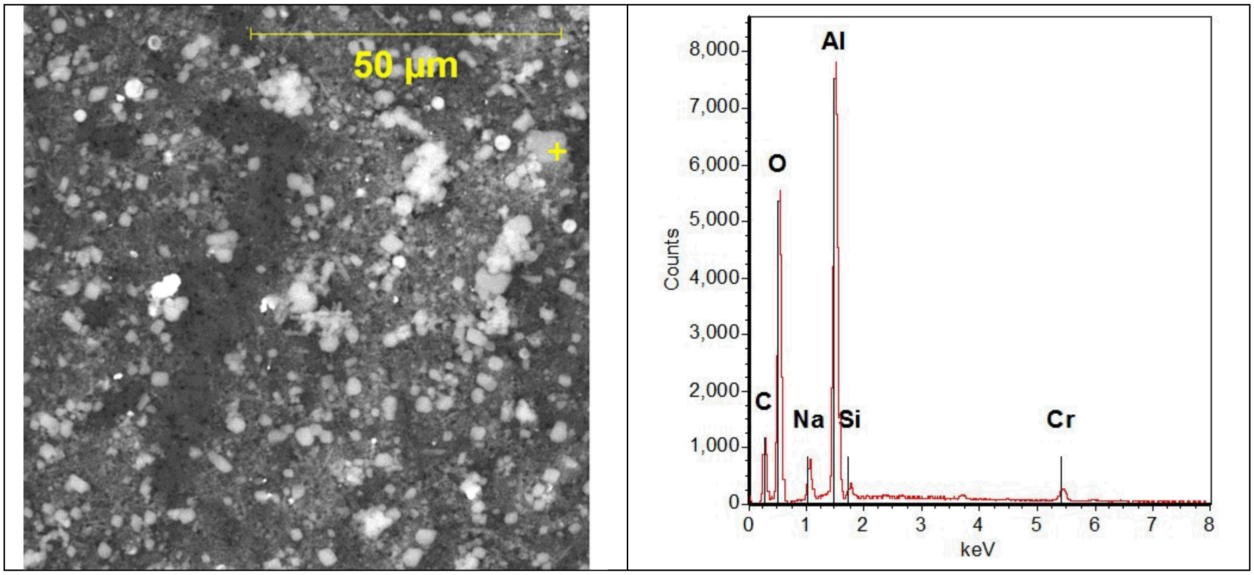


Figure C-24. Cone P Analytical Sample S16R000070 SEM Photo and EDS Spectrum Showing [Suspected] Al(O)OH.

<u>XRD (Cone P)</u>: Three major phases were identified from the data: calcium aluminum oxide sulfate, cancrisilite ($Na_7Al_5Si_7O_{24}(CO_3)\bullet3H_2O$), and silicon dioxide ($SiO_2$). (See Figure C-25 and Table C-12). It is possible that the SiO_2 phase may have been introduced during specimen grinding in the agate (SiO_2) mortar. There were no unidentified peaks, but a large portion of the sample was amorphous. In general this pattern was very weak compared to other data sets in this sample series.

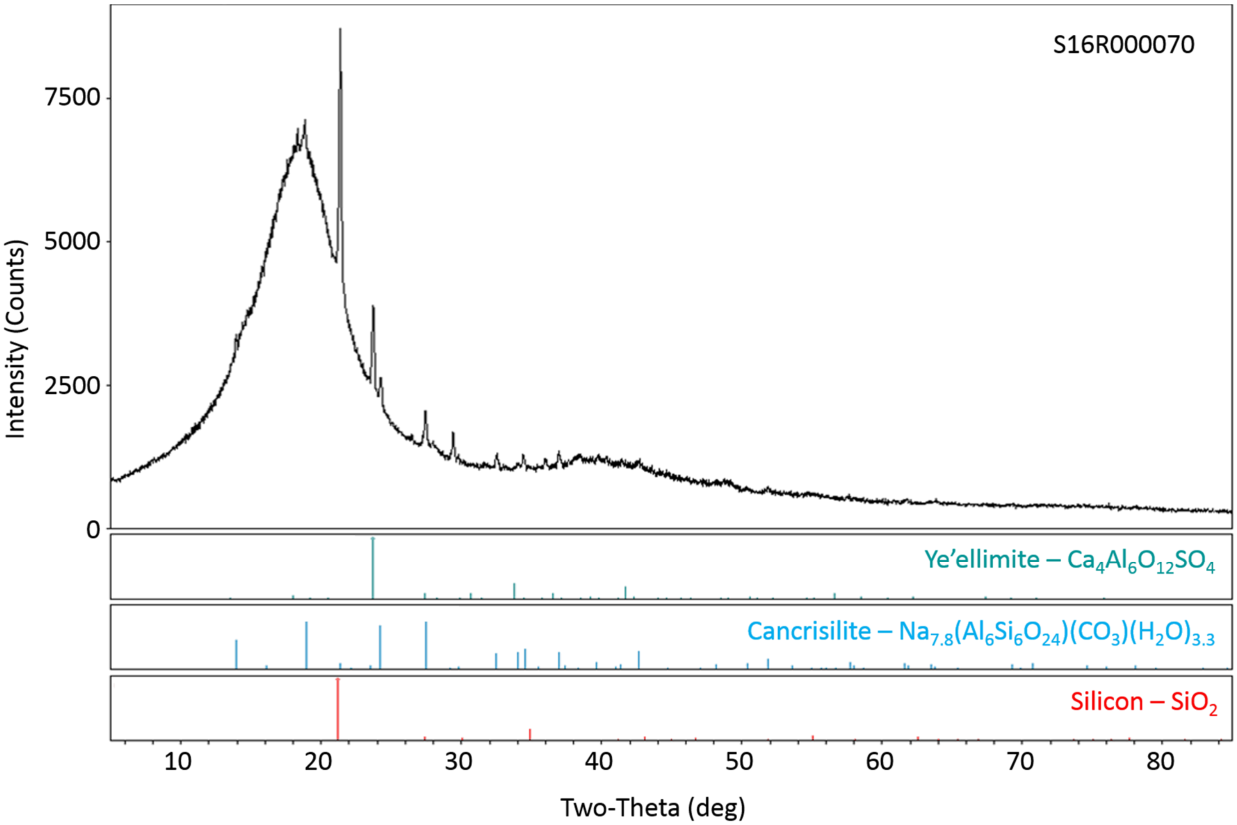
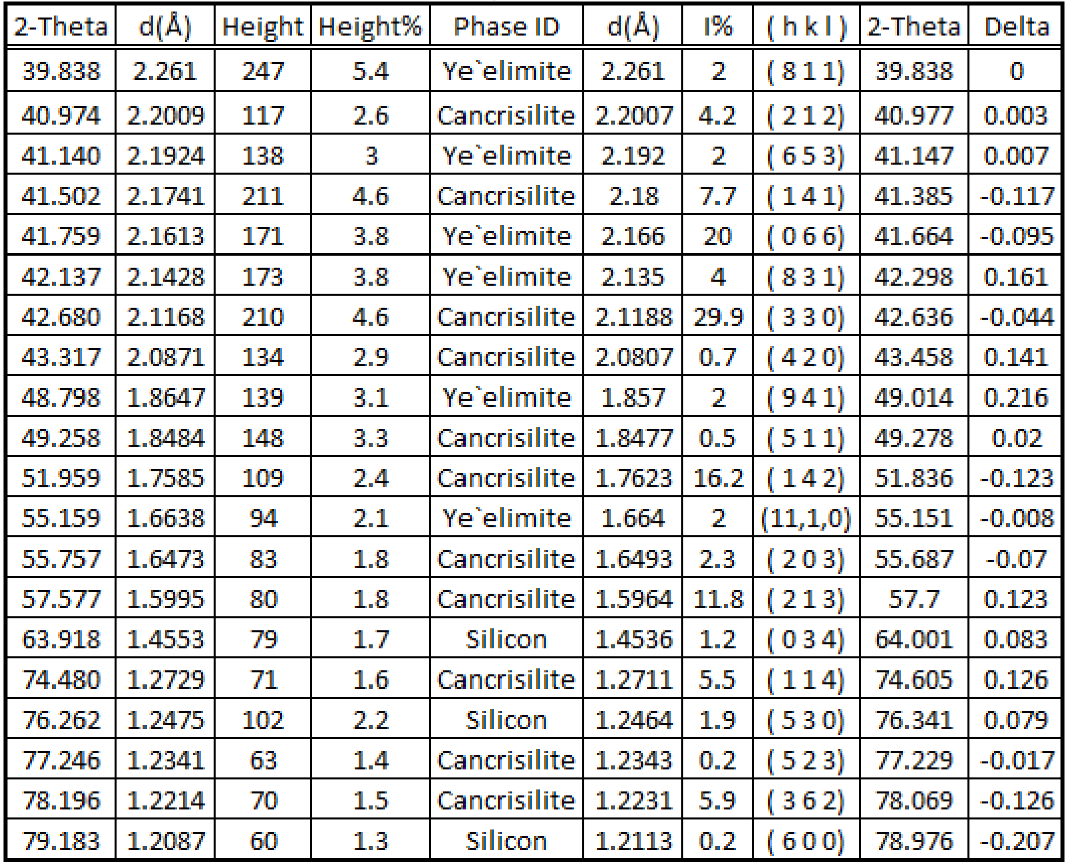


Figure C-25. Cone P Analytical Sample S16R000070 XRD Phase Identification Data.

Table C-12. Cone P Analytical Sample S16R000070 XRD Phase Identification Results.
(Page 1 of 2)

2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
14.000	6.3205	325	7.2	Cancrisilite	6.3565	47.6	(1 1 0)	13.921	-0.08
18.903	4.6908	569	12.5	Cancrisilite	4.6916	100	(1 0 1)	18.9	-0.003
21.438	4.1415	4541	100	Cancrisilite	4.1613	9.9	(2 1 0)	21.335	-0.103
23.780	3.7387	1551	34.2	Ye`elimite	3.76	100	(4 2 2)	23.643	-0.137
24.320	3.657	544	12	Cancrisilite	3.6699	70.4	(3 0 0)	24.232	-0.087
27.501	3.2407	699	15.4	Cancrisilite	3.2456	99.6	(1 2 1)	27.459	-0.043
28.078	3.1754	248	5.5	Cancrisilite	3.1783	0.4	(2 2 0)	28.052	-0.026
28.237	3.1579	177	3.9	Ye`elimite	3.16	2	(5 3 0)	28.218	-0.02
29.482	3.0273	529	11.6	Cancrisilite	3.0536	1.7	(3 1 0)	29.223	-0.259
29.862	2.9897	166	3.7	Ye`elimite	2.99	2	(6 1 1)	29.858	-0.003
31.639	2.8256	103	2.3	Ye`elimite	2.84	2	(5 4 1)	31.475	-0.164
32.617	2.7432	266	5.8	Cancrisilite	2.7525	26.5	(4 0 0)	32.503	-0.113
34.483	2.5988	239	5.3	Ye`elimite	2.6	2	(7 1 0)	34.467	-0.016
36.039	2.4901	150	3.3	Ye`elimite	2.51	2	(7 2 1)	35.744	-0.295
37.039	2.4252	273	6	Silicon	2.4226	0.8	(2 2 1)	37.079	0.04
38.160	2.3565	184	4.1	Cancrisilite	2.3458	3.4	(2 0 2)	38.34	0.18
38.481	2.3375	230	5.1	Ye`elimite	2.338	1	(6 5 1)	38.473	-0.008
38.937	2.3112	158	3.5	Silicon	2.2983	0.5	(0 1 3)	39.164	0.227
39.224	2.295	151	3.3	Ye`elimite	2.297	4	(8 0 0)	39.187	-0.036
39.443	2.2827	200	4.4	Cancrisilite	2.2708	11.1	(2 3 1)	39.658	0.216

Table C-12. Cone P Analytical Sample S16R000070 XRD Phase Identification Results.
(Page 2 of 2)



2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
39.838	2.261	247	5.4	Ye`elimite	2.261	2	(8 1 1)	39.838	0
40.974	2.2009	117	2.6	Cancrisilite	2.2007	4.2	(2 1 2)	40.977	0.003
41.140	2.1924	138	3	Ye`elimite	2.192	2	(6 5 3)	41.147	0.007
41.502	2.1741	211	4.6	Cancrisilite	2.18	7.7	(1 4 1)	41.385	-0.117
41.759	2.1613	171	3.8	Ye`elimite	2.166	20	(0 6 6)	41.664	-0.095
42.137	2.1428	173	3.8	Ye`elimite	2.135	4	(8 3 1)	42.298	0.161
42.680	2.1168	210	4.6	Cancrisilite	2.1188	29.9	(3 3 0)	42.636	-0.044
43.317	2.0871	134	2.9	Cancrisilite	2.0807	0.7	(4 2 0)	43.458	0.141
48.798	1.8647	139	3.1	Ye`elimite	1.857	2	(9 4 1)	49.014	0.216
49.258	1.8484	148	3.3	Cancrisilite	1.8477	0.5	(5 1 1)	49.278	0.02
51.959	1.7585	109	2.4	Cancrisilite	1.7623	16.2	(1 4 2)	51.836	-0.123
55.159	1.6638	94	2.1	Ye`elimite	1.664	2	(11,1,0)	55.151	-0.008
55.757	1.6473	83	1.8	Cancrisilite	1.6493	2.3	(2 0 3)	55.687	-0.07
57.577	1.5995	80	1.8	Cancrisilite	1.5964	11.8	(2 1 3)	57.7	0.123
63.918	1.4553	79	1.7	Silicon	1.4536	1.2	(0 3 4)	64.001	0.083
74.480	1.2729	71	1.6	Cancrisilite	1.2711	5.5	(1 1 4)	74.605	0.126
76.262	1.2475	102	2.2	Silicon	1.2464	1.9	(5 3 0)	76.341	0.079
77.246	1.2341	63	1.4	Cancrisilite	1.2343	0.2	(5 2 3)	77.229	-0.017
78.196	1.2214	70	1.5	Cancrisilite	1.2231	5.9	(3 6 2)	78.069	-0.126
79.183	1.2087	60	1.3	Silicon	1.2113	0.2	(6 0 0)	78.976	-0.207

Ye'elimite = $Ca_4(AlO_2)_6SO_4$

Centrifuged Solids Analytical Samples from AX-103 Composite Test Cones U (S16R000077) and V (S16R000079/81)

Cones U and V contained the largest amounts of NaOH added to the samples (relative to the size of the test samples), and – like the corresponding AX-101 samples – they contained the largest fraction of centrifuged solids, suggesting that the highest OH concentrations suppressed the solubility of $Na_2C_2O_4$. The slurry/settle/decant procedure was used for cones U and V. The cone U settled solids were used for the PLM, SEM, and XRD analyses (S16R000077), and the cone V settled solids were used for the TGA (S16R000079) and ICP (S16R000081) analyses.

The analytical samples for cone U (S16R000077) and cone V (S16R000079/81) were described as a green sludge with a watery consistency.

PLM (Cone U): Three slide mounts were prepared in the mother liquor. In Figure C-26, the PLM photo S16R000077a is representative of the phases observed, which include the same major phases as cone P, but with a higher proportion of $Na_2C_2O_4$.

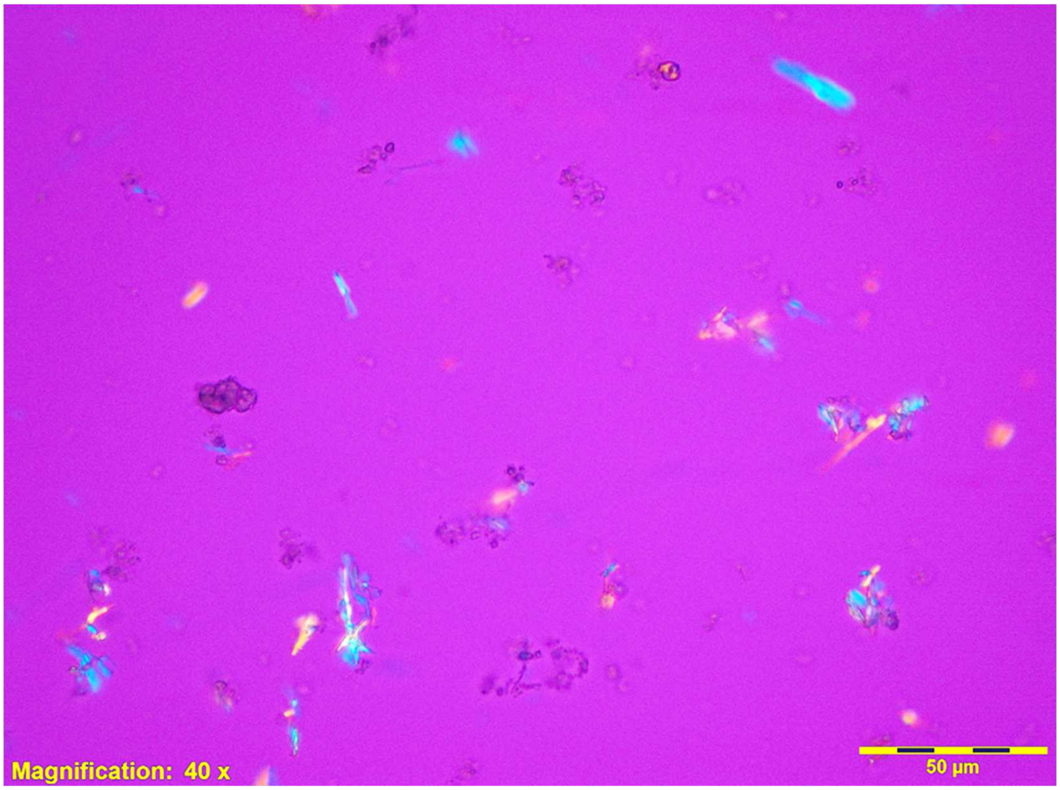


Figure C-26. Cone U PLM Photo S16R000077a Showing $Na_2C_2O_4$ and Isotropic Globular Crystals.

SEM (Cone U): The sample was mainly O-rich with Na and Al in larger concentrations. Other elements present were C, Si, Cr, Ca, P, S, and Cl. Likely phases present include $Na_2CO_3{\bullet}H_2O$ and/or $Na_2C_2O_4$ (likely $Na_2C_2O_4$, based on XRD results), "hydrouvarovite," and cancrinite.

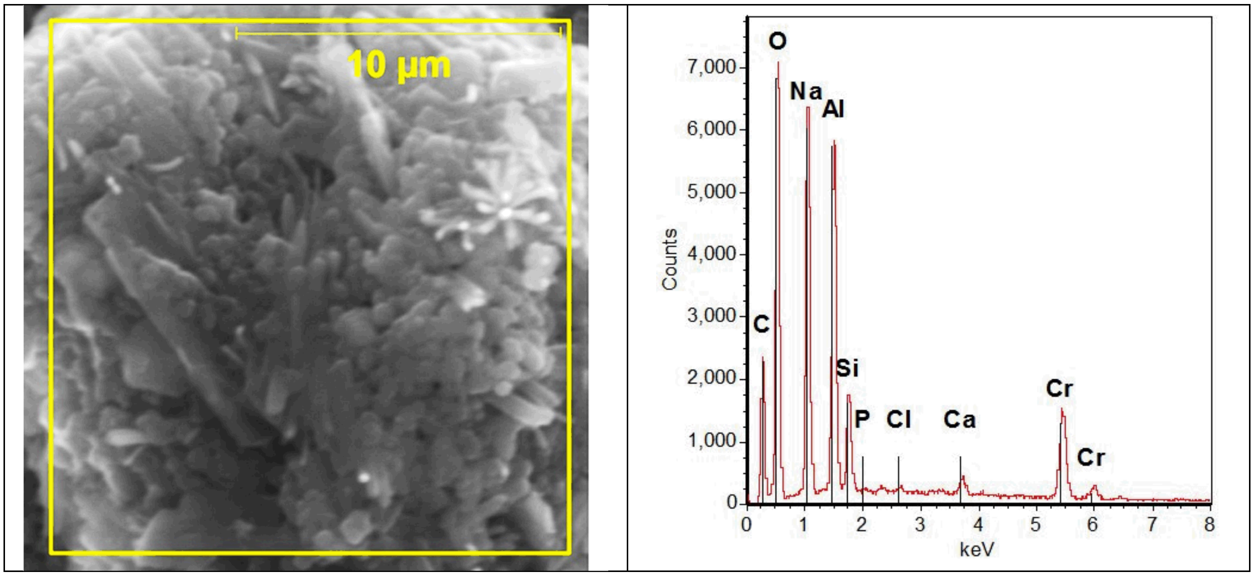


Figure C-27. Cone U SEM Photo and EDS Spectrum Area Scan.

XRD (Cone U): Two major phases were identified in the data (calcium aluminum oxide sulfate and hydrocancrinite) with five unidentified peaks (see Figure C-7 and Table C-13). Like cone P, this pattern was very weak compared to other data sets in this sample series, indicating a high proportion of amorphous material.

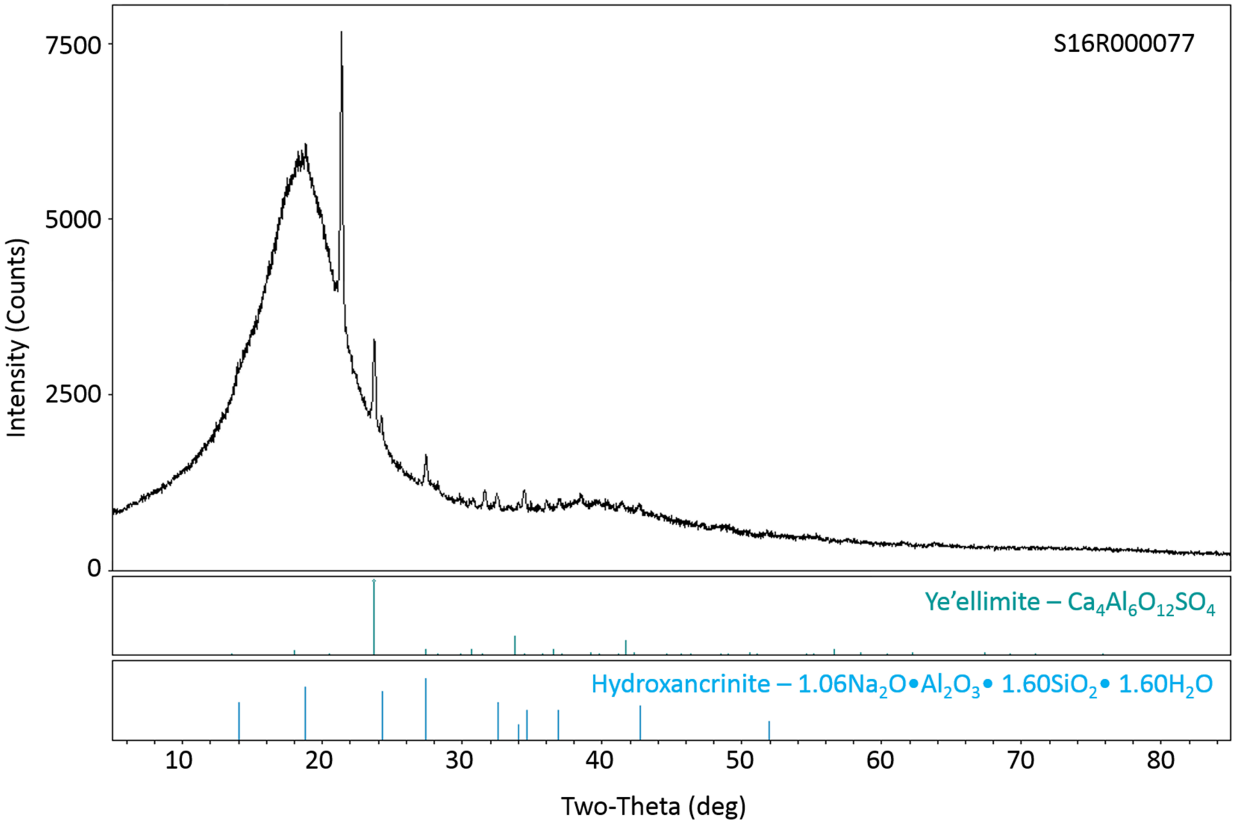
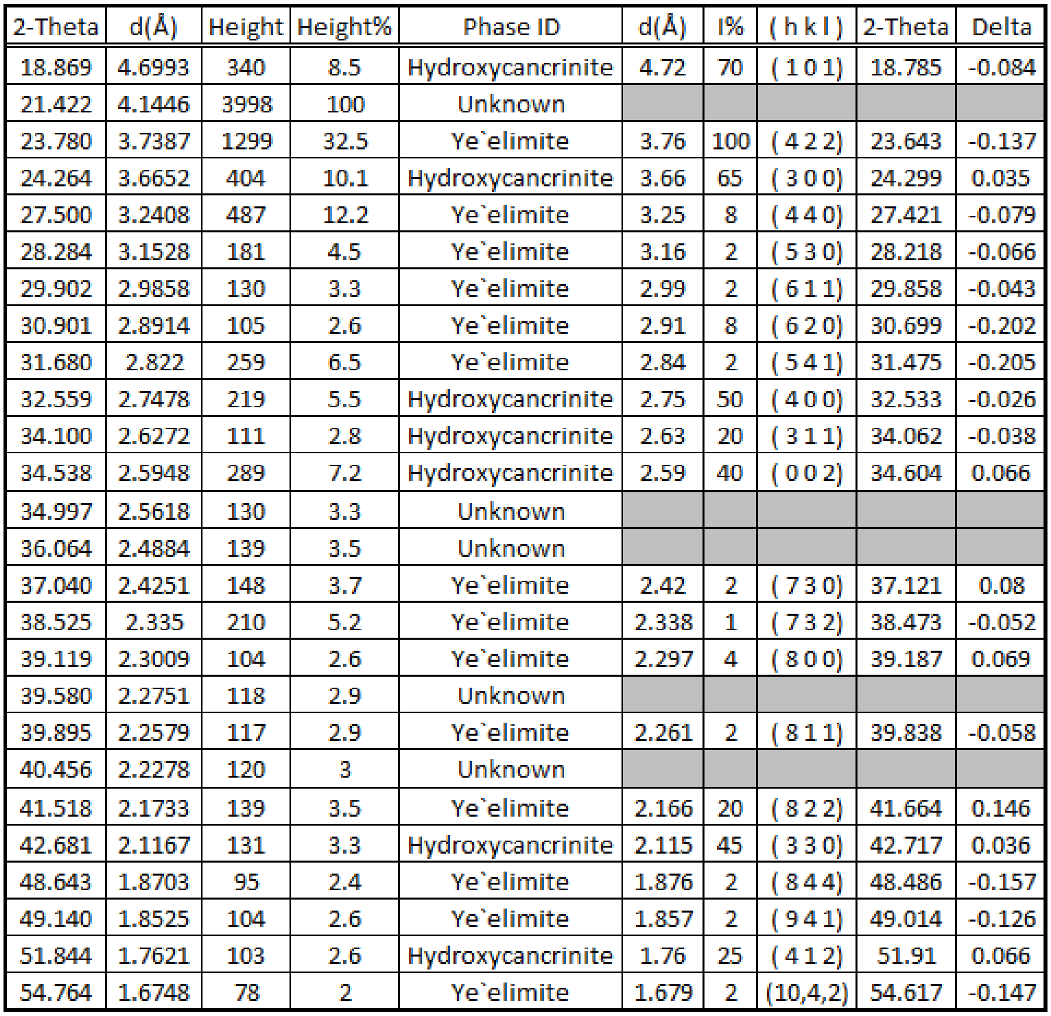


Figure C-28. Cone U Analytical Sample S16R000077 XRD Phase Identification Data.

Table C-13. Cone U Analytical Sample S16R000077 XRD Identification Results.



2-Theta	d(Å)	Height	Height%	Phase ID	d(Å)	I%	(h k l)	2-Theta	Delta
18.869	4.6993	340	8.5	Hydroxycancrinite	4.72	70	(1 0 1)	18.785	-0.084
21.422	4.1446	3998	100	Unknown					
23.780	3.7387	1299	32.5	Ye`elimite	3.76	100	(4 2 2)	23.643	-0.137
24.264	3.6652	404	10.1	Hydroxycancrinite	3.66	65	(3 0 0)	24.299	0.035
27.500	3.2408	487	12.2	Ye`elimite	3.25	8	(4 4 0)	27.421	-0.079
28.284	3.1528	181	4.5	Ye`elimite	3.16	2	(5 3 0)	28.218	-0.066
29.902	2.9858	130	3.3	Ye`elimite	2.99	2	(6 1 1)	29.858	-0.043
30.901	2.8914	105	2.6	Ye`elimite	2.91	8	(6 2 0)	30.699	-0.202
31.680	2.822	259	6.5	Ye`elimite	2.84	2	(5 4 1)	31.475	-0.205
32.559	2.7478	219	5.5	Hydroxycancrinite	2.75	50	(4 0 0)	32.533	-0.026
34.100	2.6272	111	2.8	Hydroxycancrinite	2.63	20	(3 1 1)	34.062	-0.038
34.538	2.5948	289	7.2	Hydroxycancrinite	2.59	40	(0 0 2)	34.604	0.066
34.997	2.5618	130	3.3	Unknown					
36.064	2.4884	139	3.5	Unknown					
37.040	2.4251	148	3.7	Ye`elimite	2.42	2	(7 3 0)	37.121	0.08
38.525	2.335	210	5.2	Ye`elimite	2.338	1	(7 3 2)	38.473	-0.052
39.119	2.3009	104	2.6	Ye`elimite	2.297	4	(8 0 0)	39.187	0.069
39.580	2.2751	118	2.9	Unknown					
39.895	2.2579	117	2.9	Ye`elimite	2.261	2	(8 1 1)	39.838	-0.058
40.456	2.2278	120	3	Unknown					
41.518	2.1733	139	3.5	Ye`elimite	2.166	20	(8 2 2)	41.664	0.146
42.681	2.1167	131	3.3	Hydroxycancrinite	2.115	45	(3 3 0)	42.717	0.036
48.643	1.8703	95	2.4	Ye`elimite	1.876	2	(8 4 4)	48.486	-0.157
49.140	1.8525	104	2.6	Ye`elimite	1.857	2	(9 4 1)	49.014	-0.126
51.844	1.7621	103	2.6	Hydroxycancrinite	1.76	25	(4 1 2)	51.91	0.066
54.764	1.6748	78	2	Ye`elimite	1.679	2	(10,4,2)	54.617	-0.147

Chemical Analysis (Cone V): Analytical results for the settled solids (S16R000079/81) from cone V ($[OH]_{Found}$ = 2.3 M) are shown in Table C-10. The results are dominated by the Na and Al present in the large amount of ISL in the settled solids. The small amount of Cr in the analytical sample is consistent with the SEM/EDS results for the corresponding sample from cone U (S16R000070).

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