SOLID PHASE CHARACTERIZATION OF HEEL SAMPLES FROM TANK 241-C-110

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EXECUTIVE SUMMARY

During sluicing operations of tank 241-C-110, a significant amount of solids were unable to be retrieved. These solids (often referred to as the tank “heel”) were sampled in 2010 and chemically and mineralogically analyzed in the 222-S Laboratory. Additionally, dissolution tests were performed to identify the amount of undissolvable material after using multiple water contacts. This report covers the solid phase characterization of six samples from these tests using scanning electron microscopy, polarized light microscopy, and X-ray diffraction. The chemical analyses, particle size distribution analysis, and dissolution test results are reported separately.

Two of the samples were from composites created from as-received material – Composite A and Composite B. The main phase in these samples was sodium-fluoride-phosphate hydrate (natrophosphate) – in the X-ray diffraction spectra, this phase was the only phase identifiable. Polarized light microscopy showed the presence of minor amounts of gibbsite and other phases. These phases were identified by scanning electron microscopy - energy dispersive X-ray spectroscopy as sodium aluminosilicates, sodium diuranate, and sodium strontium phosphate hydrate (nastrophite) crystals. The natrophosphate crystals in the scanning electron microscopy analysis showed a variety of erosive and dissolution features from perfectly shaped octahedral to well-rounded appearance.

Two samples were from water-washed Composites A and B, with no change in mineralogy compared to the as-received samples. This is not surprising, since the water wash had only a short period of water contact with the material as opposed to the water dissolution tests.

The last two samples were residual solids from the water dissolution tests. These tests included multiple additions of water at 15 °C and 45 °C. The samples were sieved to separate a coarser fraction of >710 µm and a finer fraction of <710 µm. These two fractions were analyzed separately. The coarser fraction contained mostly gibbsite with minor amounts of sodium aluminosilicates (cancrinite) and bismuth aluminum-rich phases. The finer fraction was mostly composed of gibbsite, the sodium aluminosilicate phase, cancrinite, and a poorly crystalline to non-crystalline phase containing varying amounts of iron, bismuth, aluminum, and phosphorus.

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LIST OF TERMS

Abbreviations and Acronyms

ATL	Advanced Technologies and Laboratories International, Inc.
BEI	Backscattered Electron Image
C-110	Tank 241-C-110
EDS	Energy Dispersive X-ray Spectroscopy
ICDD	International Centre for Diffraction Data
IR	Index of Refraction
PSEM	Personal Scanning Electron Microscope
PLM	Polarized Light Microscopy
SEI	Secondary Electron Image
SEM	Scanning Electron Microscopy
TSAP	Tank Sampling and Analysis Plan
(un)crP+	(Un)crossed Polars (Positive)
WTP	Waste Treatment and Immobilization Plant
XRD	X-ray Diffraction/Diffractometry

1 INTRODUCTION

Laboratory-scaled tests have been performed to test the dissolution behavior of the heel solids from tank 241-C-110 (C-110). These solids are the material that is unable to be retrieved after applying modified sluicing to the tank waste in 2009. The solids were sampled in 2010 for chemical and physical characterization and to evaluate the dissolution behavior during final retrieval. The analytical tests and dissolution procedure are described in the tank sampling and analysis plan (TSAP), RRP-PLAN-46196, *Tank Sampling and Analysis Plan for Waste Solids in Tank 241-C-110*, and in the test plan, LAB-PLN-10-00011, *Test Plan for Tank 241-C-110 Heel Solids Characterization and Dissolution Testing*.

For solid phase characterization, X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), and polarized light microscopy (PLM) were utilized. The analyses followed the current revisions of procedures ATS-LT-519-107, “222-S Laboratory Polarized Light Microscopy,” ATS-LT-161-100, “222-S Laboratory Sample Preparation and Operating Procedure for Scanning Electron Microscopes,” and ATS-LT-507-101, “222-S Laboratory X-Ray Diffractometry (XRD).” Sample preparation steps for these procedures are also described in the individual sections to detail any adjustments due to the sample characteristics.

Overall, six samples were analyzed: two were as-received samples, two were water washed and two were residuals of the water dissolution tests (see Table 1). The difference between the water-washed and the water dissolution test was the length of water contact and the temperature of treatment. Water-washed samples were only in contact for a brief amount of time (<1 hr) at ambient hot cell temperature; the water dissolution test included water contact over an extended period of time (multiple increments of 4 hr dissolutions, in total 60 hr) at 15 °C and 45 °C.

Table 1. Sample Identification.

Pre Water Dissolution	As-Received	S10R000354	Composite A
		S10R000362	Composite B
	Water Washed	S10R000375	water washed Composite A
		S10R000378	water washed Composite B
Post Water Dissolution	Residues	S11R000162	fine fraction (<710 µm)
		S11R000188	coarse fraction (>710 µm)

Examples of the as-received samples in their original jars are shown in Figure 1. The left image shows large chunks of crystalline material in a matrix of fine-grained whitish to pale yellow material with dark specks interspersed. The large crystals are most likely sodium-fluoride-phosphate hydrate (natrophosphate) based on the perfectly crystallized octahedral shape (see yellow ring insert with large crystal, approximately 2 cm long). The right image shows the more common appearance of the heel material.

Details of the sample descriptions and chemical analyses performed by Advanced Technologies and Laboratories International, Inc. (ATL) are presented in RPP-RPT-48654, *Final Report for*

the Analysis of Waste Solids in Tank 241-C-110, and the results of the dissolution test will be presented in a future Washington River Protection Solutions final report.

Figure 1. Images of As-Received Heel Material.

2 SOLID PHASE CHARACTERIZATION OF PRE-DISSOLUTION SAMPLES

2.1 X-RAY DIFFRACTION

The analyses of the XRD patterns of the two as-received composite samples (Figure 2) and of the water-washed composite samples (Figure 3) revealed natrophosphate as the dominant and only detectable crystalline phase. In both cases, as-received and water-washed, the sample from Composite B showed the same XRD pattern as Composite A.

Figure 2. XRD Pattern for As-Received Samples S10R000354.

Figure 3. XRD Pattern for Water-Washed Sample S10R000375.

2.2 POLARIZED LIGHT MICROSCOPY

Polarized light microscopy showed the presence of sodium-fluoride-phosphate crystals mixed with minor amounts of small gibbsite and some opaque and yellow particles (Figure 4). In the lower left, a well-crystallized natrophosphate octahedron can be seen.

Figure 4. PLM Images of As-Received Sample S10R000354.

(10x, crP+, Red I comp., mounted in 1.55 IR oil)

(10x, uncrP, mounted in 1.55 IR oil)

crP+ crossed polars (positive)
IR index of refraction
uncrP uncrossed polars

After water wash, the crystals look slightly smaller (Figure 5); however, this is also due to the sample preparation – some crystals needed to be crushed with a spatula on the sample container wall to produce an evenly thick slide. Overall, no particular change in appearance was observed.

Figure 5. PLM Images of Water-Washed Sample S10R000378.

(10x, crP+, Red I comp., mounted in 1.55 IR oil)

(40x, uncrP, mounted in 1.55 IR oil)

2.3 SCANNING ELECTRON MICROSCOPY

2.3.1 Sample Preparation

Each sample was prepared for SEM analysis using one or more of three different methods. Samples S10R000354 and S10R000362 (as-received composites) were prepared by smearing a slurry of sample material onto a Petri dish. The smear was allowed to dry, some of the coarser particulate was crushed, and the dry particulate was lifted onto a SEM stub coated with an adhesive carbon tab.

Sample S10R000375 (water-washed Composite A) was suspended by sparging the contents of the sample vial with a disposable plastic pipette and transferring a small amount (about 0.2 mL) of sample slurry onto a dry filter. The pipette tip was drawn gently across the filter surface to create streaks of particulate on the filter. The vacuum pump was then immediately turned on. When the fluid had drained from the filter surface, the clamp and funnel were removed and the filter was allowed to completely dry.

Sample S10R000378 (water-washed Composite B) and a second preparation of Sample S10R000375 was prepared by water washing an aliquot (about 1 ml) of the slurry with about 30 ml of water, which was then sonicated for about 15 min and allowed to stand overnight. This allowed the abundant sodium fluoride phosphate to dissolve completely. The resulting smaller particulate was suspended and an aliquot was transferred onto a polycarbonate filter using vacuum filtration.

To do this, a cellulose backing pad and a 45-mm diameter, 0.4- μ m pore size, Nucleopore polycarbonate filter was placed on the fritted glass base of a filtration flask connected to a trap and vacuum. A filtration funnel was placed on the filter stack and clamped into place. Approximately 5 ml of water was added, with the vacuum turned off, in order to completely cover the polycarbonate filter. The sample/water suspension was sparged with a disposable plastic pipette, and a small amount (about 0.2 ml) of sample slurry was transferred into the funnel. The vacuum pump was immediately turned on. When the fluid had drained from the filter surface, the clamp and funnel were removed and the filter was allowed to dry completely. A section of the filter was cut out and affixed with carbon paint to an aluminum SEM stub containing a carbon planchet. The resulting smear and water-washed SEM specimens were coated with a conductive coating of carbon by evaporative deposition.

Samples S11R000162 (<710 μ m fraction, post water dissolution) and S11R000188 (>710 μ m) were prepared by dispersing a representative portion in water. The disaggregated particulate was then deposited onto a 0.4- μ m pore size, 45-mm diameter polycarbonate filter using vacuum filtration. A section of the filter was cut and glued to a carbon planchet on an aluminum SEM stub. The specimens were then coated with carbon by evaporative deposition.

SEM analysis was conducted using an Aspex¹ Personal Scanning Electron Microscope (PSEM), Model II, with a Noran light element energy EDS detector for chemical analysis. The instrument was operated at an accelerating voltage of 20 kV, and the samples were mounted at a working

¹ Aspex is a registered trademark of ASPEX Instruments, Delmont, Pennsylvania.

distance of 15 to 20 mm. Most of the images were acquired in secondary electron image (SEI) mode. Particles composed of heavier elements were located using the backscattered electron image (BEI) mode. EDS spectra were acquired for 30 seconds live time (unless noted) on relatively smooth surfaces (either flat or sloping toward the detector) near the center of the image.

2.3.2 Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy Results

Few distinctions were noted between the four pre-dissolution samples examined. Therefore, the samples are described together for this discussion. The figures below consist of either an SEI or a BEI to the left and an EDS spectrum to the right. The EDS spectrum was acquired from the spot marked with the '+' on the left hand image.

Large crystals and fragments of the sodium-fluoride-phosphate hydrate (natrophosphate), dominated the smear sample preparations (Figures 6 and 7). Fracture surfaces of natrophosphate crystals as shown in Figure 7 are probably the result of crushing the dried smear sample prior to transfer to the SEM stub. Many of the natrophosphate particles show evidence of rounding of the crystal surfaces due to dissolution and erosion (Figure 8).

Figure 6. SEI Image and EDS Spectrum of a Single Crystal of Natrophosphate from Sample S10R000354 Smear.

Figure 7. SEI Image and EDS Spectrum of a Fractured Fragment of Natrophosphate from Sample S10R000362 Smear.

Figure 8. SEI Image and EDS Spectrum of a Rounded Particle of Natrophosphate from Sample S10R000375 Smear.

X-ray diffraction indicates that natrophosphate was the only identifiable crystalline component in the samples. However, several minor or trace phases were identified in the SEM examination (see Figures 9 through 18).

Figure 9. SEI Image and EDS Spectrum of Aluminum-Rich Particulate from Sample S10R000375 Smear.

Some of these phases have been observed and are well characterized in other tank waste samples. These include aluminum-rich particulates, probably gibbsite (Figure 9), a sodium aluminosilicate, presumably cancrinite (Figure 10), sodium diuranate (Figure 11), and the sodium strontium phosphate hydrate phase, nastrophite (Figure 12).

Nastrophite ($\text{NaSr}[\text{PO}]_4 \cdot 9\text{H}_2\text{O}$) is described as completely soluble in 1% HCl and partially soluble in hot water ("New Mineral Names," Fleischer et al. 1982). A fragment found in the water-washed preparation of sample S10R000375 indicates that there is some resistance to dissolution in water at room temperature (Figure 13).

Figure 10. SEI Image and EDS Spectrum of a Sodium Aluminosilicate Aggregate from Sample S10R000375 Smear.

Figure 11. SEI Image and EDS Spectrum of a Sodium Diuranate Particle from Sample S10R000375 Smear.

Figure 12. SEI Image and EDS Spectrum of a Nastrophite Crystal from Sample S10R000354 Smear.

Figure 13. SEI Image and EDS Spectrum of a Nastrophite Fragment from Sample S10R000375 Water Washed.

Two other particle types occurred in all samples but they have been less well characterized. The first of these is best called a bismuth-iron metal phosphate. It is a fine-grained phase with a variable chemistry ranging from an iron-rich metal phosphate (Figure 14) to a bismuth-rich metal phosphate (Figure 15). The phosphate peak in this continuum of particles is also variable, and sodium, aluminum, and silicon are often present.

Figure 14. SEI Image and EDS Spectrum of Iron-Rich Metal Phosphate from Sample S10R000375 Water Washed.

Figure 15. SEI Image and EDS Spectrum of a Bismuth-Rich Metal Phosphate from Sample S10R000375 Slurry.

It is unclear whether the occasional particles of phosphate-free, bismuth-rich (Figure 16) and iron-rich (Figure 17) material are related to the metal phosphate phase.

Figure 16. SEI Image and EDS Spectrum of a Bismuth-Rich Crystal from Sample S10R000375 Slurry.

Figure 17. SEI Image and EDS Spectrum of an Iron-Rich Particle from Sample S10R000375 Slurry.

The second particle type found in these samples that has been less well characterized is a sodium- aluminum-phosphate particle type. While this chemical combination has occasionally been observed in tank waste, there has been no identification of a specific phase with this type of chemical signature using XRD or PLM characteristics. In the C-110 heel samples, it takes the form of fine-grained irregular sheets that survive the water wash (Figure 18).

Figure 18. SEI Image and EDS Spectrum of the Sodium Aluminum Phosphate-Rich Particle from Sample S10R000378 Water Washed.

3 POST-DISSOLUTION RESIDUAL SAMPLE S11R000162 (<710 μM)

3.1 X-RAY DIFFRACTION

The analysis of the post-dissolution X-ray diffraction pattern revealed gibbsite or nordstrandite as the major crystalline phase(s) (see Figure 19). At least one peak (at 8.3 deg two theta) could not be conclusively identified. This peak was first thought to be an artifact from sample preparation; it did appear twice on re-prepared samples. However, no pattern with the International Centre for Diffraction Data (ICDD) database produced a satisfying match – either the phases were deemed unlikely (SiO_2 crystals) or the chemical composition is highly unlikely (e.g., uranium acetate phases).

Figure 19. XRD Pattern of Residual Sample S11R000162.

The same issue was observed during XRD of the so-called Group 1 samples within the Waste Treatment and Immobilization Plant (WTP) pretreatment testing sequence. In PNNL-17992, WTP-RPT-166, *Characterization, Leaching and Filtration Testing for Bismuth Phosphate Sludge (Group 1) and Bismuth Phosphate Saltcake (Group 2) Actual Waste Sample Composites*, an extensive description of the potential candidate minerals is presented. Again, none of these phases could be positively identified by another analytical technique.

Several other peaks could not be positively identified, such as at 22.4 and 30.9 deg two theta. A peak of significant size at 33.5 deg two theta shows either a multiplet of distinct peaks or a single peak of a purely crystalline phase. The latter feature seems to be associated with the phase that produces the peak at 8.3, since one of the re-runs shows a parallel reduction in peak size while the other peaks were unaffected. This would cause the interpretation to lean toward a multiplet of distinct peaks rather than a poorly crystallized substance.

3.2 POLARIZED LIGHT MICROSCOPY

PLM of the water dissolution sample showed some very finely grained remnants of natrophosphate and gibbsite crystals with some opaque and yellow particles (Figure 20). The sample vial contained 50% clear liquid and 50% settled brown fines.

Figure 20. PLM Images of Residual Sample S11R000162.

3.3 SCANNING ELECTRON MICROSCOPY

Sample S11R000162 was prepared by dispersing a representative portion in water onto a polycarbonate filter. Particle loading on the specimen was moderately heavy, with well-dispersed micron-sized particulate scattered on a near-continuous mat of sub-micron size particulate (Figure 21). The coarsest particles were typically less than 20 μm in size.

Figure 21. SEI Image and SEI Close-Up of Sample S11R000162 Overview.

The individual particles are dominated by three particle types. These are illustrated in Figure 22. The particles labeled #1 and #2 in Figure 22 are sodium aluminosilicates with a chemical composition consistent with cancrinite. The particle labeled #3 is gibbsite ($\text{Al}[\text{OH}]_3$). The particle labeled #4 is an iron-bismuth-aluminum-phosphorus mix that is probably non-crystalline. Note that this last particle (#4) is slightly brighter in the backscatter image due to the iron and bismuth. There are other particles on the backscatter image with similar brightness that probably share a similar chemical composition.

The fine-grained fraction that forms a near continuous mat is composed mostly of particles similar to the main particle types. There are also patches on the filter of what appear to be a colloidal or gel material. This occurs in irregular, flattened patches, larger than $20\text{ }\mu\text{m}$ (Figure 23). These appear to be a mix, primarily of gibbsite and the amorphous metal phosphate phase. The EDS spectrum in Figure 23 was collected by rastering the SEM beam over the area within the yellow box on the image.

In addition to the above, a couple of trace phases were observed. These were a uranium-rich phase, consistent with sodium diuranate mixed with the metal phosphate phase (Figure 24) and a sodium-strontium-phosphate phase with a chemistry consistent with nastrophite $\text{NaSr}[\text{PO}_4]\cdot 9(\text{H}_2\text{O})$, but with an unusual lath- or needle-like morphology (Figure 25).

Figure 22. SEI Image and EDS Spectra of Dominant Phases in Sample S11R000162.

Figure 23. SEI Image and EDS Spectrum of Gel in Sample S11R000162.

Figure 24. SEI Image and EDS Spectrum of Uranium-Rich Phase in Sample S11R000162.

Figure 25. SEI Image and EDS Spectrum of Nastrophite in Sample S11R000162.

4 POST DISSOLUTION RESIDUAL SAMPLE S11R000188 (>710 μM).

4.1 X-RAY DIFFRACTION

The analysis of the X-ray diffraction pattern revealed gibbsite and nordstrandite as the major and only identifiable crystalline phase(s) (see Figure 26).

Figure 26. X-Ray Diffraction Pattern of Sample S11R000188.

4.2 POLARIZED LIGHT MICROSCOPY

The sample vial contained dry silty material. PLM showed some very fine-grained (<5 μm) shards of natrophosphate and gibbsite crystals with some opaque and yellow particles (Figure 27); the largest particles were opaque.

Figure 27. PLM Images of Sample S11R000188.

4.3 SCANNING ELECTRON MICROSCOPY

Sample S11R000188 was prepared by dispersing a representative portion in water onto a polycarbonate filter. During cutting of the filter, several larger rounded grains detached from the filter surface and were contained in a plastic Petri dish. These particles were adhered to a second aluminum SEM stub using a lifting technique where an adhesive carbon tab was pressed onto the particles in the Petri dish.

The larger grains in Sample S11R000188 ranged between 0.5 and 1 mm in size and displayed rough surfaces with sharp edges suggesting minimal degradation from the dissolution and minimal rounding due to tumbling during the waste retrieval processes (Figure 28).

Figure 28. SEI Images and EDS Spectrum of Larger Grain from Sample S11R000188.

Further SEM examination of one of the large grains showed it to be an aggregate of small subhedral particles cemented together resulting in open pore space in the grain. This is seen in Figure 28 where a coarse grain is shown under two consecutive magnifications. An EDS analysis of one of the subhedral particles indicates the presence of an aluminum oxide phase, tentatively identified as gibbsite based upon the morphology.

Additional large grains were similar to the one in Figure 28 and were identified as gibbsite aggregates; however, some of the large grains contained a high level of iron. One of these iron-rich particles is shown in Figure 29. The iron-rich particle had lath-like smaller features, and the EDS spectrum shows a phase dominated by iron oxide with minor phosphorous.

Figure 29. SEI and BSE Images and EDS Spectra of Aluminum Oxide and Iron Oxide Grains from Sample S11R000188.

SEM analysis of the finer particulate dispersed on the filter showed moderately heavy particle loading with well-dispersed micron-sized particulate (Figure 30). The coarsest particles were typically less than 50 μm in size.

Figure 30. SEI Image Overview of Sample S11R000188 Particulate.

Areas of the image displayed in Figure 30 were further analyzed by the SEI, BEI, and EDS detectors. Two of these areas are shown in Figures 31 and 32. The larger particle in Figure 31, as highlighted by the EDS crosshair labeled by a '1', is an aluminum oxide phase. An aluminum oxide phase is also present at the spot labeled '2', and the euhedral morphology is indicative of gibbsite. The particle shown at the EDS spot labeled with a '3' is an iron-rich phase, and this phase is also present in other small particles in the area as indicated in the BEI.

Figure 31. SEI and BSE Images and EDS Spectra of an Area from Figure 30.

Figure 32. SEI and BSE Images and EDS Spectra of an Area from Figure 30.

The three selected particles in Figure 32 show three different phases. The particle with the EDS crosshair labeled '1', is an aluminum oxide phase with subhedral features indicative of gibbsite. The particle labeled '2' is an iron-aluminum-strontium-phosphate phase, and the particle labeled with a '3' is the sodium-strontium-phosphate phase, nastrophite.

The BEI detector was used to quickly scan the particulate for heavy elements. Scattered on the filter were micron-sized bismuth particles as seen in Figure 33. In addition, an occasional lath-like aluminum oxide particle was detected, as seen in Figure 34, which could be the nordstrandite.

In summary, the majority of the larger and mid-sized particles were aggregates of gibbsite, and gibbsite was seen as micron-sized single particles. An iron oxide phase was also seen throughout all the SEM specimens covering a broad particle size range similar to the gibbsite. Of the non-aluminum oxide and iron oxide phases, the larger particles were a cancrinite and an iron-bismuth-aluminum-phosphorus mix. Smaller particles were made up of the previous mentioned phases, and others consisted of nastrophite and other heavy metal elements such as uranium and bismuth.

Figure 33. BSE Image and EDS Spectrum of a Bismuth-Rich Particle from S11R000188.

Figure 34. SEI Image and EDS Spectrum of an Aluminum-Rich Lath (Nordstrandite?) from S11R000188.

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