C-104 Solid Phase Characterization of Sample 4C-13-1 From Tank 241-C-104 Closure Sampling Event

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List of Terms

Acronyms and Abbreviations

BEI	backscattered electron image
C-104	tank 241-C-104
EDS	energy dispersive X-ray detector
PSEM	personal scanning electron microscope
SEI	secondary electron image
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
XRD	X-ray diffraction

1 INTRODUCTION

At the request of Advanced Technologies and Laboratories International, Inc. and Tank Waste Inventory and Characterization personnel, one solid grab sample from closure sampling in Riser 7 of tank 214-C-104 (C-104) was examined to determine the solid phases that were present. The sample was analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The purpose of this analysis was to see if the presence of hydrated phases could provide a possible explanation for the high moisture content obtained from thermogravimetric analysis (TGA) (see Appendix A). The TGA sample split had 11.5% water added by weight to prevent dispersion of the dry particulate.

Sample S13T003832 was a split from the homogenized grab sample 4C-13-1. It consisted of mostly light tan, granular solids with a few small white and reddish/brown particles. This split had not had additional water added. Once dried, the appearance was that of a homogeneous, light tan, fine solid.

2 X-RAY DIFFRACTION ANALYSIS

A fraction of the sample was ground as required, placed in the well of a quartz zero-background slide, compressed with the plane of a glass slide, fixed with collodion binder, and allowed to dry. Preparation and analysis by XRD was performed by J. A. Pestovich during the period April 11-15, 2013, in accordance with ATS-LT-507-103, "222-S Laboratory X-Ray Diffractometry (XRD) Using the Rigaku®¹ MiniFlex II." Refer to laboratory notebook HNF-N-710-1, "Rigaku® MiniFlex II X-Ray Diffractometer (XRD) Maintenance and Operations (GD400212)," page 23, for test information and specifics. The sample compositions reported below are relative amounts based upon all the crystalline species present in each individual sample.

S13T003832 (4C-13-1). The major phases of the sample were identified as gibbsite [$\text{Al}(\text{OH})_3$] and thermonatrite [$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$]. Natrophosphate [$\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$] and cancrinite [$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3) \cdot 2.2\text{H}_2\text{O}$] were identified as minor phases, and clarkeite [$\text{Na}((\text{UO}_2)\text{O})(\text{OH}) \cdot \text{H}_2\text{O}$] appeared as a trace phase.

<u>Chemical Name</u>	<u>Mineral Name</u>	<u>Formula</u>	<u>~Rel. Amount</u>
Aluminum Hydroxide	Gibbsite	$\text{Al}(\text{OH})_3$	Major
Sodium Carbonate Monohydrate	Thermonatrite	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	Major
Sodium Fluoride Phosphate Hydrate	Natrophosphate	$\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$	Minor
Sodium Calcium Aluminosilicate Carbonate	Cancrinite	$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3) \cdot 2.2\text{H}_2\text{O}$	Minor
Sodium Uranium Oxide Hydroxide Hydrate	Clarkeite	$\text{Na}((\text{UO}_2)\text{O})(\text{OH}) \cdot \text{H}_2\text{O}$	Trace

¹ Rigaku is a registered trademark of Rigaku Americas Corporation/USA, The Woodlands, Texas.

Figure 1. X-Ray Diffraction Pattern, Sample S13T003832 (4C-13-1).

3 SCANNING ELECTRON MICROSCOPY ANALYSIS

Another portion of the dried sample was crushed lightly, and the dry solids were placed in a small petri dish. A SEM specimen was prepared by transferring the dried solids from the petri dish onto an aluminum SEM stub covered with an adhesive carbon tab. This specimen was coated with a thin layer of carbon by evaporative disposition. The resulting SEM specimen was examined on the ASPEX^{®2} personal scanning electron microscope (PSEM) equipped with an energy dispersive X-ray (EDS) detector. This instrument is located in Room 1-A at the 222-S Laboratory and is operated in accordance with the 222-S Laboratory Technical Procedure ATS-LT-161-100, "222-S Laboratory Sample Preparation and Operating Procedure for Scanning Electron Microscopes." Mr. G. A. Cooke performed the SEM analysis on April 11 and 15, 2013. Information pertaining to the preparation and analysis is contained in HNF-N-832-1, "Laboratory Controlled Notebook for SEM," page 184. The images used to illustrate the particle types that

² ASPEX is a registered trademark of Aspex Corporation, Delmont, Pennsylvania.

were observed are all secondary electron images (SEI) unless identified as backscattered electron images (BEI).

The SEM specimen consisted of a number of large fragments that, upon closer examination, appeared to consist of aggregates of smaller particles. Figure 2 shows a group of these aggregates along with an EDS spectrum obtained by rastering the beam through the area delineated by the yellow box.

Figure 2. Sample 4C-13-1: Particle Aggregates (Left) and Energy Dispersive Spectrometry Spectra (Right) from Area in Yellow Box.

Some of these large particles have an external morphology that appears to be consistent with the natrophosphate (Figure 3). However, examination of the surface chemistry with the EDS detector shows these particles are typically covered with a sodium-rich phase (probably thermonatrite, as indicated by the XRD pattern).

Figure 3. Sample 4C-13-1: Particle Aggregate Coated with Sodium Carbonate (Left) and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

The sodium-rich material is uniformly fine grained and is mostly present as coatings (Figure 4), although discrete aggregates of sodium-rich material were observed (Figure 5).

Figure 4. Sample 4C-13-1: Close-up of Aggregate Surface (Left) and Energy Dispersive Spectrometry Spectra (Right) from Areas in Yellow Box.

Figure 5. Sample 4C-13-1: Small Irregular Sodium Carbonate Aggregate (Left) and Energy Dispersive Spectrometry Spectra from Areas in Yellow Box (Right).

The next most common phases are aluminum-rich (Figure 6), usually recognized as small (<10 micron) euhedral to subhedral crystals, and sodium-uranium-rich particulate, easily found by examining the particulate in BEI mode (Figure 7). These particles correspond to the gibbsite and clarkeite identified by the XRD analysis.

Figure 6. Sample 4C-13-1: Single Crystal of Gibbsite (Left) and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

Figure 7. Sample 4C-13-1, Patch of Fine-Grained Clarkeite: Backscatter Electron Image (Left), Secondary Electron Image (Center), and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

Less common phases, located on the SEM specimen, include iron-rich (also recognized as brighter than the surrounding particulate, Figure 8), thorium-rich (again showing up as brighter in BEI, Figure 9), and a sodium-calcium-rich particulate (Figure 10).

Figure 8. Sample 4C-13-1, Patch of Fine-Grained Iron Oxyhydroxide: Backscattered Electron Image (Left), Secondary Electron Image (Center), and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

Figure 9. Sample 4C-13-1, Aggregate of Thorium-Rich Material: Backscattered Electron Image (Left), Secondary Electron Image (Center), and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

Figure 10. Sample 4C-13-1: Single Crystal of Sodium-Calcium Carbonate or Oxalate (Left) and Energy Dispersive Spectrometry Spectra (Right) from Spot Marked with Yellow Cross.

4 DISCUSSION

Solid phase characterization was performed on Sample S13T0003832 (4C-13-1) in order to seek an explanation for unusually high weight loss results from the TGA analysis. This sample was one of four grab samples taken from C-104 and analyzed at the 222-S Laboratory as directed by RPP-PLAN-44844, *Sampling and Analysis Plan for Waste Solids in Tank 241-C-104 to Support Tank Closure*.

Analysis by XRD and SEM showed the sample to consist of aggregates of mostly fine-grained material cemented with thermonatrite [$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$]. The thermonatrite and gibbsite [$\text{Al}(\text{OH})_3$] were the major phases identified by XRD, and the SEM found coatings of fine-grained thermonatrite on the surface of the particle aggregates.

The SEM BEI imaging readily detected a sodium- and uranium-bearing compound that was consistent with the clarkeite [$\text{Na}((\text{UO}_2)\text{O})(\text{OH}) \cdot \text{H}_2\text{O}$] identified as a trace phase by XRD. The broad XRD peaks associated with the clarkeite indicate that it is poorly crystalline. The discrepancy between the SEM, which showed the uranium phase to be common, and the XRD, which found only trace amounts, can be explained if most of the uranium-bearing phase is non-crystalline.

Natrophosphate [$\text{Na}_7\text{F}(\text{PO}_4)_2 \cdot 19\text{H}_2\text{O}$] and cancrinite [$\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{CO}_3) \cdot 2.2\text{H}_2\text{O}$] were identified as minor phases by XRD and could not be located on the SEM specimen. This is probably due to the heavy coating of thermonatrite that was ubiquitous on the larger particles.

Iron-rich and thorium-rich particulate were observed on the SEM specimen. No peaks on the XRD pattern could be attributed to compounds with these chemical elements. This is due to their low concentrations, their lack of crystal structure, or both.

The phases observed are all consistent with the chemical analyses for these samples (report in preparation). They are also consistent with the phases found in previous C-farm heel samples (LAB-RPT-11-00008, *Solid Phase Characterization of Heel Samples from Tank 241-C-110*; LAB-RPT-13-00002, *Solid Phase Characterization of Tank 241-C-108 Residual Waste Solids Samples*).

However, the particulate in Sample 4C-13-1 is somewhat unusual in that it consists of porous aggregates of very fine-grained material. This may play some role in the TGA results, since the abundant pore space may allow substantial water to persist in the aggregate particles and yet still appear to be dry. These porous aggregates would act to absorb water, causing the particulate to appear dryer than it really is.

5 REFERENCES

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