

Scanning Transmission Electron Microscopy of Plutonium Particles in Hanford Tanks 241-TX-118 and 241-SY-102

December 2019

EC Buck SI Sinkov ES Ilton DD Reilly TG Lach



Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830

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Final Report

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Pacific Northwest National Laboratory Richland, Washington 99352

Abstract

This is a report on the effort to characterize discrete plutonium (Pu) bearing particles from Hanford wastes, taken from tanks, 241-SY-102 and 241-TX-118. Excess plutonium-bearing materials were added to tanks SY-102 and TX-118 from the Plutonium Finishing Plant (PFP). These have been previously characterized with Scanning Electron Microscopy (SEM) by Reynolds and co-workers. Their SEM observations were confirmed in this study with SEM where the particles in 241-SY-102 and 241-TX-118 were 5 to 20 µm in length with a variable composition containing plutonium, bismuth, and phosphorus. In this investigation, the plutonium particles were extracted from surface mounts using the SEM-Focused Ion Beam (FIB) and prepared for Scanning Transmission Electron Microscopy (STEM) and Atom Probe Tomography (APT). This was the first time that high resolution STEM methods and APT have been applied to plutoniumbearing wastes from the Hanford tanks. The STEM analysis of 241-SY-102 indicated a complex coprecipitation of plutonium oxide with bismuth and phosphate. Diffraction and imaging partially matched with a plutonium oxide phase. There were both crystalline and amorphous plutonium oxide (PuO_2) associated with bismuth, phosphate, and iron. Nano-precipitates of iron, chromium, and bismuth were observed within the plutonium oxide in some particles, suggesting that these phases formed at the same time. The STEM analysis of 241-TX-118 indicated that the plutonium particles were a mixed bismuthphosphate phase and plutonium oxide. .

Executive Summary

This is a report on microscopy characterization activities at Pacific Northwest National Laboratory (PNNL) on plutonium (Pu) bearing particles from Hanford waste tank 241-SY-102 and 241-TX-118 samples.

Nuclear criticality safety concerns arise because a small fraction of plutonium inventory in the Hanford tank waste is in the form of large, dense particles that might be segregated from other waste solids by hydrodynamic conditions during waste handling. Initial characterizations have estimated that about 4% of all plutonium in the tank farms is in the particulate form that presents criticality safety concerns. Further characterization of the plutonium-bearing particles and inventories is important to develop the criticality safety evaluations necessary to allow handling and processing of these plutonium-bearing wastes. More information is needed on chemical compositions and densities of the plutonium particles to establish potentials for particle segregation under special hydrodynamic conditions.

Concerns also arise because additional, unidentified plutonium inventory might be in plutonium-bismuthrich particulate forms. While plutonium-bismuth-rich particulates have been observed in laboratory samples, the exact compositions, conditions of formation, and densities of the particles are unknown. Further characterization of particles will provide insight to the Hanford processing sources and support quantification of the plutonium inventories in support of criticality safety evaluation.

Washington River Protection Solutions (WRPS) shipped waste samples that contained plutonium particulates to PNNL for characterization. PNNL conducted experiments to determine the density of the species and provided the identity of the species so that a semi-quantitative estimate of the density can be found.

Scope

This work involved characterization of the plutonium particles in the waste samples with respect to size, density, and composition. The Pu-Bi-rich particulate forms are of special concern with density and compositions to be characterized to support analysis of their conditions of formation.

A technical report prepared to PNNL standards that provides best-available characterization of the particulate plutonium in the sample materials is the deliverable for the work scope. The technical report will be used as reference basis for criticality safety evaluation supporting the Hanford tank farms operations.

Findings

The plutonium-bearing particles observed in both 241-SY-102 and 241-TX-118 confirm the original findings by Reynolds et al.¹ The compositions and particle size ranges agree with this earlier study.

It required high resolution scanning transmission electron microscopy (STEM) and atom probe tomography (APT) before the true nature of the composition was uncovered. Some of the plutonium was crystalline and matched with PuO_2 but other particles were amorphous. The particles have both phosphorous and bismuth at varying levels.

Crystalline Particle Attachment (CPA) processes have not been documented in the Hanford tanks but were suggested as possible processes by Peterson and co-authors² that may occur in the waste tanks. However, the following observations in this investigation suggest that the formation of these larger plutonium-bearing particles may have occurred via an Oswald ripening mechanism and CPA:

(1) The occurrence of a single crystals of plutonium oxide mixed with phosphorus, bismuth, iron and chromium, aggregates and nanoparticles of plutonium oxide and other phases with different orientations in their outer rims.

(2) Different stages of nanoparticle agglomeration and aggregation as individual particles, clusters, and larger particles.

These processes suggest that CPA may have been a mechanism for the formation of the plutonium-rich particles in 241-SY-102 and 241-TX-118. If so, this mechanism suggests and upper bound on particle size that would be dependent upon the colloid interaction processes occurring in the very high ionic strength solutions and shows that the particles cannot have a density higher than that of PuO_2 .

Acknowledgments

The authors thank the Radiochemical Processing Laboratory (RPL) Management and Radiological Control for assisting in developing protocols for the analysis of plutonium-bearing materials within the Radiomaterials Microscopy Suite. We thank the staff at Building 222S for providing the SY-102 and TX-118 samples. We thank Washington River Protection Solutions (WRPS) staff David Losey, Gary Cooke, Jake Reynolds, and Bill Callaway for supporting this project. Shane Scott is thanked for providing assistance on transport of the samples.

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Acronyms and Abbreviations

atom probe tomography
atomic percent
bright field
backscattered electron
Crystalline through Particle Attachment
disintegrations per minute
X-ray Energy Dispersive Spectroscopy
Electron Energy-Loss Spectroscopy
Field Emission Gun
Fast Fourier Transform
Focused Ion Beam
High Contamination Are
high angle annular dark field
kilo-electron volt
micrometer
National Institute of Standards and Technology
nanometer
Plutonium Finishing Plant
Pacific Northwest National Laboratory
Radiochemical Processing Laboratory
Radiological Protection Technician
Selected Area Electron Diffraction
Scanning Electron Microscopy
Scanning Transmission Electron Microscopy
Transmission Electron Microscopy
Washington River Protections Solutions
weight percent

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1.0 Introduction

The Hanford Site in Eastern Washington State, has approximately 56 million gallons of nuclear waste remaining from plutonium production contained in 177 underground storage tanks. Most plutonium was extracted from the nuclear fuel prior to discharge of the waste to the storage tanks. However, small amounts of plutonium were lost, including during processing at the Plutonium Finishing Plant (PFP) and were sent directly to the waste tanks. Under alkaline conditions the solubility of plutonium is extremely low.

This report is focused on recent progress and proposed future work towards characterizing plutoniumbismuth-phosphorus (Pu-Bi-(±P))-rich particles discovered in the sludge fraction of tanks 241-SY-102 and 241-TX-118 (henceforth will be referred to as SY-102 and TX-118, respectively). The ongoing mystery concerning the source of the Bi that is closely associated with Pu in these tanks is not addressed. As summarized in Delegard and Jones³, three species of Pu-rich particles (Pu-O, Pu-Bi, and Pu-Bi-P) were discovered in tanks SY-102 and TX-118 in 2004 and 2012, respectively. A more detailed SEM-EDS (Scanning Electron Microscope-X-ray Energy Dispersive Spectroscopy) study of Pu particles in SY-102 was published in 2016 by Reynolds et al.², who preconcentrated Pu by gravitational settling and dissolution and rinsing of soluble sodium salts. The morphology of the Pu-Bi particles is striking, often attaining lengths on the order of tens of microns but only up to about five microns thick. This lath-like morphology can appear to be comprised of smaller laths yielding the so-called "petrified wood" appearance. The Pu-Bi-P particles usually had diameters less than ten microns (larger ones appear to be about 20 µm in diameter) and were described as having a "globular" morphology, indicating to the authors that they are either amorphous or aggregates of smaller particles. A major claim in the paper is that both the Pu-Bi and Pu-Bi-P are oxygen rich. If so, this would have important implications for their propensity to settle and accumulate with strong implications regarding the danger of reaching criticality.

Plutonium-bearing particles from the Z9 crib sites have been found to have a strong association with phosphorus.⁴ These particles have been examined with x-ray absorption spectroscopy⁵ and transmission electron microscopy.⁶ However, as discussed by Reynolds et al.¹, there were uncertainties in quantifying the amount of oxygen associated with the Pu particles. In this regard, an issue that is not resolvable by conventional SEM-EDS is the possibility that the particles might exist as a dense metallic core coated by a thin oxide layer. With respect to Pu-Bi-P particles, it would also be important to distinguish whether they are aggregates or single amorphous structures, where aggregates would have lower net densities. Again, Reynolds et al.¹ noted that they did not have the spatial resolution to distinguish between these two possibilities.

The advanced electron microscopy facilities recently established in the Radiochemical Processing Laboratory (RPL) at PNNL are ideal for tackling these challenging issues. First, the JEOL 300F GrandARM STEM system can routinely reach atomic scale resolution and is ideal for resolving the smallest of particles, thereby potentially settling the issue of whether the Pu-Bi-P particles are aggregates or not. Further, electron diffraction can determine whether the particles are amorphous or crystalline and possibly identify the phase. The Thermo-Fisher Helios 660 Scanning Electron Microscopy-Focused Ion Beam (SEM-FIB) can be used to select individual particles and then section them for further study by Scanning Transmission Electron Microscopy- Electron Energy-Loss Spectroscopy (STEM-EELS) and Scanning Transmission Electron Microscopy-X-ray Energy Dispersive Spectroscopy (STEM-EDS) as well as Atom Probe Tomography (APT). This enabled us to quantify the composition of a particle from the surface to its core and thus better characterize its density.

2.0 Experimental Procedure

The technical or operating procedure (RPL-EMO-1 Rev1) was utilized by this project to conduct the microscopy operations. The two samples from SY-102 and TX-118 (were received from Building 222S and partitioned into samples suitable for microscopy analysis.

222S Descriptions: Source Tank: 241-SY-102 / Core 285 / Segment 17 Sample Number: S11R000655 Subsample ID: Sludge solids with nominal particle diameters of 10-45 um collected for SEM analysis

Source Tank: 241-TX-118 / Composite Segments 1 /Sample Number: S11R000664 Subsample ID: Sludge solids with nominal particle diameters of 10-45 um collected for SEM analysis Cores 236/259/260

Sources and generation of these two samples described in LAB-RPT-12-00006, Rev. 1, *Characterization of Plutonium-Bearing Waste in the High-Level Waste Storage Tanks* 241-SY-102, 241-TX-118, and 241-AZ-101 and the Plutonium Finishing Plant Z-9 Crib.

The individual materials were a dried powder that had been previously sieved and separated as reported by Reynolds et al.¹ The following description was provided by Reynolds and co-workers.¹ Hanford tank SY-102 was core sampled and the associated sludge layers were composited and homogenized. The sludge was then water-washed with one part "inhibited water" (0.01 M NaNO₂ and 0.01 M NaOH) and one-part sludge to remove soluble salts from the sample. The initial sample was expected to have between 200 to 350 micrograms of plutonium per gram of sludge based on inductively coupled plasma mass spectroscopy. To increase the likelihood of locating dense plutonium-bearing particulates, settling tests were performed to separate the fast settling fraction from the sample, assuming that particulate that is both large and dense would most likely be found in this fraction. 39.12 grams of sample were suspended in 1 L of de-ionized water in a 30-cm high separatory funnel by stirring the sample into the de-ionized water with a small spatula. The sample was further homogenized by rotating the vessel end over end several times. The sample was then allowed to settle for 58 min, and the top 80 % of the volume was removed from the funnel. This process was repeated five more times, leaving the faster-settling fraction in the funnel each time. Each successive settling step further increased the concentration of fast settling particles in the sample left behind. The final fast settling solids fraction was recovered by opening the stopcock on the funnel and allowing the solids to flow into a beaker.

Due to the high levels of contamination, both glass vial containers of SY-102 and TX-118 materials were handled in a High Contamination Fume Hood area. To deposit these materials on the sticky carbon SEM mount, a modified technique previously used for deposition of plutonium oxide (PuO_2) and plutonium tetraflouride (PuF_4) samples was used.

Caution: Plutonium-containing materials in powdery form may be highly mobile and dispersible and need to be handled with the greatest care possible to prevent contamination. In this case a pointed Q-tip was used as a sampling tool to move a subsample from the container to the upper rim of the funnel and onto the SEM stub.

Figure 2.1 shows the experimental setup used for SEM sample preparation with pictures taken from two different angles. The vial size was 20 ml, inner diameter of the funnel stem was ~4 mm. A 0.5-inch diameter SEM stub was supported by an inverted mushroom-shaped metal piece. The vial was attached to

the funnel with a sticky tape for the photograph. During sample preparation, the vial was held securely, while a pointed Q-tip was used to minimize distance between the vial neck and the funnel opening.



Figure 2.1. SEM sample preparation using a glass funnel and a pointed Q-tip sample collector. Note: all parts shown in this image were cold duplicates of the actual set-up assembled in a High Contamination Area (HCA) fumehood (the dark red solid at the vial bottom is iron(III) hydroxide). Immediately after application all disposable parts were disposed in a waste container and the funnel was decontaminated with water, wiped with wet towels, and placed into a sealed bag to store.

The use of a bright light source under a very sharp angle is recommended to illuminate the sticky carbon surface after the first round of the material transfer through the funnel to see more clearly the amount of material and its location with respect to the center of the mount. With this light test, if no material was visible on the sticky surface, another round of transfer was performed.

Note: With highly concentrated plutonium powders (PuO₂, PuF₄, etc.) a bright light test might not be informative because it only takes a few particles of plutonium to exceed a counting rate of 10^6 disintegrations per minute (dpm) on direct measurement of the sample with alpha meter (this can only be performed by an appropriately trained Radiological Protection Technician, RPT). This level of alpha activity is considered too risky for application of a tap test and subsequent sample handling unless the requirement is to deposit as many as several hundred particles for a representative size distribution analysis.

Once the material was visibly present, the SEM sample was tap-tested (continuous RPT coverage was required during this process) to confirm that moderate mechanical disturbance of the sample did not lead to release of plutonium particles from the sticky surface to other areas. In the case of a successful tap-test (i.e., no spread of contamination was detected), under RPT instruction, smears were collected from the sides (grooved area) and bottom of the mount. If the smear results were negative the sample could be surveyed

out of the HCA. Six samples of SY-102 and two samples of TX-118 were prepared as described above, most of them on an ultra-smooth carbon tape.

2.1 Micro-structural Analysis of Samples

For SEM, a small quantity of the solid material was placed on a flat sticky carbon tape mounted on an aluminum stub using a mini-funnel. This method prevents the spread of particles and reduces the risk of contamination. The sample was then tested for loose particles by gently tapping the specimen on its side. The specimen was then surveyed and checked for smearable activity. The SEM sample was examined in a FEI Quanta250 Field Emission Gun (FEG) equipped with a backscattered electron (BSE) detector and EDAX Genesis X-ray energy dispersive spectrometer (EDS) system in the RPL. No conductive carbon coat was used for sample preparation and the instrument was sometimes operated in the low-vacuum mode. This enabled analysis of all major elements in the phases. It is not possible to extract quantitative data or even semi-quantitative data on the light elements, but the analysis can confirm their presence. Examples include the identification of a sodium phase and carbonates.

2.2 SEM Magnification Scale

Most SEM images were obtained at 20 keV with backscattered imaging to enable the high atomic number (Z) phases to be easily viewed. As the sample was not a polished flat section, it is unreliable to extract quantitative data from the EDS analyses; however, semi-quantitative analysis is reported. Analyses where the lower energy X-rays were present were deleted from consideration. The SEM magnification scale was calibrated with a National Institute for Science and Technology (NIST) traceable standard. The SEM images of this measurement standard are shown in Figure 2.2. The instrument indicated magnification was within one percent of the expected value. The energy scale was checked by looking at high and low energy X-rays from known materials. For SEM, a small quantity of the solid material was placed on a sticky carbon tape mounted on an aluminum SEM stub. The SEM sample was examined in a FEI Quanta250 FEG equipped with a BSE detector and EDAX Genesis X-ray EDS system in the RPL.



Figure 2.2. SEM images of the magnification standard (MRS-4) showing calibration checked at x200, x1000, x4000, and x10000 (Taken 09-2019)

2.3 X-ray Energy Dispersive Spectroscopy

The EDS system was calibrated with known compounds. The energy positions of peaks measured on the EDS system have been compared to literature values. The agreement between literature and experimental values was excellent, demonstrating that the system is calibrated correctly for analyzing characteristic X-rays at both low and high energies (see Figure 2.3). The error in the peak energy assignments was estimated to be ~1%. Although SY-102 and TX-118 materials were highly radioactive, they did not create any problems for the EDS system.

With the electron beam off, we can record an EDS signal and show the radioactive signature of the material. The TX-118 sample, which was more radioactive than the SY-102 sample, revealed the presence of americium (Am²⁴¹) through the detection of X-rays from neptunium. SY-102 would have given a similar signal following a much longer count but this was not attempted.



Figure 2.3. Spectrum of a bismuth standard showing peaks identified by the NIST program Desktop Spectrum Analyzer 2 (Kelvin 2018-09-26 revision)

2.4 Focused Ion Beam (FIB) SEM Sample Preparation

The SEM mounts containing the dried tank waste specimens were used for locating the Pu particles. A FEI Helios 660 NanoLabTM FEG dual beam focused gallium ion beam/scanning electron microscope (FIB-SEM) equipped with an EDAX (EDAX Inc., Mahwah, NJ) compositional analysis system was used in the Transmission Electron Microscopy (TEM) sample preparation. The current and accelerating voltage of the ion beam used for prep was 9 pA to 9 nA and 2–30 kV, respectively, depending on the progress of the thinning operation. The radioactive contamination state of the chamber was established before and after this process. The thinned specimens were attached to copper (Cu) Omniprobe grids. These were of sufficiently low radioactivity levels that they could be analyzed safely in the GrandARM STEM/TEM.

The process of isolating and extracting the plutonium particles started with locating the plutonium-rich particles using BSE imaging in the SEM-FIB. Once a particle was located, it was coated with a Pt-C mixture to protect the specimen. The sample area was then trenched out with the ion beam until the sample could be extracted using normal SEM-FIB methods (see Figure 2.4). The sample was protected from damage from the ion beam during thinning by adding carbon (see Figure 2.5). The plutonium materials were cut from the bulk solid, such that these particles represent materials that would have been unaffected by any post-separation processes such as washing, or reaction with any solutions (i.e. these were the regions that were previously exposed). This is the clear advantage of the SEM-FIB method over straight analysis using the SEM. With the SEM-FIB, the internal composition and structure of the particle was revealed. One further advantage of this approach is the ability to look for evidence of metallic plutonium in the particles. Of the samples that were prepared from both SY-102 and TX-118, there was no evidence of any metallic material.



Figure 2.4. Steps in the preparation of a lift-out specimen of a particle of Pu from Tank Waste solids



Figure 2.5. Final thinning process for preparation of samples for STEM and other techniques. This sample is described in more detailed in Section 5.2.

2.5 Scanning Transmission Electron Microscopy (STEM)

Specimens for STEM were characterized on a JEOL (Japan) ARM300F (GrandARM) probe-corrected microscope equipped with high angle annular dark field (HAADF) and bright field (BF) detectors, dual Bruker X-ray EDS, and Gatan (Gatan Inc., Pleasanton, CA) Quantum Image Filter for Electron Energy-Loss Spectroscopy (EELS). Diffraction patterns, EELS data, and electron micrographs were analyzed with Gatan DigitalMicrograph[™] 3.0 software. Resolution and diffraction were demonstrated on a plutonium oxide material shown in Figure 2.7 where the atomic columns were clearly resolved and there was a good match of electron diffraction values to literature values.



Figure 2.6 Lift-out Specimen of plutonium oxide



Figure 2.7. Atomic resolution image of a plutonium oxide material (A). The measured electron diffraction (B) had d-spacings at 0.310 nm, 0.273 nm, 0.192 nm, 0.160 nm, 0.125 nm. (C) This is in good agreement with literature values for (111) 0.3109 nm, (200) 0.2692 nm, (220) 0.1904 nm, (311) 0.1624 nm, (331) 0.1235 nm

2.6 Atom Probe Tomography (APT)

Specimens for atom probe tomography (APT) were characterized on a Cameca LEAP 4000XHR local electrode atom probe microscope. APT is a mass spectrometry technique that utilizes field evaporation to map the 3D composition of a material with part-per-million sensitivity and sub-nanometer spatial resolution, providing unique insight into the compositional and structural variation in a material. APT was performed using laser pulse mode with a pulse energy of 50-60 pJ and detection rate of 0.3% at 125 kHz and 45 K. Reconstructions and analyses were performed using Cameca's Integrated Visualization and Analysis Software (IVAS) 3.8.2. Analysis was performed using standard techniques that include two-dimensional concentration contour plots and isoconcentration surface analysis.

TX-118 particles were sectioned into needle-shaped specimens for atom probe tomography (APT) using SEM-FIB as shown in **Figure 2.8**. The final tip diameter of the specimen is under 100nm. Low energy (2kV) ions were used at the end to remove beam damage and limit Ga implantation.



Figure 2.8 Preparation of the APT tip using the SEM-FIB. (A) The specimen is cut-out from a lift-out that was also used for STEM analysis (B) the lift-out is attached to an APT post and the excess material is cut off. (C) The needle is shaped with the ion beam, and (D) the sample is analyzed in the APT instrument (schematic diagram).

APT has been used at PNNL to analyze various materials including non-conducting materials; however, this analysis of a particle from the Hanford waste tanks is the first example of this advanced technique being applied to these complex materials. Because of its ability to obtain very high spatial resolution in comparison to any other characterization tools, including STEM combined with close to part-per-million analytical sensitivity, it was used in this case, to look for the presence of elements that potentially would act as neutron modifiers (absorbers or reflectors) within the plutonium-bearing particles. It was only possible to perform a few analyzes with this tool and only with TX-118.

3.0 Results

This section presents the results of our investigation into the reflectance spectra of the SY-102 and TX-118 sample solids.

3.1 Reflectance Spectra of SY-102 and TX-118 Solids

Small portions (~20 to 25 mg) of the tank solids were placed inside ~10 ml (11.3 mm ID) borosilicate glass round bottom tubes and reflectance spectra were collected in a 380 to 980 nm range of visible spectrum using an Ocean Optics USB2000 spectrophotometer and a high intensity tungsten lamp as a light source. A white powder of aluminum hydroxide loaded into a tube of the same geometry was used as a blank sample. Figure 3.1 shows loaded containers in a horizontal position when the material was broadly spread out along side walls to provide better-quality images. For spectral acquisition the tubes were returned to a vertical position with the solids gently compacted and evenly distributed along the central axis.



Figure 3.1. Pictures of SY-102 (left tube) and TX-118 (right tube) samples. Sample colors shown in the image on the left were more realistic but were slightly out of focus. Image on the right offers a better depth of focusing (an aperture priority mode) but the colors appeared darker than they really were. Note presence of very fine and electrostatically active particles adhered to inner side of glass walls around the main mass of the material for the TX-118 sample. No such an effect was observed for the SY-102 sample represented by larger, better defined particles

Figure 3.2 shows the reflectance spectra of these samples.



Figure 3.2. Reflectance spectra of SY-102 and TX-118 samples. Spectra of partially degraded Pu(IV) oxalate and Pu(IV) tetrafluoride are added for illustrative purposes only to show typical shapes and positions of 5f-transitions for pure plutonium compounds

As follows from the spectra presented, both samples showed a broad and monotonously changing levels of reflectance signal exhibiting no characteristic peaks across the spectral range examined. This typically happens when plutonium concentration is too low to contribute to any measurable extent to a low reflectance (high absorbance) signal of interfering components represented by iron and other highly colored transition metal compounds in these mixtures. It appears that without additional partitioning to separate the plutonium-rich fraction from bulk of non-radioactive constituents the plutonium signature could not be established reliably in these samples. This was expected based on the total concentrations of plutonium in the samples.

4.0 SY-102 Characterization

The number of plutonium particles found in SY-102 was low. There were many other particles observed, including particles of heavy element thorium-bismuth and uranium. The first step in the analysis work was to examine samples in the SEM to provide an overview of the particles visible in the specimen.

4.1 Scanning Electron Microscopy (SEM) and Analysis of SY-102

The SY-102 material had a range of particle sizes. The BSE detector was used to search for the high Z (atomic number) particles. Many different high Z particles were found but most of these did not contain plutonium. Figure 4.1 and Figure 4.2 depict various particles found in the SY-102 sample. Thorium was commonly found throughout the sample. Plutonium-bearing particles were difficult to distinguish from the uranium and bismuth phases by BSE imaging in the SEM. Therefore, EDS analysis had to be used to identify Pu in such particles.



Figure 4.1. SEM image and EDS analysis of a thorium particle

All the high Z particles were extremely small, around 2-5 micrometers, μ m, in length. The samples themselves had a large variety of particle sizes. In Figure 4.3, a large central particle is shown together with a lot of other material with a diversity of shapes and sizes. Elemental mapping of this region is shown in Figure 4.4 and this shows the composition of the individual particles varied although much of the area appeared to contain bismuth, iron and silicon. There was a particle of chromium, possibly metallic based on the very strong signal obtained. Distinct aluminum phases and a calcium-phosphorus phase also were present. There was a small particle in the center of the image that may contain plutonium. The low-level signal of plutonium that appears to suggest uniform coverage was probably an artifact. Unless the particle was identified by both BSE imaging and EDS analysis, the presence of plutonium could not be verified.



Figure 4.2. SEM image a (A) plutonium-rich phase and (B) thorium-bismuth particle, and (C) EDS of both particles.



Figure 4.3. Agglomeration of particles in SY-102



Figure 4.4. Elemental maps of particles shown in Figure 4.3

The BSE imaging can be deceptive in describing the morphology of the Hanford tank waste sample. Three images are shown in Figure 4.5. Under BSE imaging, the plutonium particle is visible but high contrast is also seen for some of the larger particles in the area. As the beam energy was lowered, the surface relief became clearer. The plutonium particle was then shown to be intimately wrapped in the other non-plutonium phases within the sample. The surface had the "wooden-like" appearance which has been observed by others.

 Table 4.1. Semi-quantitative analysis of a selection of particles in SY-102 showing major compositions (element wt%)

Point	NaK	MgK	AIK	SiK	PK	SK	BiM	PuM	CaK	BaL	CrK	MnK	FeK
1	3.9	2.9	16.3	13.9	1.2	0.5	12.9	1.1	3.3	0.1	3.0	11.8	29.0
2	4.0	1.7	13.3	10.6	0.5	0.6	16.2	0.8	1.9	0.5	1.6	6.9	30.3
3	4.9	1.1	18.3	12.9	0.5	0.6	16.1	0.8	1.9	0.1	1.5	6.0	34.1
4	5.7	1.2	13.9	9.6	9.6	0.3	10.2	0.1	17.3	0.0	1.6	4.9	32.5
5	4.7	0.2	10.3	9.8	0.1	0.7	19.8	0.0	0.7	0.0	0.2	3.9	36.2
6	7.2	0.4	11.8	16.0	0.2	0.4	18.2	0.0	1.3	0.0	0.8	3.7	50.3

Several particles were analyzed during the characterization and an example set of analyses is shown in The BSE imaging can be deceptive in describing the morphology of the Hanford tank waste sample. Three images are shown in Figure 4.5. Under BSE imaging, the plutonium particle is visible but high contrast is also seen for some of the larger particles in the area. As the beam energy was lowered, the surface relief became clearer. The plutonium particle was then shown to be intimately wrapped in the other non-plutonium phases within the sample. The surface had the "wooden-like" appearance which has been observed by others.

Table 4.1. The EDS results do not include oxygen or carbon, which are not easily quantified in the SEM. All the particles indicate high concentrations of bismuth as well as silicon, aluminum, and manganese. These results are consistent with the known composition of this waste.



Figure 4.5. SEM images of a plutonium particle (shown by arrow) taken under different imaging conditions. (A) high voltage BSE image, (B) Low magnification and low voltage SE image, (C) low magnification image of plutonium particle

Elemental analysis of the region depicted in Figure 4.5 is shown in Figure 4.6. Again, much of this material appeared to be a mixed iron-bismuth oxide in agreement with the results in The BSE imaging can be deceptive in describing the morphology of the Hanford tank waste sample. Three images are shown in Figure 4.5. Under BSE imaging, the plutonium particle is visible but high contrast is also seen for some of the larger particles in the area. As the beam energy was lowered, the surface relief became clearer. The plutonium particle was then shown to be intimately wrapped in the other non-plutonium phases within the sample. The surface had the "wooden-like" appearance which has been observed by others.

Table 4.1. This type of phase has been described by Lumetta et al.⁷ in investigations of other Hanford tank waste samples. Because this sample of SY-102 had been density separated, it was reasonable to expect that most of the particles would possess higher densities, for sodium nitrate to be washed away, and the less dense low-solubility aluminum hydroxide phases to be mainly absent. This data also shows the limitations of SEM-EDS in describing these particles.



Figure 4.6. Elemental maps of the plutonium particle and surrounding area

Several small boehmite (AlOOH) particles were also observed in density separated SY-102 sample. These are very light phases that would not be expected to be present at high concentrations in these samples. Figure 4.7 shows an analysis of the particle using EDS.



Figure 4.7. Small particles of boehmite in the SY-102 waste

4.2 SEM-FIB Lift Out Preparation of SY-102

Only a few plutonium particles were observed on each SEM stub. When particles were identified they were cut out with the Ga-ion beam. The process of removing a particle from the sample stub first involved coating the sample with carbon to protect the particle from damage from the ion beam. Once the particle was isolated with the ion beam, a probe was brought in and attached to the lift out specimen. This is shown in the images in Figure 4.8.



Figure 4.8. Located plutonium particle in SY-102 and the extraction process. Elemental maps identify the location of the particle

Elemental analysis in the SEM-FIB using EDS is also shown in Figure 4.8. Another example of a located particle that was then cut out with the ion beam is shown in Figure 4.9. The plutonium was associated with bismuth and iron as was found in the SEM study. The Pu-bearing shape also seems to be associated with manganese; however, this is not completely clear with EDS using the SEM. The identification of Pm and Ti was questionable and required other techniques to confirm.



Figure 4.9. Another plutonium particle located in the SY-102 wastes with elemental maps

4.3 Scanning Transmission Electron Microscopy (STEM) of SY-102

STEM was conducted on the lift out specimens produced by the SEM-FIB. The plutonium particle was readily identified during imaging under HAADF imaging. Elemental analysis with EDS was used to establish the major phases in the specimen. In Figure 4.10, the elemental maps are shown. The central particle is plutonium oxide. There is an aluminum (hydr)oxide particle in the lower right-hand side of the image as shown by the element maps.



Figure 4.10. HAADF image (A) of plutonium particle extracted from SY-102, convergent beam electron diffraction (CBED) of the plutonium oxide (B), and elemental maps showing the distribution of major elements

Low magnification imaging in the STEM of the plutonium particle from SY-102 strongly suggested that the phase was plutonium oxide (see Figure 4.10). However, other elements were present including aluminum, iron, phosphorus, calcium, silicon, and bismuth. The iron appeared to coat the outer parts of the plutonium but there was some interface between the two phases. Phosphorus and calcium were co-located for the most part and were not directly incorporated into the plutonium phase. Silicon was also heterogeneously distributed. The distribution of bismuth was inconclusive as it appeared to be incorporated into the plutonium material. Slightly higher magnification mapping of this area is shown in Figure 4.11.



Figure 4.11. Higher magnification images of plutonium particle in STEM-HAADF mode and elemental maps

The major phase is plutonium oxide; however, this phase also has several other elements associated with it including aluminum, iron, and bismuth. The iron appeared to coat the plutonium particles, but the bismuth appeared to be entrained in the plutonium oxide. This was observed in other analyses even though, in this case, the analysis does not appear to be definitive. Higher resolution studies were conducted to determine the exact nature of this association. Another finding from the STEM investigation was that the plutonium particle appeared to have voids or holes in it. This is shown clearly in Figure 4.11. It is possible that the imaging was unable to locate the material in the hole, but the EDS analysis clearly indicates that this is a hole in the structure. The presence of voids in the plutonium phase would severely impact the effective density of the phase.

Analysis of the oxygen level in the phase is not easily accomplished with EDS; however, EELS is a much more effective technique for determining the amount of oxygen in the structure. In Figure 4.12, EELS maps of both plutonium and oxygen can be used to look at the ratio of these two elements.



Figure 4.12. Collection of STEM images (A) HAADF image, (B) BF image, Electron energy-loss images of plutonium particle in SY-102 using the (C) oxygen K-edge, and (D) the plutonium O_{4,5} edge



Figure 4.13. Elemental map of plutonium particle at the edge showing a calcium phosphate particle adjacent to the plutonium oxide and an aluminum oxide in the lower right-hand corner of the image

The association of calcium, phosphorus, and oxygen clearly indicates the presence of a calcium phosphate (apatite phase) in the waste specimen. However, this phase is not part of the plutonium phase but merely attached to this particle. An aluminum hydroxide can also be seen in the image with an association of iron at the edges. The location of bismuth was more difficult to define even at this high magnification. Nevertheless, bismuth seemed to be incorporated into the plutonium oxide phase. The occurrence of spots in the higher magnification HAADF image (see Figure 4.14A) were coincident with the bismuth patches observed in the elemental maps. An atomic resolution image showing atomic columns of the plutonium-bearing structure is shown in Figure 4.14B. Using the Fast Fourier Transform (FFT) of the high-resolution image, it is possible to obtain d-spacings. These are listed in Table 4.2. The values match with plutonium oxide but not exactly. An example of plutonium oxide is shown in the experimental section (see Figure 2.7). The measured distance between atomic columns in Figure 4.14C were calculated to be 0.195 nm.

This is not the Pu-Pu distance in PuO_2 but is close to the Pu-O distance. The Pu-O distance is between 0.18 and 0.19 nm in PuO_2 and PuO_{2+x} . Oxygen atomic columns should not be visible with HAADF imaging.⁵ This suggests that other elements are present in the phase leading to scattering. The arrow in Figure 4.14C points to one of the compositional anomalies or patches that were observed through the plutonium oxide material. The patches and their composition are clearer in the elemental maps in Figure 4.15 that show the enrichment of iron, phosphorus, and bismuth in these regions.



Figure 4.14. High-resolution HAADF image of plutonium material in SY-102 (A), FFT of the high-resolution image, and (C) HAADF atomic resolution image of atomic columns in plutonium oxide

Experimental	Literature
(d-spacings)	(PuO ₂)
nm	nm
0.348	
0.342	
0.312	0.3109
0.299	0.2692
0.194	0.1904
0.162	0.1624
0.124	0.1235

Table 4.2. List of electron diffraction d-spacings from SY-102



Figure 4.15. Elemental maps at very high magnification showing the presence of phosphorus and bismuth accumulations within the plutonium matrix

The elemental maps show patches of both bismuth and phosphorus within the plutonium oxide, but it is also evident that iron is associated with these phases. This is suggestive of a co-precipitation mechanism and may explain the reason why bismuth, phosphorus, and iron were nearly always found with plutonium in all the analyses. Further work is required to investigate these features and this type of region will benefit from analysis with atom probe tomography (APT) which offers excellent quantification capabilities.

5.0 TX-118 Characterization

This section discusses the SEM investigation and analysis of TX-118.

5.1 Scanning Electron Microscopy (SEM) and Analysis of TX-118

A limited SEM investigation of TX-118 was conducted in this period. The particle size of the TX-118 material was much more homogeneous than the SY-102 sample. Plutonium particles were readily found in this specimen. The particles had a composition that contained bismuth and phosphorus at much higher levels than in the SY-102 sample. In Figure 5.1, the analysis of three particles is shown. In each case, the composition of the particles was extremely consistent.



Figure 5.1. Three difference particles found in TX-118 with very similar compositions based on EDS analysis

In Figure 5.2, an elongated particle is shown. This particle was contained within a matrix of aluminum-rich materials. The phase again contained plutonium, bismuth, and phosphorus. Several other particles containing plutonium were found and analyzed although not all particle analyses are reported here. In Figure 5.3, an example of two particles of plutonium found in the specimens are shown. The SEM analyses confirm the findings of Reynolds et al. but these only provide a very limited amount of information. Under the SEM, the particles appear as large solid masses. The subsequent STEM analyses revealed a different nature to these particles.



Figure 5.2. SEM image of elongated plutonium particle (thin white lines) and compositional analysis



Figure 5.3. SEM images of plutonium particles in TX-118 (A) a smaller 10 μm particle and (B) a larger 20 μm particle

5.2 Scanning Transmission Electron Microscopy (STEM) and Analysis of TX-118

STEM analysis of the plutonium particles found in TX-118 was conducted to determine whether the composition observed at the SEM level was consistent. The STEM analyses would determine if the particles had a homogeneous composition, whether there were coatings of different materials, and would determine the structure of the particles, so that the density could be inferred. The particle shown in Figure 5.2 was examined as this had distinctive band-like form. Under the SEM, this appeared to be a large crystalline particle; however, under TEM and electron diffraction (see Figure 5.4), the material was amorphous. The selected area electron diffraction (SAED) pattern in Figure 5.4B, shows distinctive ring pattern of an amorphous material. The surrounding material was wispy and had a clay-like appearance.

Elemental mapping of the bands are different magnifications was performed to reveal the overall composition (see Figure 5.5 using STEM-EDS and Figure 5.6 using STEM-EELS).



Figure 5.4. (**A**) TEM image of the extracted elongated plutonium particle (arrow) and (**B**) SAED pattern from the particle showing it to be finely crystalline to partially amorphous.



Figure 5.5. Elemental map of extracted plutonium particle from TX-118 showing that the laminated structure is due to separate regions of plutonium. Bismuth is the major other element present and phosphorus is present at lower levels. Adjacent to the particle iron and manganese were observed.



Figure 5.6. STEM-HAADF image (A) and (B) Electron energy-loss images of the plutonium particle in TX-118 using the plutonium O_{4,5} edge, phosphorus K-edge, iron L_{2,3} edge, oxygen K-edge, manganese L_{2,3} edge, and the carbon K-edge.

In this case, the plutonium particle does contain oxygen, phosphorous, and bismuth. Both iron and manganese were at the edge of the particles.



Figure 5.7 Line profile across the region in Figure 5.6A revealing the composition of the phase.

A line profile across the bands is shown in **Figure 5.7**, this indicates that the phase is mainly plutoniumbismuth oxide with a very low concentration of phosphorous. The transition metals were not in the material.



Figure 5.8. Elemental map of extracted plutonium particle from TX-118 showing that the laminated structure is due to separate regions of plutonium. Bismuth is the major other element present and phosphorus is present at lower levels. Adjacent to the particle iron, chromium, and manganese were observed.



Figure 5.9. Elemental EDS and EELS maps of an extracted plutonium particle from TX-118 at higher magnification. Oxygen map was an EELS map.

EELS is more difficult to collect for many elements, but its major advantage is that the signal is not susceptible to fluorescence effects as occurs in EDS. Elemental analysis from these regions are tabulated in **Table 5.1** where the plutonium oxide phase and the transition metal-rich region are shown. A line profile of the EDS results through this region is shown in **Figure 5.10**. The two highest level elements are plutonium (yellow) and oxygen (red). There is chromium (light blue) enrichment in the middle of the profile, together with manganese (dark red) and a decrease in bismuth (dark-purple). Iron (light purple) is only slightly enriched in the middle section and phosphorus (light yellow) only slight decreased in the middle section. Silicon and aluminum were also visible but are at low levels in the material. The mix of different compositions only occurred on a sub-micron scale. Under the SEM, these regions appeared almost as a single phase. As the magnification was increased, more details emerged regarding the nature of these phases in the TX-118 wastes.

1A-110								
	Pu C	Dxide	Metal	Oxide				
Element	Wt%	At%	Wt%	At%				
Na K	5.261	20.825	1.359	2.273				
Mg K	0.369	1.380	7.822	12.379				
Al K	1.929	6.506	22.612	32.236				
Si K	1.733	5.617	9.638	13.199				
P K	9.898	29.083	11.351	14.096				
Cr K	0.792	1.386	16.475	12.187				
Mn K	0.440	0.729	6.157	4.311				
Fe K	2.706	4.410	9.543	6.573				
Bi M	22.272	9.699	14.199	2.613				
Pu M	54.600	20.365	0.844	0.133				

 Table 5.1 Compositional analysis of a plutonium-rich zone and an iron- manganese-chromium zone in

 TX 118



Figure 5.10 Compositional line profile over region shown in arrow in Figure 5.8A.

Selected plutonium-rich particles that were observed during the SEM investigation were also analyzed with EDS and the results are listed in Table 5.2. There was a slight variation in the Bi/Pu ratio that suggested different phases; however, closer inspection with STEM, showed that this was not the case.

Element	Wt%	Wt%	Wt%	Wt%	Wt%
AIK	8.8	3.6	10.1	6.0	1.5
SiK	1.1	3.7	1.6	2.6	1.2
PK	6.2	5.0	5.1	5.1	6.4
SK	0.0	0.0	0.2	0.2	0.4
BiM	15.0	14.1	16.3	14.0	20.6
UM	7.0	6.3	7.5	6.2	7.9
PuM	45.0	48.8	39.9	51.2	50.1
CaK	0.7	0.8	0.7	0.7	0.7
BaL	2.4	0.7	0.0	0.9	0.7
CrK	3.6	2.5	5.4	1.3	2.5
MnK	1.9	2.0	3.7	1.4	1.5
FeK	8.3	12.4	9.6	10.4	6.4
Bi/Pu	0.33	0.29	0.41	0.27	0.41
P/Pu	0.14	0.10	0.13	0.10	0.13

Table 5.2. Compositional analysis of selected plutonium particles in TX-118

In compositional analysis (excluding carbon and oxygen) indicated a good correlation between the bismuth, phosphorus, and plutonium concentrations. Further analysis in the STEM was used to confirm these findings. At very high magnification as shown in **Figure 5.11**, elemental mapping indicated a well-mixed material.



Figure 5.11 Higher magnification STEM-HAADF image and STEM-EDS analysis of the plutonium particle



Figure 5.12 EDS analysis of Pu particle in TX-118

Even the EDS analysis with TEM, had a composition that was very similar to that found in the SEM results produced in this study as well as the ones by Reynolds et al. **Figure 5.12** shows an EDS scan of the major plutonium phases in TX-118 and the similarity to the SEM results. The copper signal in the TEM is dominated by fluorescence from the support grid. This supports the idea that we are looking at representative material in the STEM.



Figure 5.13 High resolution HAADF images of discrete nanoparticles within a plutonium particleagglomerate from TX-118 (A-C). (D-E) EELS and EDS analysis of plutonium distribution, respectively, within the region marked in (C) and (F-G) EELS and EDS of oxygen, respectively in the same region.

STEM-EELS has far better spatial resolution than STEM-EDS which can be influenced by fluorescence from neighboring areas. For these specific elements, EELS has better counting statistics. However, the result in **Figure 5.13** shows essentially the same compositional analysis result from both EELS and EDS confirming the presence of Pu and O. The results from EDS analysis from the other elements in the region show that we have distinct Bi, Fe, and Cr particles in the region (see **Figure 5.14**). This is an exceptional result as now, for the first time, we have reached a magnification level where distinct plutonium, iron,

chromium, and bismuth phases were observed. These individual particles were on the order of 2 to 5 nm in diameter. Such particles would not be visible with SEM imaging or many other methods such as x-ray photoelectron spectroscopy.



Figure 5.14 Elemental maps from phosphorus, bismuth, chromium, carbon, iron, and aluminum, showing the distribution of these elements within the marked region from boxed region in Figure 5.13C.



Figure 5.15 HAADF Plutonium-bearing region (A) and (B) FFT of area showing crystallinity. (C) Multiple elemental map from **Figure 5.14** showing how the individual particles have aggregated.

High resolution imaging and an FFT of the image is shown in **Figure 5.15** (A and B). Electron diffraction measurements from this and other diffraction patterns (see **Figure 5.16**) are listed in **Table 5.3**. By combining the elemental maps, it was possible to produce an image that shows the separate plutonium, bismuth, iron, and chromium particles. This was possible because this area was extremely thin and devoid of other interferences.

Experimental Measurements (nm)	PuO ₂ (nm) (Lit)	Iron Oxide γ-Fe ₂ O ₃
0.3126 ± 0.006	0.3109	
		0.295
0.2442 ± 0.005	0.2692	0.252
0.1954 ± 0.004	0.1904	
0.1681 ± 0.0034	0.1624	
0.1473 ± 0.003		0.148
	0.1235	

Table 5.3 Electron diffraction d-spacings from TX-118 Plutonium Oxide Nano-particles

The match of the electron diffraction to PuO_2 was not a great match in this instance for TX-118 (see **Table 5.3**). This may not surprising considering the distribution of other phases in this region (see **Figure 5.15**C); however, changes in lattice parameters with PuO_2 association with other materials has been noted, for instance with goethite.⁸ Further analysis will be required to determine this possible change.



Figure 5.16 Electron diffraction and STEM image of plutonium particles possibly undergoing crystalline particle attachment (A) Electron diffraction pattern, (B) radial average histogram, and (C) STEM HAADF image

6.0 Atom Probe Tomography

Atom probe tomography (APT) was used to characterize the compositional variation within certain TX-118 particle specimens. The composition of one particular specimen is found in **Table 6.1**. This reconstruction is similar to two other specimens that were analyzed in that the particles contain oxygen, carbon, nitrogen, multiple transition metals, Pu, Bi, and various other elements. It must be mentioned that the mass-to-charge-state spectrum for these specimens is quite complex (as shown in **Figure 6.1**) A more complete and systematic analysis is necessary to understand the correct identities and remove isobaric interferences among the peaks. APT allows for quantitative analysis of the composition spatial variation within the material as depicted in **Figure 6.2**, which has 2D compositional contour plots. Oxygen is present fairly uniformly throughout, while iron, chromium and manganese are separated from one another. While the composition in Table 6.1suggests that this material contains an oxidized steel (Fe, Cr, Ni, Mn), these elements may have been dissolved and reprecipitated as these elements do not overlap with one another. Also, shown in Figure 6.2 is the clustering of Bi and Pu on the order of up to 5nm in size. As shown in the circled regions, Pu and Bi appear to gather together. Though these regions do still represent relatively low concentrations, the small nature of these clusters likely cause aberrations that results in mixing with matrix atoms during reconstruction.

Further evidence of the segregation of the transition metals from one another and the clustering of Pu and Bi together is highlighted by the proximity histogram analysis shown in **Figure 6.3**. Proximity histograms, or proxigrams, are measures of the concentration at a given distance from the interface of an isoconcentration surface. The isoconcentration surface is generated around regions that are connected by the same concentration of a given element. For example, the inset in **Figure 6.3** a shows regions that have 28 at% Fe. The proxigram then measures the concentration at distances inside (positive) and outside (negative) of these interfaces. Inside of these surfaces will have higher concentrations of the given element, but they also will show if other elements collect with, or away from, the particular element. It is clear that Fe, Mn, and Cr all gather together, confirming what is seen in **Figure 6.2**. These analyses also confirm that Pu and Bi co-locate slightly.

Element	At%	Element	At%	Element	At%
0	34.39	Р	1.02	F	0.28
Fe	23.08	Bi	0.99	N	0.19
Mn	9.62	Mg	0.97	Y	0.16
S	6.20	Ca	0.81	La	0.07
Н	4.40	Th	0.72	Ru	0.06
Cr	4.24	U	0.57	Мо	0.06
С	3.92	Zr	0.47	Cu	0.03
AI	2.04	Si	0.45	Sc	0.03
Na	1.63	Rh	0.37	Тс	0.02
Pu	1.41	Pb	0.36		
Ni	1.10	Со	0.31		

Table 6.1 Composition in atomic percent from the TX-118 specimen as measured by APT (caveat that there are isobaric interferences that may limit compositional accuracy.



Figure 6.1 Mass-to-charge-state ratio spectrum of one TX-118 specimen



Figure 6.2 2D compositional contour maps of the reconstructions showing spatial variation in composition of the TX-118 specimen. Each panel is the summation of 5nm thick and 75nm X 120nm. The percent range below each panel is the concentration range from blue to red.



Figure 6.3 Proximity histograms showing concentrations at a distance from isocentration surfaces of (a) Fe 28 at%, (b) Cr 7 at%, (c) Mn 13 at%, (d) 2.5 at% Bi, (e) Pu 5 at%, and (f) O 37 at%.

7.0 Discussion

The plutonium oxide material in SY-102 was crystalline but contained numerous voids and a significant amount of bismuth and phosphorus. These results may suggest a co-precipitation of the phosphate and bismuth with the plutonium which has resulted in a mixed phase. Because the SEM-FIB was able to cut through the particles, the observations made in this study should not have been impacted by any washing procedures used in the preparation of the samples and we are observing the true nature of the particles when they were initially formed. The overall density of this plutonium phase is less than pure plutonium oxide because of the element precipitates and the voids. The reason for the voids is still unclear. Similar observations were made for TX-118 although voids in the plutonium oxide were not found. There was mixing of several other metal oxides with the plutonium oxide that would also reduce the expected density of this material. The observation of phosphorus in association with plutonium oxide as nano-precipitates was also found in Z9 crib samples by a team led by Reilly (PNNL) using APT (see **Figure 7.1**) and is very similar to the results of APT on TX-118 (see section 6.0).



Figure 7.1 SEM and APT Analysis of Particles from Z9 crib (taken from Reilly et al. 2018)

In TX-118, many of the observed plutonium particles also contained moderate levels of bismuth and phosphorus; however, much of the time the material was amorphous or only partially crystalline. The high-resolution images of detached particles indicate that the primary particles in the observed features is a 2 to 5 nm spherical nano-crystallites. We observed a variety of these particles; bismuth, iron, and chromium, as well as plutonium.

7.1 Crystalline Particle Attachment

These nano-particles may have formed during the initial contact of soluble (acidic wastes) with the alkaline tanks forming colloids. The particles are very similar to the ones observed by Lumetta et al. in the BiPO₄ wastes where nanoparticles of a mixed iron-bismuth phase were found.^{7, 9} When contacted with alkaline conditions, plutonium nitrate would readily form nano-sized PuO₂.¹⁰ It is possible that such particles when formed in close proximity would start to aggregate and given sufficient time, might form single particles.

For many decades, materials scientists and engineers have sought to understand the links between chemical conditions and subsequent crystal morphology.¹¹ Typically, industrial processes such as PuO₂ production at Hanford that used plutonium oxalate formation, use non-equilibrium conditions that favor non-classical nucleation, as shown in **Figure 7.2**. Depending on production conditions, historic microscopy of plutonium oxalate particles shows a variety of oriented growth habits, ranging from "puffballs" of radially precipitated crystals to "desert rose" structures of plates that are formed from polycrystalline precipitation.¹²⁻¹⁴



Figure 7.2 Possible mechanisms for the formation of the observed plutonium particles using the pathways to nucleation and crystal growth concepts developed by de Yoreo and others¹¹ (adapted from schematic diagrams from de Yoreo et al.). Rapid precipitation from oversaturation—typical for industrial processes—may lead to the formation of metastable crystallites that can evolve into the bulk crystal, given sufficient time.

Nanoparticles on the surface and in the outer rim of the plutonium oxide precipitates appear to indicate that the growth of the larger plutonium particles has occurred via a crystallization through particle attachment (CPA) process, and colloidal particle interaction. This process may place an upper limit on the size of the particles and provides a mechanistic pathway for the observed microstructures and compositions.

Crystallization through Particle Attachment (CPA) is a mechanism by which crystals may nucleate and grow.¹¹ However, evidence for CPA can only be truly found through in-situ observations of particle growth because, in many cases, the resulting crystalline particle exhibits no clear evidence if the particle had formed by atom-by-atom processes or be colloidal particle attachment processes. There has been some discussion that evidence for CPA may be found by looking for defects or looking at the outer edges of a particle where the growth process had not completed. CPA can occur with amorphous nanoparticles or crystalline particles. It is possible that the amorphous assembled particle will undergo crystallization. For nanocrystalline particles, the colloidal particles aggregate through a surface attachment mechanism and then undergo re-orientation to form a bulk crystal devoid of defects or evidence of prior surfaces. The crystal grows from nanoparticles with different orientations where larger crystal will grow at the expenses of smaller crystals attaching to the surfaces.¹¹ CPA has been in observed or proposed in: titanium oxides such as anatase and rutile; iron oxides including hematite, magnetite and goethite; calcium phosphate; and in natural uraninite (uranium oxide) crystals. De Yoreo and co-workers¹¹ have argued that in complex energy environments, with lower degrees of supersaturation (i.e. environments where chemical species have low solubility), and where the formation of metastable nanoparticles is favorable, CPA may be both thermodynamically and kinetically advantageous compared to monomer-by-monomer growth.¹¹ Hence, the conditions in the Hanford tanks which are highly alkaline and where the aqueous plutonium solubility is so low, it is more likely that large plutonium-bearing particles would form through a CPA mechanism from the addition of soluble plutonium that would have almost instantly formed colloidal plutonium oxides⁸. ¹⁵. Such a process does explain the variability in composition of the observed particles, possibly also the deviation from the PuO_2 structure although with a close match to crystalline plutonium oxide (PuO_2), and the presence of bismuth, phosphorus, iron, and chromium, seemingly entrained within the larger particles.

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