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## **Investigation of In-Line Monitoring Options at H Canyon/HB Line for Plutonium Oxide Production**

*H Canyon and HB Line have a production goal of 1 MT per year of plutonium oxide feedstock for the MOX facility by FY17 (AFS-2 mission). In order to meet this goal, steps will need to be taken to improve processing efficiency. One concept for achieving this goal is to implement in-line process monitoring at key measurement points within the facilities. In-line monitoring during operations has the potential to increase throughput and efficiency while reducing costs associated with laboratory sample analysis. This project has focused on identifying key measurement points in the AFS-2 process, investigating alternate technologies that could be used for in-line analysis, and conducting a throughput benefit analysis.*

### **Awards and Recognition**

N/A

### **Intellectual Property Review**

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

### **SRNL Legal Signature**

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**Signature**

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**Date**

## Investigation of In-Line Monitoring Options at H Canyon/HB Line for Plutonium Oxide Production

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### Introduction

In 2011, the H Canyon and HB Line facilities were chosen to begin dissolving and purifying excess plutonium oxide for initial feedstock material for the Mixed Oxide (MOX) Fuel Fabrication Facility. The goal for production is to provide 1 metric ton (MT) per year of MOX feedstock by FY17. Meeting this goal will be challenging unless measures are taken to reduce waste and/or increase throughput. In-line process monitoring could provide the needed tools to help meet H Canyon/HB Line production goals.

For process monitoring and accountability, H Canyon and HB Line typically pull samples at various points during processing, which are sent to F/H Laboratory or HB Line Laboratory for analysis. The analyses performed in F/H Laboratory can take several days to complete leading to pauses in production. Setting up in-line monitoring equipment at the key measurement points within the process could lead to significant time savings and increased processing efficiency. Reducing the number of samples pulled for laboratory analysis would also lead to a reduction in cost for facility operation.

### Approach

In the work discussed here, we completed five tasks to investigate the benefits that could result from implementation of in-line analysis. The first task was to map the H Canyon/HB Line processing path for plutonium oxide production. This included developing a flow chart of the process with current sampling locations and analysis techniques used at each point. The second task was to identify key measurement points during the process for quality control and accountability and identify any gaps in the current monitoring scheme. The third task was to identify alternate technologies that could be used in-line for process control and accountability to replace the currently used laboratory techniques. Task four was to conduct initial proof-of-concept testing with the proposed in-line instruments. The final task was to perform a benefit analysis to provide an estimate of the potential gains in processing efficiency resulting from implementation of in-line monitoring.

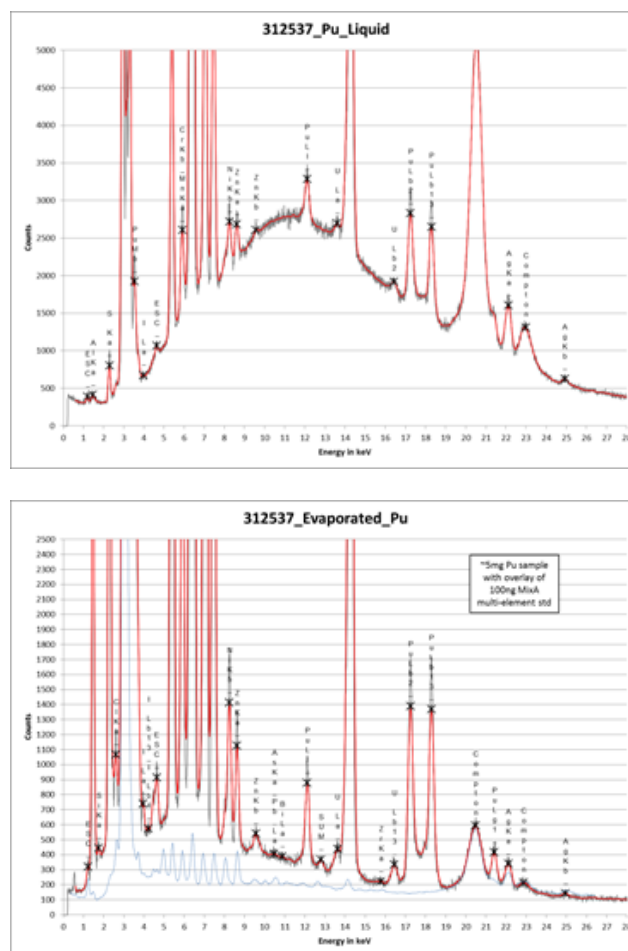
## Summary of Results

The plutonium oxide production processing path in H Canyon and HB Line was mapped out using documentation on the AFS-2 mission and expert input from the facilities. Sampling points and analytical techniques used on collected samples were also identified. The key measurement points for process control and accountability were also identified through H Canyon/HB Line documents and interviews with personnel. Key measurement points/hold points identified in H Canyon include several tanks prior to transfer to HB Line that measure for Pu valence state, process related conditions (acidity, impurities, Pu concentration) and accountability (isotopics & Am-241). Several hold points for total Pu and acidity were identified in HB Line. Hold points were also identified on the back end of the process (i.e., solution returning to H Canyon from HB Line) for verifying the oxalate kill step was completed.

Several technologies amenable to in-line utilization were suggested to replace the currently used laboratory techniques. These include:

- X-ray fluorescence (XRF) to replace inductively coupled plasma mass spectrometry (ICP-MS) for metal impurity analysis (F/H Lab),
- In-line gamma spectroscopy to replace isotope dilution mass spectrometry (IDMS) for Pu isotopics and total Pu (F/H Lab) and alpha spectroscopy and ChemCheck for Pu isotopic ratio analysis and U concentration (F/H Lab)
- UV-vis spectroscopy to replace free acid titration (F/H Lab) and oxalate titration (HB Line Lab) for acidity and Pu DAS for total Pu (HB Line Lab)

After identification of these technologies, XRF and gamma spectroscopy were selected for initial proof-of-concept studies. XRF spectra was taken of a liquid Pu sample and an evaporated sample on a thin polymer film (Figure 1). Liquid sampling shows good sensitivity however, the background is limited by Compton scattering from water. The evaporated sample shows much better sensitivity due to the reduction in background from the water. However with both samples a wide range of

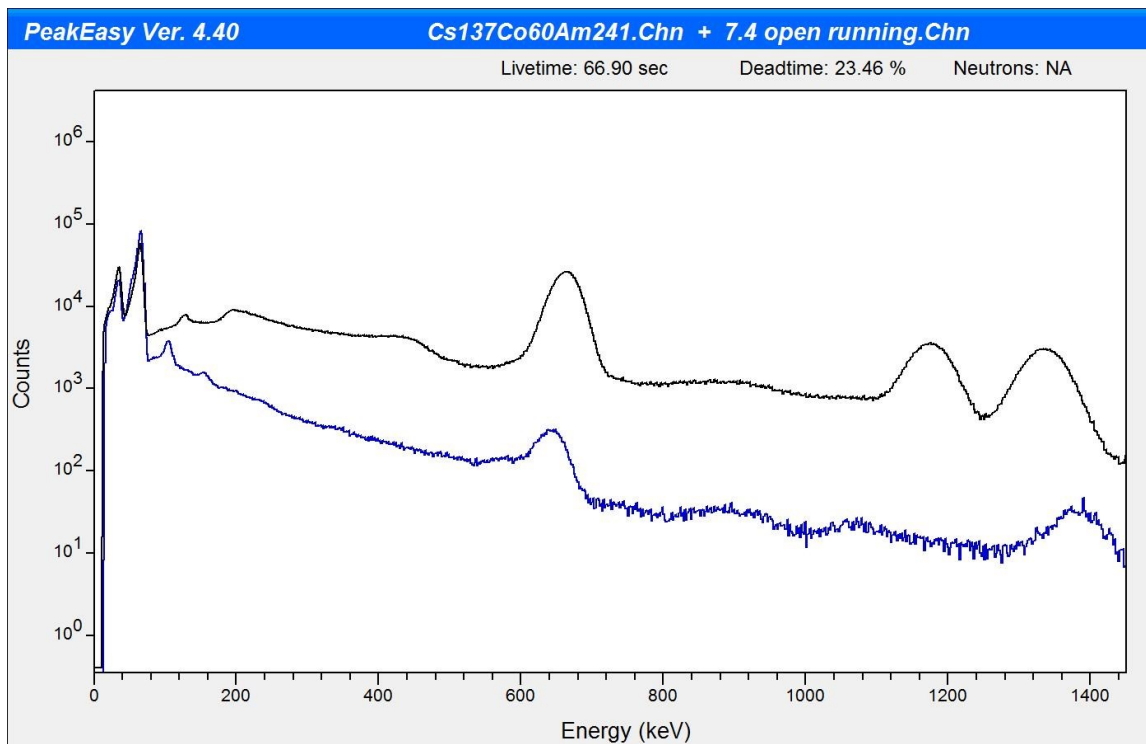


**Figure 1.** (top) XRF Spectra of liquid Pu sample from batch 3 of AFS-2 campaign, (bottom) XRF Spectra of evaporated Pu sample and a 100 ng mix multi-element standard

impurities can be detected and based on data obtained with multi-element standards the limit of detection is estimated to be around 10-50 ppm.

Several measurements were taken as part of this work with both HPGe (High Purity Germanium) and NaI detectors. The HPGe measurements were carried out in F-area labs on both AFS-2 and UNF samples. The samples remained inside a fume hood while the detector measured the samples from outside. It was not possible to shield the detector adequately in the lab these measurements were taken. As a result, the scatter background from Cs-137 present in the area (Cs-137 is somewhat ubiquitous in F-area) obscured any signal from the plutonium in the AFS-2 solution.

Several of the sampler's in the H-canyon sampler aisle were measured while circulating solution both with the sampler boxes closed and open. Again, the scatter background from the significant Cs-137 peak made it difficult to identify features associated with Pu but in several spectra, these features are visible. For example, a spectrum taken at the 7.4 sampler with the door open shows the 104 keV Pu-241 peak. The two spectra below are a reference spectrum taken the previous day with a Co-60, a Cs-137 and an Am-241 source, and the spectrum obtained at the 7.4 sampler while the door was open and the sampler was running. This demonstrates that even an appropriately shielded NaI detector may be able to quantify Pu in solution although an HPGe would make this determination more precise.



**Figure 2.** Reference spectrum (black) and spectrum from 7.4 sampler while open and running (blue).

In FY15 a subcontract was also established with Clemson University to investigate a liquid sampling–atmospheric pressure glow discharge (LS-APGD) source for potential utilization for on-line or at-line measurements in H Canyon. Direct LC detection uses the mobile phase itself as an electrode in the source plasma circuit. This idea was first realized by Couch and Brenner and the Marcus group at Clemson has capitalized on this concept to develop a liquid sampling–atmospheric pressure glow discharge (LS-APGD) source that operates at relatively low currents (<30 mA) and solution flow rates (<50  $\mu\text{L min}^{-1}$ ), that has been interfaced with a LC-MS mass analyzer yielding a relatively simple alternative for ICP mass spectrometry applications. Clemson University conducted the following tasks with guidance and feedback from SRNL: (1) develop a conceptual design for an in-line or on-line analytical instrument that could be used in H Canyon. (2) Address issues that may be related to exhaust of Pu produced during ionization. (3) Perform initial testing of surrogate materials.

The conceptual design for operation of the technology in H Canyon was developed in the context of a small footprint optical emission and mass spectrometer system. The system was designed to accept aliquots of system samplings with use of a discrete injection system, potentially with an autosampler. In the case of the optical system, a multichannel optical spectrometer was utilized for testing. In the case of MS, a ThermoScientific LCQ ion trap analyzer system was employed. Although it has many analytical limitations, it is an excellent test bed for microplasma source design and evaluation.

The basic operation of the LS-APGD microplasma involves the complete vaporization of the electrolyte/sample solution. In principle, all of this vapor would need to be exhausted in order to quantitatively capture radionuclides that are present in each sample. Clearly, these species will only exist during the course of an actual source injection, with the remainder of the time of source operation producing a vapor consisting of 5%  $\text{HNO}_3$ .

An initial test matrix, two different matrices, were employed for the source evaluation. In the first case, a “high-solids” surrogate solution (High Purity Standards (Charleston, SC) MS-744-001 (ADS Mix 1) Solution A) consisting of 22 elements at concentrations of 1000 mg L<sup>-1</sup> each was evaluated. Thus the total solids content of this test solution was 2.2%. This solution was employed to test the ability of the microplasmas to operate stably under high solids conditions, as would be expected in the upstream end of H-canyon. Three test elements (Ag, Cs, and Ce) were added at final concentrations of 100  $\mu\text{g mL}^{-1}$  in the matrix solutions at dilutions of 0, 10, 100, and 1000 X. In principle, maintaining a constant spike content will reveal any potential matrix effects related to the source operation and analytical performance. As a general rule, both plasma sources operated most consistently having greater test matrix dilution factors.

The second test matrix was composed of a 3 g L<sup>-1</sup> uranium nitrate solution in 5%  $\text{HNO}_3$  (High Purity Standards (Charleston, SC)). In this case, the test solution was prepared as a surrogate for the predominately-plutonium containing solutions at the downstream end of the H-canyon process. The challenge here was the role of the high matrix concentration on the precision of the measurements.

The initial evaluation of the use of the LS-APGD microplasma ionization source for the analysis of what could be termed as “heavy matrices” indicated that there is little detrimental effect on the overall operation of the plasma nor its analytical performance for solutions having less than ~0.1% dissolved solids. With regards to the two test samples, the 2% multielement solution was best analyzed following 100 and 1000X dilution, while the 3 g L<sup>-1</sup> (0.3%) uranium solution was readily analyzed following 10 – 100X dilution. In the case of the multielement solution, limits of detection for the three spike elements (Ag, Cs, and Ce) were on the single  $\mu\text{g mL}^{-1}$  level. To be clear, there is much to be learned about de-clustering of background water-related ions and in the use of an ion trap mass spectrometer for quantitative analysis. Based on the initial efforts, though, it seems clear that the physical attributes of the LS-APGD microplasma, its tolerance of complex matrices, and low sample/waste volumes are in line for implementation on-line or in-line for analysis of measurement points in H-canyon.

An H Canyon/HB Line AFS-2 throughput model was used to estimate processing efficiency gains that could be expected by reducing sample analysis turn around times. Assumptions used in the model included: AFS-2 is only process running, no labor restrictions, oxalate kill performed in HB Line, 1 precipitator/1 furnace running, and 1 kg cans. The model was run using four different scenarios, described below:

Traditional Sampling Scenarios:

- 1) 48 hour sample turn around times for all H Canyon samples, 48 hour sample turn around times for JT-72, NT-21, and 8 hour sample turn around times for NT-51
- 2) 48 hour sample turn around times for all H Canyon samples, 4 hour sample turn around times for all HB Line samples

In-line Monitoring Scenarios:

- 3) 12 hours sample turn around times for all H Canyon samples, 0.5 hour sample turn around times for JT-72 and NT-21, 0.1 hour sample turn around time for NT-51 – *In-line UV-vis, XRF, and gamma systems at key measurement points*
- 4) 0 hour sample turn around times for all samples – *completely automated system with in-line monitoring and feedback control*

\*48 hour turn around time is an estimate based on historical turn around times associated with ICP-MS and Pu-IDMS analysis performed in F/H Laboratory.

\*\* Variations in HB Line Laboratory turn around times based on information from different sources.

\*\*\*Sample analysis turn around times for in-line monitoring scenarios are estimates

**Results from the model suggest, using traditional sampling scenario 2 as a base, that one could expect a 40% increase in throughput by moving to in-line monitoring scenario 3 and a 70% increase in throughput by moving to scenario 4.**

## **FY2015 Accomplishments**

*LDRD-2014-00140*

*LDRD External Report Summary*

- Continued investigation of gamma spectroscopy analysis of H Canyon solutions.
- Subcontract established for collaborative work with Clemson University
- Throughput model to determine on-line monitoring benefits in H Canyon/HB Line complete

### **Total Number of Post-Doctoral Researchers**

- SRNL: 1
- Clemson University: 1