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Demonstration of In Situ Down Blending During ZIRCEX Process

March 2023

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ABSTRACT

The Material Recovery Pilot Plant (MRPP) has successfully demonstrated in situ down-blending of Highly Enriched Uranium (HEU) fuel to support INL's commitment to High-Assay Low-Enrichment Uranium (HALEU) production technologies. Depleted uranium pellets, along with an HEU fuel piece were placed in the hydrochlorinator and subsequently declad and oxidized. UOx product was recovered, analyzed, and demonstrated to have reduced enrichment within the targeted range of 20 – 30 % U-235. This first attempt at in situ down-blending will be followed by continued process refinement over the remaining fuel operations at MRPP.

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ACRONYMS

DOE	Department of Energy
HALEU	High-Assay Low-Enrichment Uranium
DU	Depleted Uranium
HEU	Highly Enriched Uranium
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
INTEC	Idaho Nuclear Technology Engineering Center
MRPP	Material Recovery Pilot Plant
SM&A	Safeguards Measurements and Analysis
ZIRCEX	Zirconium Removal prior to Extraction

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Demonstration of In Situ Down Blending During ZIRCEX Process

PURPOSE

The United States Department of Energy (DOE) has a vested interest in making high-assay low-enriched uranium (HALEU) available to support operation of advanced nuclear reactors. HALEU may be sourced from reprocessing used nuclear fuels that contain highly enriched uranium (HEU) which is subsequently down-blended to HALEU enrichment levels.

HEU materials, particularly after separation and purification from fission products and other contaminants, present security challenges for handling and transportation. Down blending to HALEU enrichment during head-end reprocessing can mitigate those security issues as well as simplify front-end HALEU production processes. Moving down-blending to occur concurrently with decladding is intended to ensure purified HEU is never present in a processing facility and provides consistent HALEU without complicated mixing of dry materials downstream.

BRIEF MRPP PROCESS DESCRIPTION

The Material Recovery Pilot Plant (MRPP) resides at the Idaho Nuclear Technology Engineering Center (INTEC) complex in building CPP-653. It is designed to test the Zirconium Removal prior to Extraction (ZIRCEX) decladding process. The ZIRCEX process involves the removal of zirconium (Zircaloy) or aluminum cladding from unirradiated fuel by exposing it to hydrogen chloride gas (HCl) in a hydrochlorinator, which is a fluidized bed reactor. The HCl gas reacts with the zirconium or aluminum to form zirconium tetrachloride ($ZrCl_4$) or aluminum chloride ($AlCl_3$, or its dimer Al_2Cl_6) which are volatile at elevated temperatures. After volatilization, the $ZrCl_4$ or $AlCl_3$ gas is filtered in a packed bed filter before being sent to the pyrohydrolyzer where it is reacted with steam or O_2 to convert it to a ZrO_2 or Al_2O_3 solid. The off-gas, consisting of primarily HCl with approximately 15% H_2O and trace amounts of H_2 is sent through an off-gas scrubber treatment system. The ZrO_2 or Al_2O_3 solids are collected in the ZrO_2 filter.

Once the fuel pieces are declad, the uranium, all of which should remain in the hydrochlorinator during decladding, is reacted with a mixture of NO_2 and O_2 gases to convert it to U_3O_8, with potential for conversion to UO_3. The resultant solids, with size ranging between 8 – 12 μm, is then elutriated from the hydrochlorinator with N_2 flow and captured in the UOx filter. The UOx filter contains four 2-μm sintered metal filters that collect the UOx. The N_2 passes through the filters and on to the scrubber system. After UOx elutriation is complete, a SafeVac centrifugal HEPA vacuum, which is hard piped to the UOx filter drain, is used to collect the UOx powder into a 300 – 1000 mL stainless steel vessel.

The main process and scrubber skids reside inside a PermaCon. The main system blower is used to convey process gases and to provide air turnover in the PermaCon, thus maintaining a negative pressure differential across the PermaCon. Downstream from the scrubber, process gases are mixed with PermaCon exhaust. the mixed gases pass through two 24” x 24” x 11.5” HEPA filters in series and the blower, then to the stack at a rate of up to 2000 cfm. A simplified diagram of the MRPP process can be seen in Figure 1.

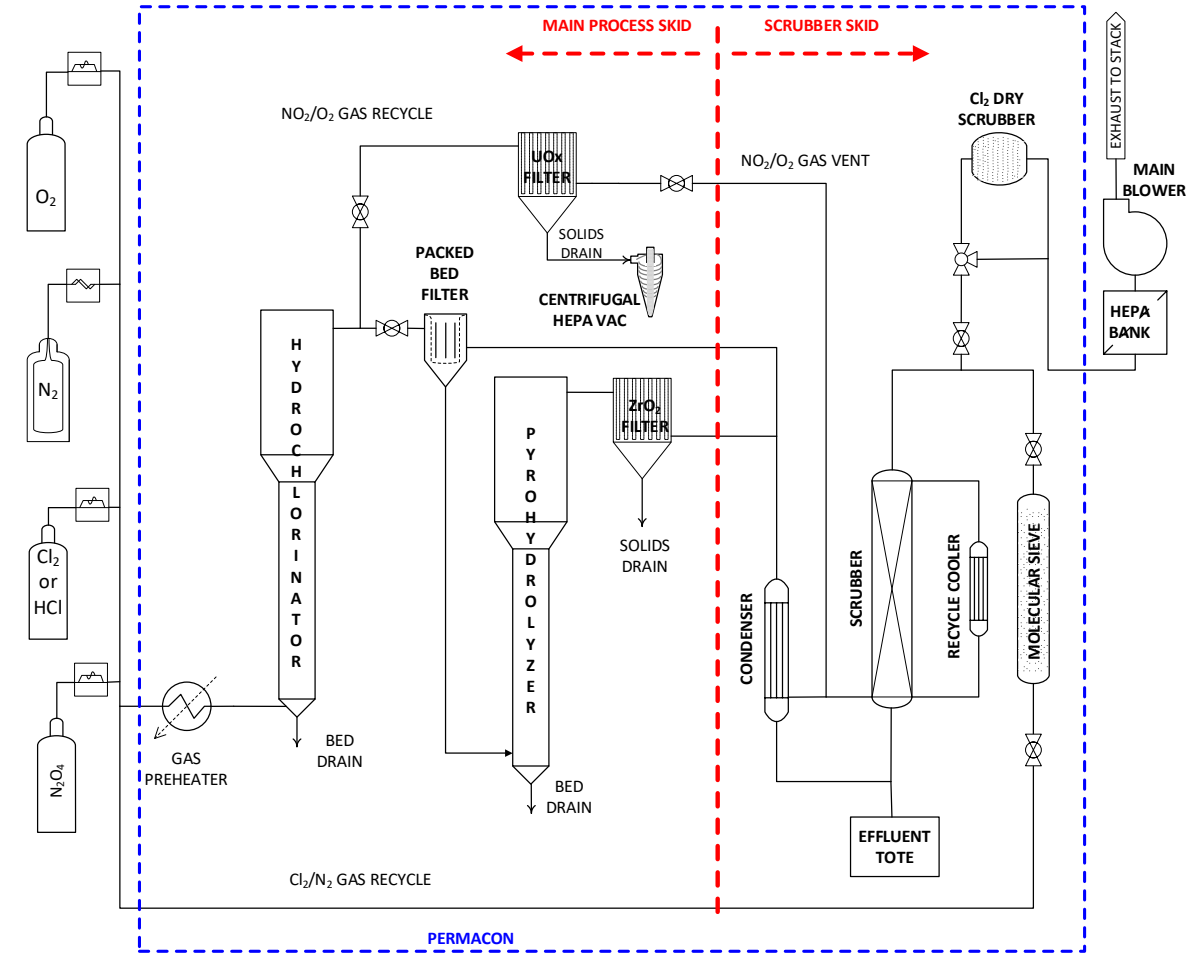

Figure 1. Simplified MRPP process diagram.

DOWN BLENDING DEMONSTRATION

Preparatory Testing

MRPP was intended to process pieces of HEU fuel. In order to down blend the HEU, addition of depleted uranium (DU) is necessary. The DU pellets available for use are UO_2 cylinders, approximately 1 cm in diameter, with mass of approximately 27 g each. Theoretically, DU in the UO_2 form should behave similarly to the uranium present in fuel pieces. However, it's physical and chemical form is disparate from the HEU fuel meat. Preliminary testing was required to ensure the MRPP equipment is capable of converting pellets of DU into a uranium oxide (UOx, either as U_3O_8 or UO_3) product that may be collected in the same manner as the product from fuel processing. To that end, three tests were conducted using DU only. Those tests provided the following information:

1. DU reaction with oxidizing gases is possible under the same conditions as those used for HEU fuel.
2. No additional oxidation time appears necessary for DU pellets compared to HEU fuel.

3. System holdup of UOx materials is higher than initially anticipated. This is due to high total internal surface area of the hydrochlorinator and the UOx filter relative to the amount of UOx produced.
4. UOx product can be collected under the same conditions as those used for HEU fuel.
5. Due to system holdup, in situ down blending is not only desirable for the aforementioned reasons, but also necessary to accomplish the MRPP mission while adhering to required material balance area constraints.

In Situ Down Blending

Batches of DU were prepared to provide sufficient U-238 to down blend each fuel piece to near-HALEU values. Due to the size of the DU pellets, it is not possible to produce a precise down-blend for each batch. A range of between 20 and 30% enrichment was chosen in order to demonstrate down blending without overshooting and producing material that would require further enrichment.

For this initial demonstration, one piece of fuel along with one batch of DU pellets were loaded into the hydrochlorinator simultaneously. The normal MRPP zirconium declad process was then performed, followed by oxidation and UOx product collection. It was noted after product collection that the material was not homogenous. Portions of the material were deep black in color, with the visual appearance of U_3O_8. Other areas were golden orange and appeared to be a mixture of some other uranium compound (most likely UO_3 or UO_2Cl_2) and alumina fines. Samples collected for analysis were required to be small, <100 mg, making it challenging to collect representative samples of the bulk material. The collected UOx product was analyzed using three different instruments.

Non-destructive analysis

Safeguards Measurements and Analysis (SM&A) personnel performed non-destructive analysis on the UOx product canister using quantitative passive gamma spectroscopy. They also provided enrichment measurements, with the following results:

Table 1. Non-destructive analysis results

Isotope	Abundance (wt%)	Uncertainty (%)
U-234	0.3075	14.23
U-235	27.29	7.62
U-238	72.40	2.91

Typically, the SM&A group uses their portable detector for passive gamma spectroscopy only, so it was not configured for optimal enrichment results. This analysis resulted in uncertainties large enough that the results are considered inadequate to stand alone and it must be accompanied by destructive analytical chemistry analysis techniques. However, the reported uncertainties in the passive measurements are considered reasonable and agree with those seen historically in other enrichment measurements.

ICP-OES

One sample was sent to the Radiochemistry Lab for analysis using inductively coupled plasma optical emission spectroscopy (ICP-OES). There, it was analyzed using two different methods. The first was an isotopic method built into the instrument's software. This method uses a standard of known isotopic abundance and compares it to the unknown sample, then applies a mass discrimination factor. The second method is achieved by building a calibration curve from data obtained for HALEU samples of known enrichment. The intensity data from MRPP samples are then compared to the calibration curve to determine concentration. Enrichment was calculated by dividing the concentration of U-235 by the sum of concentrations for U-238 and U-235.

Table 2. ICP-OES results.

	U-235 (wt%)
Isotopic Method	8.4
Calibration Curve	9.99

Although there is some disparity between the two methods, it is well within error. The isotopic method had a relative standard deviation (RSD) of 0.15%, while the calibration curve method had an RSD of 0.9%. However, the calibration curve method is considered more accurate since it applies a specific calibration curve at each analysis to account for changes in the instrument over time.

ICP-MS

A second sample was sent to CFA-625 for analysis using ICP mass-spectroscopy (ICP-MS). Due to unforeseen circumstances, this analysis had to be performed within a limited time frame, so it was executed using a single-point isotopic ratio calibration curve. The isotopic standard has a certified U-235/U-238 ratio of 0.0072543 ± 0.0000040. The result of the sample analysis was a U-235/U-238 ratio of 0.352 ± 0.002 with a 0.5% RSD.

Table 3. ICP-MS results.

	U-235 (wt%)
U-235	26.0
U-238	74.0

DISCUSSION AND CONCLUSIONS

Clearly, there is wide discrepancy among the enrichment results reported from the various measurements. The noted non-homogeneity of the collected product made obtaining a uniform representative sample very difficult. The differences in the results are attributed to samples being collected individually from the stratified collection canister. Regardless, the results of the samples demonstrated good agreement to known enrichments for each respective method. Therefore, all of the analytical results are believed to be accurate for the individual samples

analyzed. Fully representative sampling of non-homogenous product, collected in a glove bag with awkward positioning, will continue to present challenges. For that reason, multiple samples will be collected from each MRPP batch. More vigorous mixing will also be attempted prior to sample collection.

Despite the described challenges, all analysis is in agreement on the important point: MRPP has successfully demonstrated in situ down blending from HEU fuel. This method will continue to be used and refined for the remainder of the fuel research at MRPP.