Characterization of Mixed-Oxide Powder and Pellets from Modified Direct Denitration

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INTRODUCTION

Modified Direct Denitration (MDD) is a process that was developed at Oak Ridge National Laboratory (ORNL) in the 1980s to produce fuel-grade UO_2 from uranyl nitrate solutions and fuel-grade mixed-oxide powder from coprocessed U-Pu nitrate solutions.[1,2] As part of the Advanced Fuel Cycle Initiative (AFCI), MDD was reexamined on a glove-box scale for use in co-conversion of mixed-actinide nitrate solutions (U+TRU) into mixed oxides suitable for use in fuel fabrication or as a storage or disposal form.[3] The current (and proposed future) development work supports advanced fuel reprocessing and fuel fabrication technologies as part of ORNL's Coupled End-to-End (CETE) Demonstration within the Global Nuclear Energy Partnership (GNEP). This work utilizes an existing glove-box MDD unit for the co-conversion of the U/Pu/Np product stream from hot cell separation processes of spent nuclear fuel. Four new glove boxes have been procured to house equipment to be used to characterize the products.

DESCRIPTION OF ACTUAL WORK

In MDD, an inorganic salt is added to a metal nitrate solution, and the double salt that forms is decomposed inside a sloped and rotating heated pipe to continuously produce mixed-oxide powder. Direct decomposition from the double salt to the mixed oxide eliminates the problems associated with blending individual oxides, as well as the difficulties associated with transition through the "mastic" phase encountered in conventional thermal denitration of uranium. The MDD product is a free-flowing powder from which acceptable fuel pellets can be fabricated with minimal work with the powder. Acceptable pellets can be made from the product simply by deagglomerating and sieving, which can be done in a single operation.[1, 4]

In prior work supporting the AFCI,[3] co-conversion tests were performed using the following actinide mixtures as feed solutions: (a) 90% U/10% Pu, (b) 90.4% U/ 9.1% Pu/ 0.5% Np, and (c) 90.4% U/9.0% Pu/0.3% Np/0.3% Am. The powder was free-flowing and did not require milling or grinding. Subsequently, the mixed-oxide products were calcined/reduced under varying conditions and pellets were pressed using an existing uniaxial press located in a glove box. Powder characterization was limited by the unavailability of equipment and the presence of plutonium.

Under the CETE Demonstration, a powder characterization laboratory has been established and will be used to analyze the MDD-produced uranium and U/P/Np mixed oxide. Characterization equipment has been installed in glove boxes, including the following: a surface area analyzer, a helium pycnometer for skeletal density, an AutoTap for tap density, a powder rheometer for quantifying the flow properties of the powder, an X-ray diffractometer for material composition and crystalline structure determination, a laser-light-scattering particle-size analyzer, and a stereomicroscope for imaging of the powders. A related glove-box line and equipment have been procured to press and sinter pellets made from the MDD product. These studies will be used to adjust the operating parameters of the MDD unit to achieve the required density of a sintered MOX pellet.

A "cold" MDD unit was built for runs with depleted uranium (DU). This unit has been used to optimize operating conditions and to provide MDD-produced uranium for initial measurements with the characterization equipment. DU from the operational checkout of the hot cell mixer-settlers has been processed in the glove-box MDD unit. Operationally, the uranium solution from the hot cell solvent extraction behaved identically to the uranium solutions prepared by dissolving uranium oxide.

The first MOX material that will be converted (January 2008) under the CETE Demonstration is the U/Pu/Np nitrate solution obtained from the hot cell separation of Dresden spent nuclear fuel. The feed composition is 87% U and 13% Pu/Np. The second batch of material (May 2008) will have a higher Pu/Np composition. Final values are still being determined but should be between 20 and 50% Pu/Np.

RESULTS

Various runs were made using the cold MDD unit, and the resulting DU oxide underwent characterization and pellet sinterability studies. Samples of the results are shown in Table I.

TABLE I. MDD-Produced DU.

Powder ID	Calcination/ Reduction Conditions	Surface Area (m^2/g)	Green Pellet (% TD)[a]	Sintered Pellet (% TD)[a]
062507	Dry 4% H_2/Ar	3.0	49	95
	Moist 4% H_2/Ar	2.2	51	91
062707	Dry 4% H_2/Ar	1.8	54	92
	Moist 4% H_2/Ar	1.6	56	90

[a]TD = theoretical density.

The first run with U/Pu/Np from the hot cell separation processing will be made in January 2008, and the powder characterization will be performed immediately following the run. Results to be presented will include analysis of the operation, as well as powder density, surface area, particle size, impurity analysis, pellet densities, and integrity.

REFERENCES

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