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Plutonium oxide polishing for MOX fuel fabrication

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Abstract

Los Alamos National Laboratory (LANL) successfully polished 120 kg of plutonium from surplus nuclear weapons for the European Mixed Oxide (MOX) Lead Test Assembly (LTA), managed by Duke, COGEMA, and Stone & Webster (DCS). The purified oxide was fabricated into fuel pellets, which comprised the LTAs. The LTAs have been inserted into the Catawba (SC, USA) nuclear reactor, where they are presently being used to generate electricity. The material used in the MOX LTA represents the first plutonium oxide from LANL to be polished under the quality requirements set forth by the Nuclear Regulatory Commission (NRC). In addition, the MOX project has been hailed as the "largest single nonproliferation project in history" by US Ambassador Linton Brooks (23/9/04). The process flow for PuO_2 purification was based on aqueous recovery that included various unit operations (dissolution, ion exchange, oxalate precipitation, and calcination). Data from a variety of chemical and physical analyses demonstrate product quality and process consistency. Further process optimization experiments will be performed prior to polishing an additional 330 kg of PuO_2 for the Mixed Oxide Fuel Fabrication Facility (MFFF) at Savannah River Site. During LTA production in 2004, approximately 500 L of 7 M nitric acid was used for washing impurities from the plutonium in order to meet product purity specifications. The majority of this acid was sent to the LANL Radioactive Liquid Waste Treatment Facility (TA-50) as effluent. Optimization experiments during 2006 and 2007 will investigate the use of recycled HNO_3 for PuO_2 washing and ion exchange. If successful, aqueous polishing processes will re-use almost all of the nitric acid that would otherwise have been sent to TA-50. In addition, an overall reduction in the volume of nitric acid used during ion exchange will be tested. The use of new Inconel calcination boats will also be verified. Additional process optimization activities will be conducted to validate the use of 100% quaternized Reillex ion exchange resin. Qualification exercises will include a series of process runs, followed by chemical analyses to assess product oxide impurity levels. Once the optimized processes have been qualified, the production phase of the project will begin.

Keywords: Anion exchange; Plutonium purification; Precipitation; Oxalate; Calcination; MOX fuel

1. Introduction

In 2001 LANL was authorized to begin purifying PuO_2 for MOX Lead Test Assemblies for NRC licensing. The objectives of the project were to polish impure weapons-grade plutonium dioxide to provide 120 kg of high-purity PuO_2 for the fabrication of MOX fuel lead test assemblies (LTA) by August 2004. Purified PuO_2 was blended to produce 10 kg lots and analyzed for Pu and U assay, Pu and U isotopic composition, trace element impurities, and moisture content. The physical characteristics of the oxide powders, such as bulk and tap density, surface area, and particle size distribution were also measured. The PuO_2 product was then packaged into a COGEMA convenience container, and an ARIES (Advanced Recovery and Integrated Extraction System) inner can.

2. Process conditions

Impure plutonium oxide feed is obtained from weapons disassembly in the ARIES line at Los Alamos. This may generate high-fired oxide due to the relatively high temperatures of the

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conversion process. The PuO_2 feed is dissolved in a mixture of 15.6 M nitric acid and 0.2 M hydrofluoric acid. During the demonstration phase of the project, glass dissolution vessels were replaced with Teflon® vessels for greater dissolution efficiencies. The Teflon® dissolution vessel is refluxed at 110 °C for 4 h with mechanical stirring. Typical dissolution efficiencies are between 70 and 90%. Undissolved PuO_2 heels from the first dissolution are recycled through the dissolution process using 15.6 M HNO_3 and 0.3 M HF. Typical dissolution efficiencies for the second pass are 30–60%.

In preparation for ion exchange, the solution is filtered, treated with $Al(NO_3)_3$ to complex the fluoride, and HNO_3 molarity adjusted to 7.0. Plutonium(VI) in solution is adjusted to Pu(IV) using H_2O_2 [1]. The solution is loaded onto 32 L columns containing 100% quaternized Reillex HPQ™ resin. Impurities are removed using 500 L of 7 M HNO_3. The final phase of the anion exchange purification involves elution of the plutonium using 0.35 M HNO_3. Approximately, one column volume of 0.35 M nitric acid is added to the column to convert the plutonium nitrate complex to a species that is easily removed from the Reillex HPQ™ according to the equilibrium reaction [2] Pu^{4+} (aq) + $6NO_3^-$ (aq) ⇔ $Pu(NO_3)_6^{2-}$ (org). By allowing the solution to sit overnight, it is possible to approach an equilibrium state that minimizes acid usage and maximizes the plutonium concentration. The plutonium is eluted using approximately 30 L of 0.35 M HNO_3, resulting in a purified Pu solution with a concentration of about 50–60 g/L.

After adjusting the HNO_3 concentration to 2.5 M, and reconverting any Pu(VI) to Pu(IV) with H_2O_2, a 0.7 M oxalic acid solution is slowly added to the precipitation vessel to precipitate plutonium oxalate. Formation of the Pu(IV) oxalate complex is indicated by a brownish-orange color. The mixture is stirred at 65 °C, allowed to digest and cool prior to filtration.

Plutonium oxalate is calcined for 4 h in a muffle furnace at 650 °C to convert the oxalate to PuO_2. The powder is cross-blended in a Turbula® blender for 20 min to produce 10 kg lots. Product characterization, including Pu and U assay, Pu and U isotopic composition, trace element impurity analyses, and powder properties (moisture content, bulk and tap density, surface area, and particle size distribution) is completed prior to packaging in the COGEMA convenience container, which is placed inside an ARIES inner can.

3. Results

Los Alamos produced oxide met the proposed chemical and physical specifications [3] outlined in ASTM INTERNATIONAL Industrial Standard C757-90 “Specification for Nuclear-Grade Plutonium Dioxide Powder, Sinterable” [4]. The product also had moisture levels, which meet the DOE 3013 Standard [5] which provides guidance for the stabilization, packaging and safe storage or plutonium-bearing metals and oxides. Los Alamos produced oxide contained an average of 87.8% plutonium by weight. Certain elements were more difficult to remove in order to meet purity requirements. Silicon and boron were problematic, and necessitated the use of Teflon® dissolution vessels to allow higher HF concentration during high-fired oxide dissolution. Gallium was extremely difficult to remove to program specifications, and necessitated increased wash volumes, which required the installation of new process lines. These changes were implemented after the fourth process run. Fig. 1 shows Ga levels before and after these changes were implemented. Fig. 2 shows the measured levels of Al, B, Si, C and halogens in the measured MOX samples compared to the required levels. Figs. 3–5 show particle size, moisture content and surface area of the final product.

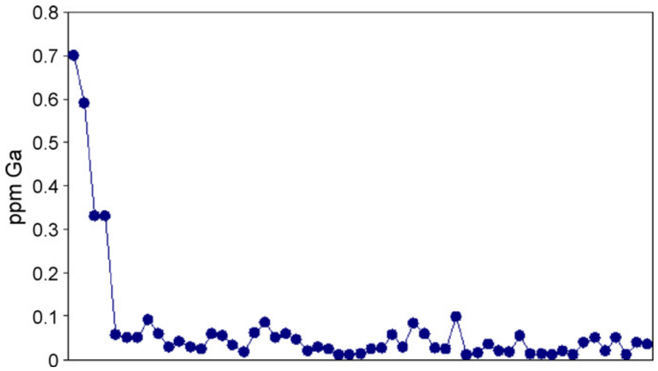

Fig. 1. Gallium concentration for 45 process runs.

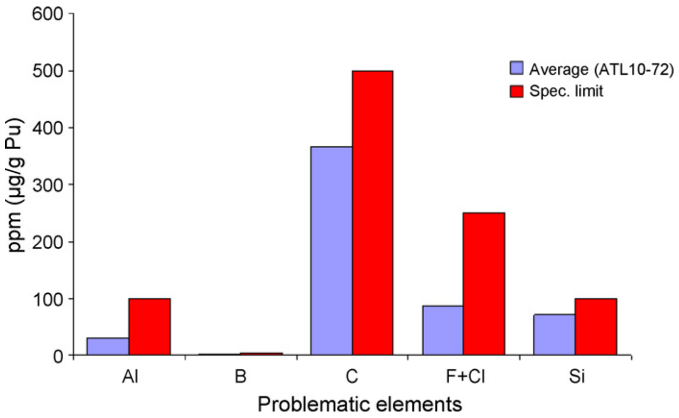

Fig. 2. Concentration of problematic elements compared with specification limit.

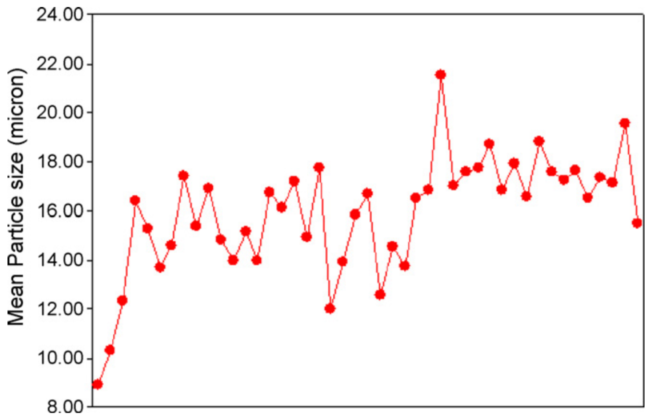

Fig. 3. Mean particle size for 45 process runs.

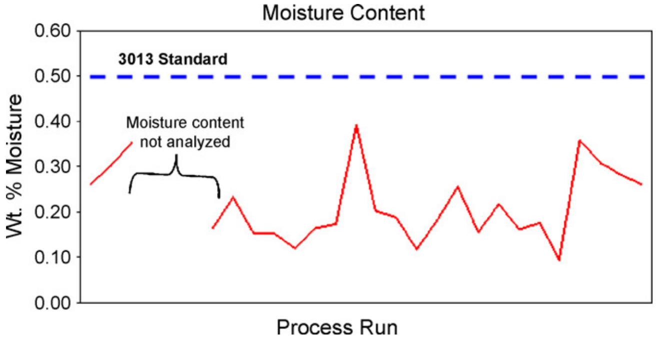

Fig. 4. Moisture contents for approximately 45 process runs.

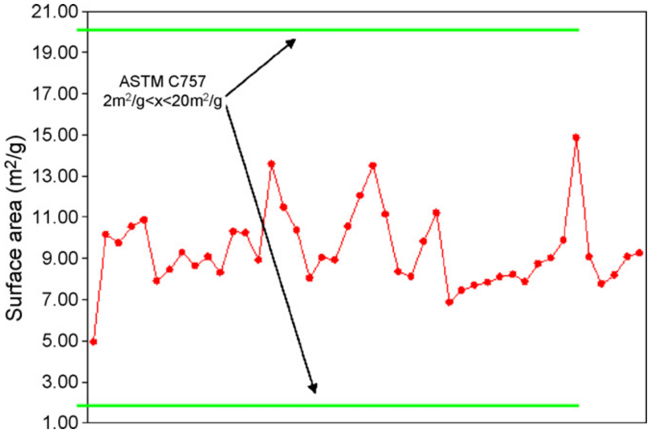

Fig. 5. Specific surface area for 45 process runs.

4. Process improvements

Process optimization activities are being conducted to (1) reduce the volume of HNO_3 used for washing during ion exchange (IX), (2) validate the use of recycled HNO_3 for washing, (3) validate the use of 100% quaternized Reillex HPQ^{TM} Polymer (4) improve the dissolution efficiency of high-fired PuO_2 and undissolved heel material and (5) validate the use of Inconel 601^{TM} calcination boats.

Experiments are planned using varying volumes of nitric acid IX wash. The objective is to examine the effect of reducing the total volume of IX wash on product PuO_2 purity from the present volume of 500 L. Wash volumes will be varied from 450 to 350 L. Los Alamos is also evaluating the use of recycled nitric acid for the IX wash. At a production capacity of 90 kg/year of purified PuO_2, the purification process alone generates 30,855 L of Transuranic Waste (TRU) liquid that must be dispositioned by evaporation and sent to the treatment facility at TA-50. Instead of treating the distillates as waste, we will recycle the distilled HNO_3 back into the aqueous polishing process. Currently, testing of the recycled acid is conducted to ensure that it does not introduce contaminants back into the ion exchange process, thereby causing the product oxide to exceed the purity specifications.

Los Alamos is investigating the impact of changing from 70% quaternized Reillex HPQ^{TM} Polymer to 100% quaternized Reillex HPQ^{TM} Polymer (Reilley Industries, Inc. no longer makes the 70% quaternized Reillex HPQ). It is expected that the 100% Reillex HPQ^{TM} will be more efficient as there are more quaternized sites for absorption. For the dissolution efficiency studies, we examined milling the material to smaller particle sizes to enhance dissolution rates by providing greater particle surface area, as well as varying HF and HNO_3 concentrations during dissolution. During 2004, we found that the physical deterioration of fused silica calcination boats was contaminating the oxide product with silicon. We conducted experiments using tantalum, Inconel 601^{TM}, and platinum calcination boats to evaluate which boat material would provide the cleanest calcination at the lowest cost. Results have shown that product purity can be maintained using calcination boats constructed of Inconel 601^{TM}.

5. Conclusions

LANL successfully polished plutonium oxide for the fabrication of MOX Lead Test Assemblies, which have been inserted into a reactor at the Catawba Nuclear Power Plant (SC, USA). The conversion of plutonium from nuclear weapons into MOX reactor fuel has been demonstrated [6]. Los Alamos is currently in the optimization and process improvements project phase. Current optimization process runs are being conducted to confirm the use recycled nitric acid and smaller volumes of nitric acid in the anion exchange process. If successful, these steps will significantly decrease the amount of liquid waste generated during purification. Validation of the use of 100% quaternized Reillex HPQ^{TM} for ion exchange, and Inconel 601^{TM} calcination boats for calcination is ongoing. Dissolution efficiency experiments on high-fired oxide and heel material are also being conducted. The completion of optimization and qualification activities, along with planned equipment installations, will allow the project to move on to production of 330 kg of plutonium oxide for the MOX Fuel Fabrication Facility at Savannah River Site.

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