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PLUTONIUM OXIDE DISSOLUTION (U)

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INTER-OFFICE MEMORANDUM

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SUMMARY

Several processing options for dissolving plutonium oxide (PuO_2) from high-fired materials have been studied. The scoping studies performed on these options were focused on PuO_2 typically generated by burning plutonium metal and PuO_2 produced during incineration of alpha contaminated waste.

At least two processing options remain applicable for dissolving high-fired PuO_2 in canyon dissolvers. The options involve solid solution formation of PuO_2 with uranium oxide (UO_2) and alloying incinerator ash with aluminum.

An oxidative dissolution process involving nitric acid solutions containing a strong oxidizing agent, such as cerium (IV), was neither proven nor rejected. This uncertainty was due to difficulty in regenerating cerium (IV) ions during dissolution. However, recent work on silver-catalyzed dissolution of PuO_2 with persulfate [1] has demonstrated that persulfate ions regenerate silver (II). Use of persulfate to regenerate cerium (IV) or bismuth (V) ions during dissolution of PuO_2 materials may warrant further study.

INTRODUCTION

Historically the dissolution of high-fired PuO_2 has been difficult to accomplish. With an abundance of this refractory PuO_2 available at DOE sites, the need for large-scale, efficient processing methods was identified as part of the effort to de-inventory sites and reduce residue and waste accumulations.

Selection of canyon dissolvers for processing these materials was a logical choice provided certain processing and waste-handling constraints were satisfied. These constraints minimized use of certain chemicals and eliminated materials which would be incompatible with waste forms. The criticality safety constraints directed these scoping

studies towards production of stable pellets which would dissolve uniformly, vigorously, and rapid enough to eliminate unwanted accumulations of either dissolved or undissolved plutonium.

Although processing options involving alloys, solid solutions, and strong oxidants are promising, further demonstration of these technologies would be required before acceptance. Demonstration of production and dissolution of stable pellet forms using the actual high-fired materials could become necessary.

DISCUSSION

The selection of processing options for laboratory evaluation was based on previous recovery operations of plutonium from incinerator ash in canyon dissolvers, [2] lab-scale dissolution of refractory PuO_2 with silver (II),[3] an apparent improvement in the dissolution rates for refractory PuO_2 due to solid solution formation with UO_2, [4] and the successful canyon dissolution of scrub alloy materials.[5] Each of these processing approaches had included some modifications to satisfy criticality and waste-handling constraints.

Another processing approach considered but not directly pursued in the laboratory was reductive dissolution of PuO_2 in nitric acid solutions containing strong reducing agents. Previous work reported in the literature[6] suggested that reductive dissolution rates were slow and inferior to oxidative dissolutions. However, the dissolution rate for the PuO_2 -UO_2 solid solution prepared for laboratory testing appeared to have improved significantly.

Solid Solution Formation of Uranium and Plutonium Oxides

The solid solution of PuO_2 with UO_2 used in the laboratory was prepared by microwave heating an equimolar mixture of the two oxides. An X-Ray Diffraction analysis of the fused material verified that a one-to-one solid solution of PuO_2 and UO_2 had formed.

Following the microwave preparation, a portion of the fused material was dissolved in boiling nitric acid containing fluoride. The fused material appeared to have dissolved uniformly and no undissolved particles were remaining after dissolution.

With the apparent successful dissolution of the PuO_2-UO_2 solid solution, the technology needed to prepare stable forms of the solid solution suitable for canyon dissolution still requires development. Use of microwave heating is a possible approach for preparation of stable solid solution pellets.

Preparation and Dissolution of Incinerator Ash Alloy

In the 1960's incinerator ash was mixed with aluminum and an aluminum fluoride-lithium fluoride fluxing agent and heated to form a plutonium-aluminum alloy. The resulting aluminum alloy and spent flux were subsequently dissolved in nitric acid solutions to recover the plutonium.

For laboratory testing, a flyash stand-in for incinerator ash was mixed with aluminum and the fluxing agent and heated to form the alloy. This alloy material dissolved in nitric acid solutions, but the spent flux did not without the presence of mercury. However, dissolution of spent flux may not be necessary if this material can be recycled and eventually stored as transuranic waste. Further development of the alloying process with

incinerator ash and dissolution of the alloy products is needed before processing of incinerator ash inventories can begin.

Oxidative Dissolution of Plutonium Oxide

The oxidative dissolution process accelerates the dissolving of high-fired PuO_2 because of the oxidation of tetravalent plutonium to hexavalent plutonium by the oxidizing agent. Unfortunately dissolution rates will decrease rapidly unless the oxidizing agent is continuously regenerated. Incomplete dissolution of PuO_2 did occur during laboratory experiments because attempts to regenerate bismuth (V) or cerium (IV) were unsuccessful.

The use of persulfate ions to regenerate oxidants was not tried in these laboratory experiments. This approach should work with either bismuth or cerium based on the continuous regeneration of silver (II) with persulfate ions during PuO_2 dissolution studies conducted at other laboratories.

RECOMMENDATIONS

Because high-fired PuO_2 may become a suitable waste form for storage, further development of the dissolution technology for this refractory material appears to be unwarranted at this time. However, by alloying incinerator ash with aluminum, this processing option could provide a way to reduce the volume of material eventually being stored. This volume reduction assumes the incinerator ash alloys and spent flux would be dissolved, solutions sent to waste, and the plutonium converted to PuO_2 . Further development of the production and dissolution of the incinerator ash alloys is recommended.

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