Oxidation of Pu-Bearing Solids: A Process for Pu Recovery from Rocky Flats Incinerator Ash

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Summary

High-fired PuO₂, RFP ash heels, and synthetic RFP incinerator ash were easily soluble after oxidation of Pu(IV) to Pu(VI) by heating with Na₂O₂ or K₂O to 450° for two hours. This offers a route to the recovery of Pu from these and similar PuO₂-bearing solids that can be carried out in present equipment. Evidence for new compounds K₂PuO₄, K₄PuO₆, and K₆PuO₆ is presented. A process for recovery of Pu from RFP incinerator ash is presented.

Introduction

Several DOE sites have Pu-bearing powders or residues that, under current regulations, must have the Pu recovered and/or immobilized to allow disposal of the remaining material as waste. Examples are glovebox sweepings at SRS and incinerator ash and ash heels at RFP. In general, these solids contain Pu at substantial levels (>5 wt.%) too high to meet the limits for WIPP storage. Pu is usually present in these solids as "high-fired" PuO₂. "High-fired" PuO₂ dissolves slowly and with difficulty in HNO₃-HF solutions. One successful aqueous process for dissolving Pu from such solids depends on oxidation of Pu(IV) in the difficultly-soluble PuO₂ to the Pu(VI) by oxidation with Ag(II). As this process operates by electrolytically re-oxidizing Ag(I) to Ag(II), the equipment for its operation is rather complex. A simpler method is the object of this study.

Keller and co-workers²,³ report preparing ternary oxides of Np, Pu, and Am with Li and Na by reacting actinide dioxides with Li₂O and Na₂O₂ in a oxygen atmosphere at 400-900°. The products were Ac(V) and Ac(VI) compounds such as Li₄PuO₆ and Na₄PuO₆. Yamashita, et.al., report preparing Li₄PuO₆ and Li₄PuO₄ by reacting LiOH with PuO₂ at 900° in an oxygen atmosphere; the resulting products dissolved easily in 1M HNO₃. This work explores these and similar reactions on PuO₂, RFP ash heels and synthetic RFP incinerator ash.
Experimental Methods

Reactions were performed on a gram scale in a muffle furnace enclosed in a glovebox. Li₂CO₃, LiOH, and Na₂O₂ were reagent grade; KO₂ (Alfa Chemicals, Inc.) was technical grade, >95% pure. Two types of PuO₂ were used, a material fired at 900° and material prepared fired at 450°. A synthetic incinerator ash simulating RFP ash was tested in some experiments; this material contained 21 different components with SiO₂ (42%), carbon (19%), Fe₂O₃ (5.6%) and MgCO₃ (4.5%) as major materials in the mixture. High-fired PuO₂ was added to this mixture for testing. A sample of actual RFP ash heels was also tested.

Weighed amounts of the materials tested mixed with the oxidizing agent were heated in a muffle furnace for 2 to 4 hours at temperatures from 275 to 900°. The products were normally x-rayed to determine if the PuO₂ had reacted. This amounts to a "yes-no" test for a reaction. If there was no reaction, the PuO₂ lines will be strong, and the x-ray will show little else. When there is a complete reaction, the PuO₂ lines will not be seen. New lines usually appear which may or may not be found in the x-ray catalog.

Dissolution of the reaction products under mild conditions (HNO₃, RT, 1-2 hrs) provided a semi-quantitative measure of the success of the oxidation. It was assumed that PuO₂ would only dissolve under strenuous conditions (6M HNO₃, 80-100°, 4-8 hours) and therefore any Pu dissolved was Pu(VI). This assumption appears to be sound; spectra of the solutions identified only Pu(VI).

Results

Three different treatments were investigated for high-fired PuO₂, low-fired PuO₂, RFP "ash heels" and a synthetic incinerator ash mixed with high-fired PuO₂. An initial experiment reacted high-fired PuO₂ with a 25% mole excess of Na₂O₂, calculated by assuming the reaction was

\[
\text{PuO}_2 + 2\text{Na}_2\text{O}_2 \rightarrow \text{Na}_4\text{PuO}_5 + 1/2 \text{O}_2
\]

The mixture was heated at 450° for 5 hours. The x-ray powder pattern of the black product was similar to that of Ca₂PuO₅; no PuO₂ lines were present. The product dissolved in 8M HNO₃ in 1/2 hour and 88% of the theoretical Pu present was recovered.

Rather than react the synthetic ash heels directly—which would involve oxidizing both the PuO₂ and 18 wt.% carbon content of the synthetic ash with Na₂O₂—the synthetic incinerator ash was heated overnight at 700° to burn out the carbon (weight loss, 17%) then reacted with Na₂O₂. Based on the amount of PuO₂ present, Na₂O₂ was 300% in excess. PuO₂ was detected by x-ray in the fired sample. This experiment was repeated with 500% excess Na₂O₂; no PuO₂ lines were found in the x-ray pattern of the product. The large excess
of Na₂O₂ required was due to competing reactions with other components of the synthetic ash, particularly SiO₂.

A sample of RFP ash heels was also reacted at 450° for 7 hours with Na₂O₂ in a weight ratio of 1g ash heels to 1.16g Na₂O₂. The product was a brown cake that showed a few PuO₃ lines in its x-ray. Recovery of Pu by dissolving was 8.9 wt.% of the sample. From earlier work, this sample of ash heels is about 10 wt.% Pu.

Although Yamashita, et. al. were able to prepare Pu(VI) compounds by reacting LiOH or Li₂CO₃ in 100% oxygen atmosphere, attempts to reproduce this result on synthetic ash heels or PuO₂ (heating at 900° for 4 hours) failed. The x-ray patterns for both showed strong PuO₂ lines and dissolving in 8M HNO₃ recovered only 5% of the Pu present. The failure of this approach is attributed to firing in air instead of 100% oxygen.

Potassium superoxide, KO₂, has more oxygen on a weight basis than Na₂O₂, 45 wt.% vs 41 wt.%, but decomposes above 300° to a mixture of K₂O₂ and KO₂. Tests with KO₂ as an oxidizing agent were run on low-fired PuO₂ over the temperature range 275° to 450°. X-ray powder patterns of the products identified three patterns; PuO₂, a pattern isostructural with potassium uranium oxide (K₂UO₄), and a pattern isostructural with plutonium oxide sulfide, Pu₂O₂S. The K₂UO₄ pattern is assumed to be that of K₂PuO₄, the identity of the compound represented by the Pu₂O₂S pattern has not been established. Qualitative results of the reaction between PuO₂ and KO₂ are shown in Table 1.

Table 1
X-Ray Patterns of the PuO₂-KO₂ Reaction

<table>
<thead>
<tr>
<th>2KO₂/PuO₂ **</th>
<th>Time hr</th>
<th>Temp., °C</th>
<th>K₂UO₄</th>
<th>&quot;Pu₂O₂S&quot;</th>
<th>PuO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>mole ratio*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>275</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>350</td>
<td>x</td>
<td></td>
<td>x</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>450</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>275</td>
<td>xx</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>275</td>
<td>x</td>
<td>xx</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>350</td>
<td>xx</td>
<td></td>
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<tr>
<td>4</td>
<td>6</td>
<td>450</td>
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<tr>
<td>6</td>
<td>3</td>
<td>275</td>
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<td></td>
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<td>6</td>
<td>4</td>
<td>350</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>450</td>
<td>x</td>
<td></td>
<td></td>
</tr>
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</table>

* Calculated for KO₂/PuO₂ = 1
** PuO₂ fired at 450°

The lines of the x-ray patterns of K₂PuO₄ and "Pu₂O₂S" are listed in Table 2. Figures 1 and 2 show the powder patterns of K₂PuO₄ and "Pu₂O₂S".
Table 2

<table>
<thead>
<tr>
<th>&quot;Pu₂O₂S&quot;</th>
<th>K₂PuO₄</th>
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<tbody>
<tr>
<td>d., Å</td>
<td>I(rel.)</td>
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<tr>
<td>6.75</td>
<td>20</td>
</tr>
<tr>
<td>6.08</td>
<td>7</td>
</tr>
<tr>
<td>4.28</td>
<td>5</td>
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<tr>
<td>3.49</td>
<td>1</td>
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<td>3.38</td>
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<td>3.03</td>
<td>10</td>
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<td>1.51</td>
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<td>1.42</td>
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</table>

The products of the 4/1 and the 6/1 reactions dissolved completely in 1M HNO₃ at room temperature. There was a small residue of PuO₂ when the 3/1 product dissolved; the 2/1 product dissolved to leave PuO₂, as expected from the x-ray data.

The reaction between KO₂ and high-fired PuO₂ was investigated at a 4/1 2KO₂/PuO₂ ratio at 350° and 400°. No PuO₂ was detected in the x-ray patterns of the products; 73% of the Pu in the PuO₂ product dissolved in 1M HNO₃ to yield a Pu(VI) solution. About 5% of the sample did not dissolve, possibly because of insufficient acid.

RFP ash heels and KO₂ were reacted for 4 hours at 275° in a weight ratio of 0.5g KO₂ per g ash heels. The product cake showed a strong PuO₂ pattern on x-ray and two other patterns identified as silicates; dissolving in 1M HNO₃ recovered only 1-2% of the Pu but did dissolve 35% of the sample. Evidently a more KO₂ is necessary to accommodate the reaction of SiO₂ with KO₂. The low yield of Pu from the dissolving suggests that the PuO₂ in RFP ash heels is coated with SiO₂. (Ash heels are the residue from repeated leaching of incinerator ash with hot 8M HNO₃-0.2M HF.)

PuO₂ and KO₂ were reacted with each in stoichiometric excess to determine the K/Pu (mole) ratio of products of the PuO₂-KO₂ reaction. The product of the reaction with excess PuO₂ at 275° was leached with 0.25M HNO₃ and the excess PuO₂ filtered, dried and weighed. From the initial reactant weights and the weight of the excess PuO₂, the K/Pu ratio of the product was found to be 2.0.
suggesting that the product was $K_2PuO_4$. A second experiment reacted $KO_2$ with excess $PuO_2$ at $450^\circ$; the $K/Pu$ ratio was found to be 2.7. A mixture of $K_2PuO_4$ and $K_4PuO_5$ is a possible explanation.

Excess $KO_2$ reacted with $PuO_2$ at $400^\circ$ was leached with water, and the potassium in the leach water determined by acid-base titration. ($KO_2$, $K_2O_2$, and $K_2O$ all decompose to $KOH$ in water). From the initial weights and the excess potassium determination the $K/Pu$ ratio was calculated to be 5.9. This suggests that the red-brown product of the reaction was $K_6PuO_6$.

Application to Processing Rocky Flats Incinerator Ash

Rocky Flats Plant (RFP) incinerator ash has the nominal composition 18 wt.% graphite, 40 wt.% $SiO_2$, 5 wt.% $Fe_2O_3$, 3 wt.% $Al_2O_3$, 5 wt.% $PuO_2$ and minor amounts of about 20 other oxides. Several of these oxides react with $Na_2O_2$ and thus increase the amount of $Na_2O_2$ required to oxidize $PuO_2$. Three of the major components were reacted with $Na_2O_2$ to determine the amount of $Na_2O_2$ they would require.

The reaction with powdered graphite was tested by heating a $Na_2O_2$-graphite mixture to $450^\circ$ for 2 hours; $Na_2O_2$ was 30% excess for the reaction

$$C + 2Na_2O_2 \rightarrow CO_2 + 2 Na_2O \rightarrow Na_2CO_3 + Na_2O$$

The product dissolved in acid with the evolution of $CO_2$ and left no residue.

The reaction between $SiO_2$ and $Na_2O_2$ is assumed to be

$$Na_2O_2 + SiO_2 \rightarrow Na_2SiO_3 + 1/2 O_2$$

Two experimental tests found that 66% of the $SiO_2$ reacted when the ratio of reactants was 1/1, and 89% of the $SiO_2$ reacted when the ratio was $1.36 Na_2O_2/SiO_2$. Both experiments calculate that 150% of the stoichiometric amount of $Na_2O_2$ is necessary to consume all the $SiO_2$.

A test of the reaction between $Na_2O_2$ and $Fe_2O_3$ found a barely detectable reaction at $450^\circ$ for 2 hours. An estimated 95% of the $Fe_2O_3$ did not react.

A processing scheme for recovery of Pu from RFP incinerator ash involves the following steps:

1. Seiving the ash to -50 mesh.

2. Roasting the ash at 700° for several hours to oxidize graphite. This method of disposing of graphite is chosen over oxidation because of the large amount $Na_2O_2$ required, 13 g per g graphite.

3. The graphite-free ash is mixed with an equal weight $Na_2O_2$. 

5
4 The mixture is heated to 450° for two hours. In this work it was found that a food can is a satisfactory container. Should this and the preceding steps be performed at RFP, after oxidation the can could be capped and shipped to Savannah River for aqueous processing.

5. The treated ash is charged to a dissolver and dissolved, can and all, in 8 M HNO₃.

6. After dissolving, 10 vol.% 1 wt.% gelatin is added to the solution to coagulate silica, and the solution filtered.

7. The Pu(VI) solution is reduced to Pu(IV) with NaNO₂ and Pu recovered by anion exchange.

Discussion

Oxidation of residues containing PuO₂ by heating with either Na₂O₂ or KO₂ is a low-temperature treatment that could be easily adapted as a pre-treatment to dissolving PuO₂-bearing material. Present equipment would be sufficient for the oxidation; a dissolver that could be flushed would be required, since some components of the residues would probably be insoluble and their accumulation could lead to interference with succeeding processing.

The reaction of PuO₂ with Na₂O₂ is an adaptation of an analytical method for treatment of difficultly-soluble solids. If a large excess of Na₂O₂ is used essentially everything will be converted to water-soluble salts. Potassium superoxide, KO₂, was used as a substitute for K₂O₂, which reacts violently with O₂ to form KO₂. About 300°, KO₂ begins to decompose to KO₂, K₂O₂ and O₂. The reaction reverses on cooling. Either Na₂O₂ or KO₂ will oxidize PuO₂ satisfactorily and allow an easy dissolving of the Pu(VI) ternary oxide.

The two compounds produced by heating KO₂ with PuO₂ were not found in a literature search, although the analogous compounds for the other alkali metals have been reported. The reactions with excess PuO₂ do allow a separation of unreacted material, but the x-ray patterns of the Pu(VI) were swamped by the strong PuO₂ lines. The qualitative evidence suggests that K₂PuO₄ and K₄PuO₅ are the two compounds formed.

The reaction of PuO₂ with excess KO₂ indicated that the residue after water leaching was K₅PuO₆, however it is not certain that this was the original compound, since the ternary oxide may have reacted with the water leach.

Acknowledgements: The author is indebted to Alice Murray for calling his attention to the Pu(VI) ternary oxides, and to Beverly Wall for experimental assistance.
References


