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

by

D. G. Karraker

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

**MASTER
MASTER**

DOE Contract No. DE-AC09-96SR18500

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

Keywords: Pu(VI) Ternary Oxides, PuO₂ Dissolving, Peroxide Oxidation of PuO₂, Treatment of PuO₂-Bearing Residues

WSRC-TR-97-0231

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

D. G. Karraker
Chemical and Hydrogen Technology Section
Savannah River Technology Center
Aiken, SC 29808

18 July 1997

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 KO₂ 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, K₄PuO₅ 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-workers^{2,3} 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 Li₅PuO₆ and Na₄PuO₅. Yamashita, et.al., report preparing Li₄PuO₅ and Li₃PuO₄ 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. Li_2CO_3 , LiOH , and Na_2O_2 were reagent grade; KO_2 (Alfa Chemicals, Inc.) was technical grade, >95% pure. Two types of PuO_2 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 SiO_2 (42%), carbon (19%), Fe_2O_3 (5.6%) and MgCO_3 (4.5%) as major materials in the mixture. High-fired PuO_2 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 PuO_2 had reacted. This amounts to a "yes-no" test for a reaction. If there was no reaction, the PuO_2 lines will be strong, and the x-ray will show little else. When there is a complete reaction, the PuO_2 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 (HNO_3 , RT, 1-2 hrs) provided a semi-quantitative measure of the success of the oxidation. It was assumed that PuO_2 would only dissolve under strenuous conditions (8M HNO_3 , 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 PuO_2 , low-fired PuO_2 , RFP "ash heels" and a synthetic incinerator ash mixed with high-fired PuO_2 . An initial experiment reacted high-fired PuO_2 with a 25% mole excess of Na_2O_2 , calculated by assuming the reaction was

The mixture was heated at 450° for 5 hours. The x-ray powder pattern of the black product was similar to that of Ca_2PuO_5 ; no PuO_2 lines were present. The product dissolved in 8M HNO_3 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 PuO_2 and 18 wt.% carbon content of the synthetic ash with Na_2O_2 --the synthetic incinerator ash was heated overnight at 700° to burn out the carbon (weight loss, 17%) then reacted with Na_2O_2 . Based on the amount of PuO_2 present, Na_2O_2 was 300% in excess. PuO_2 was detected by x-ray in the fired sample. This experiment was repeated with 500% excess Na_2O_2 ; no PuO_2 lines were found in the x-ray pattern of the product. The large excess

of Na_2O_2 required was due to competing reactions with other components of the synthetic ash, particularly SiO_2 .

A sample of RFP ash heels was also reacted at 450° for 7 hours with Na_2O_2 in a weight ratio of 1g ash heels to 1.16g Na_2O_2 . The product was a brown cake that showed a few PuO_2 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.⁴ were able to prepare Pu(VI) compounds by reacting LiOH or Li_2CO_3 in 100% oxygen atmosphere, attempts to reproduce this result on synthetic ash heels or PuO_2 (heating at 900° for 4 hours) failed. The x-ray patterns for both showed strong PuO_2 lines and dissolving in 8M HNO_3 recovered only 5% of the Pu present. The failure of this approach is attributed to firing in air instead of 100% oxygen.

Potassium superoxide, KO_2 , has more oxygen on a weight basis than Na_2O_2 , 45 wt.% vs 41 wt.%, but decomposes above 300° to a mixture of K_2O_2 and KO_2 . Tests with KO_2 as an oxidizing agent were run on low-fired PuO_2 over the temperature range 275° to 450° . X-ray powder patterns of the products identified three patterns; PuO_2 , a pattern isostructural with potassium uranium oxide (K_2UO_4), and a pattern isostructural with plutonium oxide sulfide, $\text{Pu}_2\text{O}_2\text{S}$. The K_2UO_4 pattern is assumed to be that of K_2PuO_4 , the identity of the compound represented by the $\text{Pu}_2\text{O}_2\text{S}$ pattern has not been established. Qualitative results of the reaction between PuO_2 and KO_2 are shown in Table 1.

Table 1 X-Ray Patterns of the PuO_2 - KO_2 Reaction						
$2\text{KO}_2/\text{PuO}_2$ **	Time hr	Temp., $^\circ\text{C}$	Pattern			
mole ratio*			K_2UO_4	" $\text{Pu}_2\text{O}_2\text{S}$ "	PuO_2	
2	2	275			x	
2	4	350		x	x	
2	6	450	x	x	x	?
3	4	275	xx	x		
4	3	275	x	xx		
4	4	350		xx		
4	6	450	x	x		
6	3	275		x		
6	4	350	x	x		
6	6	450		?		

* Calculated for $\text{KO}_2/\text{PuO}_2 = 1$

** PuO_2 fired at 450°

The lines of the x-ray patterns of K_2PuO_4 and " $\text{Pu}_2\text{O}_2\text{S}$ " are listed in Table 2. Figures 1 and 2 show the powder patterns of K_2PuO_4 and " $\text{Pu}_2\text{O}_2\text{S}$ ".

Table 2

Lines and Intensities for K_2PuO_4 and " Pu_2O_2S "

" Pu_2O_2S "		K_2PuO_4	
d., Å	I(rel.)	d., Å	Rel I (%)
6.75	20	6.43	40
6.08	7	6.05	48
4.28	5	4.25	72
3.49	1	3.45	40
3.38	9	3.12	25
3.03	10	3.01	100
2.25	2	2.67	18
2.13	3	2.29	20
1.98	1	2.13	42
1.97	2	2.01	24
1.88	1	1.91	34
1.74	2	1.74	46
1.56	1	1.51	17
1.51	1	1.46	15
1.42	1	1.42	24

The products of the 4/1 and the 6/1 reactions dissolved completely in 1M HNO_3 at room temperature. There was a small residue of PuO_2 when the 3/1 product dissolved; the 2/1 product dissolved to leave PuO_2 , as expected from the x-ray data.

The reaction between KO_2 and high-fired PuO_2 was investigated at a 4/1 $2KO_2/PuO_2$ ratio at 350° and 400° . No PuO_2 was detected in the x-ray patterns of the products; 73% of the Pu in the the 400° product dissolved in 1M HNO_3 to yield a Pu(VI) solution. About 5% of the sample did not dissolve, possibly because of insufficient acid.

RFP ash heels and KO_2 were reacted for 4 hours at 275° in a weight ratio of 0.5g KO_2 per g ash heels. The product cake showed a strong PuO_2 pattern on x-ray and two other patterns identified as silicates; dissolving in 1M HNO_3 recovered only 1-2% of the Pu but did dissolve 35% of the sample. Evidently a more KO_2 is necessary to accommodate the reaction of SiO_2 with KO_2 . The low yield of Pu from the dissolving suggests that the PuO_2 in RFP ash heels is coated with SiO_2 . (Ash heels are the residue from repeated leaching of incinerator ash with hot 8M HNO_3 -0.2M HF.)

PuO_2 and KO_2 were reacted with each in stoichiometric excess to determine the K/Pu (mole) ratio of products of the PuO_2 - KO_2 reaction. The product of the reaction with excess PuO_2 at 275° was leached with 0.25M HNO_3 and the excess PuO_2 filtered, dried and weighed. From the initial reactant weights and the weight of the excess PuO_2 , 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° ; 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° 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° for 2 hours; Na_2O_2 was 30% excess for the reaction

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

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 $1.36Na_2O_2/SiO_2$. 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° 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 .

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 HNO_3 .

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 NaNO_2 and Pu recovered by anion exchange.

Discussion

Oxidation of residues containing PuO_2 by heating with either Na_2O_2 or KO_2 is a low-temperature treatment that could be easily adapted as a pre-treatment to dissolving PuO_2 -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 PuO_2 with Na_2O_2 is an adaptation of an analytical method for treatment of difficultly-soluble solids. If a large excess of Na_2O_2 is used essentially everything will be converted to water-soluble salts. Potassium superoxide, KO_2 , was used as a substitute for K_2O_2 , which reacts violently with O_2 to form KO_2 . About 300° , KO_2 begins to decompose to K_2O_2 , K_2O and O_2 . The reaction reverses on cooling. Either Na_2O_2 or KO_2 will oxidize PuO_2 satisfactorily and allow an easy dissolving of the Pu(VI) ternary oxide.

The two compounds produced by heating KO_2 with PuO_2 were not found in a literature search, although the analogous compounds for the other alkali metals have been reported. The reactions with excess PuO_2 do allow a separation of unreacted material, but the x-ray patterns of the Pu(VI) were swamped by the strong PuO_2 lines. The qualitative evidence suggests that K_2PuO_4 and K_4PuO_5 are the two compounds formed.

The reaction of PuO_2 with excess KO_2 indicated that the residue after water leaching was K_6PuO_6 , 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

1. L. A. Bray and J. L. Ryan, "Catalyzed Electrolytic Dissolution of Plutonium Dioxide", Radioactive Waste Management, 6, 127 (1982).
2. C. Keller, L. Koch and K. H. Walter, J. Inorg. Nucl. Chem., 27, 1205 (1965).
3. C. Keller, L. Koch, and K. H. Walter, J. Inorg. Nucl. Chem., 27, 1225 (1965).
4. T. Yamashita, K. Ohuchi, K. Takahashi and T. Fujino in "Transuranium Elements" ed. L. R. Morss and J. Fuger. American Chemical Society, Washington, DC 1992 p441 et seq.
5. C. A. Kraus and E. F. Whyte, J. Am. Chem. Soc., 48, 1781, (1926).
6. D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc. N.Y. (1946) p 386.