This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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 for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

Recovery of Plutonium from Refractory Residues Using a Sodium Peroxide Pretreatment Process

Tracy S. Rudisill

Westinghouse Savannah River Company
Aiken, SC 29808

Abstract

The recycle of plutonium from refractory residues is a necessary activity for the nuclear weapon production complex. Traditionally, high-fired plutonium oxide (PuO_2) was leached from the residue matrix using a nitric acid/fluoride dissolving flowsheet. The recovery operations were time consuming and often required multiple contacts with fresh dissolving solution to reduce the plutonium concentration to levels where residual solids could be discarded. Due to these drawbacks, the development of an efficient process for the recovery of plutonium from refractory materials is desirable. To address this need, a pretreatment process was developed which utilizes a sodium peroxide (Na_2O_2) fusion to oxidize plutonium from the 4+ to the 6+ valence forming an acid-soluble ternary oxide. The development program utilized a series of small-scale experiments to optimize processing conditions for the fusion process and demonstrate the plutonium recovery efficiency using ceramic materials developed as potential long-term storage forms for PuO_2 and an incinerator ash from the Rocky Flats Environmental Technology Site (Rocky Flats) as test materials.

Process optimization studies using high-fired PuO_2 demonstrated that the efficiency of plutonium recovery increased with the Na_2O_2 fusion temperature (up to 700°C), increasing Na_2O_2 to PuO_2 ratio, and a decrease in the Na_2O_2 particle size. Complete recovery of high-fired PuO_2 was obtained by dissolving the fused product in 8M nitric acid following fusion at 700°C for 2 h with 100% excess in the amount of Na_2O_2 required for complete conversion to the ternary oxide. The amount of Na_2O_2 required to maximize plutonium recovery is also dependent upon other materials associated with the PuO_2 which readily oxidize. Carbon or organic materials should be removed by calcination prior to fusion and nominally 100% excess Na_2O_2 should be added for impurities which react to form ternary oxides.

The recovery of plutonium following pretreatment by Na_2O_2 fusion was demonstrated using two residues containing high-fired PuO_2. Initially, ceramic materials developed as potential long-term storage forms for PuO_2 were fused and dissolved in 8M nitric acid. Plutonium recovery efficiencies ranging from approximately 95% to essentially complete recovery were obtained following fusion at 700°C for 2 h using 100% excess Na_2O_2.

The second demonstration of the fusion process was performed using incinerator ash from Rocky Flats. In experiments with ash containing 17-18 wt% plutonium (based on accountability data), 90-95% recovery was obtained following dissolution of the fused product in 8M nitric acid. The fusions were performed at 700°C for 2 h using 75-100% excess Na_2O_2 based on the estimated plutonium concentration and assuming the ash contained 50 wt% silicon oxide (SiO_2). The

reduction in excess Na_2O_2 had no effect on the plutonium recovery efficiency; however, it is likely the excess Na_2O_2 was more than sufficient for complete oxidation as the analyzed SiO_2 concentration was only 21-28 wt%.

In subsequent experiments with ash containing only 8-9 wt% plutonium, the recovery efficiencies were significantly less, ranging from 60-90% for experiments performed using similar conditions. The general reduction in the recovery efficiency was attributed to at least a 2-3 fold increase in the SiO_2 concentration. Because the ash was predominately SiO_2, a material which reacts with Na_2O_2, it is doubtful that sufficient Na_2O_2 was added to completely oxidize the plutonium. The plutonium recovery efficiency was sensitive to the excess Na_2O_2. When the excess reagent was reduced from 100 to 50%, the recovery efficiency decreased to only 40-50%.

Introduction

The generation of refractory materials containing residual amounts of plutonium and other actinides is a frequent byproduct of nuclear weapon production activities. For example, approximately 20,000 kg of incinerator ash accumulated at the Rocky Flats Environmental Technology Site (Rocky Flats) during many years of operation. Traditionally, a nitric acid/fluoride dissolution flowsheet was used to leach plutonium from residues of this type. Multiple contacts with fresh dissolver solution were generally required to dissolve a majority of the plutonium. Rather than use a traditional, but inefficient, nitric acid/fluoride dissolution flowsheet, the development of a simple solid state fusion process for oxidation of plutonium from the 4+ to the more soluble 6+ valence state would produce a more effective and economical recovery. The recovery of plutonium from existing residues or from residues generated by future plutonium disposition or weapon production activities could then be accomplished by dissolving the pretreated residue in nitric acid followed by subsequent purification.

Fusion reactions are routinely used to solubilize minerals, glasses, and other refractory materials prior to dissolution and elemental analyses.(1) Fusion techniques have also been applied to dissolve small samples of refractory plutonium oxide (PuO_2) in preparation for analysis.(2-4) These analytical procedures involve the fusion of the PuO_2 sample with sodium peroxide (Na_2O_2) or a combination of Na_2O_2 and either sodium hydroxide (NaOH) or potassium pyrosulfate. The fused products were then dissolved in nitric or hydrochloric (HCl) acid and the solution analyzed for plutonium. The feasibility of extending a Na_2O_2/NaOH pretreatment to a plutonium recovery process was demonstrated by Partridge et al. (5) for small samples of incinerator ash and centrifuge sludge. Plutonium recoveries greater than 95% were obtained with some ashes when a 7:1 ratio of (an equal mass mixture of) Na_2O_2/NaOH was fused at 500-700°C with this material. Small-scale experiments were also performed by Karraker and Rudisill et al. (6,7) to demonstrate the feasibility of developing a recovery process using this approach for refractory materials containing PuO_2 and neptunium oxide (NpO_2). In these experiments, 1-2 g of PuO_2 or NpO_2 were calcined at 900°C, mixed and heated with the fusing reagents, and dissolved. Actinide recoveries approaching 90% were obtained with several materials. Of these materials, Na_2O_2 was identified as the most promising material for the development of a pretreatment process based on high recovery efficiencies achieved following fusion of both refractory PuO_2 and NpO_2.

The focus of this work was the development and demonstration of optimal processing conditions for the fusion of refractory PuO_2 with Na_2O_2. Initially, parametric studies were performed to optimize the processing conditions using pure PuO_2 calcined at 900°C. Following these studies, demonstrations of the recovery process were performed using ceramic materials developed as potential long-term storage forms for PuO_2 and incinerator ash from Rocky Flats.

Experimental

Process Optimization Studies

A series of small-scale experiments was performed to develop optimal processing conditions for the fusion of refractory PuO_2 with Na_2O_2 as a pretreatment to dissolution. In these experiments, PuO_2 calcined at 900°C, was used as the test material. Nominally 1 g of high-fired PuO_2 was fused for 2 h with varying amounts of Na_2O_2 using fusion temperatures ranging from 450 to 700°C. In additional experiments, the ratio of Na_2O_2 to PuO_2 was varied and the particle size of the Na_2O_2 was reduced to measure the impact on the recovery of plutonium following the fusion process. Once formed, the fused product was dissolved in 8M nitric acid and analyzed for plutonium. The success of a fusion experiment was determined by calculating the plutonium recovery efficiency using the measured plutonium concentration in the dissolving solution and the known amount of PuO_2 used in the experiment.

Fusion Temperature

In previous studies with refractory actinide oxides, the oxidation efficiency of Na_2O_2 was shown to increase with increasing temperature.(7) Based on this work, a series of experiments was performed in which the fusion temperature was increased from 450 to 700°C in 50°C increments. In each experiment, a 1 g sample of high-fired PuO_2 was fused with a 50% excess in the stoichiometric amount of Na_2O_2 required to form the ternary oxide shown in equation 1.

$$\mathrm{PuO_2 + 2Na_2O_2 \rightarrow Na_4PuO_5 + \frac{1}{2}O_2} \qquad 1$$

The Na_2O_2 used in these experiments was a granular mixture with a +140 mesh particle size distribution. The fusions were performed by transferring the PuO_2 into a 100 mL alumina crucible and adding the required amount of Na_2O_2. The Na_2O_2 was premeasured in a nitrogen atmosphere glovebox and added to the alumina crucible at the last minute to prevent reaction with moisture in the air. Following addition of the Na_2O_2, the crucible contents were mixed and the crucible placed in a small muffle furnace. The desired temperature was maintained for 2 h once the setpoint was reached. The alumina crucible and fused products were allowed to cool prior to dissolution. The dissolutions were performed in the crucible by initially adding 65 mL of 8M nitric acid and a magnetic stirring bar. The crucibles were placed on a hot plate/stirrer, covered with a watch glass containing water to reduce evaporation, and stirred and heated at

70-80°C for 1 h. The dissolving solution was then filtered using 0.45 μm filter paper and sampled for analysis. The plutonium concentration was determined by liquid scintillation counting and gamma pulse height analysis.

Excess Reagent

To measure the impact of increasing the Na_2O_2 to PuO_2 ratio on plutonium recovery, experiments were performed in which the excess Na_2O_2 was increased to 100, 200, and 300% based on the formation of the ternary oxide shown in equation 1. The experiments were performed in the same manner as discussed in the previous section. Nominally 1 g of high-fired PuO_2 was fused with the desired amount of (+140 mesh) Na_2O_2 using a fusion temperature of 700°C for 2 h. The fused product was dissolved in 8M nitric acid at 70 to 80°C for 1 h. The dissolver solution was filtered and a sample analyzed for the plutonium concentration.

Reagent Particle Size

The Na_2O_2 used in the fusion temperature and excess reagent studies was removed directly from the reagent container. Combining the granular, +140 mesh Na_2O_2 with the high-fired PuO_2, which typically has a maximum particle size of about 45 μm (325 mesh), (8) does not result in efficient mixing of the materials prior to fusion. For this reason, a series of experiments was performed in which the Na_2O_2 was ground using a mortar and pestle to a particle size less than 200 mesh (74 μm) to measure the impact on plutonium recovery. Grinding and screening were performed in a nitrogen atmosphere glovebox to prevent reaction with moisture in the air. Each experiment was performed at 700°C for 2 h. The fused products were dissolved in 8M nitric acid at 70 to 80°C for 1 h. The dissolver solution was filtered and a sample analyzed for the plutonium concentration.

Recovery of Plutonium from Ceramic Materials

To demonstrate the Na_2O_2 pretreatment process on a larger scale, a series of experiments was performed using several plutonium-containing ceramics as test materials. These materials were fabricated as potential long-term storage forms for PuO_2. The intent of the program was to produce a material with a high plutonium content with long-term stability. The ceramic materials contained 65-80 wt% PuO_2, 1-20 wt% zirconium oxide, and 0-30 wt% cerium oxide.

Three ceramic samples containing nominally 20 g of material each were selected as test cases for pretreatment by Na_2O_2 fusion. Initially, the samples were ground to a powder using a mortar and pestle and calcined at 1000°C for 2 h. The test materials were fused with a 100% excess in the stoichiometric amount of Na_2O_2 required to react completely with the estimated amount of PuO_2 in each sample. The fusions were performed in 250 mL alumina crucibles by adding the required amount of (+140 mesh) Na_2O_2, mixing, and heating to 700°C and holding for 2 h. After cooling, the fused product was dissolved in the crucible by adding nominally 150 mL of 8M nitric acid, a magnetic stirring bar, and stirring/heating at 80-90°C for 1 h. The dissolving solution was filtered and sampled for analysis.

Complete solubilization of the ceramic materials was not obtained during dissolution of the fused products. To ensure that all of the plutonium was recovered, the residues from Samples 1 and 2 were calcined at 600°C for 1 h, ground, and fused a second time. The fusions were performed at 700°C for 2 h with 100% excess Na_2O_2 assuming the residues contained 0.5 g of PuO_2. The fused products were dissolved and analyzed following the method described above.

The residue from Sample 1 was completely dissolved following the second fusion; however, a small amount of solids remained from Samples 2 and the initial dissolution of the fused product from Sample 3. The residue from these samples was calcined at 600°C for 1 h and dissolved in nominally 125 mL of an 8M nitric acid/0.06M (hydrogen) fluoride solution by heating at 90-100°C while stirring for 3 h.

Recovery of Plutonium from Rocky Flats Incinerator Ash

During past nuclear weapon production activities at Rocky Flats, an incinerator ash was produced by burning job control wastes from the site's plutonium-containing gloveboxes. The volume and mass reductions achieved during the incineration process resulted in an ash residue which contained plutonium concentrations well above economic discard limits in effect at that time. For this reason, the ash was stored, and periodically, plutonium was recovered from the material by leaching with a nitric acid/calcium fluoride (CaF_2) solution at elevated temperature. To dissolve a majority of the plutonium, multiple contacts with fresh dissolving solution were routinely required. To achieve high plutonium recoveries, it was often necessary to dry and calcine the residual solid remaining from a dissolution prior to contacting with fresh dissolving solution.(9-11)

Since the efficient recovery of plutonium from incinerator ash was difficult to accomplish using traditional aqueous dissolution flowsheets, the use of an ash as a "worst case" test material was chosen to identify potential limitations of the Na_2O_2 fusion process. Four cans of Rocky Flats incinerator ash previously shipped to the Savannah River Site in 1992 were obtained for the test program. The bulk mass and plutonium content of the ash based on accountability data are given in Table 1.

Table 1 Rocky Flats Incinerator Ash Characterization

Can No.	Ash Mass	Plutonium Mass	Plutonium Concentration
	(g)	(g)	(wt%)
1	952	82	8.6
2	992	87	8.8
3	311	55	17.7
4	505	91	18.0

The fusion experiments were performed by initially calcining a 6-7 g sample of ash at 1000°C for 2 h to remove volatile components such as organic material and moisture. The calcined ash was mixed and fused with 50-100 excess Na_2O_2 based on the estimated PuO_2 and silicon oxide (SiO_2) concentrations and the stoichiometry given by equations 1 and 2.

$$Na_2O_2 + SiO_2 \rightarrow Na_2SiO_3 + \frac{1}{2}O_2 \tag{2}$$

The presence of other oxides (of much lower concentration) which react with Na_2O_2 was ignored. The PuO_2 concentration was calculated from accountability data (see Table 1) and the SiO_2 concentration was estimated from characterization data available for Rocky Flats incinerator ash.(11,12) An SiO_2 concentration of 50 wt% was assumed for the initial experiments performed with ash from cans 3 and 4. A slightly higher concentration of 60 wt% was assumed for the ash from cans 1 and 2 due to the lower plutonium concentration.

Fusion experiments were performed using Na_2O_2 with three different particle size distributions. The Na_2O_2 used in the experiments was obtained as a granular mixture with a +140 mesh particle size distribution. For a majority of the experiments, the Na_2O_2 was ground to pass through either a 100 or 200 mesh screen. The Na_2O_2 was prepared in the same manner as discussed in the previous sections. The calcined ash and Na_2O_2 were transferred to a 100 mL alumina or 125 mL stainless steel crucible and mixed with a metal spatula. The crucible was heated at 700°C for 2 h. After cooling, the fused product was dissolved in the crucible using 8M nitric acid at 80-90°C for 1 h. The dissolving solution was filtered using 0.45 μm filter paper and sampled for analysis. The residual solids were rinsed with a 15 mL aliquot of 8M nitric acid prior to sampling the filtrate. The plutonium concentration of the filtrate was determined by liquid scintillation counting and gamma pulse height analysis. The concentrations of other metals in the filtrate were determined by inductively-coupled plasma emission and atomic absorption spectroscopy. The insoluble residues from many of the experiments were also characterized by x-ray diffraction analysis.

Results and Discussion

Process Optimization Studies

Fusion Temperature

The measured plutonium concentration and filtrate volume were used to calculate the plutonium recovered during each dissolution. The plutonium recovery (see Figure 1) generally increased with increasing temperature from 50 to 60% at 450°C to approximately 90% at 700°C. Fusion temperatures above 700°C were not used since Na_2O_2 melts at 675°C.(13) Higher fusion temperatures would likely lead to excessive volatilization of the Na_2O_2 and increased corrosion of the alumina crucible. Analytical procedures used to solubilize high-fired PuO_2 by fusing with Na_2O_2 or Na_2O_2/NaOH mixtures are typically performed below 500°C to prevent excessive contamination of the dissolving solutions with the crucible materials.(2,3) However, the increased plutonium recovery efficiency obtained at higher fusion temperatures is desirable and a subsequent purification step would be used to remove impurities from the plutonium-containing solution.

Excess Reagent

The plutonium recovery as a function of the excess Na_2O_2 used in the fusion is shown in Table 2.

Table 2 Effect of Excess Na_2O_2 on Plutonium Recovery

Excess Na_2O_2 (%)	Plutonium Recovery (%)
50	91
100	100
200	103
300	101

The data show that complete recovery of the high-fired PuO_2 can be achieved at an excess Na_2O_2 value between 50 and 100% using a fusion temperature of 700°C for 2 h.

Particle Size

The plutonium recovery data obtained for this series of experiments are plotted as a function of fusion temperature on Figure 2. Data from the initial series of experiments in which +140 mesh Na_2O_2 was used for the pretreatment process are included for comparison. The recovery data from the experiments using the –200 mesh Na_2O_2 show a steady increase in plutonium recovery from approximately 75% at 550°C to essentially 100% at 700°C. A comparison of this data with the plutonium recoveries obtained with the +140 mesh material shows an approximate 10% improvement in plutonium recovery over the range of temperatures. The improvement in plutonium recovery can be attributed to better mixing of the materials which resulted from the use of a finer Na_2O_2 particle size. Increasing the availability of Na_2O_2 to a larger portion of the PuO_2 particles results in a higher extent of reaction. This result is consistent with the fusion of many refractory materials where the rate of decomposition (or conversion to a more soluble material) is highly dependent upon the exposed surface area of the material.(14)

Recovery of Plutonium from Ceramic Materials

The results of the fusion experiments performed to recover plutonium from the ceramic materials are summarized in Table 3. The table includes the plutonium recovery efficiencies obtained following the initial Na_2O_2 fusions as well as recovery data for the second fusions and the nitric acid/fluoride dissolutions.

Table 3 Recovery of Plutonium from Ceramic Materials

Sample	Total Plutonium Recovered	1st Na_2O_2 Fusion/8M Nitric Acid Dissolution		2nd Na_2O_2 Fusion/8M Nitric Acid Dissolution		8M Nitric Acid/0.06M Fluoride Dissolution	
	(g)	(g)	(%)	(g)	(%)	(g)	(%)
1	8.32	8.31	99.9	0.01	0.1		
2	7.88	7.46	94.7	0.04	0.5	0.38	4.8
3	11.76	11.38	96.8			0.38	3.2

The recovery efficiencies obtained following the initial fusions were very good. Recovering 95% or more of the plutonium in a single dissolution step from a refractory material is difficult to obtain with traditional nitric acid/fluoride dissolution flowsheets. A recovery flowsheet developed in the 1980's at the Savannah River Technology Center for high-fired PuO_2 produced in the Rocky Flats foundry required dissolving in 13.7M nitric acid/0.1M fluoride at 110°C. Under these conditions, approximately 88% of the plutonium dissolved in 3 h. Subsequent treatment of the remaining solids with fresh dissolving solution solubilized most of the remaining PuO_2 in 2 h.(15) Difficulty in dissolving the last fraction of refractory PuO_2 in a given batch is not atypical of nitric acid/fluoride dissolution flowsheets which generally require periodic removal of the dissolving solution and addition of fresh reagent to approach complete dissolution of the material.(16) A plutonium recovery approaching 100% was only obtained in one experiment with the plutonium-containing ceramics; however, an increase in the recovery efficiency could likely be obtained by decreasing the Na_2O_2 particle size used to perform the fusions

Recovery of Plutonium from Rocky Flats Ash

Cans 3 and 4

The initial plutonium recovery experiments using the Rocky Flats incinerator ash were performed using the material from cans 3 and 4 which contained the ash with the highest plutonium concentration. The objective of the experiments was to demonstrate the Na_2O_2 fusion process using the ash and compare the plutonium recovery efficiency with the efficiency obtained with traditional nitric acid/fluoride dissolution flowsheets. Experiments were also performed to measure the effects on plutonium recovery when the amount of excess Na_2O_2 was reduced and when the Na_2O_2 powder was increased from a –200 to a –100 mesh particle size distribution. The experimental details for each fusion including the mass of reactants and the mass lost during calcination are summarized in Table 4.

Table 4 Fusion of Incinerator Ash from Cans 3 and 4

Exp't No.	Can No.	Mass of Ash (g)	Mass of Calcined Ash (g)	Volatilized Mass (%)	Mass of Na_2O_2 (g)	Excess Na_2O_2[(b)] (%)
1A[(a)]	3	7.2080	6.7348	6.6	9.9255	80
1B[(a)]	3	7.2165	6.7427	6.6	10.3122	87
2	4	6.5060	6.1669	5.2	9.9215	100
3	4	6.5490	6.1578	6.0	9.9806	99
4	3	6.5016	5.9353	8.7	9.9443	100
5	4	6.5028	6.1372	5.6	9.9197	100
6	3	6.5104	6.0520	7.0	8.7212	75
7	4	6.5102	6.1352	5.8	8.7197	75

(a) Ash sample was divided into two portions following calcination.
(b) Excess Na_2O_2 was based on the accountability data for PuO_2 and 50 wt% for SiO_2 in the ash.

Pretreatment of the incinerator ash with Na_2O_2 generally produced a fused product which adhered to the crucible wall; however, in most cases, the fused material dissolved to the point where the residual solids were easily washed from the crucible. Once the filtration was complete, the solids were stirred with approximately 100 mL of water at 50-75°C for 30 min to dissolve excess sodium nitrate ($NaNO_3$). The $NaNO_3$, generated from the neutralization of excess Na_2O_2, exceeded its solubility limit in the dissolving solution. As an alternative, washing with water prior to the dissolution of the fused product could be used to remove a majority of the excess Na_2O_2 as soluble NaOH. Following the dissolution and water wash, the remaining solids were calcined at 1000°C for 1 h. After cooling, the mass of the solids was noted for use in estimating the composition of the ash and the solids stored for subsequent x-ray diffraction analysis.

The plutonium recovery efficiency for each experiment (see Table 5) was calculated using the mass of recovered plutonium and the accountability data for each can. Relying upon the accountability data raises concerns associated with uncertainties in the plutonium analyses and the possibility of obtaining nonrepresentative samples; however, the ash appeared very consistent in color and particle size. The ash was likely ground and screened prior to analysis and shipment from Rocky Flats. Pretreatment in this manner would improve the accuracy of the plutonium analyses and minimize sampling concerns.

In all experiments, the solubilized plutonium was greater than 89 % based on the accountability data. Recoveries of this magnitude generally compare favorably with plutonium recoveries obtained by refluxing multiple times with nitric acid/fluoride solutions. In studies at Rocky Flats, a 90% recovery was not obtained until the third or fourth contact with fresh dissolving solution when crushed incinerator ash was refluxed (at 110-115°C) in a 12.5M nitric acid/0.2M CaF_2 solution (at a solids-to-liquid ratio of nominally 100 g/L).(10) From this comparison, it is clear that the Na_2O_2 fusions greatly improved the solubility and recoverability of the plutonium from the incinerator ash samples.

Table 5 Plutonium Recovery Efficiency – Cans 1 and 2

Exp't No.	Can No.	Na_2O_2 Particle Size (mesh)	Excess Na_2O_2 (%)	Plutonium Concentration (Accountability) (wt%)	Plutonium Concentration (Measured) (wt%)	Recovery Efficiency (%)
1A	3	–200	80	17.7	16.9	96
1B	3	–200	87	17.7	15.8	89
2	4	–200	100	18.0	16.8	93
3	4	–200	99	18.0	16.9	94
4	3	–100	100	17.7	16.4	93
5	4	–100	100	18.0	16.0	89
6	3	–100	75	17.7	15.7	89
7	4	–100	75	18.0	16.9	94

From the recovery data in Table 5, it does not appear that reducing the excess Na_2O_2 from 100 to 75% had an effect on the plutonium recovery efficiency. It is likely that the excess Na_2O_2 was more than sufficient to convert SiO_2 to a ternary oxide and oxidize the PuO_2 and other minor metal oxides present in the ash. This assumption is based on an estimated SiO_2 concentration of 21-28 wt% in the ash obtained from the mass of insoluble solids. The excess Na_2O_2 in each experiment was based on a concentration of 50 wt%; therefore, the excess Na_2O_2 in each experiment was actually well above 300%, a value which was likely sufficient to drive to near completion the conversion of PuO_2 in the ash to the nitric acid-soluble ternary oxide. Inspection of the recovery data also shows that increasing the Na_2O_2 particle size distribution from –200 to –100 mesh did not have a noticeable effect on the plutonium recovery efficiency. It appears that as long as the Na_2O_2 particles are small enough to provide good mixing, the oxidation efficiency of the Na_2O_2 is not reduced. Additional fusion experiments were performed with the ash from cans 1 and 2 using Na_2O_2 with a +140 mesh particle size distribution. The results of these experiments are discussed in the following section.

Cans 1 and 2

A series of experiments using the ash from cans 1 and 2 was performed to measure the efficiency of the Na_2O_2 pretreatment process in solubilizing the plutonium in a lower assay material. The plutonium assay for the ash from these cans was only 8-9 wt%, which would typically provide a greater challenge for a recovery process; plutonium recovery efficiency generally decreases with decreasing plutonium concentration in a residue. To accomplish this task, several methods were employed to quantify the amount of plutonium remaining in the insoluble residues following dissolution of the fused product. Experiments were also performed to measure the effects on plutonium recovery from the ash when the amount of excess Na_2O_2 was reduced and when the Na_2O_2 powder was increased from a –100 to a +140 mesh particle size distribution. In addition, several experiments were performed in which a stainless steel crucible was used to contain the reactants during fusion which is prototypical of a way the pretreatment process can be implemented on a production scale.

The fusion experiments with the incinerator ash from cans 1 and 2 were performed using the same general procedures used for the initial experiments. The details of each experiment including the mass of reactants and the mass lost during calcination are summarized in Table 6.

Table 6 Fusion of Incinerator Ash from Cans 1 and 2

Exp't No.	Can No.	Mass of Ash (g)	Mass of Calcined Ash (g)	Volatilized Mass (%)	Mass of Na_2O_2 (g)	Excess Na_2O_2[(b)] (%)
8	1	6.5010	6.2926	3.2	9.8943	82
10	1	6.5029	6.3737	2.0	9.9610	83
11	2	6.5030	6.3466	2.4	10.8219	99
12	1	6.5030	6.4779	0.4	10.7889	99
13	1	6.5018	6.5083	(a)	9.4643	74
14	2	6.5019	6.3676	2.1	9.4546	74
15	1	6.5052	6.4365	1.1	8.0963	49
16	2	6.5093	6.3958	1.7	8.0956	49
17	1	6.5010	6.3221	2.8	10.8633	100
19	1	6.5006	6.9807	(a)	10.8939	101
20	2	6.5040	6.3742	2.0	10.7741	98
21	1	6.5024	6.5436	(a)	10.8092	99
22	2	6.5024	6.3700	2.0	10.8349	99
23	2	6.5049	6.4947	0.2	9.4819	74

(a) A small mass gain was observed following calcination.
(b) Excess Na_2O_2 was based on the accountability data for PuO_2 and 60 wt% for SiO_2 in the ash.

The plutonium recovery efficiencies from the initial experiments using samples of ash from cans 1 and 2 were only 60-75% based on the accountability data. To determine if the low plutonium recovery efficiencies were real or biased low due to poor nondestructive assays, additional measures were taken to estimate the amount of plutonium remaining in the insoluble solids. The solids from two of the experiments were fused a second time with Na_2O_2 in an attempt to recover additional plutonium. The amount of Na_2O_2 used in the fusions was based on the assumption that the solids were SiO_2 and the use of nominally 100% excess in the stoichiometric requirement for complete reaction (see equation 2). The Na_2O_2 was ground to a –100 mesh particle size distribution and the fusions were performed at 700°C for 2 h. The fused product was dissolved in 8M nitric acid at 80-90°C for 1 h; the solution was then analyzed for plutonium. Based on the recovered plutonium and the mass of insoluble solids, the plutonium content of the solids was 2-3 wt%.

The residual plutonium content of the solids from a number of the experiments was determined by x-ray diffraction. A series of standards containing known ratios of PuO_2 and aluminum oxide (Al_2O_3) powders was used to measure the PuO_2 concentration in the insoluble solids from the ratio of peak intensities. Initially an x-ray diffraction spectrum of the solids from each experiment was obtained to screen for the presence of Al_2O_3. Only the solids from experiment 21 showed the presence of Al_2O_3; however, an estimate of the PuO_2 concentration was obtained by comparison of the x-ray spectrum from these solids with the spectra from the other samples. The amount of plutonium in the solids was then calculated from the plutonium concentration and the mass of solids. Using the estimated plutonium content of the insoluble solids obtained from the second Na_2O_2 fusions and x-ray diffraction analyses, the plutonium recovery efficiencies from the ash samples were calculated for the initial Na_2O_2 fusion and subsequent nitric acid dissolution (see Table 7).

Table 7 Plutonium Recovery Efficiency – Cans 1 and 2

Exp't No.	Can No.	Na_2O_2 Particle Size (mesh)	Excess Na_2O_2 (%)	Plutonium Recovery (%)	Plutonium Concentration (Accountability) (wt%)	Plutonium Concentration (Measured) (wt%)
8	1	–100	82	72	8.6	8.2
10	1	–100	83	74	8.6	7.5
11	2	–100	99	66	8.8	10.1
12	1	–100	99	60	8.6	9.9
13	1	–100	74	57	8.6	9.6
14	2	–100	74	56	8.8	10.7
15	1	–100	49	41	8.6	11.3
16	2	–100	49	51	8.8	10.2
17	1	+140	100	21(a)	8.6	(b)
19	1	–100	101	92	8.6	32.5
20	2	–100	98	79	8.8	7.9
21	1	–100	99	88	8.6	26.2
22	2	+140	99	15(c)	8.8	(b)
23	2	+140	74	12(c)	8.8	(b)

(a) Total plutonium in ash sample based on average value measured in experiments 8, 10, 12, 13, and 15.
(b) Not measured.
(c) Total plutonium in ash sample based on average value measured in experiments 11, 14, 16, and 20.

Based on the plutonium recoveries given in Table 7, the Na_2O_2 fusions were clearly less efficient in solubilizing the plutonium in the lower assay ash. A 90-95% recovery was obtained using the ash containing 17-18 wt% plutonium; however, only a 60-90% efficiency was obtained from the lower assay material using comparable excesses of Na_2O_2. Interestingly, in the two experiments performed with ash from cans 1 and 2 in which a plutonium recovery efficiency of nominally 90% was achieved, the estimated plutonium content of the ash was uncharacteristically greater that 25 wt%. The reduction in the plutonium recovery efficiency for the material from cans 1 and 2 was attributed to a very high SiO_2 concentration in the ash samples.

To illustrate this point, the compositional range for the ash used in both series of experiments was estimated using data for each experiment. The ash compositions were calculated from the mass of insoluble solids and the elemental analysis of the nitric acid solution used to dissolve the fused product and the wash solution used to remove soluble $NaNO_3$ from the solids. Although, the x-ray diffraction spectra showed the presence of small amounts of other materials (PuO_2, silicon carbide, Al_2O_3, and a sodium aluminosilicate), the mass of the insoluble solids was assumed to be SiO_2. The composition of the ash samples were obtained by assuming all elements were present as oxides and summing the total recovered oxide mass. A comparison of the range of oxide concentrations in the ash from the two sets of cans is shown in Table 8.

From Table 8, one can see that the SiO_2 concentration of the incinerator ash from cans 1 and 2 was at least a factor of 2-3 higher than the concentration in cans 3 and 4. Since the ash was predominately SiO_2, a material which reacts with Na_2O_2, it is doubtful that sufficient Na_2O_2 was added to completely oxidize the PuO_2 to the acid-soluble ternary oxide. The plutonium recovery efficiency was sensitive to the excess Na_2O_2 used in the experiments. The recovery efficiencies obtained using the ash samples from cans 1 and 2 are plotted on Figure 3 as a function of the excess Na_2O_2 used in the experiments. The data exhibit a good deal of scatter, especially around 100% excess Na_2O_2; however, the recovery efficiency decreased in a linear fashion to only 40-50% at 50% excess Na_2O_2.

The reduction in the oxidation efficiency of the Na_2O_2 was attributed to the morphology of the ash. Microscopic analysis of plutonium-containing incinerator ash has shown that much of the plutonium occurs in rich deposits surrounded by larger nonplutonium-bearing particles.(17) The presence of an agglomeration of SiO_2-containing particles at the surface of PuO_2-rich regions in the ash would limit the rate and extent of reaction with Na_2O_2 due to the mass transfer resistance provided by the reacted and unreacted particles and the depletion of reactant. Higher plutonium recovery efficiencies could be obtained by crushing the ash to release the plutonium-bearing regions or increasing the amount of Na_2O_2 used to perform the fusion. An increase in the excess Na_2O_2 would yield higher plutonium recoveries; however, it also generates additional waste which must be balanced against the increased plutonium recovery. Although the plutonium recovery efficiencies obtained with samples of ash from cans 1 and 2 were generally less than obtained with the richer material from cans 3 and 4, the recoveries still compared favorably with values reported for nitric acid/fluoride dissolution flowsheets.(10)

The metal oxide concentration ranges presented in Table 8 are typical of values reported by Johnson (11) and Behrens et. al. (12) for ash from Rocky Flats. The material balance closures for the experiments performed with ash from cans 3 and 4 were reasonably good, ranging from about 76 to 98 %. Much of the missing material could likely be accounted for by sodium oxide (Na_2O) and the oxides of elements for which an analysis was not performed. The material balance closures for the experiments performed with ash from cans 1 and 2 exceeded 100% in many cases; the recovery of excess mass was attributed to the accumulation of mass during the handling of the insoluble solids (which were the bulk of the recovered mass). Sources of excess mass likely included crucible fragments from experiments in which failure occurred and an attempt to recovery plutonium from the solids by dissolving in HCl.

Table 8 Comparison of Rocky Flats Incinerator Ash Compositions

Oxide	Cans 1 and 2 Concentration Range (wt%)	Cans 3 and 4 Concentration Range (wt%)
Ag_2O	0.0	(a)
Al_2O_3	3.2 - 5.7	5.3 - 20.1
As_2O_3	0.0	(a)
B_2O_3	0.1 - 0.9	1.0 - 1.7
BaO	0.1 - 0.2	0.2 - 0.4
BeO	0.0 - 0.1	(a)
CaO	6.1 - 7.4	7.9 - 10.5
CdO	0.0	0.0
CoO	0.0 - 0.6	0.0
Cr_2O_3	0.3 - 0.8	0.7 - 1.3
Cu_2O	0.0 - 0.2	0.1
Fe_2O_3	4.3 - 6.5	6.7 - 12.5
HgO	0.0	(a)
K_2O	0.5 - 0.8	(a)
La_2O_3	0.0	0.0
Li_2O	0.0	0.0
MgO	0.8 - 1.0	0.8 - 1.1
MnO_2	0.1 - 1.2	0.1 - 0.2
MoO_2	0.0 - 0.1	0.0 - 0.1
NiO	0.4 - 0.8	0.8 - 1.1
P_2O_5	1.3 - 2.7	3.5 - 4.6
PbO	0.0 - 0.2	0.1
PuO_2	1.9 - 36.8	17.8 - 19.2
SeO_2	0.0	(a)
SiO_2	55.5 - 103.9	21.5 - 28.3
SnO_2	0.0	0.0 - 0.1
SrO	0.0	0.0 - 0.1
Ta_2O_5	0.0 - 0.1	(a)
TiO_2	1.4 - 2.2	1.3 - 2.6
V_2O_5	0.0 - 0.1	0.0 - 0.1
ZnO	0.1 - 0.4	0.4 - 1.0
ZrO_2	0.0	0.0
Volatile Components	0.0 – 3.2	5.2 - 8.7
Total Recovered Mass	88.1 – 156.4	76.4 - 97.6

(a) Not measured.

In three experiments with ash from cans 1 and 2, Na_2O_2 with a +140 mesh particle size distribution was used to perform the fusions. In each case, an extremely low plutonium recovery efficiency was obtained (see Table 7). The reduced recovery efficiencies were attributed to inefficient mixing of the Na_2O_2 and ash. The rate and extent of reaction is directly proportional to the surface area of PuO_2 which is exposed to Na_2O_2; therefore, a low conversion to the acid-soluble ternary oxide was obtained in these experiments. To maximize plutonium recovery from incinerator ash or other refractory materials, the Na_2O_2 particle size distribution should be fine enough to provide efficient mixing of the solids. If necessary, the residue should be ground to improve mixing or to expose regions rich in PuO_2 which are encapsulated by nonplutonium-bearing materials.

In experiments 21, 22, and 23, a 125 mL stainless steel beaker was used to perform the Na_2O_2 fusion and fused product dissolution. During experiment 21, corrosion of the beaker was minimal but observable based on a comparison of the recovered masses of iron, nickel, and chromium in the dissolving solutions with average values from the other experiments. However, in experiments 22 and 23, when the same beaker was used, the recovered mass of these elements was much higher. The increased corrosion was attributed to the removal of the protective oxide coating from the surface of the stainless steel during the dissolutions. However, corrosion of the container used to perform the fusion on a production scale should not be a major issue. In fact, one strategy for implementing the process in a production facility would be to perform the fusion in a mild steel vessel and dissolve both the vessel and the fused product in nitric acid. Performing the fusion and dissolution in the same metal container would also be feasible since corrosion products are easily removed during subsequent plutonium purification. It may also be possible to minimize corrosion by using a container fabricated from a metal alloy other than stainless steel.

Conclusions

A series of small-scale experiments was performed to optimize processing conditions for the pretreatment of refractory plutonium-containing residues by Na_2O_2 fusion. Using high-fired PuO_2 as the test material, the experimental program demonstrated that the efficiency of plutonium oxidation (measured by plutonium recovery) increased with fusion temperature up to 700°C. Fusion temperatures above this value were not tested since Na_2O_2 melts at 675°C and higher temperatures could lead to excessive volatilization and increased corrosion of crucible materials. Fusion of the high-fired PuO_2 at 700°C for 2 h was considered the optimal conditions for the pretreatment process.

Increasing the Na_2O_2 to PuO_2 ratio led to an increase in plutonium recovery efficiency. Complete recovery of high-fired PuO_2 was obtained following fusion at 700°C for 2 h using a 100% excess in the amount of Na_2O_2 required for complete conversion to the ternary oxide. The optimization studies also demonstrated that decreasing the Na_2O_2 particle size distribution from +140 to –200 mesh improved the plutonium recovery efficiency. The improvement in recovery was attributed to better mixing of the reactants due to the finer Na_2O_2 particle size distribution.

The finer particles exposed additional PuO_2 surface area to Na_2O_2 which resulted in a higher extent of reaction and enhanced solubility of the high-fired PuO_2.

The recovery of plutonium following pretreatment by Na_2O_2 fusion was demonstrated using two residues containing high-fired PuO_2. Initially, ceramic materials developed as potential long-term storage forms for PuO_2 were fused and dissolved in 8M nitric acid. Plutonium recovery efficiencies ranged from nominally 95% to essentially complete recovery. The fusions were performed at 700°C for 2 h using a 100% excess in the amount of Na_2O_2 required for complete conversion to the ternary oxide. Sodium peroxide with a +140 mesh particle size distribution was used to perform the fusion experiments; therefore, it would be a reasonable expectation that even higher plutonium recovery efficiencies were obtainable if the Na_2O_2 was ground to a finer particle size prior to fusion.

In the second demonstration of the pretreatment process, incinerator ash from Rocky Flats was used as the test material. Two series of experiments were performed using samples of ash containing 17-18 wt% and 8-9 wt% plutonium. In both series of experiments, the ash samples were initially calcined at 1000°C for 2 h to remove volatile components. Following this treatment, no problems due to the oxidation of residual organic materials were encountered.

In the first series of experiments with ash containing 17-18 wt% plutonium, the fusions were performed at 700°C for 2 h using 75-100% excess Na_2O_2 based on the estimated plutonium concentration and assuming the ash contained 50 wt% SiO_2. Using these conditions, 90-95% of the plutonium was recovered (based on accountability data for the ash) following dissolution of the fused product. Variations in the excess Na_2O_2 had no effect on the plutonium recovery efficiency; however, it is likely that the excess Na_2O_2 was more than sufficient to convert SiO_2 to a ternary oxide and oxidize the PuO_2 and other minor metal oxides present in the ash. The analyzed SiO_2 concentration in the ash was only 21-28 wt%; therefore, the excess Na_2O_2 in each experiment was actually well above 300%. The plutonium recovery efficiencies obtained for these experiments were much better than would be expected for traditional nitric acid/fluoride dissolution flowsheets. To achieve recoveries of this magnitude, multiple contacts with fresh dissolving solution are required.

Pretreatment experiments with the ash containing 8-9 wt% plutonium were performed using essentially the same conditions as experiments with the higher assay material. However, the plutonium recovery efficiencies for these experiments were significantly less, ranging from 60-90%. The general reduction in the recovery efficiency was attributed to the significant increase in the ash's SiO_2 concentration. Since the ash was predominately SiO_2, a material which reacts with Na_2O_2, it is doubtful that sufficient Na_2O_2 was added to completely oxidize the PuO_2 to the ternary oxide. In addition, the encapsulation of the PuO_2 by an agglomeration of SiO_2-containing particles likely reduced the extent of the oxidation and the resulting plutonium recovery efficiency.

The plutonium recovery efficiency obtained during experiments with the lower assay ash was sensitive to the excess Na_2O_2. In experiments when the excess reagent was reduced from 100 to 50%, the recovery efficiency decreased in a linear fashion to only 40-50%. The reduction in the oxidation efficiency was attributed to the morphology of the ash. Microscopic analysis of plutonium-containing incinerator ash has shown that much of the plutonium occurs in rich deposits surrounded by larger nonplutonium-bearing particles. The presence of an agglomeration of SiO_2-containing particles at the surface of PuO_2-rich regions would limit the rate and extent of reaction with Na_2O_2 due to mass transfer limitations and depletion of reactant. Higher plutonium recovery efficiencies could be obtained by crushing the ash to release the plutonium-bearing regions or increasing the amount of Na_2O_2 used to perform the fusion. An increase in the excess Na_2O_2 would yield higher plutonium recoveries; however, it also generates additional waste which must be balanced against the increased plutonium recovery.

In the ash fusion experiments, three different Na_2O_2 particle size distributions were used. In the experiments with the higher assay ash, increasing the particle size distribution from –200 to –100 mesh did not have a noticeable effect on the plutonium recovery efficiency. However, when (unground) Na_2O_2 with a +140 mesh particle size distribution was used in fusion experiments with the lower assay ash, extremely low plutonium recovery efficiencies were obtained. The reduced recovery efficiencies were attributed to inefficient mixing of the Na_2O_2 with the ash. Because the particle size distribution of the Na_2O_2 was much larger than the distribution of the ash, mixing of the reagents was poor, resulting in regions of ash in poor contact with Na_2O_2. Since the plutonium oxidation rate and extent of reaction is proportional to the surface area of exposed PuO_2 particles, a low conversion to the ternary oxide was obtained. To maximize plutonium recovery from incinerator ash or other refractory materials, the Na_2O_2 particle size distribution should be fine enough to provide efficient mixing of solids.

In three ash experiments, the Na_2O_2 fusions were performed using a stainless steel crucible to demonstrate a possible strategy for implementing the process in a production facility. During the initial experiment, corrosion of the beaker was minimal based on the recovered masses of iron, nickel, and chromium; however, in two subsequent experiments which used the same beaker, significant corrosion occurred. The increased corrosion was attributed to the removal of the protective oxide coating from the surface of the stainless steel beaker. However, corrosion of the container used to perform the fusion on a production scale should not be a major issue. In fact, a second strategy for implementing the process in a production facility would be to perform the fusion in a mild steel vessel and dissolve both the vessel and the fused product in nitric acid. Performing the fusion and dissolution in the same metal container would also be feasible since any corrosion products are easily removed during subsequent plutonium purification. It may also be possible to minimize corrosion by using a container fabricated from a metal alloy other than stainless steel.

References

1. Z. Šulcek and P. Povondra, *Methods of Decomposition in Inorganic Analysis*, CRC Press, Inc. Boca Raton, FL, pp. 167-229 (1989).

2. G. W. C. Milner, D. Crossley, I. G. Jones, and G. Phillips, "The Rapid Dissolution of Plutonium Dioxide by a Sodium Peroxide Sinter, Followed by Determination of the Plutonium Content by Differential Spectrophotometry," *Analyst*, 90, 732 (1965).

3. G. W. C. Milner, and D. Crossley, "The Rapid Dissolution of Plutonium Dioxide by a Sodium Peroxide − Sodium Hydroxide Fusion, Followed by Determination of the Plutonium Content by Controlled-Potential Coulometry," *Analyst*, 93, 429 (1968).

4. J. K. Patterson, "Investigation into the Dissolution and Direct Assay of High-Fired Plutonium Oxide (Fusion-Melt with Potassium Pyrosulfate and Sodium Peroxide)," Report RFP-2402, Rockwell International, Atomics International Division, Golden, CO (1976).

5. J. A. Partridge and E. J. Wheelwright, "Plutonium Recovery from Incinerator Ash and Centrifuge Sludge by Peroxide Fusion," Report BNWL-B-419, Battelle Memorial Institute, Richland, WA (1975).

6. D. G. Karraker, "Oxidation of Pu-Bearing Solids: A Process for Pu Recovery from Rocky Flats Incinerator Ash," Report WSRC-TR-97-0231, Westinghouse Savannah River Company, Aiken, SC (1997).

7. T. S. Rudisill and D. G. Karraker, "Fusion Techniques for the Oxidation of Refractory Actinide Oxides," Report WSRC-TR-99-0021, Westinghouse Savannah River Company, Aiken, SC (1999).

8. J. A. Porter and A. E. Symonds, Jr., "Precipitation of Plutonium(III) Oxalate and Calcination to Plutonium Dioxide," Report DP-981, E. I. du Pont de Nemours and Co., Aiken, SC (1965).

9. G. F. Molen and R. O. Wing, "Dissolution of Plutonium-Bearing Residues in a Nitric Acid-Calcium Fluoride Solvent System," Report RFP-776, The Dow Chemical Company, Rocky Flats Division, Golden, CO (1966).

10. G. F. Molen, "Effects of Acid Concentration and Feed-Particle Size on the Dissolution of Plutonium-Bearing Materials," Report RFP-890, The Dow Chemical Company, Rocky Flats Division, Golden, CO (1968).

11. T. C. Johnson, "Recovery of Plutonium from Incinerator Ash at Rocky Flats," Report RFP-2520, Rockwell International, Atomic International Division, Golden, CO (1976).

12. R. G. Behrens, E. C. Buck, N. L. Dietz, J. K. Bates, E. Van Deventer, and D. J. Chaiko, "Characterization of Plutonium-Bearing Wastes by Chemical Analysis and Analytical Electron Microscopy," Report ANL-95/35, Argonne National Laboratory, Argonne, IL (1995).

13. J. A. Dean, Editor, *Lange's Handbook of Chemistry*, 13th Edition, McGraw-Hill Book Company, New York, NY (1985).

14. Z. Šulcek et al., p. 167.

15. G. A. Burney, "Dissolution of Rocky Flats Foundry PuO_2," Report DPST-84-782, E. I. du Pont de Nemours and Co., Aiken, SC (1984).

16. L. W. Gray, "Dissolution of Plutonium Dioxide," Report DPST-83-460, E. I. du Pont de Nemours and Co., Aiken, SC (1983).

17. E. C. Buck, "Microscopic Analysis of Pu-Contaminated Incinerator Ash: Implications for Immobilization," in Plutonium Futures – The Science, Topical Conference on Plutonium and Actinides, Report LA-13338-C, Los Alamos National Laboratory in Cooperation with the American Nuclear Society, Santa Fe, NM, (1997).

Figure 1 Effect of Fusion Temperature on Plutonium Recovery

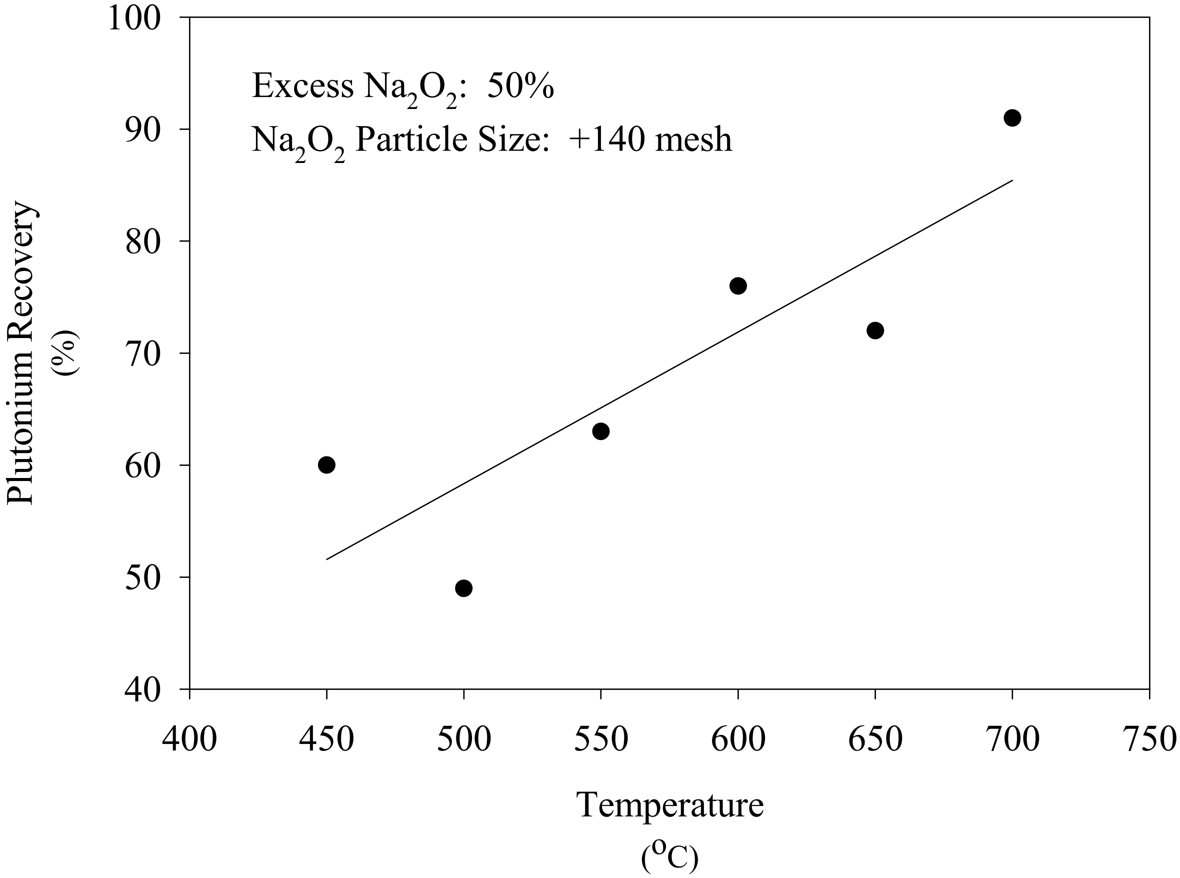

Figure 2 Effect of Na_2O_2 Particle Size on Plutonium Recovery Efficiency

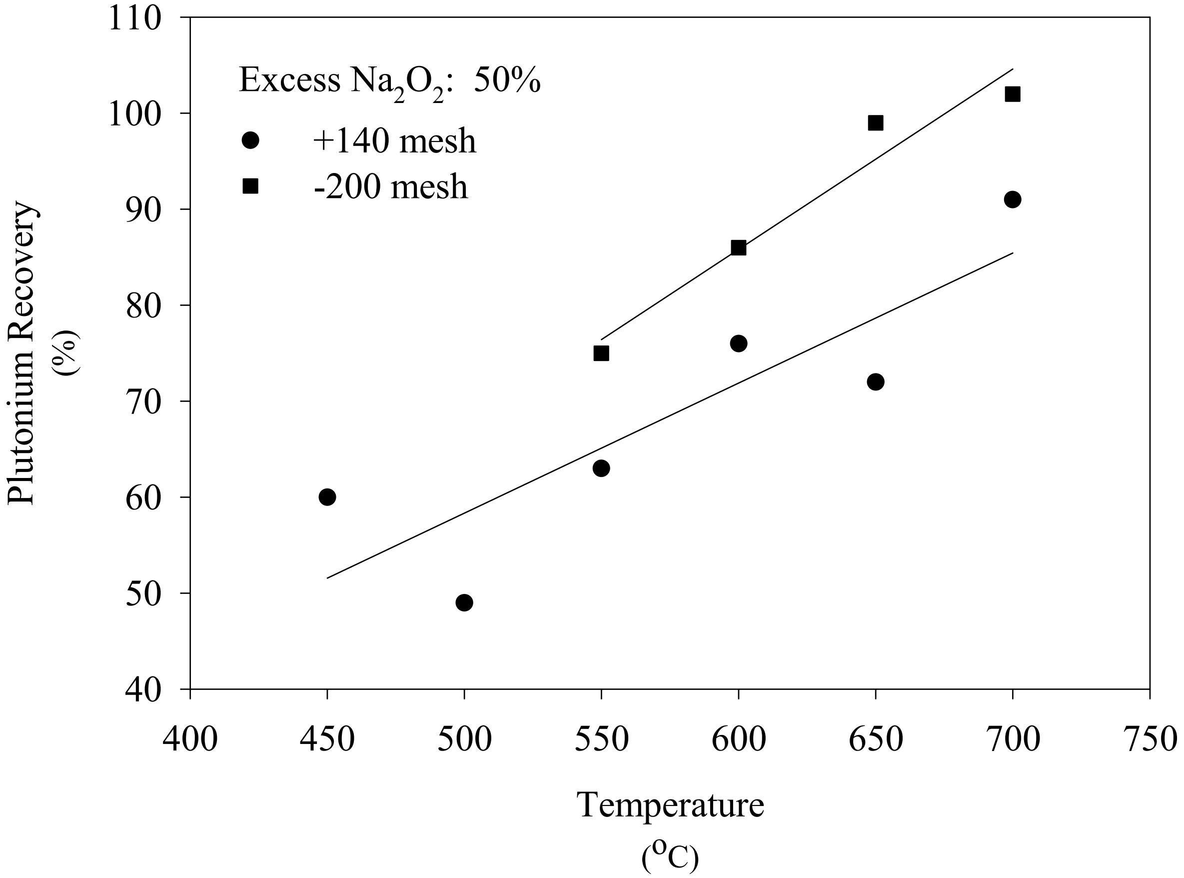

Figure 3 Effect of Excess Na_2O_2 on the Recovery of Plutonium From Rocky Flats Incinerator Ash
(Cans 1 and 2)