Chemical Treatment of Plutonium with Hydrogen Peroxide Before Nitrate Anion Exchange Processing

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CHEMICAL TREATMENT OF PLUTONIUM WITH HYDROGEN PEROXIDE BEFORE NITRATE ANION EXCHANGE PROCESSING

by

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ABSTRACT

The major aqueous process used to recover and purify plutonium at the Los Alamos Plutonium Facility is anion exchange in nitric acid. This process is highly selective for plutonium; however, all plutonium must be as Pu(IV) to form the strongly sorbed anionic nitrato complex. The previous "full-reduction treatment" used at Los Alamos to obtain Pu(IV) results in a three- to fourfold increase in the feed solution volume and the introduction of kilogram quantities of extraneous salts immediately before a process whose function is to remove such impurities. That treatment has been successfully replaced by a single reagent, hydrogen peroxide, which converts all plutonium to Pu(IV), minimally increases the feed volume, and introduces no residual impurities. Safety aspects of this revised chemical treatment are addressed.

I. INTRODUCTION

The nitrate anion exchange process used to separate and purify plutonium at Los Alamos is especially well suited for purifying plutonium because Pu(IV) exhibits the highest distribution coefficient of any ion, and because few other elements show even moderate sorption on the resin.¹ Use of this anion exchange process to efficiently recover plutonium requires, however, that plutonium be in the tetravalent state that forms the strongly sorbed anionic nitrato complex.

Plutonium possesses four oxidation states (III, IV, V, and VI) that readily exist in aqueous solution. The similarity of the oxidation potentials of the plutonium ion pairs in nitric acid, shown in Table I,² demonstrates why at least three oxidation states can exist simultaneously at equilibrium concentrations in nitric acid. The similarities in the potentials of these multiple oxidation states also explain why conversion of all plutonium to Pu(IV) can be challenging.

Hydroxylamine³ and nitrite⁴ have been used to reduce Pu(IV) to Pu(III) in nitric acid. These reductants, however, require nitric acid concentrations of less than 1.4 M and elevated temperatures to reduce Pu(VI) at a useful rate.^{5,6} Investigators have found that the reduction of Pu(VI) to Pu(V) is rapid, but the reduction of Pu(V) to Pu(IV) requires tens to hundreds of hours.⁴ The slow reduction of Pu(V) is attributed in part to the necessity of breaking plutonium-oxygen bonds, as compared to the much faster reactions that involve only electron transfer.⁷

Colvin⁵ found the reduction rate with nitrite in 7 M nitric acid was too low to be of practical use. In another study,⁸ no reduction of Pu(VI) by 0.15 M nitrite in 4 M nitric acid was observed after even 16 hours. Consequently, the conversion of plutonium to Pu(IV) has often been attained in a two-step process that uses a strong reductant such as ferrous ion to reduce all plutonium to Pu(III), after which nitrite selectively reoxidizes Pu(III) to Pu(IV).

Table I. Apparent Potential of Pu Ion Couples in Nitric Acid^a

HNO ₃ , M	Pu(III)-Pu(IV)	Pu(IV)-Pu(VI)	Pu(III)-Pu(VI)
0.10	0.952	0.925	0.934
0.20	0.939	0.949	0.946
0.30	0.935	0.973	0.961
0.40	0.927	0.993	0.972
1.00	0.914	1.054	1.006

^aFrom Chesne.²

The "full-reduction pretreatment" procedure previously used to attain Pu(IV) at Los Alamos is long and tedious. It first requires dilution of the feed solution to a nitric acid concentration of less than 3 M (in which the reduction reaction can occur safely and rapidly), followed by the addition of (1) urea to destroy any nitrite (which otherwise would consume the reductant), (2) hydroxylammonium nitrate to reduce Pu(IV) to (III), (3) ferrous ammonium sulfate to reduce Pu(VI) to (III), and (4) sodium nitrite to reoxidize Pu(III) to (IV). Finally, an appropriate quantity of concentrated nitric acid is added to restore the acid concentration to 7 M, from which Pu(IV) is sorbed on the anion exchange resin.

Disadvantages of this lengthy and complicated procedure are numerous. The initial volume of feed solution often is increased more than threefold as a consequence of the need to dilute and then reconcentrate the nitric acid. This increase in volume not only requires more time for ion exchange processing, it also generates unnecessarily large volumes of highly salted, highly radioactive, acid waste solution, for which concentration and disposal are time consuming and expensive. Moreover, it is counterproductive to load feed solution with large quantities of extraneous salts immediately before a purification process whose purpose is to remove such impurities.

The objective of this investigation was therefore to replace the full-reduction procedure for converting plutonium to Pu(IV) with a simpler procedure that minimizes the dilution of feed solution and the introduction of reagent salts.

II. SAFETY CONSIDERATIONS

Hydrogen peroxide has been shown to rapidly reduce Pu(VI) to Pu(IV) on an analytical scale in 7 to 8 M nitric acid.⁹ Myers¹⁰ in 1956 found hydrogen

peroxide to be a suitable process-scale reductant for Pu(VI). Although hydrogen peroxide is routinely used to precipitate plutonium, this reagent has not found routine application as a reductant in the nuclear industry. The peroxide precipitation procedure, however, requires caution and close adherence to safety regulations, as iron and certain other transition metals are known to catalyze the decomposition of hydrogen peroxide.

Because potential safety hazards are of particular concern within the nuclear industry, the issue of safety was specifically addressed in the study by Myers.¹⁰ Myers found that iron decreases the rate of Pu(VI) reduction, and if present at sufficiently high levels, iron may prevent the reaction from going to completion. However, the tolerance for iron is surprisingly high. A Pu(VI) solution of at least 12.5 grams per liter in 6 M nitric acid was completely reduced in 10 minutes by hydrogen peroxide in the presence of iron at 0.88 grams per liter. The next higher level of iron studied by Myers was 5 grams per liter, and at even this level the reduction was 80% complete in 10 minutes.

It is useful to convert the weight ratios reported by Myers to mole ratios. In the first case, reduction is complete in 10 minutes when the mole ratio of iron to plutonium is 0.30. In the second case, the reduction is 80% complete in 10 minutes even when the mole ratio of iron to plutonium is 1.7! Because levels of iron in process solutions are rarely this high, nothing in the Myers data indicates that hydrogen peroxide is unsuitable for our application. Nor did Myers report unusually vigorous reactions, even at the higher concentrations of iron.

The interaction between hydrogen peroxide and ion exchange resin also has been studied. Bibler and Orebaugh¹¹ reported that Dowex-50, a strong-acid cation exchange resin, can be dissolved completely in one hour in a solution of 6% hydrogen peroxide, 0.1 M

nitric acid, and 0.001 *M* iron at 80°C. These investigators concluded, however, that the iron must be sorbed by the resin for dissolution to proceed, because unsulfonated cross-linked polystyrene beads did not dissolve in an identical solution. This study would seem to preclude the attack of anion exchange resin by peroxide, as iron cannot be sorbed on anion exchange resin as a nitrate complex. Kalkwarf¹² cites evidence that ions of copper, iron, and manganese catalyze the oxidation of resin by nitric acid, even in the absence of peroxide.

Baumann¹³ studied the interaction of hydrogen peroxide with both cation and anion exchange resins. Baumann reported that only anion exchange resins in the hydroxide form reacted appreciably with dilute peroxide. She found the resin to sorb peroxide by ion exchange processes under these conditions, after which peroxide decomposed. Baumann also reported that up to 15% of the strong base exchange sites of this resin could be converted to weak base sites by repeated contact with 0.05 *M* hydrogen peroxide solutions.

Elston¹⁴ reported that Pu(IV) is, in general, 10³ times as effective a catalyst as either Fe(III) or Cu(II) for decomposing hydrogen peroxide in nitric acid. In view of the results of the cited safety-related investigations, and the fact that relatively small quantities of hydrogen peroxide would be required, hydrogen peroxide seemed to be a reasonable and safe candidate for reducing Pu(VI) in our process feed solutions.

III. EXPERIMENTAL

A. Measurement of Pu(VI)

Plutonium processed at Los Alamos always contains americium impurity, the beta-decay daughter of ²⁴¹Pu. Uranium also is a common impurity. A periodic chart display of the anion exchange behavior of 60 elements from nitric acid¹ (Figure 1) shows Pu(IV) to be the most strongly sorbed ion, whereas U(VI) is weakly sorbed, and Am(III) is not sorbed at all. Any plutonium present as Pu(III) or Pu(VI) would be expected to follow the sorption behavior of Am(III) and U(VI), respectively. The non-retention of Pu(III), in fact, is the basis for the rapid elution of purified plutonium, following its reduction to Pu(III) with hydroxylammonium nitrate.

One of the recent advances in plutonium processing at Los Alamos is an On-Line Gamma Monitor.¹⁵ This instrument allows the operator to monitor the behavior of uranium, plutonium, and americium in the effluent stream as it emerges from an anion exchange process. The intended function of this instrument was to provide real-time process status information from

which the operator can verify complete removal of impurities, and also define the elution profile of the plutonium product as it is recovered.

An unexpected fringe benefit of this On-Line Monitor is that it clearly indicates the presence of any Pu(VI) that accompanies U(VI) impurity, as shown in Figure 2. (The presence of Pu(VI) is explained by its incomplete reduction during chemical treatment of feed solution.) This confirmed our suspicion that Pu(VI) was being lost to the effluent waste stream. Consequences of such plutonium loss are (1) a decrease in plutonium product recovery, and (2) the need to recycle waste streams to recover this plutonium.

Because the On-Line Gamma Monitor detects Pu(VI) with high sensitivity, it not only identifies when Pu(VI) is being lost, it also serves as a diagnostic instrument to measure in real time the effectiveness of alternative chemical pretreatments designed to eliminate Pu(VI) from the feed solution.

B. Feed Treatment with Hydrogen Peroxide

A new feed treatment based on hydrogen peroxide was investigated to adjust plutonium to the required (IV) oxidation state. Based on the readout of the On-Line Gamma Monitor, we estimated the Pu(VI) content of typical feed solutions to rarely exceed 10% of the total plutonium. The amount of hydrogen peroxide added was sufficient to stoichiometrically reduce nearly half of the total plutonium, assuming that the reaction proceeds according to

Hydrogen peroxide was added to the feed solution after its adjustment to 7 *M* in nitric acid. This addition was made at least a day before the ion exchange loading, in the proportion of 200 ml of 30% solution per kilogram of plutonium. (A minimum of 100 ml of 30% hydrogen peroxide was added per 25 liters of solution, regardless of the plutonium content, to maintain an adequate peroxide concentration).

The hydrogen peroxide was slowly added in increments of 20 to 25 ml as the feed solution was vigorously mixed by air sparging in a criticality-safe glass column that had at least 20 liters of free space above the solution to allow for expected frothing. The solution was mixed thoroughly for an additional five minutes by air sparging. Finally, the treated solution was allowed to react overnight to allow sufficient time for the conversion of plutonium to Pu(IV) and the decomposition of excess peroxide to go to completion.

Fig. 1. Removal of Elements from Nitric Acid Solution with Strong-Base Anion Exchange Resin.

This treatment procedure has been tested on actual feed solutions that were subsequently processed by full-scale ion exchange at Los Alamos. The outcome of the peroxide treatment was measured by the On-Line Gamma Monitor, near-IR spectrophotometry, and radiometric assay. Stripcharts from the On-Line Gamma Monitor shown represent two identical portions of actual feed solution: without treatment (Figure 2), and with the peroxide treatment (Figure 3). Portions of effluent solution that coincided with the Pu(VI) peak position were collected and assayed for Pu(VI) on a Cary 17D spectrophotometer, with the results shown in Figures 4 and 5.

The visible/near-IR spectrum in Figure 4 shows the characteristic absorbance peak of Pu(VI) at 831 nm, whereas the feed solution after the recommended treatment (Figure 5) shows insignificant Pu(VI) at this same point in the effluent stream. Radiometric assay of these same solutions established that the recommended peroxide treatment of the feed solution decreased the quantity of Pu(VI) that accompanies the uranium impurity in the effluent stream by a factor of approximately 1000.

C. Caution

If incomplete conversion of plutonium to Pu(IV) is suspected, the feed solution may be spectrophotometrically analyzed for the intense 831-nm peak of Pu(VI) before loading the solution on an ion exchange column.

An unusually vigorous reaction when the small increments of hydrogen peroxide are added may indicate higher-than-normal levels of metal ions that catalyze the decomposition of hydrogen peroxide. In those few cases, it may be advisable to use the traditional full-reduction treatment for increased safety.

IV. CONCLUSIONS

1. Hydrogen peroxide, when used as directed, is a simple and safe chemical reductant for converting Pu(VI) to Pu(IV) in 7 M nitric acid feed solutions.
2. The use of hydrogen peroxide reductant eliminates the previous need for a large dilution of the feed solution; this results in substantial savings in processing time and waste treatment costs.
3. Hydrogen peroxide adds no residual impurities to the feed solution, in contrast to the kilogram quantities of reagent salts previously used to obtain Pu(IV). Benefits include significantly higher purity plutonium product and a substantial reduction in the salt content of aqueous waste streams that are concentrated before recycling or disposal.
4. The effectiveness of hydrogen peroxide reductant was initially proven by the On-Line Gamma Monitor developed at Los Alamos, and subsequently by satisfactory performance during several months of routine operations.

Fig. 2. Stripchart Record of Untreated Feed Solution Showing Pu(VI) Peak.

Fig. 3. Stripchart Record of Peroxide-Treated Feed Solution Showing the Absence of a Pu(VI) Peak.

Fig. 4. Absorbance Spectrum Showing Characteristic Pu(VI) Peak at 831 nm.

Fig. 5. Absorbance Spectrum Showing the Absence of Pu(VI) Peak at 831 nm.

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