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ANION EXCHANGE RECOVERY OF PLUTONIUM FROM THE
HANFORD 234-5 BUILDING BUTTON LINE - TASK I OXALATE FILTRATE

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INTRODUCTION

The Hanford 234-5 Building Button Line - Task I Flowsheet calls for the continuous precipitation of plutonium from a 2.7 to 3.1 M nitric acid solution by the continuous addition of 1 molar oxalic acid. The plutonium oxalate precipitate is then continuously removed by a mechanical drum filter. The plutonium losses in this operation range from 0.2 to 1.0 grams per liter and are assumed to be normally about 0.4 grams per liter. In the past, the plutonium was recovered from the oxalate filtrate by a procedure involving several oxalate kill steps, a thermal concentration and a final recovery by solvent extraction.

This document reports the results of a laboratory investigation undertaken to adapt the plutonium anion exchange process⁽¹⁾ to the direct recovery of the plutonium lost to the Task I oxalate filtrate, thus making the Button Line independent of Recuplex operations or backcycle to the separations plants.

SUMMARY

The plutonium left in the Button Line Task I Filtrate can be successfully recovered by the nitric acid anion exchange process, thus isolating the Button Line from any solvent extraction process. Direct acidification of the filtrate to 9M HNO_3 will dissolve the precipitated plutonium oxalate and yield an ion-exchange feed which will permit the resin to be loaded to 70 grams of plutonium per liter of resin. No added resin damage will be caused by the increase in nitric acid concentration, and feed containing fluoride at least as high as 0.2 M can be used when aluminum is added to complex the fluoride. If a high throughput rate is necessary, the process should be operated at 58 to 60 C. For low throughput plants, ambient temperature is permitted. Permutit SK is the resin of choice because of its superior kinetics and resistance to chemical and radiolysis damage.

DISCUSSION

Twenty eight liters of Task I oxalate filtrate were obtained in four 2-gal polyethylene bottles. Preliminary experimental work showed that approximately 90% of the plutonium contained in each bottle had precipitated out and settled to the bottom of the bottles. Furthermore, after removal of the supernate, the plutonium oxalate precipitate dissolved quite rapidly in 15 M HNO_3 and remained in solution when the 15 M HNO_3 was diluted to 7.2 M with water. When the 15 M HNO_3 solution of plutonium was recombined with the oxalate supernate and the resultant solution adjusted to 7.2 M HNO_3 , some of the plutonium reprecipitated. The rate of reprecipitation was quite slow. The amount which reprecipitated was proportional to both the oxalate and plutonium concentrations. No exact solubility measurements were made.

A preliminary experiment was performed to determine the plutonium capacity of Permutit SK resin from an oxalate filtrate solution adjusted to 7.2 M HNO_3 . Fourteen liters of oxalate filtrate were transferred from two 2-gal polyethylene transfer bottles to a feed preparation bottle. The plutonium oxalate precipitate remaining in the two bottles was dissolved in 15 M HNO_3 and combined with the oxalate filtrate in the feed bottle. Sufficient concentrated HNO_3 was then added to the combined solution to bring the concentration up to 7.2 M HNO_3 . After mixing for several hours, the feed was pumped through a 0.28 $\text{cm}^2 \times 110 \text{ cm}$ bed of Permutit SK 30-50 mesh resin at 18.6 ml per min cm^2 . The resin column was thermostated to 58 C. The column effluent solution was sampled periodically during the absorption cycle and the plutonium content of each sample was determined. The concentration of plutonium in the feed for this run was 0.138 grams per liter, and the resin plutonium absorption capacity at 50% plutonium breakthrough was found to be only 20.3 grams per liter of resin. The absorption or so called "breakthrough" curve is given as A in Figure 1 with two other breakthrough curves for comparison.

In a second experiment, a feed solution containing 0.177 grams of plutonium per liter in 7.2 M HNO_3 was prepared. No oxalic acid or other impurities were present. This feed was then pumped through a 0.28 cm^2 x 110 cm bed of 30-50 mesh Permutit SK resin, thermostated to 58 C, at a flow rate of 19.6 ml per min, cm^2 and the effluent solution was examined for plutonium. The breakthrough curve shown as B of Figure 1 was obtained from this data. This run was repeated but with a feed solution containing 0.718 grams of plutonium per liter. The breakthrough curve for the more concentrated feed is shown as C of Figure 1. A capacity of 74 grams of plutonium per liter of resin at 50% plutonium breakthrough, calculated from curve C, is the maximum capacity obtainable for Permutit SK with any feed solution under reasonable operating condition.⁽¹⁾

The lower resin capacity in run A, compared to run B, clearly shows the adverse effect of oxalate complexing on plutonium absorption from 7.2 M HNO_3 . Run B yielded a lower capacity than run C because of the adverse effect on the equilibrium of the lower feed concentration in run B. It has been shown⁽¹⁾ that at 60 C and at reasonable mass flow rates, the plutonium capacity of Permutit SK is but little affected by changes in the feed concentration above a threshold concentration of approximately 0.25 grams of plutonium per liter of feed. Below this value, a decrease in the feed concentration lowers the resin capacity. At 25 C and a 50% slower flow rate, the threshold concentration is decreased by the favorable temperature shift of the equilibrium. Curves B and C were included in Figure 1 in order to point out that the resin capacity in run A was lower than the theoretical maximum of 70 to 74 grams of plutonium per liter of resin for two reasons: (1) the relatively low total plutonium concentration of the feed would result in a lower capacity with the flow rate and temperature conditions used, i. e. curve B; (2) in addition, in 7.2 M nitric acid sufficient oxalate complexing of the plutonium takes place that the capacity of the resin is further decreased, i. e., curve A.

Higher Nitric Acid Feed Concentrations

Several attempts were made to reduce the oxalate complexing of plutonium in 7.2 M HNO_3 anion-exchange feeds by the addition of cations which form strong, stable oxalate complexes. The most effective of these was iron but the increase in resin capacity was slight.

The disassociation of oxalic acid was suppressed and the complexing of plutonium quite effectively decreased, however, by increasing the nitric acid concentration to a value between 9 and 10 molar. This was demonstrated in two runs.

Fourteen liters of Task I Oxalate Filtrate, ranging in concentration from 0.6 to 0.9 grams of plutonium per liter, were next obtained. The solution and the settled oxalate precipitate were transferred to a 25-liter feed-preparation bottle and the acid content increased to 7.0 M HNO_3 . This treatment caused the solution to turn slightly green, and part but not all of the plutonium oxalate precipitate to dissolve. The stock solution was then vigorously stirred to homogenously suspend the precipitate and four 5-liter fractions were withdrawn. The feed for run D was then prepared by adding one additional liter of concentrated HNO_3 to one of the 5-liter fractions and mixing the solution vigorously. The addition of the extra acid increased the nitric acid concentration of this feed to 8.7 M and caused all but a very small trace of the precipitate to go into solution. The feed supernate had a plutonium concentration of 0.687 grams per liter. The feed was pumped through a $0.28 \text{ cm}^2 \times 110 \text{ cm}$ bed of 30-50 mesh Permutit SK resin at a rate of 17.2 ml per min, cm^2 . The column was thermostated to 58 C. The breakthrough curve for this run is D of Figure 2 and the resin capacity at 50% breakthrough was 75 grams of plutonium per liter of resin. This high value shows that use of the slightly higher acid concentration overcomes the effect of oxalate complexing (probably by inhibiting the ionization of oxalic acid) and allows the theoretical capacity of the resin to be achieved.

The effect of an even higher nitric acid concentration was determined in run E. This run was similar to the previous run except 2 liters of concentrated HNO_3 were added to a 5-liter stock feed solution. The nitric acid and plutonium concentrations of the feed were 10 M and 0.592 grams per liter respectively. The temperature was again 58 C and the feed flow rate was 18.8 ml per min, cm^2 . The breakthrough curve is given in Figure 2 as curve E, and the plutonium capacity to 50% breakthrough was 68 grams per liter. Curves A and C of Figure 2 are the same curves, respectively, in Figure 1. They are presented in Figure 2 for comparative purposes.

The results and observations of runs D and E yield several important facts. There seemed to be a very definite change in the feed solution as the nitric acid concentration was increased from 7 M to 8.6 M. The color changed to a much more intense green and the precipitate dissolved. The color intensification was due to the increased concentration of the hexanitrate plutonium IV species, accomplished in part by the solubilization of the precipitated plutonium and in part by the destruction of soluble plutonium oxalate complex species. Figure 2 clearly indicates that there is an optimum nitric acid concentration and that it is in the region of 8.8 M. This optimum acid concentration would be shifted by the absorption temperature and by the oxalate concentration but the shift would not be significant from a process point of view. The decrease in absorption capacity at 10 M HNO_3 is real and is a result of the formation of the protonated plutonium species described elsewhere.⁽¹⁾ In run D at a resin loading of approximately 40 grams of plutonium per liter of resin, i. e., after 55 resin bed volumes of feed had passed through the column, the concentration of plutonium in the column effluent had increased to only 0.004 grams per liter. Since only plutonium in the +4 oxidation state is able to form absorbable anionic nitrate complexes, run D clearly demonstrated the absence from this particular sample of Task I filtrate of any significant amounts of plutonium in oxidation states other than +4.

Fluoride Feed Solutions

The possible adverse effect of a large amount of fluoride in the Task I oxalate filtrate was examined. Twenty-five ml of 29 M HF were added to one of the 5-liter feed fractions described in the previous section of this report. This would correspond to a fluoride concentration of 0.21 M in the Task I oxalate filtrate. After vigorous stirring for a period of several hours, 250 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 2 liters of concentrated HNO_3 were also added. The added aluminum would correspond to a concentration of 0.20 M in the Task I oxalate filtrate. The molar ratio of aluminum to fluoride would therefore be 1.00:1.09, respectively. The feed mixture was stirred over night. Then the precipitate-free solution was forced through a $0.28 \text{ cm}^2 \times 110 \text{ cm}$ bed of 30-50 mesh Permutit SK at a flow rate of 16.5 ml per min, cm^2 . The column was thermostated at 58 C. The 50% breakthrough capacity of 69 grams of plutonium per liter of resin from this 10 M HNO_3 feed was essentially identical with run E and indicates that fluoride concentrations in the oxalate filtrate, at least as high as 0.21 M and perhaps higher, do not trouble the absorption process when an equivalent molar amount of aluminum is added to the feed. It is possible that less aluminum would be equally effective.

Effect of Temperature

The effect of temperature upon resin plutonium capacity was investigated in run F. This run was an exact duplicate of run D (described earlier) except the column temperature was decreased from 58 to 25 C and the flow rate was decreased from 17.2 to 8.7 ml per min, cm^2 . The breakthrough curve is shown in Figure 3 and the resin capacity at 50% breakthrough was 43 grams of plutonium per liter of resin. The resin capacity for run F was decreased because of the adverse effect of the lower temperature on the absorption kinetics. By reducing the feed flow rate to a very low value (too low for a practical plant process), curve F could be shifted to a point slightly beyond curve D. This is possible because, while the lower temperature

adversely affects the absorption rate, it favors the absorption equilibrium.⁽¹⁾ In process applications not demanding high throughputs, ambient temperature operation is successful with Permutit SK resin because of its very fast elution kinetics.

Resin Stability in 10 M HNO_3

The general stability of anion resins is described elsewhere.⁽¹⁾ Due to some concern over possible changes in the stability of Permutit SK resin on increasing the nitric acid concentration from 7.2 to 10 molar, one experiment was made to investigate this problem. A 0.28 cm² jacketed column was filled with 30-50 mesh Permutit SK resin. The resin was converted to the nitrate cycle with 0.6 M HNO_3 (before treatment with more concentrated acid) to minimize cracking. The resin bed had a depth of 120 cm in the nitrate cycle. The column jacket temperature was increased to 58 C and fresh 10 M HNO_3 was allowed to flow through the bed for 7 weeks at a rate of 1 liter per day. At the end of 7 weeks, the resin was allowed to stand static in 10 M HNO_3 for 1 week at 25 C. The resin plutonium absorption capacity at 50% breakthrough was then measured and found to be 70 grams of plutonium per liter of resin. The feed flow rate was 19.3 ml per min, cm², the temperature 58C, and the plutonium feed concentration 0.62 grams per liter. The breakthrough curve (G of Figure 4) is quite similar to the standard curve C for fresh resin under similar loading conditions. Obviously increasing the nitric acid from 7 M to 10 M has little harmful effect on the resin.

Potential Applications

Although this effort was aimed at a solution to a particular problem, the results obtained are valid for other feed solutions of this general type. If large volumes of solutions are to be processed, continuous contactors similar to that used in the Hanford Purex Plant could be used. The increase in the nitric acid concentration of the feed would have little effect upon the operation of the equipment. Where smaller volumes of feed must be processed, a series of two or three static-bed columns of appropriate size can be used to give continuous or near-continuous processing.

One possible column arrangement is illustrated in Figure 5. With columns 1 and 2 connected in series as shown in Part A, feed solution would be pumped through columns 1 and 2 until the monitors indicated that the plutonium concentration in the effluent from column 1 was 50% or more of the plutonium concentration in the influent feed solution, and at the same time the effluent from column 2 was free of plutonium. At this point the feed cycle would be interrupted and a volume of 7.2 M HNO_3 wash equivalent to 2 to 4 resin bed volumes would be pumped through columns 1 and 2. No plutonium will be lost to waste during either of these two steps as long as the feed cycle is terminated with the leading edge of the plutonium absorption band sufficiently high on column 2 to allow absorption room for the feed solution contained in the bed void space. Following the wash cycle, the eluting solution (0.6 M HNO_3) is pumped down-flow through column 1 at 1 to 2 ml per min, cm^2 until the elution band nears the bottom of column 1 and the 7.2 M HNO_3 , previously contained in column 1, is nearly completely displaced into column 2. At this point column 1 is disconnected and columns 2 and 3 are connected as shown in Figure 4, Part B. The feed absorption cycle on columns 2 and 3 is then initiated and run concurrently with the product elution cycle from column 1. If the point at which column 1 is disconnected from the system and the collection of product started is made when the column 1 effluent contains 1 to 2 grams of plutonium per liter, a high average product concentration (greater than 40 grams of plutonium per liter) can be obtained with no recycle. The desirable time to make the valve change can be determined by an effluent monitor or visually if glass columns are used. The cyclic operation is then repeated with columns 2, 3 and 1. Plutonium mass flow rates up to 50 mg per min, cm^2 can be used if the columns are thermostated and operated at 50 to 60 C. The rate should be cut to 30 mg per min, cm^2 for room temperature operation and even less if a resin other than Permutit SK is used.

This research work was nearing completion prior to the Recuplex criticality incident. As a result of that incident and on the basis of preliminary information, a system of columns similar to those shown in Figure 4 was designed and is now being constructed for processing Button Line Oxalate filtrates^(2, 3)

FIGURE 1

The Effect of Oxalate on Resin Absorption of Plutonium

FIGURE 2

The Effect of a Higher Nitric Acid Concentration on Resin Absorption of Plutonium

FIGURE 3

The Effect of Absorption Temperature on Resin Capacity

FIGURE 4

Resin Stability in 10 Molar Nitric Acid

FIGURE 5

Multi-Column Anion Exchange Operation

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