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S. Fredric Marsh

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MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

THE EFFECT OF FLUORIDE AND ALUMINUM ON THE ANION EXCHANGE OF PLUTONIUM FROM NITRIC ACID

by

S. Fredric Marsh

ABSTRACT

Anion exchange in nitric acid is a prominent aqueous process used to recover and purify plutonium from impure nuclear materials. This process is sensitive to fluoride ion, which complexes plutonium in competition with the anionic nitrate complex that is strongly sorbed on the anion exchange column. Fluoride interference traditionally has been counteracted by adding a masking agent, such as aluminum, that forms competing complexes with fluoride. The interfering effect of fluoride is known to be a function not only of the fluoride-to-aluminum ratio but also of the fluoride-to-plutonium ratio, yet no comprehensive study of this three-component system has previously been reported. This report summarizes a Los Alamos study of the effect of 25 fluoride-aluminum-plutonium combinations on the anion exchange sorption of plutonium. Five aluminum-to-plutonium ratios ranging from 0.10 to 10 were each evaluated at five fluoride-to-aluminum ratios that ranged from 0 to 6. The fluoride-to-plutonium ratio has a greater influence on plutonium sorption than does the fluoride-to-aluminum ratio. Aluminum was less effective as a masking agent than had been assumed, because measurable fluoride interference occurred at all levels of added aluminum.

INTRODUCTION

Anion exchange in nitric acid is the principal aqueous process used to recover and purify plutonium at the Los Alamos Plutonium Facility. A Los Alamos development effort directed at improving this process has resulted in (1) the replacement of previously used gel-type resin with macroporous resin,¹ (2) an improved feed treatment procedure that uses only hydrogen peroxide,² and (3) a systematic evaluation of the effect of plutonium concentration and solution flow rate on the effective capacity of the selected macroporous resin.³

Aqueous feed solutions used in this process always contain fluoride, which is required to dissolve refractory plutonium oxide feed materials at an acceptable rate. Fluoride also is required to dissolve the large quantities of silicate materials often found in plutonium-contaminated scrap materials.

Fluoride accelerates the dissolution of difficult-to-dissolve compounds of plutonium because it forms highly stable complexes with plutonium. The anion exchange separation that follows, however, depends on the anionic nitrate complex of plutonium that strongly sorbs on the resin. Hence, the plutonium fluoride complex that is an asset during dissolution is a liability

during the subsequent anion exchange separation because it interferes with formation of the plutonium nitrate complex.

Fluoride interference can be reduced by adding a masking agent known to form a competing, high-stability, soluble fluoride complex. Aluminum commonly is added to plutonium feed solutions for this purpose. The resulting solutions contain plutonium, fluoride, and aluminum in relative amounts that vary over wide ranges. The many competing equilibria involved in such solutions make subsequent anion exchange behavior of plutonium difficult to predict.

Interference by fluoride during the processing of plutonium by anion exchange is known to be a function of not only the fluoride-to-plutonium ratio but also the aluminum-to-fluoride ratio. Aluminum commonly has been added to mask the interference of fluoride during most of the nearly thirty years that nitrate anion exchange has been used to purify plutonium. Yet we are unable to find a published, systematic study of the effect of specific quantities of aluminum and fluoride on the plutonium anion exchange process. Our investigation provides this previously unavailable information, which should facilitate the processing of fluoride-containing solutions of plutonium.

EXPERIMENTAL

Experimental Design

Plutonium. The plutonium concentration was maintained at a constant level of four grams per liter throughout this series of experiments. The oxidation state of all plutonium used in this study was adjusted to Pu(IV) with hydrogen peroxide,² after which the absence of Pu(VI) and Pu(III) was confirmed by spectrophotometric analysis.

Aluminum. Five levels of aluminum, relative to plutonium, were obtained by adding appropriate quantities of 2.2 *M* aluminum nitrate solution. The selected aluminum-to-plutonium mole ratios were 0.10, 0.33, 1.0, 3.0, and 10.

Fluoride. Fluoride was added, as hydrofluoric acid, to provide five fluoride-to-aluminum ratios at each level of aluminum to plutonium. The selected mole ratios of fluoride to aluminum were 0, 1.5, 3.0, 4.5, and 6.0.

Nitric Acid. Sufficient nitric acid and water were added to maintain the total acid concentration

at 7 *M*. (The small amount of hydrogen ion present as hydrofluoric acid was included in the calculation of total acid concentration.)

Nitrate. Because aluminum was added as the aluminum nitrate salt, three moles of additional nitrate were added with every mole of aluminum. This provided additional nitrate that contributed to a varying total nitrate concentration in excess of the nitrate present as 7 *M* nitric acid.

Resin. Lewatit MP-500-FK (40- to 70-mesh) macroporous anion exchange resin (obtained from M bay Chemical Company, Philadelphia, Pennsylvania) was used in this study. Individual 10-milliliter portions of these solutions were contacted with portions of air-dried, nitrate-form Lewatit resin. A weighed amount of air-dried resin that corresponded to a 2-milliliter volume of nitrate-form resin in water was taken for each contact. (The specified volume of wet resin weighed 0.66 gram in air-dried form.)

Assay Technique

Dynamic batch contacts of each combination of solution and resin were achieved using a wrist-action shaker. Each solution initially contained the selected quantities of plutonium, aluminum, and fluoride. After each dynamic contact period, a measured portion of solution was removed for assay of plutonium using gamma spectrometry, by assaying the 129-keV gamma ray of ²³⁹Pu.

After the first dynamic contact period was completed, the shaker was stopped only long enough to remove a solution aliquot for radioassay. The dynamic contact was quickly resumed until the second contact period had been completed, after which another aqueous portion was removed for assay. This procedure was repeated until three aqueous portions had been removed for assay after dynamic contact periods of 10, 20, and 60 minutes.

The fraction of initial plutonium in each contacted solution was calculated relative to the quantity of ²³⁹Pu in an identical portion of uncontacted solution. From these data, plutonium distribution coefficients were calculated for three contact periods at each of the 25 fluoride-to-aluminum-to-plutonium ratios. Sequential measurements for multiple contact periods provided important sorption kinetics data for the plutonium nitrate complex, whose sorption rate is known to be particularly slow.

Distribution coefficients (*K_d*) were calculated as follows:

$$Kd = \frac{\text{concentration of element per milliliter of wet resin}}{\text{concentration of element per milliliter of solution}}$$

In practice, Kd values were calculated by the equation:

$$Kd = [(A_i - A_f)/A_f] / (V_l/V_r),$$

where

A_i is the activity of the actinide initially in the liquid,

A_f is the actinide activity in the liquid after contact,

V_l is the liquid volume, and

V_r is the volume of wet resin.

Because each fluoride-to-aluminum-to-plutonium combination was used for a series of three sequential contact measurements, the liquid-to-resin ratio changed as each aqueous portion was removed for assay. We corrected for this changing ratio as well as for the decrease in the total activity remaining in the vial after the removal of each aqueous portion.

We elected to express Kd in terms of wet-resin volume, contrary to the common practice of expressing Kd in terms of dry-resin weight, for reasons explained in detail in a previous report.¹ Whichever convention is used, however, the relative effect of fluoride and aluminum remains the same.

RESULTS AND DISCUSSION

All solutions used in this study were prepared to initially contain the appropriate amounts of fluoride, aluminum, nitric acid, and resin. Plutonium was added last, immediately before the dynamic contact began. Under normal circumstances, the olive green color of the plutonium nitrate complex appears promptly when Pu(IV) is added to 7 M nitric acid. When plutonium was added to these solutions that contained varying ratios of fluoride and aluminum, however, a wide range of colors was observed. Some solutions showed the expected green color, some showed a lighter shade of green, and some showed no green. The intensity of the green color indicates the concentration of plutonium nitrate complex remaining in solution, and thus, the extent of fluoride interference in each case.

Because the maximum aluminum-to-plutonium ratio was 10 and the maximum fluoride-to-aluminum ratio was 6, the highest fluoride-to-plutonium ratio in this study was 60. At this maximum fluoride-to-plutonium ratio, and in a few other solutions where the fluoride-to-plutonium ratio was high, the expected

green color of the plutonium nitrate complex was either absent or quite pale. Furthermore, in those solutions in which the fluoride-to-plutonium ratio was 60 or 45, a straw-colored precipitate, assumed to be PuF_4 , was observed.

If plutonium were being precipitated from certain solutions, in competition with removal from solution by ion exchange processes, an assay of plutonium remaining in the liquid portion after the contact would seriously overestimate the quantity of plutonium sorbed on the resin.

The total absence of green color in certain high-fluoride solutions confirmed that the fluoride level was sufficient to prevent formation of the plutonium nitrate complex. In the three solutions in which precipitate formation precluded measurement of the quantity of plutonium sorbed on the resin, we can confidently conclude that fluoride interference was severe, even though we are unable to provide quantitative values.

Experimental Data

The experimental data are presented in two formats. In Figs. 1 through 5, the ratio of aluminum-to-plutonium is held constant to demonstrate the effect of varying fluoride-to-aluminum ratios. In Figs. 6 through 10, the fluoride-to-aluminum ratio is held constant to demonstrate the effect of varying aluminum-to-plutonium ratios.

Figure 1 shows that even small amounts of fluoride measurably suppress the distribution coefficient of Pu(IV) onto the resin. The interference of fluoride increases for a given fluoride-to-aluminum ratio as the fluoride-to-plutonium ratio increases, as shown in Figs. 1 through 5. (The fluoride-to-plutonium ratio is the product of the fluoride-to-aluminum ratio and the aluminum-to-plutonium ratio in Figs. 1 through 5.)

Figure 6 shows the effect of increasing levels of aluminum nitrate when fluoride is absent. The increasing distribution coefficient of Pu(IV) at the higher aluminum-to-plutonium ratios is attributed to the increasing concentration of nitrate ion present as aluminum nitrate. In the maximum case of Al/Pu = 10, the concentration of additional nitrate ion is 0.5 M.

Figures 7 through 10 present the same data shown in Figs. 1 through 5 in a different format. These figures show the effect of increasing total amounts of fluoride when the fluoride-to-aluminum ratio is held constant. The increasing interference of fluoride at the higher fluoride-to-plutonium ratios is apparent. (The

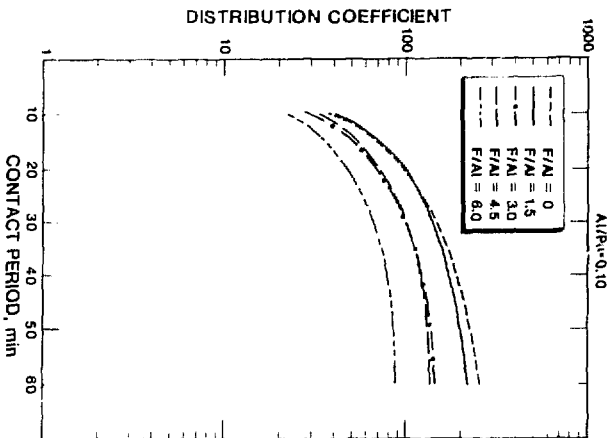


Fig. 1. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of fluoride to aluminum for $\text{Al/Pu} = 0.1$, as a function of dynamic contact time.

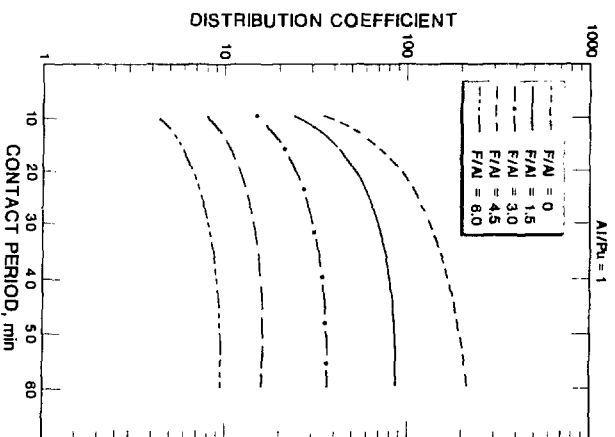


Fig. 3. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of fluoride to aluminum for $\text{Al/Pu} = 1$, as a function of dynamic contact time.

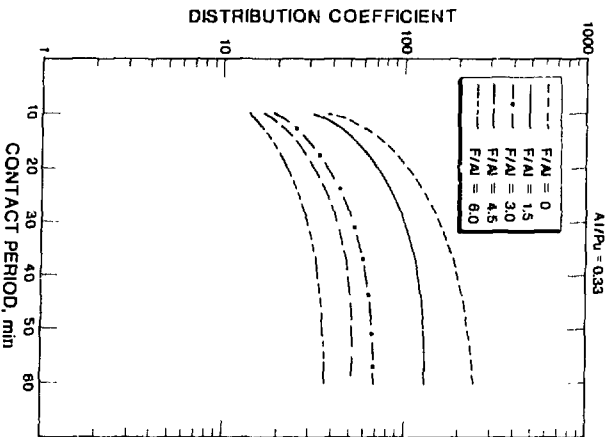


Fig. 2. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of fluoride to aluminum for $\text{Al/Pu} = 0.33$, as a function of dynamic contact time.

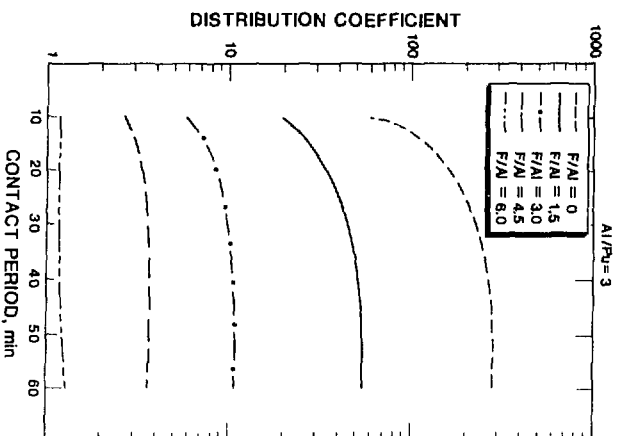


Fig. 4. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of fluoride to aluminum for $\text{Al/Pu} = 3$, as a function of dynamic contact time.

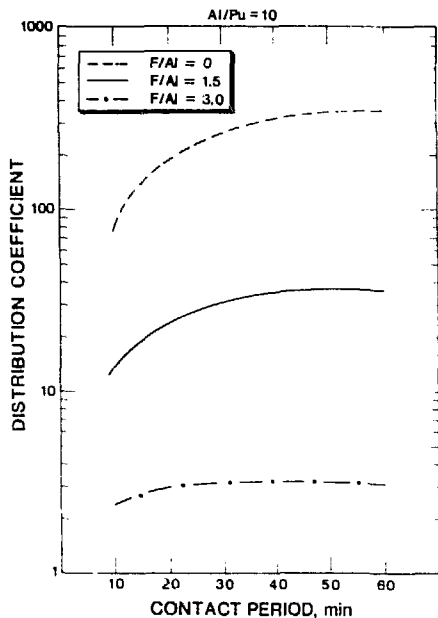


Fig. 5. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of fluoride to aluminum for Al/Pu = 10, as a function of dynamic contact time.

fluoride-to-plutonium ratio may be calculated as previously explained for Figs. 1 through 5.) Figures 9 and 10 show the almost total interference of fluoride in solutions in which Al/Pu = 3. Precipitation prevented measurement of distribution coefficients at the highest levels of fluoride in solutions for which Al/Pu = 10, as shown in Figs. 9 and 10.

CONCLUSIONS

1. All levels of fluoride tested measurably suppress the distribution coefficient of plutonium, no matter how much aluminum is added. Although aluminum counteracts the interference of fluoride to a

large extent, some interference always occurs. Aluminum therefore is less effective for masking fluoride than had been supposed.

2. Aluminum is much more effective as a masking agent at a given fluoride-to-aluminum ratio when the fluoride-to-plutonium ratio is low, than when the fluoride-to-plutonium ratio is high. This indicates that the anion exchange sorption of plutonium is more affected by the fluoride-to-plutonium ratio than by the fluoride-to-aluminum ratio.

3. On the basis of this study, we recommend that the quantity of aluminum added be approximately equimolar with the amount of fluoride present. Even at this ratio, however, some interference is to be expected, particularly when fluoride is high relative to plutonium.

4. Excessive aluminum should be avoided, as its competition for fluoride converts soluble fluoro complexes of elements such as silicon and tungsten to insoluble oxides, which can coat ion exchange resin and plug process filters and valves.

5. We had hoped that this study would result in a general equation that would define the level of aluminum required to mask any specified amount of fluoride. Unfortunately, the complex interactions of this chemical system do not lend themselves to such simplistic interpretation. It appears, instead, that each specific fluoride-to-plutonium ratio may require a unique amount of aluminum to effectively mask fluoride, without causing the precipitation problems described in the preceding paragraph.

We therefore are generating digitized, visible/near-infrared spectra for all 25 solutions examined in this study. These data will be processed by modern chemometric techniques to produce an initial data base that eventually will allow us to use on-line spectrophotometric measurements as a basis for controlling and operating the anion exchange process at near-optimum efficiency.

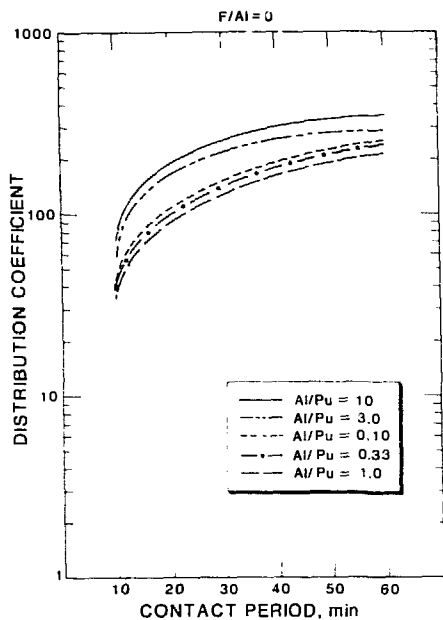


Fig. 6. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for $F/AI = 0$, as a function of dynamic contact time.

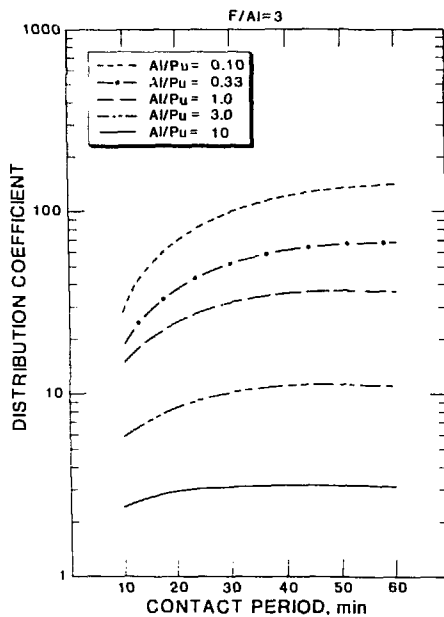


Fig. 8. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for $F/AI = 3$, as a function of dynamic contact time.

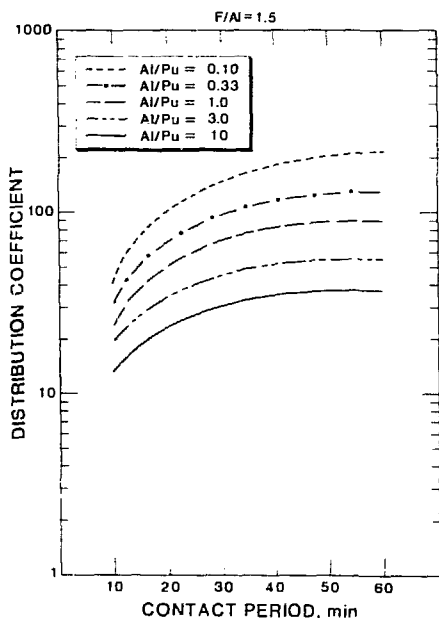


Fig. 7. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for $F/AI = 1.5$, as a function of dynamic contact time.

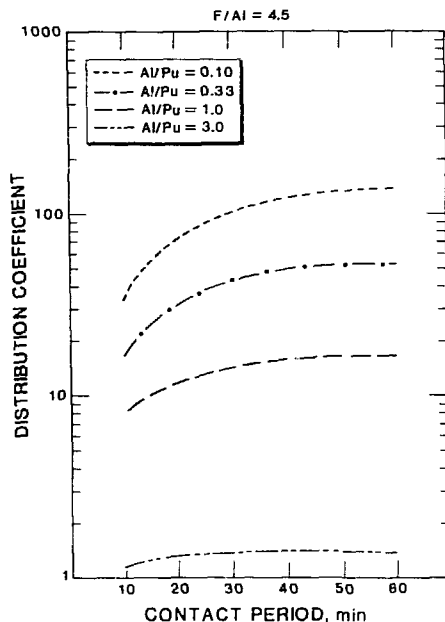


Fig. 9. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for $F/AI = 4.5$, as a function of dynamic contact time.

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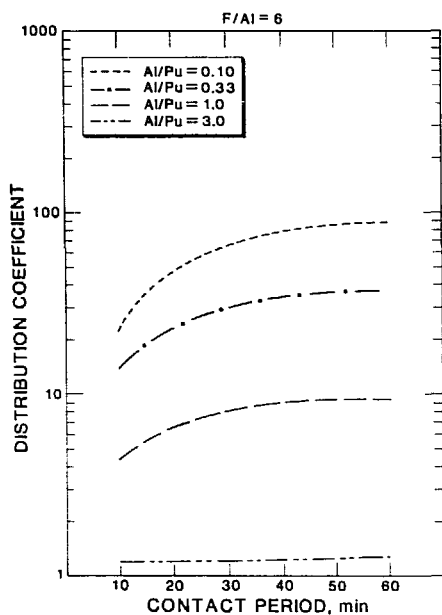


Fig. 10. Sorption of Pu(IV) on Lewatit MP-500-FK anion exchange resin from 7 M nitric acid that contains varying ratios of aluminum to plutonium for $F/Al = 6$, as a function of dynamic contact time.