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Separation of Thorium Impurity from Plutonium in the Nitrate Anion Exchange Process

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SEPARATION OF THORIUM IMPURITY FROM PLUTONIUM IN THE NITRATE ANION EXCHANGE PROCESS

by

S. Fredric Marsh, Bobby J. Phillips,
Elizabeth A. Aldaz, and Willard E. Williams

ABSTRACT

Thorium is a common impurity in many materials processed at the Los Alamos Plutonium Facility. Although the thorium impurity level is usually less than 1000 ppm, it frequently exceeds the maximum allowable limit of 100 ppm. Thorium is especially difficult to separate from plutonium because it accompanies plutonium in the three aqueous nitrate processes used at Los Alamos: nitrate anion exchange, oxalate precipitation, and peroxide precipitation. Nitrate anion exchange, the major aqueous plutonium purification process, has recently been modified to remove most of the thorium from sorbed plutonium by washing the column with 4.7 *M* nitric acid-0.007 *M* hydrofluoric acid. This chromatographic washing technique requires careful process control that is readily attainable with the recently developed Los Alamos On-Line Gamma Monitor. The successful separation of thorium using this modification has been demonstrated in routine, full-scale, nitrate anion exchange operations.

INTRODUCTION

Since 1959, the Los Alamos Plutonium Facility has used anion exchange in nitric acid as the major aqueous process to recover and purify plutonium from a wide variety of impure materials. Similar nitrate anion exchange processes are also routinely used in many other nuclear processing facilities. This system is nearly ideal for plutonium (Fig. 1) because no ion of any other element is more strongly sorbed than Pu(IV), and few other ions show even moderate sorption from nitric acid.

Figure 1 shows that Np(IV) and Th(IV) are the second and third most strongly sorbed metal ions, respectively. Neptunium is routinely separated from plutonium at the Savannah River Plant by controlling the multiple oxidation states of these two actinides. The fact that thorium exists only as Th(IV) in solution, however, makes it considerably more difficult to separate from plutonium.

Thorium is of particular concern at Los Alamos because the thorium level in most of our impure feed materials exceeds the 100 ppm specification limit. Relatively few feeds, however, contain thorium levels above 1000 ppm, which means that a decontamination factor of 10 would be adequate to bring the thorium level of most feed materials to within specifications.

Figure 2 is a diagram of the plutonium purification process. If the PuO_2 product from the ion exchange process is sufficiently pure, this oxide can be converted to metal directly using a highly efficient process whose waste is essentially free of plutonium. If the ion exchange process yields impure oxide, however, additional purification must be done using electrorefining to obtain specification-grade metal.

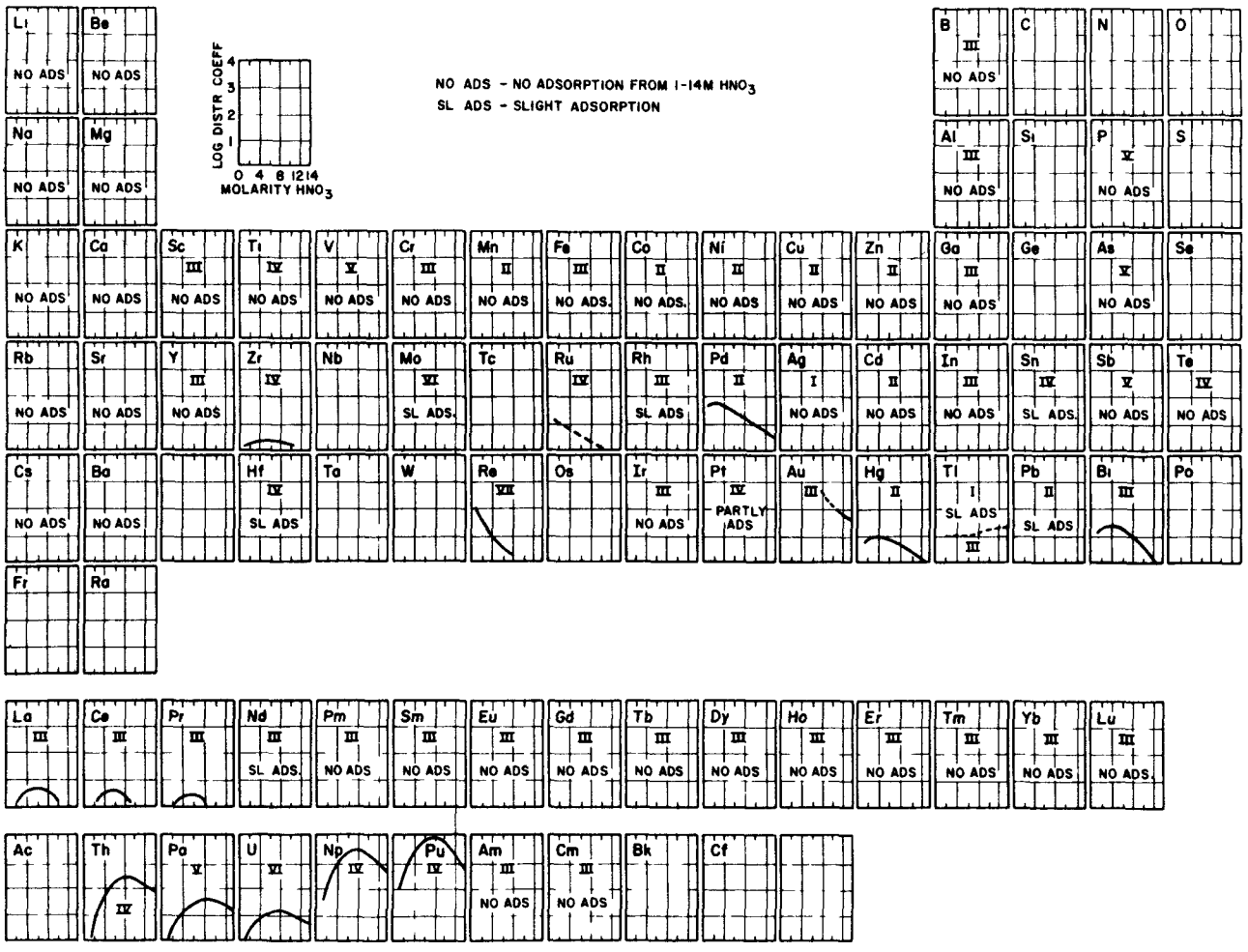

Fig. 1. Distribution of elements from nitric acid onto strong-base anion exchange resin [1]

The electrorefining process produces a significant recycle loop (Fig. 2) in which all of the impurities, now at higher relative concentrations, accompany the recycled plutonium. Thus, impurities not separated initially are processed repeatedly (at increasingly higher concentrations) as part of the electrorefining recycle stream. Thorium, which in the past has accompanied plutonium almost quantitatively, has been recycled repeatedly in this manner.

The objective of this development effort was to eliminate thorium as one of the major remaining impurities from this recycled waste stream by achieving a thorium decontamination factor of at least 10, without major modifications to the existing nitrate anion exchange procedure.

DISCUSSION

In a traditional nitrate anion exchange procedure, the anionic Pu(IV) nitrate complex is first sorbed on the resin from 7 *M* nitric acid, and then washed with pure 7 *M* nitric acid to elute all weakly sorbed and entrained impurities. The decision to use 7 *M* acid to sorb Pu(IV) is reasonable because the sorption of Pu(IV) peaks at this nitrate concentration. The use of 7 *M* nitric acid wash solution to remove weakly held impurities thus ensures that Pu(IV) remains sorbed on the resin. A consequence of using 7 *M* nitric acid wash, however, is that Th(IV) also exhibits peak sorption from this acid concentration, which guarantees that essentially no decontamination from thorium is achieved.

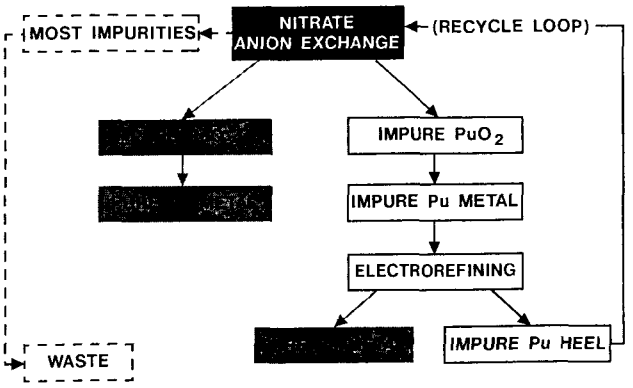

Fig. 2. Diagram of the plutonium purification process used at Los Alamos.

The Pu(IV) distribution coefficient of >3000, as determined by Faris and Buchanan,[1] is much higher than that required to ensure its complete retention on the resin. It therefore seemed reasonable that a lower concentration of nitric acid in the wash solution might adequately retain Pu(IV), yet allow a significant portion of the Th(IV) to be eluted and thereby separated from plutonium.

This idea was tested during small-scale, 15-minute batch contact experiments using Lewatit^{TM} MP-500-FK resin with radiotracers of uranium, thorium, and plutonium. This short dynamic contact time was selected to simulate the actual residence time of feed solutions as they pass through the resin bed during the process, whereas published distribution coefficients typically are equilibrium values obtained after contact periods as long as many days. The Lewatit^{TM} MP-500-FK resin used for this study is the same resin used in full-scale process columns.[2] From the small-scale experimental results (Fig. 3), it appeared that nitric acid concentrations between 4 and 5 M would adequately retain Pu(IV), while achieving some separation from Th(IV). Based on this, a nitric acid wash concentration of 4.7 M (30 vol% concentrated nitric acid) was selected for full-scale evaluation.

When 6-inch by 2-foot process-scale columns were washed with 4.7 M nitric acid, the band of sorbed plutonium was observed to migrate more rapidly, as expected, than when 7 M nitric acid wash was used. Because all sorbed species migrate in this medium, but at different rates, we refer to the technique as "chromatographic washing." Migration of the plutonium

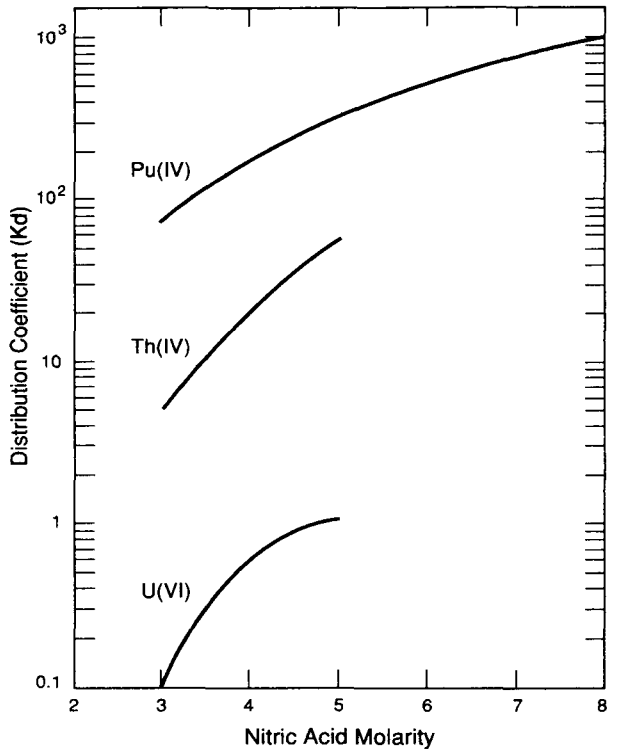

Fig. 3. Distribution of Pu(IV), Th((IV), and U(VI) onto Lewatit^{TM} MP-500-FK anion exchange resin during a 15-minute dynamic contact period as a function of nitric acid concentration.

band is tolerable, particularly if it promotes thorium separation, as long as significant quantities of plutonium are not lost to the waste stream.

Fortunately, we routinely monitor uranium, plutonium, and americium in all nitrate anion exchange processes with an On-Line Gamma Monitor that was developed at Los Alamos.[3] This instrument continuously profiles uranium, plutonium, and americium in real time as these elements emerge from the anion exchange column.

A typical gamma monitor stripchart record (Fig. 4) shows the expected anion exchange behavior of these three actinides. Americium appears first in the effluent waste stream as soon as the feed solution front reaches the column exit. Americium quickly reaches a constant value that confirms that this element is being added and removed from the column at equal rates during the feed-loading step.

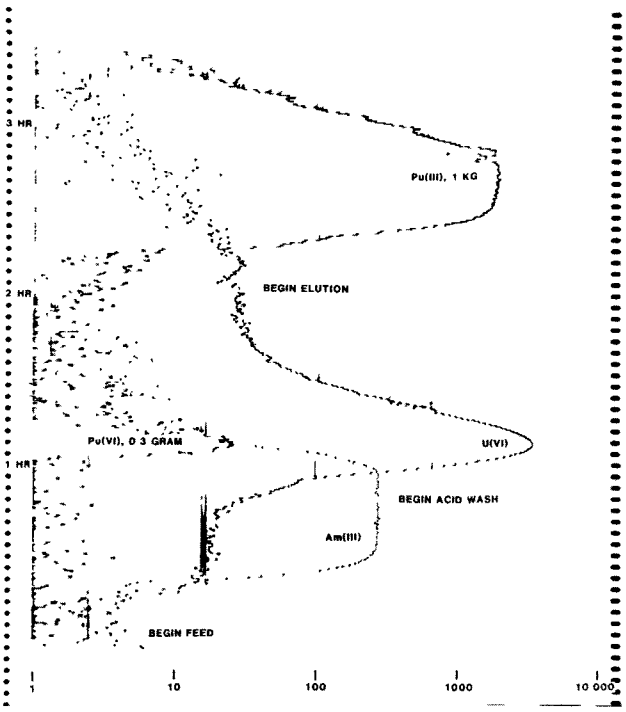

Fig. 4. Typical stripchart record from the On-Line Gamma Monitor for an anion exchange separation process for plutonium.

Uranium is slower to appear in the effluent stream because its weak sorption (Fig. 1) is sufficient to delay its exit from the column. In a properly operating anion exchange process, plutonium does not appear in the effluent, but remains strongly sorbed as Pu(IV) until it is chemically converted to nonsorbed Pu(III), which elutes as shown.

Unfortunately, thorium has neither color nor sufficient gamma activity to allow its presence to be detected at the 1000 ppm and lower impurity levels that typify our impure feeds. The gamma monitor, however, indirectly provides an estimate of the position of thorium because it falls between those of uranium and plutonium, both of which are shown. Because eluting thorium impurity is known to precede plutonium, the most complete separation of thorium is achieved when effluent solution continues to be discarded until the leading edge of the plutonium band appears.

The real-time information provided on the stripchart in Fig. 4 allows the operator to immediately detect the first indication of early plutonium breakthrough and promptly redirect the solution from the waste tank to the appropriate eluate collection tank. The gamma monitor thereby provides real-time guidance that allows the operator to reject the maximum volume of solution that contains unwanted thorium impurity.

EXPERIMENTAL RESULTS

Full-scale tests were performed with impure plutonium oxide feed materials of known (~700 ppm) thorium content. The entire effluent waste solution was collected in sequential 10-liter portions during the loading and washing cycles, after which the plutonium eluate solution was collected in three separate portions that represent the first 10%, the next 45%, and the final 45% of the total eluate volume. Each collected portion was thoroughly mixed and then sampled for thorium analysis by the Los Alamos Analytical Chemistry Group using a spectrophotometric assay technique.

Four full-scale tests were performed. Two used 7.0 *M* nitric acid wash and two used 4.7 *M* nitric acid wash. One at each nitric acid concentration contained no fluoride and one at each concentration contained 0.007 *M* hydrofluoric acid, as suggested by Jack L. Ryan of Pacific Northwest Laboratories, to improve thorium decontamination. Prior to these tests, we evaluated hydrofluoric acid levels of 0.01 and 0.005 *M* and found no significant difference in the extent of thorium removal. (The level of 0.007 *M* was selected for convenience, as it corresponds to 5 milliliters of concentrated hydrofluoric acid per 20 liters of wash solution.)

Figure 5 shows that 100% of the thorium impurity accompanies the eluted plutonium when 7 *M* nitric acid wash is used. Figure 6 shows the effect of adding 0.007 *M* hydrofluoric acid to 7 *M* nitric acid; in this case nearly half (44%) of the thorium impurity is separated from plutonium.

When the column was washed with 4.7 *M* nitric acid (Fig. 7), nearly 60% of the thorium impurity is separated. When 0.007 *M* hydrofluoric acid is added to 4.7 *M* nitric acid, however, more than 90% of the thorium impurity is separated, as shown in Fig. 8. Thus, these tests indicate that 4.7 *M* nitric acid-0.007 *M* hydrofluoric acid wash exceeds our initial objective of reducing the thorium contaminant level by a factor of 10.

RESULTS OF ROUTINE CHROMATOGRAPHIC WASHING

The "chromatographic wash" step was incorporated in routine operations of the three ion exchange process systems, with the following results. The level of thorium impurity decreased from an average of 416 ppm before the change to 42 ppm after the change in the Lean Residue system. The level of thorium decreased from an average of 185 ppm before the change to

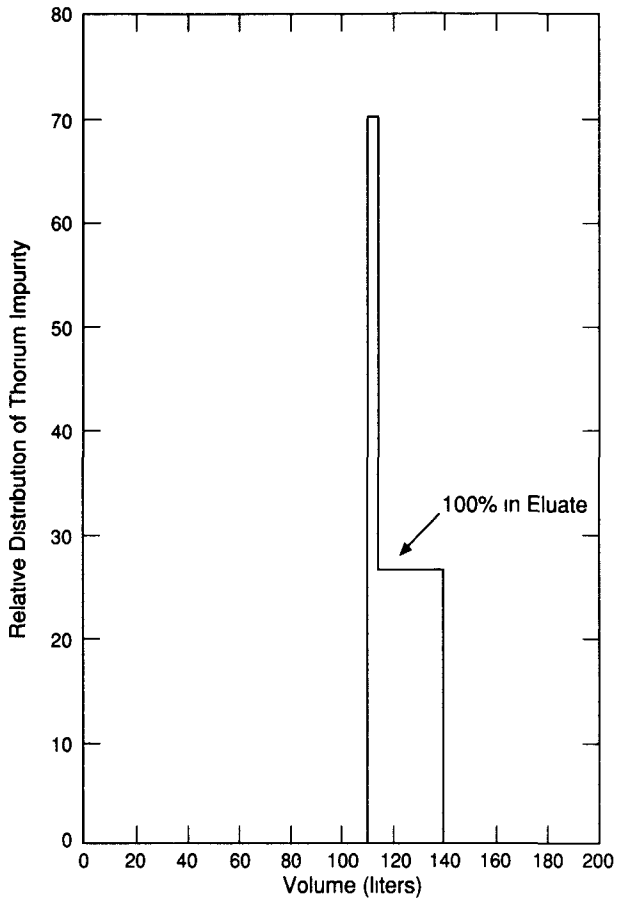

Fig. 5. Distribution of thorium impurity in wash and eluate solutions from the nitrate anion exchange process for plutonium using 7 0 *M* nitric acid wash

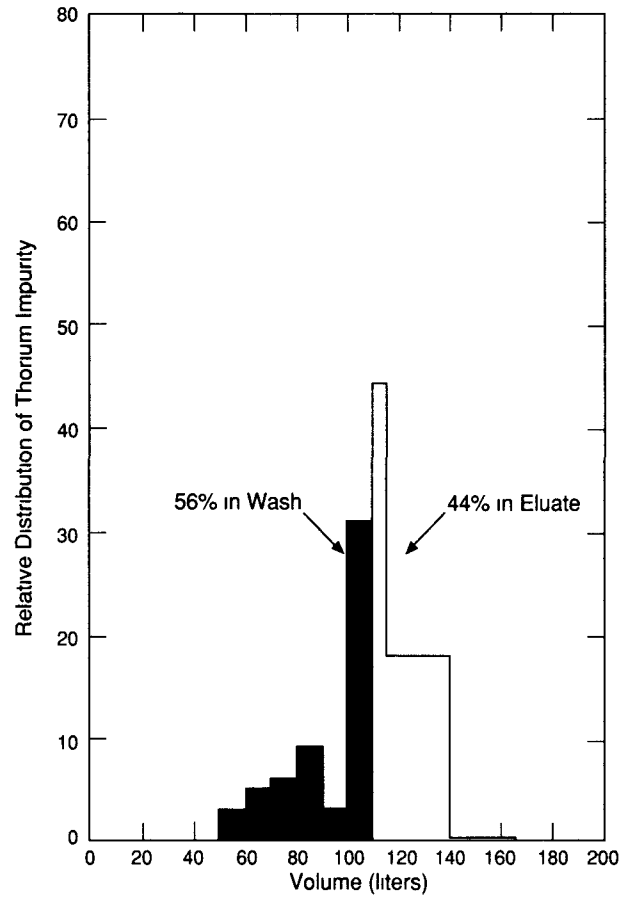

Fig. 6. Distribution of thorium impurity in wash and eluate solutions from the nitrate anion exchange process for plutonium using 7 0 *M* nitric acid-0 007 *M* hydrofluoric acid wash

27 ppm after the change in the Rich Residue system Thus, both of these routine ion exchange process systems confirm the approximate tenfold reduction in thorium indicated by our earlier tests.

Although comparable thorium impurity measurements were not readily available for a third ion exchange process, the Dissolver Solution system, thorium impurity averaged only 54 ppm during the 40 runs since this change was made. Overall, 88% of all full-scale production runs have yielded plutonium product with thorium <100 ppm. In the few cases when thorium exceeds 100 ppm, the levels are usually sufficiently low to allow these products to be blended with other plutonium products that contain an extra-low concentration of thorium to achieve a blended material that is below the 100-ppm limit.

SUMMARY

A relatively minor modification of the established nitrate anion exchange process for plutonium has resulted in the level of thorium impurity being decreased by a factor of 10 during routine production operations. This modification consists of changing the wash solution from previously used 7 *M* nitric acid to 4.7 *M* nitric acid-0.007 *M* hydrofluoric acid.

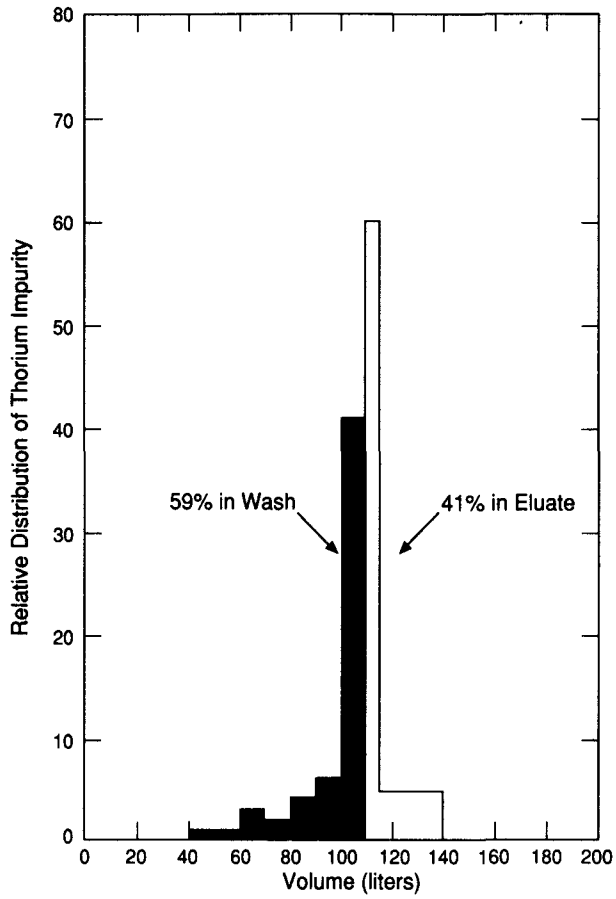

Fig. 7. Distribution of thorium impurity in wash and eluate solutions from the nitrate anion exchange process for plutonium using 4.7 *M* nitric acid wash.

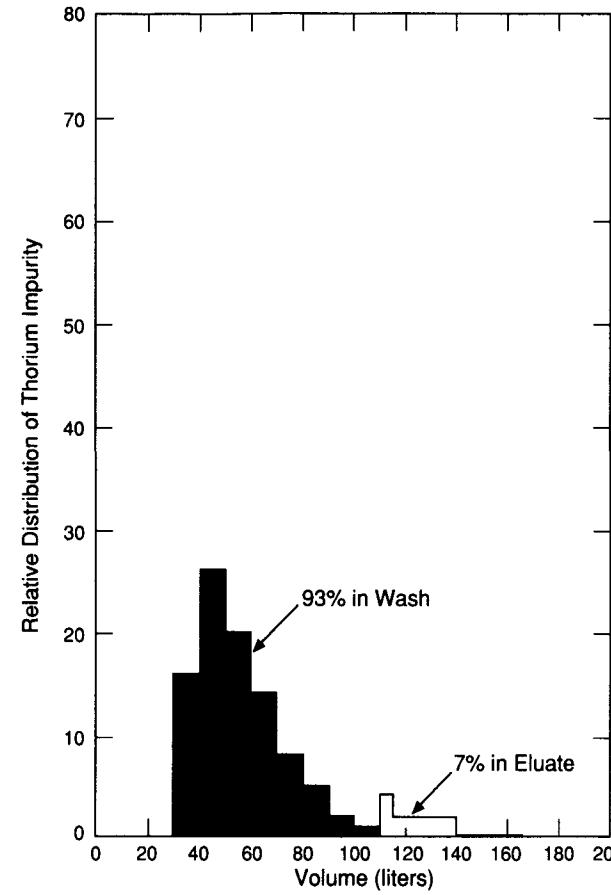

Fig. 8. Distribution of thorium impurity in wash and eluate solutions from the nitrate anion exchange process for plutonium using 4.7 *M* nitric acid-0.007 *M* hydrofluoric acid wash.

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