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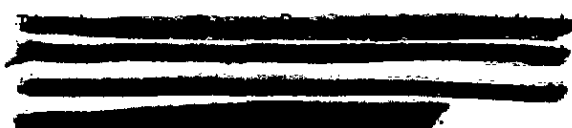
Nuclear Technology - Chemistry
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RECOVERY OF NEPTUNIUM FROM STORED PUREX WASTE

by



M. D. Snyder
Separations Chemistry Division

September 1962



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Aiken, South Carolina



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by

Mark D. Snyder

September 1962

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ABSTRACT

A process was developed for the recovery of neptunium from the sludge in stored alkaline wastes from the Purex process at Savannah River. The process involves dissolution of the sludge with HNO_3 , addition of KF to the solution and heating to avoid gel formation, addition of $\text{Al}(\text{NO}_3)_3$ to complex the fluoride, and adjustment to about 8M total NO_3^- , 0.10M N_2H_4 , and 0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ for absorption of the neptunium by an agitated bed of anion resin. Laboratory tests with actual sludge showed a recovery of about 90% of the neptunium and a separation factor from fission products in excess of 10^3 . Data on the viscosity of sludge-supernate mixtures and on the settling rate of the sludge particles were obtained for possible use in the design of equipment to remove sludge from the waste tanks.

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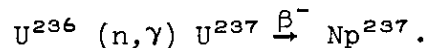
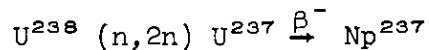
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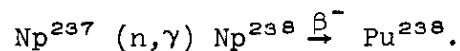
RECOVERY OF NEPTUNIUM FROM STORED PUREX WASTE

INTRODUCTION

In the production of plutonium by neutron irradiation of natural uranium, Np^{237} is produced by the nuclear reactions



Irradiation of Np^{237} produces Pu^{238} by the reaction



Because of an increased demand for Pu^{238} , sources of Np^{237} were considered to supplement the recovery from the irradiated fuels currently being processed. One such source is the stored wastes from the chemical processing of irradiated natural uranium.

In the Purex process, the irradiated uranium metal is dissolved in nitric acid, and plutonium and uranium are separated from fission products by extraction with tributyl phosphate. During the extraction of uranium and plutonium, the majority of the neptunium and fission products remains in the aqueous waste stream. To reduce the volume of waste from chemical processing, the aqueous waste is concentrated by evaporation. This solution is then neutralized with sodium hydroxide and is transferred to tanks for "permanent" storage. The insoluble hydroxides and manganese dioxide from the head end step of the Purex process settle to the bottom of the waste tanks and form a layer of sludge. Prior to the installation of a process for recovering neptunium from the acidic waste by anion exchange⁽¹⁾, a major fraction of the neptunium from the Purex process accumulated in the sludge in the waste tanks.

This study was undertaken to devise a process for recovering the neptunium from the sludge. Data on the physical nature of the sludge were required to assist in determining whether the sludge in the waste tanks could be suspended and pumped to the chemical processing building. Once the sludge was transferred, dissolution of the solids in strong nitric acid and isolation of the neptunium from solution by anion exchange was considered an attractive concept for the recovery process. Since an anion exchange process⁽¹⁾ for the recovery of neptunium from acidic Purex waste was already being operated successfully at Savannah River Plant, a similar process for the solutions of sludge would be reasonably assured of success.

SUMMARY

A concept for a chemical process was developed for the recovery of neptunium from stored Purex waste. The alkaline Purex waste consists of a sludge and a supernatant solution; essentially all of the neptunium in the waste is present in the sludge. In the chemical process that was developed the sludge was dissolved in 10M HNO_3 , and neptunium was absorbed from the solution by anion exchange resin. More than 90% of the neptunium was recovered and was separated from more than 99.9% of the fission products. Formation of a gelatinous precipitate in solutions of the dissolved sludge was avoided by adjusting the solution to 0.3M KF and then heating at 80 to 90°C. The resulting solution was adjusted to 0.6M $\text{Al}(\text{NO}_3)_3$ to complex the fluoride, which would otherwise interfere with the absorption of neptunium by anion exchange.

The sludge from the waste tanks was viscous and extremely sticky. However, the solids in the sludge could be suspended by vigorous agitation with an equal volume of the supernatant solution or water. These suspensions had viscosities of 30 to 70 centipoises and did not settle appreciably over a period of a few days.

DISCUSSION

GENERAL PROPERTIES OF THE SLUDGE

The sludge in the tanks of waste from the Purex process forms a layer of partially consolidated, sticky solids. In most tanks, this layer is two to three feet thick and amounts to about 100,000 gallons or about one tenth of the total volume of each tank. In Tanks 12 and 14, which were sampled for this study, about three fourths of the sludge was compacted into a sticky mass, and about one fourth was loosely settled. Samples of the packed sludge were obtained as plugs in a pipe-like sampling device, and samples of the loosely settled sludge were taken in bottles. The general consistency of the packed sludge can be visualized from the observation that massive solids clinging to the outside of the sampling cylinder were not removed in raising the cylinder through about twenty feet of supernate in the waste tanks.

The properties of the sludge and the supernatant solution are shown in Tables I and II. The composition of the solids in the loosely settled layer was not significantly different from the composition of those in the packed layer. When the packed sludge was slurried with tank supernate or with water, the viscosity of the resulting suspensions decreased as the ratio of liquid to solid volume was increased (Figure 1). The viscosity was measured by the flow of the suspensions from transfer pipettes that were calibrated with glycerine solutions of known viscosity in the range of 1.5 to 1000 centipoises. The results of tests with both actual sludge and synthetic sludge indicated that about 1:1 slurries of packed sludge and supernate would represent an optimum balance between volume of material to be handled and degree of fluidity necessary for pumping.

TABLE I
Properties of Sludge^(a)

| | <u>Tank 12</u> | <u>Tank 14</u> |
|---|----------------------|----------------------|
| Viscosity of 50% slurry, centipoises | 70 | 30 |
| Settling rate of 10% slurry, coarse, in./hr | 6 | 2 |
| Settling rate of 10% slurry, fines, in./hr | 1 | 0.1 |
| Coarse particles, % | ~95 | ~90 |
| Hydroxides, % | ~30 | ~25 |
| MnO ₂ , % | ~60 | ~60 |
| Acid insolubles, % | 10 | 15 |
| Neutralization equivalent, mols/liter | 15 | 10 |
| Neptunium content, mg/liter | 12-25 | 18-37 |
| Plutonium content, mg/liter | ~30 | ~30 |
| Neptunium in acid insolubles, % of total Np | 0.01 | - |
| Plutonium in acid insolubles, % of total Pu | 3 | - |
| Gross gamma, d/(min)(ml) | 8.0x10 ⁹ | 3.2x10 ¹⁰ |
| Gross beta, d/(min)(ml) | 8.5x10 ¹⁰ | 2.4x10 ¹¹ |

(a) Samples of sludge were centrifuged for 5 minutes at 1500 G prior to sampling for tests and analyses.

TABLE II
Analysis of Supernate

| <u>Component</u> | <u>Tank 12</u> | <u>Tank 14</u> ^(a) |
|---------------------------------------|---------------------|-------------------------------|
| OH ⁻ , as NaOH, M | 1.07 | 2.78 |
| SO ₄ ²⁻ , M | 0.12 | 0.09 |
| NO ₃ ⁻ , M | 2.27 | 2.62 |
| NO ₂ ⁻ , M | 2.23 | 0.96 |
| PO ₄ ³⁻ , M | 0.006 | 0.01 |
| CO ₃ ²⁻ , M | 0.62 | Not determined ^(b) |
| Al, M | 0.05 | 0.12 |
| U, g/l | 0.08 | Not determined |
| Neutralization equivalent, mols/liter | 3 | Not determined |
| Gross gamma, d/(min)(ml) | 2.7x10 ⁹ | 4.6x10 ⁹ |
| Gross beta, d/(min)(ml) | 1.7x10 ⁹ | 2.0x10 ⁹ |
| Density, g/ml | 1.25 | Not determined |

(a) Contained some waste from the processing of irradiated U-Al alloy.

(b) Material did not "gas" during acidification. Tank 12 supernate gave off copious amounts of gas.

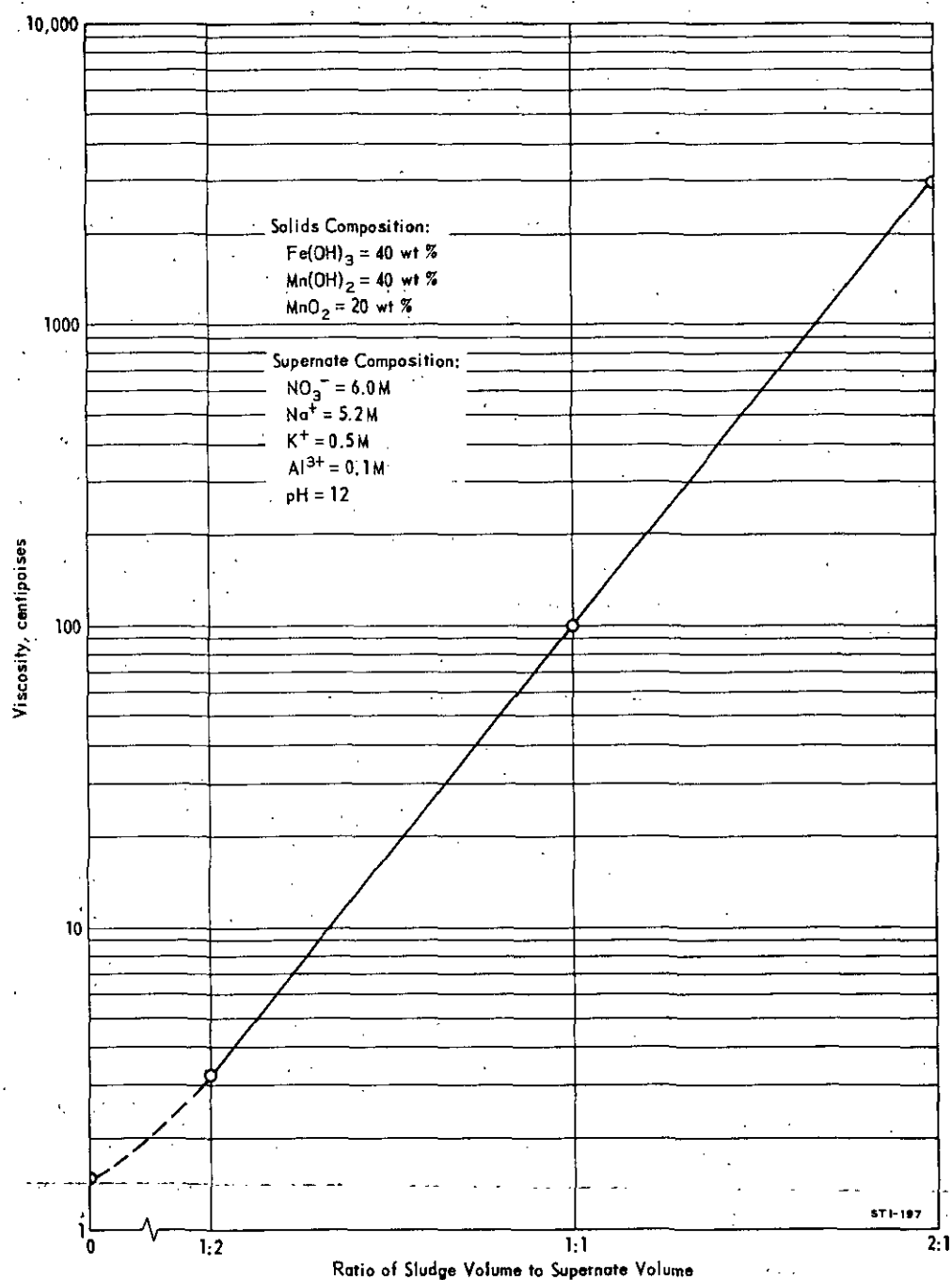


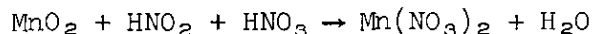
FIG. 1 EFFECT OF CONCENTRATION ON VISCOSITY OF SLUDGE SUSPENSIONS

About 90% of the solids in the sludge were large in size, and settled through the supernate at a rate of about 2 to 6 inches/hr. The remaining 10% of the solids settled at a slower rate; solids apparently consisted of two groups of particles that were fairly uniform in size. Data on the settling properties of the solids are included in Table I. After standing a few days, the settled layer consisted of about one part of solids and one part of supernate.

DISSOLUTION OF SLUDGE

About 90% of the solid matter in the sludge was readily soluble in 10M HNO_3 and the acid-insoluble material consisted of easily dispersed solids that contained virtually no neptunium. After dissolution two different precipitates formed from the solution, a brownish floc and a transparent sticky gel. Precipitation required one to two days at room temperature and ten to sixty minutes at 60 to 90°C. Normally, the reaction mixture was cooled to avoid gelation during the dissolution. Spectroscopic analysis of the precipitates showed silicon, iron, and zirconium to be the major components, and it is presumed that the brown floc was mainly iron silicate. The transparent gel probably contained a complex silicate of zirconium. Two sets of tests demonstrated that the metastable compounds were derived from the solids of the sludge. In one set of tests, the precipitates appeared even when the sludge was well rinsed with water and NaOH solutions to remove supernate before dissolution in HNO_3 . In the other tests, no more than a trace of precipitate formed when a sample of the supernate was acidified and heated.

Since a major constituent of the sludge was MnO_2 , it was advantageous to have the supernatant solution present during dissolution. The supernate contained nitrite from the radiolysis of the alkaline nitrate, which reacted with MnO_2 in acid solutions as follows:



Less than half a volume of supernatant solution was required for the complete dissolution of the MnO_2 in one volume of sludge; thus any slurry of sludge that was suitable for transfer and handling would contain an adequate volume of supernate for the dissolution. The presence of a large amount of carbonate in the supernates from Tank 12 complicated the dissolution by gassing and severe foaming. Because of a much shorter storage period, supernate from Tank 14 contained very little carbonate.

STABILIZATION OF SLUDGE SOLUTIONS

Due to the large volume and the sticky nature of the gel that is formed in solutions of sludge, these solutions must be stabilized against the formation of gel before the neptunium can be recovered by anion exchange. The composition of the gel was not determined, but its instability in the alkaline waste, initial solubility in acid, and probable polymerization to an insoluble silicate suggested that it might contain zirconium or a

similar agent. It was found that the formation of the gel could be prevented by adding fluoride to the solutions and heating. A small amount of a white floc (probably silica) appeared during heating, but its presence did not interfere with the operation of the agitated ion exchange bed. No additional precipitate formed when aluminum ion was later added to complex the excess fluoride and prevent interference with the absorption of neptunium by the anion resin.

Fluoride for stabilization was provided by the addition of 2 to 10M KF to freshly prepared sludge solutions. It was not feasible to add KF, or HF, to the 10M HNO_3 used for dissolution of the sludge because the MnO_2 in the sludge became coated with an insoluble fluoride of manganese. This insoluble material prevented rapid reaction of MnO_2 with the HNO_3 ; a rapid reaction was necessary to dissolve all the MnO_2 because the HNO_3 was unstable in the presence of acid and was lost from the reaction medium if MnO_2 were not readily available. Tests of the dissolution with HNO_3 -HF, and subsequent treatment of the residual MnO_2 with H_2O_2 , gave rather slow dissolution of the MnO_2 and further demonstrated the desirability of dissolving the sludge in HNO_3 alone.

The effectiveness of fluoride for preventing gel formation depended on the concentration of fluoride. A concentration of 0.3M was required to stabilize solutions of sludge from either Tank 12 or Tank 14. At 0.2M fluoride a slight amount of gel was formed, and at 0.1M fluoride the volume of gel was about half the initial volume of sludge.

Since fluoride is deleterious to the absorption of neptunium by anion exchange, tests were made to determine the degree of interference and to determine the optimum amount of aluminum for complexing the fluoride. The tests depended on determining the distribution of neptunium between "Dowex" 1-X4, 20-50 mesh anion resin and synthetic sludge solutions. The distribution values were then interpreted in terms of losses to be expected⁽¹⁾ in the absorption of neptunium by an agitated bed of the resin under similar conditions. The moderate nitrate concentration of 7M was selected to give high sensitivity to the effects of variables in the test and to indicate a lower practical operating value for the nitrate concentration. The results shown in Figures 2 and 3 indicate that losses would be increased about four times with a concentration of only about 0.03M fluoride, unless aluminum were added to complex the fluoride. The optimum amount of aluminum required was about two mols per mol of fluoride. By comparing these results with extensive results from tests with other anions⁽¹⁾, it was estimated that the necessary concentration of 0.3M fluoride and 0.6M aluminum in sludge solutions would require a total nitrate concentration of 8.5 to 9.0M for recovery of at least 90% of the neptunium. Measurements of the distribution of neptunium between the anion resin and an actual sludge solution 0.2M in fluoride, 0.4M in aluminum, and 8.0M in total nitrate indicated that recovery of neptunium on an agitated bed would be about 93%.

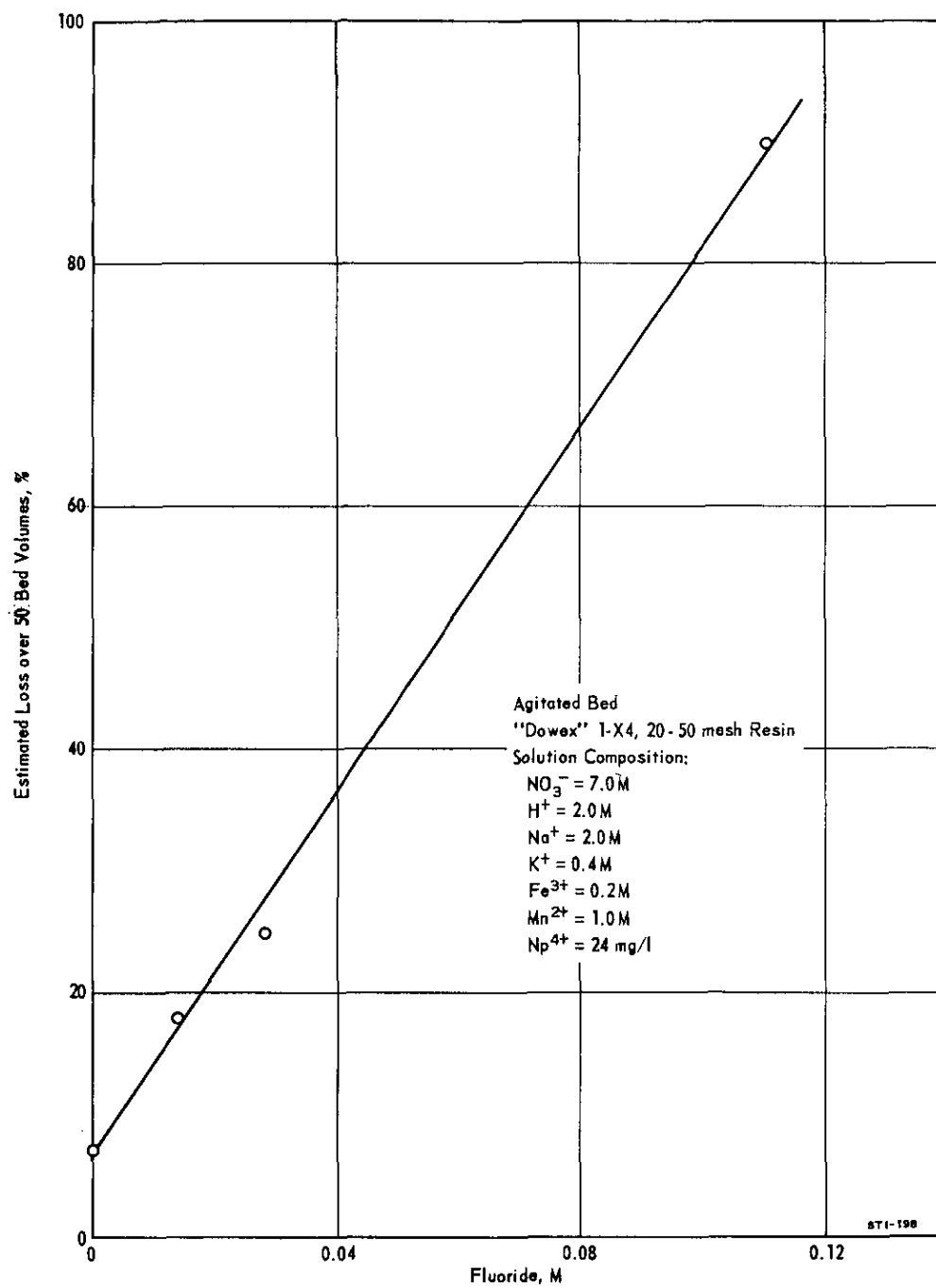


FIG. 2 EFFECT OF FLUORIDE ON RECOVERY OF NEPTUNIUM FROM SLUDGE SOLUTIONS

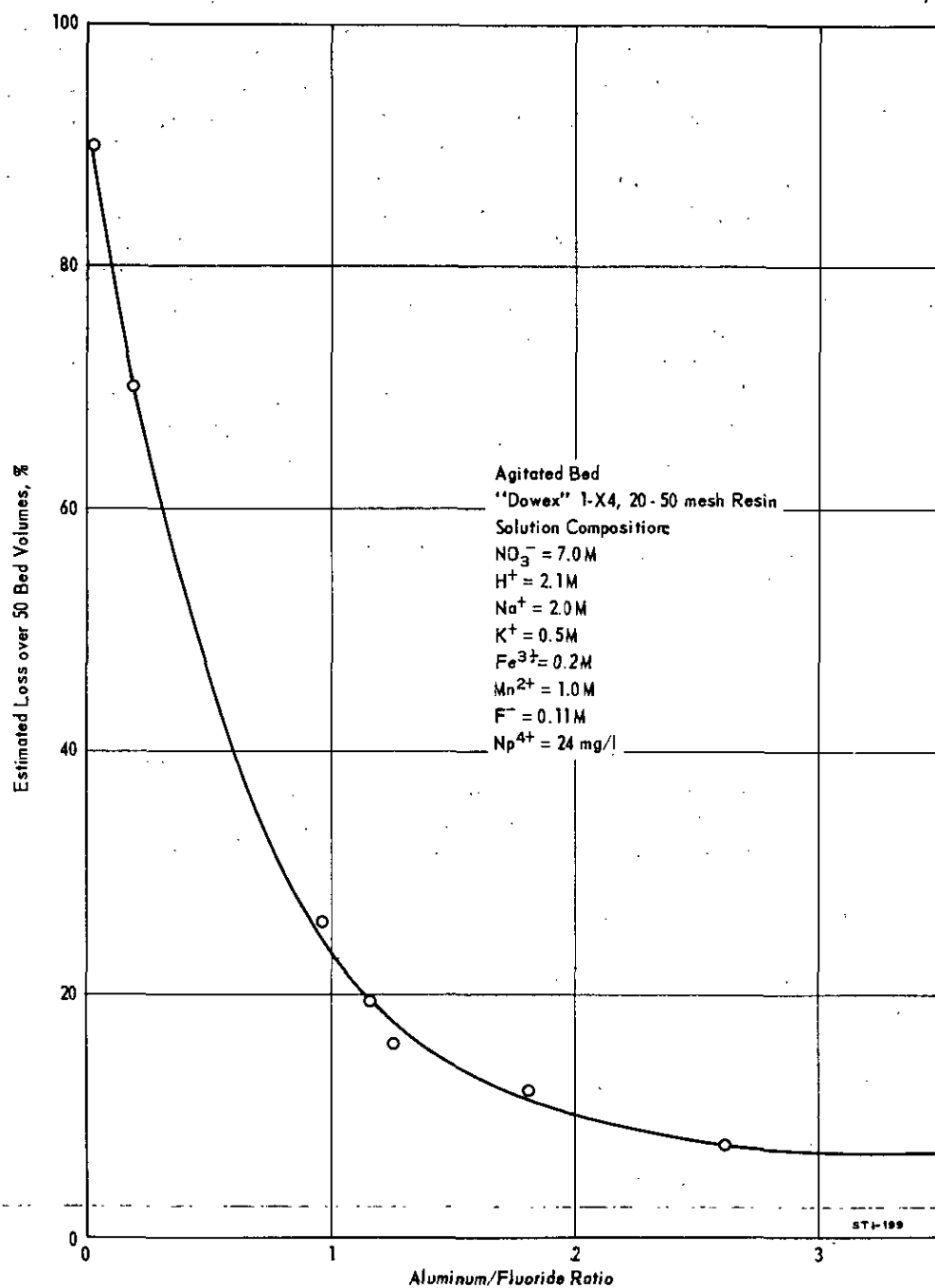


FIG. 3 EFFECT OF ALUMINUM/FLUORIDE RATIO ON RECOVERY OF NEPTUNIUM FROM SLUDGE SOLUTIONS

SMALL-SCALE DEMONSTRATION OF THE PROCESS

Two demonstrations of the process for recovering neptunium from sludge showed neptunium recoveries of 93 to 96% and decontamination factors from fission products of 600 to 5000 (Table III). The feed prepared from the sludge of Tank 12 consisted partially of sludge dissolved and stabilized in the proposed manner and partially of several sludge solutions prepared under a variety of conditions in the development of the final process. Extra neptunium was added to small portions of the original sample of sludge and subjected to the entire sequence of dissolving and stabilizing operations. Analysis of solutions from the different steps indicated that recovery was virtually quantitative until the final isolation by anion exchange. The feed prepared from the sludge of Tank 14 contained only the neptunium initially present in the sludge. The construction and operation of the agitated bed of anion resin were described previously⁽¹⁾. The 6.5 ml of resin in this apparatus represented a scale-down of about 15,000 from plant equipment.

TABLE III
Recovery of Neptunium from Sludge

| | Sample | |
|---|-----------------------|-----------------------|
| | Tank 12 | Tank 14 |
| Volume of centrifuged sludge, ml | 40 | 70 |
| Volume of supernate, ml | 20 | 50 |
| Volume of 10M HNO ₃ , ml | 80 | 115 |
| Volume of centrifuged acid insolubles, ml | 4.0 | 8.6 |
| Concentration of fluoride ion in sludge solution, M | 0.2 | 0.3 |
| Concentration of aluminum ion in sludge solution, M | 0.5 | 0.6 |
| Concentration of nitrate ion in sludge solution, M | 7.5 | 8.8 |
| Volume of adjusted feed, ml | 202 | 260 |
| Volume of adjusted feed, bed volumes | 31 | 40 |
| Neptunium in feed solution, mg | 5.00 ^(a) | 2.40 |
| Neptunium in absorption effluent, % | 3.7 | 2.1 |
| Neptunium in 8M HNO ₃ wash, % | 2.5 | 2.1 |
| Neptunium in first eluate (4.5 bed volumes), % | 90 | 94 |
| Neptunium in second eluate (4.5 bed volumes), % | 2.9 | 2 |
| Plutonium in feed, mg | 1.22 | 5.70 |
| Plutonium in absorption effluent, % | - | 5.3 |
| Plutonium in first eluate, % | 58 | 70 |
| Plutonium in second eluate, % | 21 | 7 |
| Thorium in feed, mg | 0.92 | 0.55 |
| Thorium in first eluate, % | 7 | 4 |
| Total gross gamma activity in feed, d/min | 2.95x10 ¹¹ | 2.25x10 ¹² |
| Total gross gamma activity in first eluate, d/min | 4.4x10 ⁸ | 4.2x10 ⁸ |
| Decontamination factor | 660 ^(b) | 5400 ^(c) |
| Total gross gamma activity in second eluate, d/min | 1.85x10 ⁸ | 2.45x10 ⁸ |

(a) Includes 4.00 mg added to sludge

(b) After sixteen bed volumes of wash

(c) After twenty bed volumes of wash

The basic steps of the process are as follows:

1. One volume of solid sludge is slurried with approximately an equal volume of the supernate.
2. The suspension of sludge is treated with an equal volume of 10M HNO_3 , with cooling to maintain a temperature of 25 to 40°C.
3. The solution of sludge, plus about 10% acid insolubles, is adjusted to 0.3M KF and is heated for two to four hours at 80 to 90°C. During this step about one-fourth volume of silica-like precipitate is formed.
4. The solution from Step 3 is adjusted to 0.6M $\text{Al}(\text{NO}_3)_3$ and is concentrated to 8 to 9M total nitrate.
5. The removal of the solids formed in Step 3 is recommended; the solids may be removed either before or after Step 4.
6. The solution from Step 5 is adjusted to 0.10M N_2H_4 and 0.05M $\text{Fe}(\text{NH}_2\text{SO}_3)_2$. This treatment reduces neptunium to the absorbable (IV) state.
7. The adjusted solution is passed through an agitated bed of "Dowex" 1-X4, 20-50 mesh anion resin at a flow of six bed volumes of solution per hour. During this step, most of the neptunium and associated plutonium is absorbed by the anion resin. The effluent is discarded to waste.
8. The resin is washed, without agitation, with twenty bed volumes of 8M HNO_3 at a rate of six bed volumes per hour to remove most of the absorbed fission products. In plant operation, only the first two bed volumes of effluent would be discarded to waste.
9. The neptunium, as well as the plutonium, is eluted from the resin with four to five bed volumes of 0.3M HNO_3 at a rate of two bed volumes per hour. The product solution contains at least 90% of the neptunium and about 80% of the plutonium initially present in the sludge. Less than 0.1% of the fission products are present.

The recovery of neptunium from Purex sludge by this process yields five to eight volumes of final neutralized waste per unit volume of solid sludge.

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