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ABSTRACT

The work described in this paper is part of a leaching study being conducted for the Battelle Pacific Northwest Laboratory's Waste Isolation Safety Assessment Program (WISAP). Simulated high-level nuclear waste glass were leached with three solutions, one of which is a saturated-salt brine. Because chemical separation of Np and Pu using organic extraction or anionic exchange is not effective for the brine samples, a procedure has been developed to first separate neptunium and plutonium from high concentrations of brine before proceeding with an extraction of neptunium from plutonium.

Samples were equilibrated with tracers, Np and Pu were coprecipitated with $La(OH)_3$, and interfering ions were removed by washing the hydroxide precipitate with water. Pu and Np were separated by reducing Pu to Pu^{3+} and extracting the Np^{4+} into thenoyltrifluoroacetone (TTA); control of oxidation states and contaminant concentration is critical.

INTRODUCTION

Neptunium and plutonium are of particular interest in leaching studies because it is a goal of the Waste Isolation Safety Assessment Program (WISAP) to understand the rate at which these long-lived radionuclides are released to groundwater which could invade the repositories. The single-pass leaching of simulated waste glass doped with actinides[1,2] has been described.[3] The concentration of ^{239}Pu and ^{237}Np in

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the glass is [illegible] active waste glass.[7] Samples were studied over eleven time intervals within the 3-year experiment. It was necessary to develop a radiochemical procedure to separate ^{239}Pu and ^{237}Np in the high-salt samples generated by this leaching study, because the concentration of the brine hinders their measurement by direct alpha counting.

The composition of the leach brine was based on the composition of a salt rock core from the Waste Isolation Pilot Plant in New Mexico (WIPP). The major salt component in the WIPP brine is sodium chloride (Table I). Samples containing sulfates, fluorides, and phosphates have been shown to interfere with neptunium extraction.[8] However, in these brine solutions there was no measurable fluoride or phosphate, nor was either used in the procedure as precipitating agents. Sulfate was present, but the massive amount of sodium chloride probably accounted for the major extraction interference.

TABLE I.

Composition of New Mexico Salt Rock Core

WIPP Brine B	Composition (mg/l)
Na^+	11[illegible]
K^+	15.
Mg^{+2}	1[illegible].
Ca^{+2}	900.
Sr^{+2}	1.5
Cs^+	1.
Cl^-	175,000.
SO_4^{-2}	3,500
BO_3^{-3}	10.
HCO_3^-	10.
Br^-	400.

PH 6.5   0.5

In order to approximate a brine of the composition shown in Table I, we prepared [illegible] the following reagents:

[illegible]	[illegible]	g/l
Na_2SO_4	[illegible]	g/l
[illegible]	[illegible]	mg/l
[illegible]	[illegible]	mg/l
NaBr	[illegible]	mg/l
KCl	19.	mg/l
$MgCl_2 \cdot 6H_2O$	[illegible]	mg/l
$CaCl_2$ anhyd.	2.49	g/l
$SrCl_2 \cdot 6H_2O$	4.52	mg/l
CsCl	1.3	mg/l

All attempts to separate neptunium and plutonium before removing the salts had previously failed. Trial separations were attempted using larger dilutions of the brine. At even 90. dilution (0.5 M NaCl), only 50% of the neptunium could be recovered by extraction techniques. Similar losses were experienced using the more time-consuming ion exchange procedures. In addition to the salt interference, the presence of calcium in the sample during a Pu-fluoride precipitation also caused losses of plutonium. Coleman[5] also observed that calcium must be removed because it was one of the elements which he found interfered with LaF_3 co-precipitation.

The goal of the work described here was to separate neptunium and plutonium in a brine medium so each isotope could be measured quantitatively. The procedure developed is described below, and its critical aspects are discussed.

PROCEDURE

Tracer levels of ^{239}Np and ^{242}Pu were added to each 10-milliliter sample in order to measure chemical yield. Ten milligrams of La^{+3} were added. Initially, equilibrium between tracers and samples was attained by using 1 M sodium nitrite in 8 M nitric acid solution. The solution was evaporated by boiling to about 2 ml, then diluted with water to 20 ml. Fifty percent sodium hydroxide was added to pH 12 or greater. The resultant lanthanum hydroxide co-precipitated Np and Pu, and provided an effective separation from the massive concentrations of other ions, which remained in solution. The precipitate was dissolved in 1 ml concentrated HCl and diluted to 10 ml, adjusted to a concentration of 4 M HCl. Two ml of hydroxylamine hydrochloride were added and the solution was heated in a hot water bath for 1-2 minutes. Next, 3/4 ml 1 M $SnCl_2$ and 8 ml 4 M KI were added and the solution was heated for 10 minutes in a hot water bath.[4] The solution, cooled to room temperature, was transferred to a separatory funnel. An equal volume of a 0.4 M solution of thenoyltrifluoroacetone (TTA) in toluene was added. Under these conditions the neptunium 4+ is extracted into TTA and Pu 3+ is not. The neptunium fraction was back-extracted from the organic with 9 M HCl.

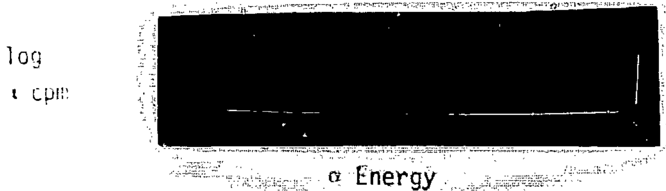
The plutonium fraction must undergo further purification. Ten milligrams of La^{3+} and 5 ml HF were added to the Pu solution; LaF_3 was co-precipitated with PuF_3. The resulting precipitate was dissolved in 10 M HCl and the solution was placed on an anionic exchange column, preconditioned with 10 M HCl. After the column was washed and converted to a NO_3^- column with 8 M HNO_3, the column was converted back to a Cl^- column with 10 M HCl. The plutonium was selectively eluted with 10 M $HCl \cdot 0.5$ M NH_4I.

The final separated and purified samples of neptunium and plutonium were electroplated onto platinum disks from a barely acidic sulfate medium for one hour at 1/2 ampere. The disks were counted on alpha detectors controlled by a Nuclear Data Model 600 Multichannel Analyzer (MCA). Pictures were taken of the alpha spectra using a scope camera attached to the ND600 to document the quality of the spectra (Fig. 1).

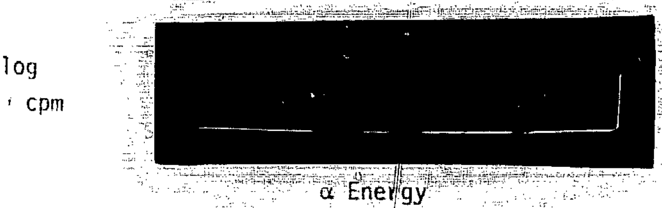
The procedure requires approximately two days for eight samples. Typical yields were in the range of 70-80% for neptunium and slightly less for plutonium.

FIG. 1

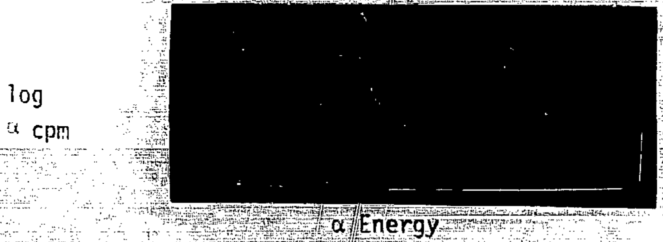
Illustration of Alpha Spectra



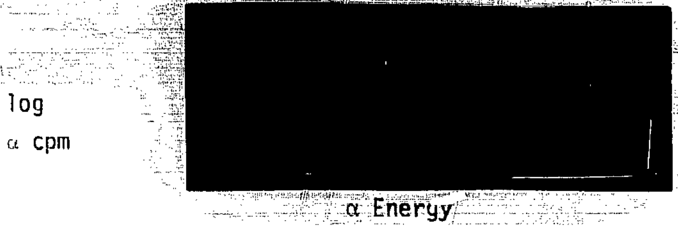
Evaporated brine



Evaporated carbonate



Separated neptunium



Separated plutonium

DISCUSSION AND CONCLUSIONS

The ^{242}Pu tracer was obtained from the isotopic separation of Pu isotopes. The ^{239}Np tracer was prepared by extraction from a ^{243}Am solution into TTA. Because ^{239}Np has a short half-life ($t_{1/2}$ = 2.35 days), it was necessary to expedite the chemical separation of neptunium and plutonium. Neptunium-239 was selected as a chemical yield tracer for neptunium because it is easily detected in an end-window, lead-shielded NaI crystal counter. Neither ^{239}Pu nor ^{242}Pu emit radiations which interfere with detection of ^{237}Np or ^{239}Pu (respectively). The oxidation states of the neptunium and plutonium during extraction are critical. The presence of interfering salts will jeopardize the separation and reduce the ultimate yields. The presence of small amounts of I_2 in the final plating solution will cause severe losses of plutonium. If these critical factors are controlled, Np and Pu can be effectively separated from highly concentrated brine solutions.

ACKNOWLEDGMENTS

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