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NEAR-QUANTITATIVE RECOVERY OF ACTINIDES FROM NITRIC ACID WASTE STREAMS BY SOLVENT EXTRACTION USING DHDECMP

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INTRODUCTION

Plutonium is recovered and purified from a wide variety of impure materials at the Los Alamos Plutonium Facility. Anion exchange and peroxide precipitation, the major aqueous separation processes, both recover plutonium from nitric acid media. The acidic waste streams from these processes typically contain small quantities of residual plutonium intermixed with all radioactive and nonradioactive impurity elements.

These waste streams usually are reduced in volume by evaporation, after which the concentrated residue is assayed for plutonium content. If the plutonium level is sufficiently low, the residue is discarded according to approved disposal procedures. If plutonium exceeds the discard level, however, the entire batch of residue must be recycled.

Recycle of such residues to recover small quantities of plutonium from already-separated impurities, including Am-241, the main source of gamma activity in these materials, is highly undesirable. It is far to eliminate the need for recycle by initially keeping plutonium out of the waste stream. Yet even those waste solutions that are free of plutonium contain the total quantity of separated americium intermixed with kilogram quantities of nonradioactive impurities.

If all actinide elements could be adequately separated from these waste solutions, the large volumes of liquid could then be discarded inexpensively as low-level waste. The multikilogram quantities of nonradioactive impurity salts dissolved in the liquid waste also could be disposed of as low-level waste, rather than require cement-fixation and burial as is now done. The economic (and political) incentive to selectively recover the alpha-emitting actinides from the bulk of the nonradioactive waste components is therefore great.

SELECTIVE EXTRACTION OF ACTINIDES

Certain carbamoylmethylphosphoryl extractants are of special value within the nuclear industry. Of these compounds, carbamoylmethylphosphonates and carbamoylmethylphosphine oxides appear to be the most selective for extracting actinides from nitric acid. Of particular significance is that actinides are highly extractable in their (III), (IV), and (VI) oxidation states, which often eliminates the usual need for prior oxidation state adjustment.

The value of dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) has been known for the past decade. More recently, researchers have developed octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) as the extractant for the proposed TRUEX process.[1] (The structures of DHDECMP and CMPO are shown in Fig.1.) CMPO unquestionable is a stronger extractant than DHDECMP; however, the stronger extraction from dilute acid, as well, makes back-extraction of actinides from CMPO into dilute acid more difficult.

By contrast, most actinides that extract well into DHDECMP from moderate concentrations of nitric acid, readily back-extract into dilute nitric acid. DHDECMP also is more selective in rejecting common impurity elements (Fig. 2). Until very recently, however, the lack of a commercial source of high-purity DHDECMP precluded its evaluation on a plant scale.

That disadvantage was eliminated in 1987 when high-purity DHDECMP became available from Occidental Chemical Corp., who uses a patented phase transfer catalysis process[3] to synthesize this compound. The advent of this new source of the pure compound prompted us to evaluate DHDECMP for removing actinides from nitric acid waste streams at Los Alamos. We also elected to include a comparable evaluation of CMPO as part of our study.

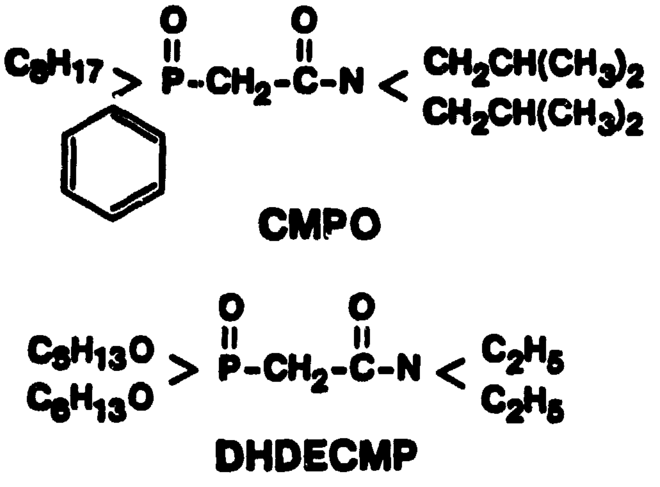

Fig. 1. Chemical Structures of octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP).

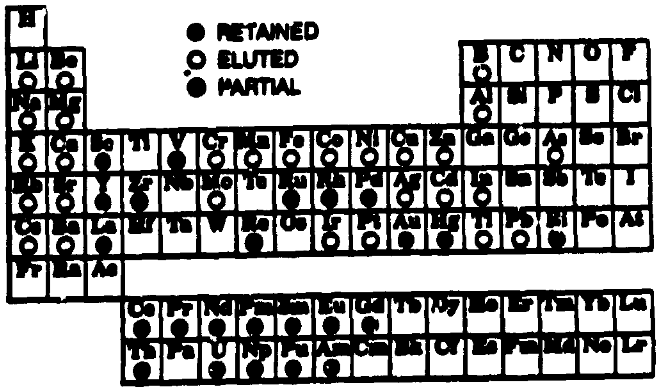

Fig. 2. Distribution of many elements on DHDECMP extraction chromatography column from 5.5 M nitric acid.[2]

Variables of this study included the extractant (DHDECMP or CMPO), the ratio of extractant to added tributylphosphate (TBP), the selected diluent, nitrate concentration, the ratio of nitrate salt to nitric acid, fluoride level, and contact time.

EXPERIMENTAL RESULTS AND DISCUSSION

Experimental distribution data usually are presented in a format that illustrates the effect of a single variable. Because our study evaluated multiple variables, however, we selected a format that allows individual and interactive effects to be presented in a single figure. This "tree" format suggested by Richard J. Beckman, Los Alamos National Laboratory Statistics Group, simultaneously illustrates the effects of total nitrate, nitrate salt/nitric acid ratio, and fluoride concentration.

The two diluents evaluated in our study were tetrachloroethylene (TCE) and Isopar-H, a purified mixture of C_9 to C_{12} isoalkanes. Of these, Isopar-H was preferred because TCE caused persistent organic dispersions that were difficult to separate from the aqueous phase, and also because TCE is an order of magnitude more volatile than Isopar-H.

A major conclusion of our study was that the more-than-adequate extraction of actinides from high nitrate solutions and the efficient back-extraction from low nitrate solutions make DHDECMP the preferred extractant for this application. Because space limitations restrict the number of Figures that can be included in this article, only Isopar-diluted DHDECMP extraction data are presented herein. However, a more complete data presentation is available elsewhere.[4]

Cpmparative extraction data for Am(III), Pu(IV), and U(VI) are presented in Figs. 3, 4, and 5, respectively. The behavior of these three actinides can be assumed to represent the general behavior of other actinides in their trivalent, tetravalent, and hexavalent oxidation states.

CONCLUSIONS

1. DHDECMP extracts Am(III), Pu(IV), and U(VI) well from solutions that contain moderate to high levels of nitrate, either as nitric acid or nitrate salts.

2. Higher nitrate salt levels increase the extraction of all three actinides; however, the enhancement is greatest for Am(III).

3. The extraction of Am(III) is essentially unaffected by the maximum level of 0.05 M fluoride. U(VI) extraction is slightly suppressed by this level of fluoride, whereas Pu(IV) extraction is strongly suppressed.

4. Fluoride suppresses the extraction of Pu(IV) most at low nitrate concentrations. The intentional addition of fluoride therefore could be used to facilitate the back-extraction of Pu(IV) into dilute acid.

5. Am(III) readily back-extracts from DHDECMP into dilute nitrate solutions. Fluoride enhances the back-extraction of Pu(IV) into dilute nitrate solutions. U(VI), however, does not easily back-extract, even with fluoride present.

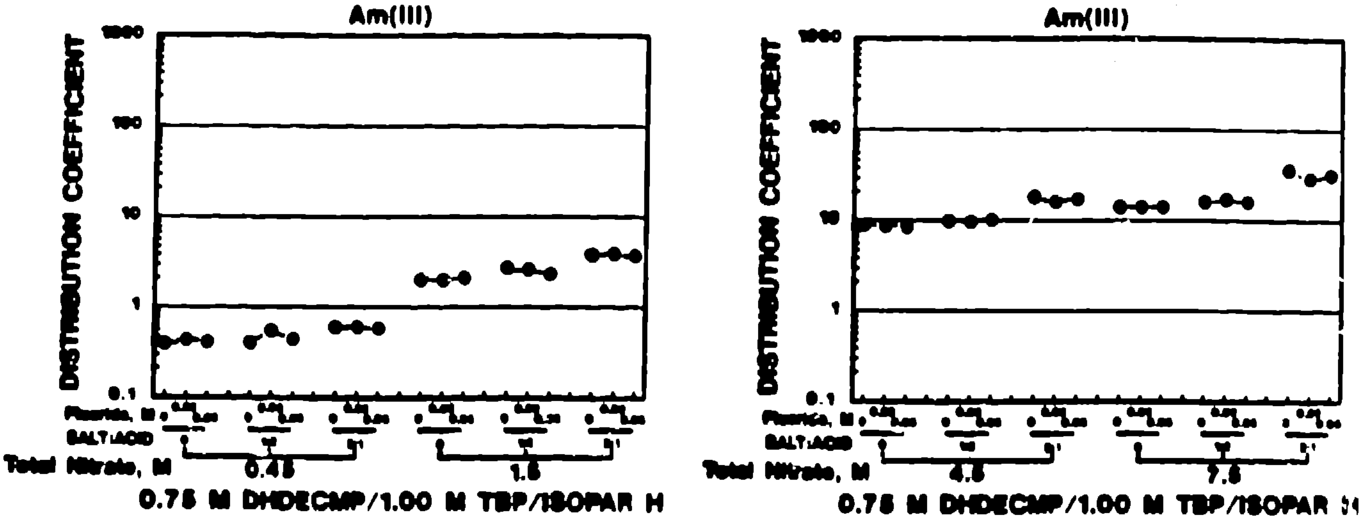

Fig. 3. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

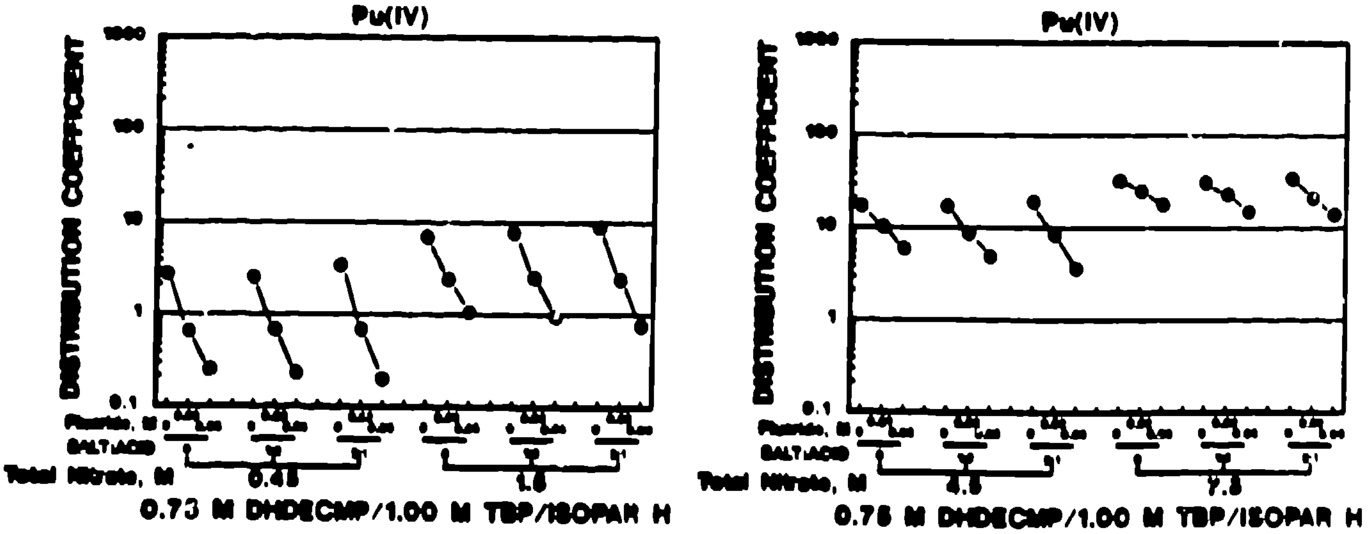

Fig. 4. Extraction of Pu(IV) into 0.75 M DHDECMP/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

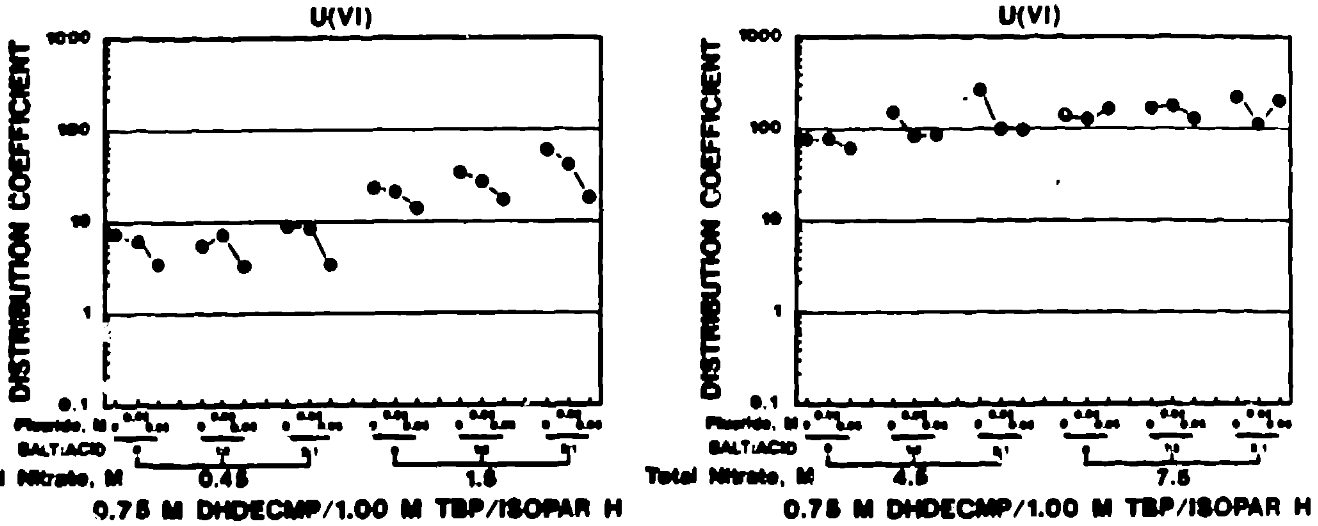

Fig. 5. Extraction of U(VI) into 0.75 M DHDECMP/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

6. The unique combination of adequate extraction from moderate-to-high nitrate solutions and efficient back-extraction from low nitrate solutions justifies the selection of DHDECMP as the extractant of choice for recovering actinides from aqueous nitrate waste streams from plutonium process operations.

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