RFP-2625

RFP-2625

uc

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

EVALUATION OF EXTRACTION CHROMATOGRAPHY FOR AMERICIUM RECOVERY

March 23, 1977

Charlotte E. Alford and James D. Navratil

MASTER

Chemistry Research and Development
Chemical Research

Rockwell International
Atomics International Division
Rocky Flats Plant
Golden, Colorado

To be presented at Colorado-Wyoming Academy of Sciences meeting, Air Force Academy, Colorado Springs, Colorado, April 22, 1977.

EXB
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Extraction, or reverse-phase partition chromatography, as used mostly for analytical separations, employs an organic solvent extractant as a stationary phase on an inert support material. This technique, which has the advantage of utilizing the versatility of solvent extraction systems with the less expensive operation of ion exchange equipment, was evaluated for a process to recover low level concentrations of americium from acidic process waste streams at Rocky Flats. The bidentate organophosphorous extractant DHDECMP (dihexyl-N, N-diethylcarbanylmethylene phosphonate) was used as the stationary phase since it was shown to effectively scavenge americium from acidic waste streams without significantly extracting impurity ions. Over 30 support materials were evaluated for DHDECMP capacity and for their ability to retain the extractant. Of the supports tested, the Amberlite^R XAD macroreticular sorbents were found to have the highest DHDECMP capacity. Amberlite XAD-4 beads retained the extractant significantly better than the other supports evaluated. Thus, this solvent was tested for americium breakthrough capacity and compared to the theoretical capacity.

INTRODUCTION

Extraction chromatography techniques are being evaluated to remove low level concentrations of americium from nitric acid waste. The nitric acid waste is generated during plutonium processing operations at Rocky Flats.

In our new plutonium recovery facility, all acidic waste containing $>10^{-5}$ g/l plutonium and americium will be sent to a secondary anion exchange process. (first slide) The secondary recovery process will reduce the plutonium concentration in the nitric acid waste from 10^{-3} g/l to 10^{-5} g/l. However, americium, also present in the nitric acid, will not be recovered.

Therefore, a process is needed to recover the americium as well as additional amounts of plutonium from the waste. Our long range objective is to reduce the actinide concentrations in the nitric acid waste down to drinking water levels.

A survey of americium recovery methods was made. Solvent extraction was selected as the best method. The bidentate organophosphorous extractants appeared the most attractive for the process because they were the only extractants available which extract essentially only actinides from high concentrations of nitric acid (7^M HNO_3).

Extraction chromatography techniques are being evaluated using a bidentate organophosphorous extractant as the stationary phase. This technique, which is used mainly in analytical chemistry separations and not for preparative scale work, involves sorbing the extractant onto a support material so ion exchange column equipment can be used. This was decided since we would like to use our existing ion exchange columns rather than install expensive solvent extraction equipment.

SLIDE 1. Conceptual Flow Sheet for Acidic Waste at Rocky Flats

Slide 2 shows the structure of the bidentate organophosphorous extractant DHDECMP.

The DHDECMP was obtained from Wateree Chemical Company, Lugoff, South Carolina, on a custom synthesis basis. Presently, Wateree is the only U.S. supplier of this extractant. The extractant was technical grade, thus it contained percentage amounts of the corresponding dihexyl ester of phosphoric acid and other impurities. The dihexyl ester needed removing since it caused difficult back extraction or stripping of the americium from the loaded organic. Caustic scrubbing was not sufficient for removing this impurity, but acid hydrolysis or contact with Amberlyst A-26^R (OH form) resin was sufficient to remove it.

SLIDE 2

Dihexyl N,N, diethylcarbamylnmethylene phosphonate

DHDECMP Capacity Studies

Slide 3 shows the capacity results for several supports. Over 30 support materials were tested. Since a capacity of 1 gram/millilitre was desired only the materials with the highest capacities are shown in the slide. All the other materials had a capacity of 0.15 gram/millilitre or less. The data were obtained by rinsing each support with 15ml of CCl_4 followed by 30ml of water. The supports were then equilibrated with 7^{M} HNO_3 , washed with 30ml of water and allowed to dry at 60°C under vacuum for three days. Next the columns of support material were tared and equilibrated with a 50 volume percent DHDECMP- CCl_4 solution for 3 days. Excess extractant was removed under vacuum and the DHDECMP loaded support washed with 7^{M} HNO_3 until no visible extractant was observed in the wash. Finally the residual 7^{M} HNO_3 was removed by washing with water and the DHDECMP loaded support was dried and weighed. The capacity of the support for DHDECMP was taken as the grams of DHDECMP sorbed on a millilitre of dried, loaded material. Each result is the average and standard deviation of three determinations. Amberlite XAD-4 had the highest capacity.

Washing Studies

Seven of the supports exhibited a high enough capacity to warrant further testing and thus were tested for extractant losses (by solubility). The results are shown in slide 3. The extractant losses were determined by passing 300 column volumes of 7^{M} HNO_3 over the DHDECMP loaded material. The residual 7^{M} HNO_3 was removed by washing with water and the DHDECMP loaded support material was dried and weighed. The extractant losses from the support materials were reported as the percent decrease in the DHDECMP capacity. Amberlite XAD-4 has the lowest extractant losses.

SLIDE 3. DHDECMP Capacity of Various Support Materials

<u>Support Material</u>	<u>DHDECMP Capacity (g/ml)</u>	<u>Decrease in Capacity After Washing (%)</u>
Amberlite XAD-4	0.34 $\pm$ 0.03	18
Amberlite XAD-7	0.32 $\pm$ 0.04	59
Poly M Phenyl Ether Chromosorb*	0.29 $\pm$ 0.01	37
Amberlite XAD-1	0.24 $\pm$ 0.04	39
Bio-Rad SM-2	0.24 $\pm$ 0.02	31
Amberlite IRA-93	0.22 $\pm$ 0.02	52
Amberlite XAD-2	0.22 $\pm$ 0.02	40

*80 to 100 mesh beads; all others 20 to 50 mesh beads.

Americium Breakthrough

Amberlite XAD-4 macroreticular sorbent was tentatively chosen for further testing because of the favorable DHDECMP capacity and low extractant losses. The support was tested for americium breakthrough capacity. The support material loaded with a known amount of DHDECMP was contained in 0.6 cm bore columns with a wet support bed height of 10 cm. The flow rate was controlled at approximately two ml/min.

Each experiment consisted of loading the column with a synthetic americium feed. Fractions (5 ml) of the column effluent were collected and analyzed for americium. The americium loading breakthrough results are shown in slide 4. The ordinate axis is the ratio of the concentration of americium in the ion column effluent to the concentration in the feed (c/c_0) and the abscissa is the milligrams of americium fed to the support bed $\times 10^{-4}$. The americium breakthrough capacity was mg Am/ml support at % breakthrough.

Elution Studies

The americium elution behavior of DHDECMP loaded Amberlite XAD-4 was studied. The columns were eluted with 0.35M HNO_3 . Fractions (15 ml) were collected and analyzed for americium. The results of these experiments are presented in Slide 5. The plot is fraction americium eluted versus millilitre of elutriant passed.

Summary

The elution of americium is very slow and creates too much waste solution. Although the capacity and retention of DHDECMP on Amberlite XAD-4 was good, the poor elution is a definite disadvantage. Other eluting reagents will be tested, as well as smaller bead supports, to improve the americium elution kinetics.

Am Breakthrough of XAD-4

SLIDE 5. Am Elution of XAD-4