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Although solvent extraction technology had its beginning more than 100 years ago, it owes a significant amount of its present prominence as a separation technique to its successful application with actinide elements. Solvent extraction plays a vital role in actinide separation, recovery and purification. The use of thorium, uranium and plutonium and other actinides in nuclear energy programs has led to the rapid development of many new solvent extraction processes that display simplicity, selectivity and speed.

The scientific literature abounds with articles on new solvent extractants [1-6]. While many of the reagents are only of academic interest, several types of extractants show promise in improving actinide recovery, separation or purification. In the last decade, American and Russian workers have evidenced much interest in the potential application of certain neutral and acidic bifunctional organophosphorus compounds in actinide separations. Triggering this interest is the ability of some carbamoylmethylenephosphorus (CMP) and carbamoylmethylenephosphine oxide compounds to extract trivalent actinides from strong nitric acid solutions, a property which distinguishes them from monofunctional organophosphorus compounds [5].

Because CMP strongly extracts actinides and lanthanides, and does not extract more than 40 other elements from 5-7 M nitric acid, the extractant has been found useful for an americium recovery and purification process [7]. Dihexyl-N,N-diethylcarbamoylmethylphosphonate is sorbed on a non-ionic macroporous resin and used in an extraction chromatography mode. The process effectively separates and purifies americium from impurities such as aluminum, calcium, chloride, copper, fluoride, iron, lead, magnesium, plutonium, potassium, sodium and zinc.

Using solvent extractants sorbed onto a solid (extraction chromatography) is well known [7]. The technique combines the attractive properties of solvent extraction (high selectivity, fast rates, high loading capacities, etc.) with the advantages of column adsorption and ion exchange (applicability to the treatment of very dilute solution, ease of liquid/solid phase separation associated with lack of serious problems, such as crud formations and solvent losses into the aqueous phase, ease of handling and simplicity of equipment, etc.)

Recently some additional advantages have been reported using the technique for actinide recovery [8]. The system uses solid supports, such as styrenedivinylbenzene beads, polyurethane foam, activated carbon, etc., loaded with a solid solvent extractant, such as octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO). The extractant (without diluent) is equilibrated with the support at a temperature just slightly above the melting point of the extractant. In addition to efficient sorption of ionic actinide species, polymeric species of

lutonium (IV) are also effectively removed from aqueous mineral acid solutions by the solid extractant-solid support. The actinide loaded material is removed from the column and incinerated, leaving the plutonium in the residue for further recovery.

The advantages of the technique are as follows: (1) The CMPO removes actinides in all oxidation states as well as actinide polymers. (2) The purity of the extractant is not critical since no back extraction step is needed. Thus acid hydrolysis or radiation damage to the reagent should not be a problem, and solvent clean-up steps and solvent pollution problems are eliminated. (3) No diluent is needed, only an inexpensive and combustible support material. (4) The process yields high recoveries and has a high concentration factor.

Besides the importance of the solvent extractant selection in the above extraction chromatography-incineration stripping" process, the proper support is vital to the success of the system. The support must have a high capacity for the extractant and must maintain that capacity during use. Bleeding of the extractant can, however, be prevented by having a small amount of support material free of extractant at the end of the column. The extraction kinetics of the extractant-support must also be comparable to a liquid-liquid system. Finally, the complete combustion properties of the support material are important to provide an ash free residue. The process could also be designed to use the waste heat during the combustion step in other process steps such as initial drying or activation of the support.

A recent study [9] has suggested the best candidate column material for tertiary plutonium recovery is trioctylphosphine oxide (TOPO) sorbed on Amberlite XAD-4 non-ionic resin (20-50 mesh); the recommendation was based on the following: (1) TOPO has a high capacity for plutonium with consistently lower effluent concentrations than other materials tested, (2) although TOPO cannot be satisfactorily eluted with typical reagents, acid digestion or incineration can be used with a consequently large concentration factor of the plutonium recovered, and (3) TOPO removes plutonium (IV) polymer from nitric acid, whereas anion exchange resins do not sorb polymer.

Several inexpensive support materials for sorbing TOPO were evaluated since the use of Amberlite XAD-4 would have an economic impact on the tertiary process since the support is used only once. The following sorbents were tested for TOPO capacity: 1) "Cotton" filler material from the Micro-Wynd II filter cartridge supplied by AMF CUND Division, Meriden, Connecticut; 2) "cord" material from the Micro-Wynd filter; 3) Micro-Klean II filter cartridge also supplied by AMF; 4) typical polystyrene-type packing material which was washed with methanol, dried, frozen and ground to 20-50 mesh; 5) two different sources of polyurethane sponge packing material, washed with methanol; 6) 3M pillow material; 7) Amberlite XAD-4, 20-50 mesh, non-ionic resin supplied by Rohm and Haas Co.; 8) household sponge; and 9) treated peat, described in Ref.10.

In the work, flint-glass Pasteur pipets (5.7mm i.d. x 14cm), containing a small amount of glass wool at the bottom, were washed with acetone, dried, and tared. Weighed sorbent materials were placed in the columns (6-8cm high), which were then heated for one hour at 60°C, cooled and tared. The

support volumes ranged between 1.5 and 2.0 ml. All of the columns were then heated to 60°C and about 5 ml of molten TOPO (60°C) was passed through each of the columns. The columns were kept upright for one hour at 60°C, then cooled and weighed. Finally, 100 ml of 7M nitric acid was passed through each of the columns. Again, the columns were dried and weighed. Control columns containing the glass wool and support material, but not contacted with TOPO, were also processed along with the TOPO columns. These were used to determine the weight loss or gain by the support material during the heating and nitric acid washing steps.

Table 1. Summary of TOPO Capacity of Support Materials

Support Material	Bulk TOPO Capacity g/ml	Washed TOPO Capacity g/ml	Capacity Loss on Wash(%)
Polyurethane 1	0.61	(a)	(a)
Polyurethane 2	0.58	0.57	2
Amberlite XAD-4	0.41	0.41	0
3 M Pillow	0.38	0.37	3
Micro-Klean	0.32	0.32	0
"Cotton"	0.30	0.21	30
Treated Peat	0.30	0.27	10
Household Sponge	0.28	0.13	54
"Cord"	0.25	0.19	24
Polystyrene	0.15	0.10	33

(a) decomposed.

Table 1 summarizes the results of the highest capacity supports. The values are an average of at least three determinations. The average standard deviation of the determinations was $\pm 5\%$. Scrutiny of the capacity data shows that polyurethane sponge material (Source 2) has the highest capacity with only 2% loss of TOPO after passing 50 column volumes of nitric acid through the column. Not only is a high TOPO capacity support material required for the tertiary plutonium recovery process, but the TOPO must be retained by the support material after large volumes of 7 M nitric acid are passed. The polyurethane sponge material meets these requirements. Furthermore, a small amount of unloaded support could be placed at the exit of the column to sorb any TOPO physically removed from the support. The polyurethane material also has excellent liquid flow characteristics; the column back pressure is very low, just as with using 20-50 mesh resins.

More work is needed to compare polyurethane on a larger scale in comparison with the second best material, Amberlite XAD-4. However, since there could be stability problems with polyurethane foam contacted with strong nitric acid solutions, a study of the safety hazards associated with using the polyurethane materials should be a first priority. It should be emphasized that there are many different types of polyurethane foams, some of which are more stable than others [11]. This was observed in this work. The first source of TOPO loaded polyurethane sponge, washed with

nitric acid, decomposed at 50°C; the same material with no TOPO did not decompose, however.

We are continuing to test other inexpensive natural and waste materials for use as combustible solvent extractant supports, such as Victorian brown coal, rice hull ash, waste wool, etc. Furthermore, we are looking at other hydrometallurgical applications and extractants. For example, in the uranium ore process, an inexpensive and impure amine reagent, which strongly extracts uranium, could be used to reduce costs and avoid phosphorus contamination to the incinerated residue opposed to using an organophosphorus extractant. A column operation may also be replaced by a moving conveyor bed or other novel technique for ease of extraction-incineration stripping.

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