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J. J. Hines[a]; H. Diamond[a]; J. E. Young[a]; W. Mulac[a]; R. Chiarizia[a]; E. P. Horwitz[a]
[a] Chemistry Division, Argonne National Laboratory, Argonne, IL

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DECONTAMINATION OF WASTE SOLUTION FROM DAVIES-GRAY ANALYSES IN A PILOT-FACILITY FOR PROCESS DEVELOPMENT

J. J. Hines, H. Diamond*, J. E. Young, W. Mulac, R. Chiarizia,
and E. P. Horwitz,
Chemistry Division, Argonne National Laboratory, Argonne IL 60439-4831

ABSTRACT

A pilot plant for removal of radioactivity from solutions has been built and tested. In an initial trial, uranium remaining in a Davies-Gray-analysis waste-solution was reduced 300,000-fold to 0.2 ppb by passing the solution through Diphonix™ ion-exchange columns. The columns were regenerated (and the uranium was recovered) with HEDPA (1-hydroxyethane-1,1-diphosphonic acid). The latter was destroyed with H_2O_2, and the uranium was reduced and precipitated as a phosphate. Final purification of the dissolved precipitate employed a U/TEVA•Spec™ (dipentyl pentylphosphonate) extraction chromatographic column. Studies of matrix effects upon the uptake of uranium by the Diphonix™ led to an initial dilution of the waste solution and to a reduction of ferric ion.

INTRODUCTION

Disposal of waste solutions can be facilitated by removing activity below prescribed levels, and treating the residue as non-radioactive (either hazardous or non-hazardous) liquid waste. Although all of the legal aspects have not been resolved, it is anticipated that such separations can result in substantial saving in the disposal of laboratory waste and can ultimately be useful on a large scale. Toward

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*Author to whom correspondence should be addressed.

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this end, a facility has been built to develop and test new processes for the removal of actinides from liquid mixed waste contained in 55-gallon drums.

The separation of actinides from solution by the gem-diphosphonic acid ion exchange resin, Diphonix™, has been extensively studied (1-6): actinides are selectively removed from acid solutions (Figure 1), while most mono- and di-valent elements do not remain on the resin. The actinides, particularly uranium, are held so strongly that it requires a gem-diphosphonic stripping agent to regenerate the resin. This, in turn, must be destroyed for further processing of the actinides. We describe a successful decontamination of a real uranium waste-solution resulting from Davies-Gray[7] analyses. The uranium was fully recovered, and purified. Processing of wastes where other actinides might be encountered are discussed.

EXPERIMENTAL

Facility

A schematic of the facility is shown in Figure 2. All of the equipment is contained in a 42" x 156" x 80" enclosure made of stainless steel, with polycarbonate sliding doors that are edged with stainless steel. The enclosure is exhausted to a wing-wide system; the exhaust encounters HEPA filters before it reaches the exterior. The equipment is attached to a framework of fiberglass-reinforced plastic. The floor-load is supported on a series of fiberglass-reinforced plastic 4" I-beams, beneath which is a 6" deep stainless steel pan with a capacity of 115 gallons. Metering pumps on a shelf within the enclosure are remotely controlled by computer.

There is room in the frame for a 55-gallon drum in a Department of Transportation-approved plastic overpack. The mixed waste from this (or other) container is pumped through cartridge filters into a 110-gallon polyethylene mixing tank supported by a fiber-glass-reinforced shell. The tank, with a conical bottom for ease of emptying, is fitted with a stirring motor and a lid with a small polystyrene door for viewing the contents and for adding reagents.

The mixed waste, adjusted for acidity and any required additives, is then transferred to the columns. The Spectrum™ five cm diameter columns are fitted with plungers to allow for variable bed-height. They can be vented and operated in

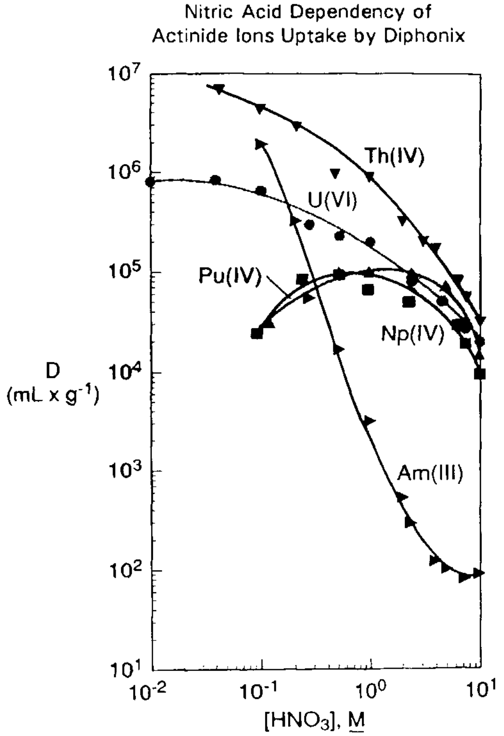

FIGURE 1. Uptake of actinide ions by Diphonix™. From reference (1).

the descending or ascending mode. Porous plastic septa confine the resin and allow expansion and contraction of the resin-bed. Each column contains about 0.5 L of resin. Two columns were operated in series.

The progress of a column-run can be followed with samples taken at either end of each column. The effluent is collected in smaller several-gallon containers, and assayed before combining into the activity-free final container.

The columns are stripped (and regenerated) in the reverse direction; this reduces the volume of stripped activity and leaves the bottom of the second column quite free of activity.

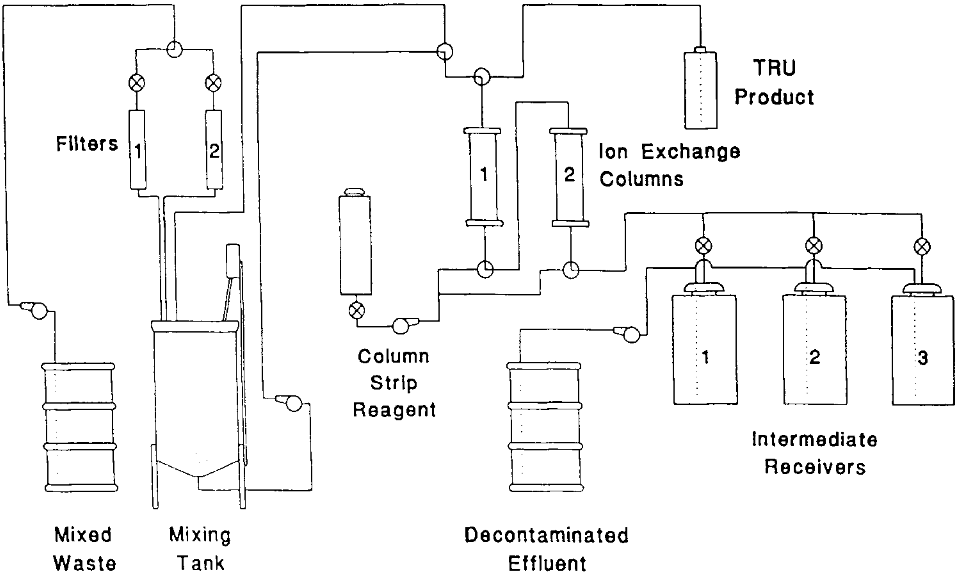

FIGURE 2. Schematic of facility within vented enclosure.

Materials

Diphonix™ (Eichrom Industries, Darien IL) is a new chelating ion- exchange resin containing gem-diphosphonate as its most active exchange site, and sulfonate and carboxylate moieties. An operating bed contains about 2/3 mmole diphosphonate/mL. The 100-200 mesh resin columns were operated at a very conservative flow-rate of 0.25 (mL/min)/cm^2. A recent kinetic study (4) shows that Diphonix™ absorbs and releases elements at a rate similar to BioRad™ AG MP-50; higher flow-rates are reasonable, but they have not yet been tested.

U/TEVA•Spec™ (8) (Eichrom Industries, Darien IL) is 40% (w/w) dipentyl pentylphosphonate on Amberchrom™ CG-71 resin. The latter material, washed with water and methanol and dried under vacuum, formed a guard-tube used in the recovery of uranium from the U/Teva.Spec™ column. This removed the small amount of solvent that bleeds from the column.

The elutriant, 0.5 M HEDPA, 1-hydroxyethane-1,1-diphosphonic acid was obtained as a 1.7 M aqueous solution, IonQuest 201™ from Albright & Wilson Co., Richmond, VA. It was used without purification.

Hydrogen peroxide (Mallinckrodt AR, Paris, KY, 30%) was kept chilled and used directly.

The reductant, SFS, sodium formaldehyde sulfoxylate (9), (Rongalite C) (Eastman Kodak, Rochester, NY) is capable of reducing uranium in 2 M HNO_3 (10) . It was kept refrigerated, and added as a solid since it has limited stability in acid solution.

Analytical grade HNO_3 and 17 Mohm cm Mille Q™ water were used.

Analyses

Uranium and other elements were determined by ICP/AES (Induction Coupled Plasma/Atomic Emission Spectroscopy) using a JY-86 ICP System (Instruments SA, Edison, NJ).

Successively more sensitive uranium measurements were made using a ChemChek Kinetic Phosphorescence Analyzer (ChemChek, Richland WA), and by ICP/MS (inductively coupled plasma/mass spectrometry) using a (Fison Instruments) VG Elemental Quad II Plus instrument.

The decline of HEDPA was observed by ^{31}P-NMR (nuclear magnetic resonance) using a GE-293-based Omega GN 300 instrument.

OPERATION

Loading and Scrubbing the Diphonix™ Column

Five gallons of waste generated by Davies-Gray analyses of uranium (principal composition in Table 1) were chosen to test the decontamination facility. Fe(III) competes (2) with U(VI) for sites on the Diphonix™; hence ascorbic acid was added to reduce the iron. Fe(II) is not held strongly by the resin.

One-thousandth scale tests showed that uranium would be very close to breaking through the two columns. This was surprising in view of its D (dry

TABLE 1. COMPOSITION OF DAVIES-GRAY WASTE

ELEMENT	moles/L	ACIDS	moles/L
uranium	5×10^{-4}	HNO_3	0-7
iron	.024	H_2SO_4	0.2
vanadium	0.0016	sulfamic	0.06
chromium	4×10^{-4}	H_3PO_4	2.8
molybdenum	0.0011		

weight distribution ratio) between 10^5 and 10^6 shown in Figure 1. However, a two-fold dilution reduced the matrix interference to a point where we could expect the uranium to be retained by the Diphonix™ resin. Batch tests with the waste-solution as received, showed that the uranium distribution ratio with respect to Diphonix increased 10-fold by tripling the volume with water, and more than 10-fold further by another volume-doubling. Reference 5 reports the effect of H_3PO_4 upon the uptake of uranium and other actinides by Diphonix.

A flow-diagram of the complete separation and purification scheme is shown in Figure 3.

Periodic samples were taken from the effluent of the two columns, operated in series. Assays of samples from the second column indicated a combined uranium content of ~0.2 ppb for the 40 L of load and scrub solutions. (A comparable analysis of water removed from an Argonne drinking fountain indicated 2 ppb U.)

Stripping the Diphonix™ Column

The stripping agent, 0.5 M HEDPA, was introduced at the bottom of the second column and was collected from the top of the first column. Uranium analyses of periodic samples from the top of the first and second columns are shown in Figure 4. In order to maximize the uranium yield in this demonstration run, 2 L of the effluent were taken for the next procedure. The results in Figure 4

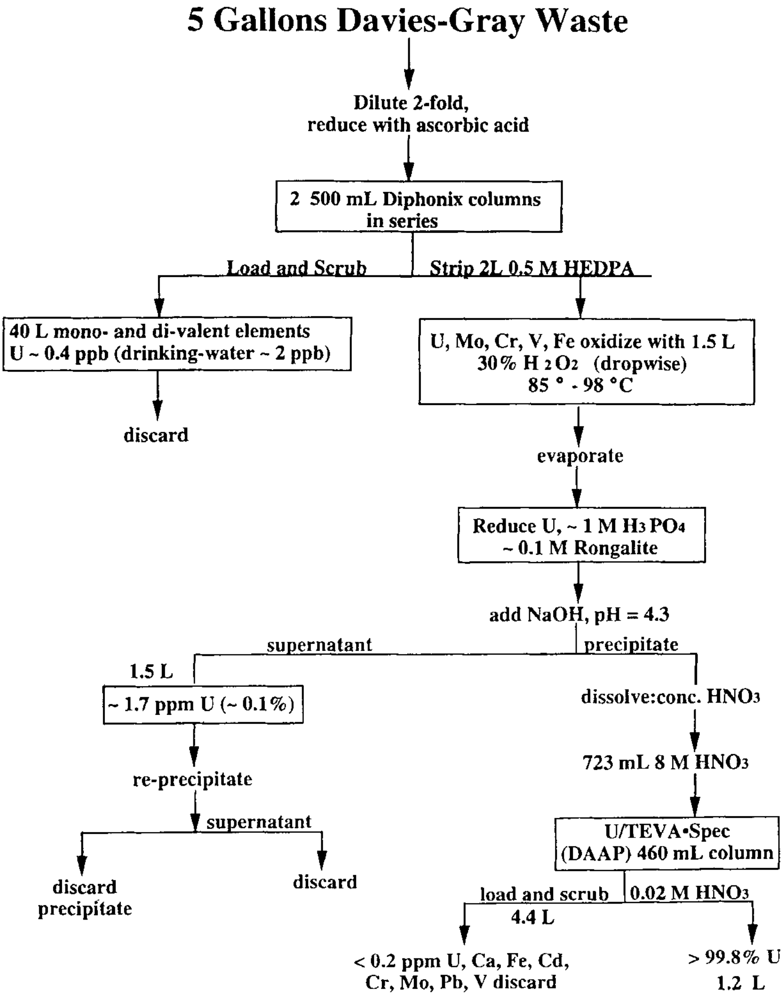

FIGURE 3. Removal of uranium from the waste solution and recovery of the uranium.

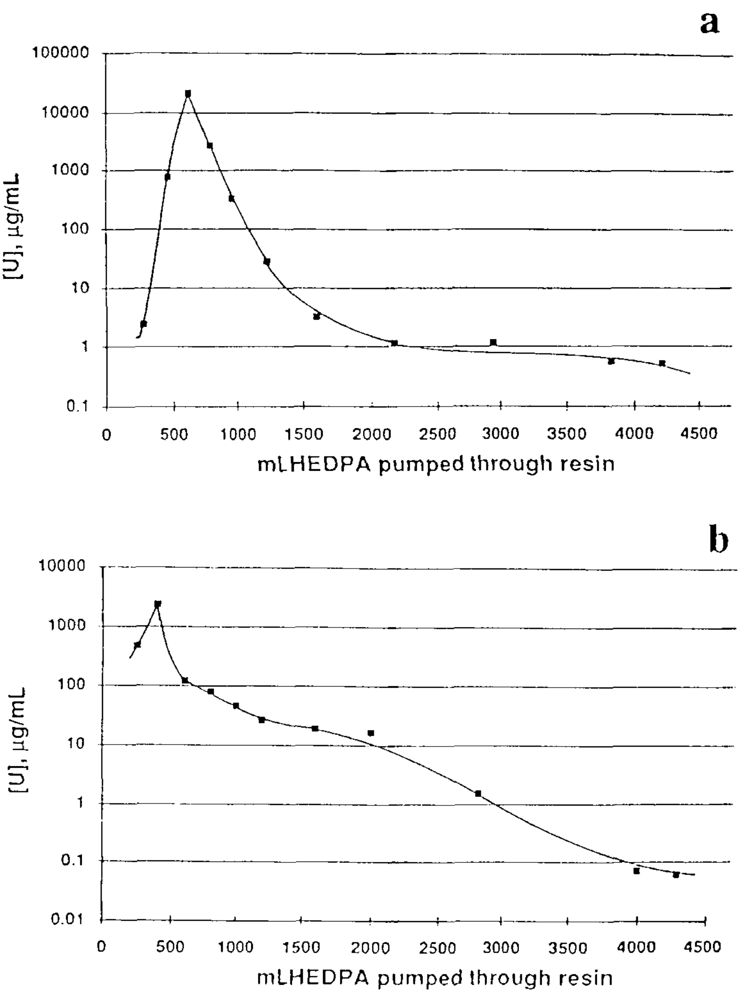

FIGURE 4. Uranium concentration of the strip-solution (a) from the top of the first column, and (b) from between the columns.

show that the second column was a necessary component of the system for the conditions of this demonstration.

Oxidation of HEDPA

Studies by E. Appelman (11) show that HEDPA can be destroyed by H_20_2 at 85-100 C. The efficiency of the peroxide is highest around a pH of 1, but even then, a mole ratio of H_20_2/HEDPA >10 is recommended. In this demonstration, 1.5 L of 30% H_20_2 (~15 moles) was used with 1 mole of HEDPA. Vanadium catalyst (0.001 M) is required. The original waste solution (Table 1) had an excess of vanadium, one-fourth of which remained on the Diphonix™ column and was removed with the uranium.

Alternatively, sodium peroxydisulfate could also have been used(11) at room (or slightly higher) temperature, and in a little more than stochiometric amounts. Silver and copper catalysts are needed for the peroxydisulfate oxidation.

The addition of 30% hydrogen peroxide to a 0.5 M HEDPA solution, is highly exothermic, so additional heat was only required initially. The H_20_2 must be added slowly to a well-stirred solution to avoid overheating and to reduce side-reactions. Early tests with 50% H_20_2 were unsuccessful. The progress of the HEDPA-destruction was observed by ^{31}P-NMR. In an alternative analytical procedure, ^{233}U was added to a 1/1000th portion of the solution; the uranium was reduced, and >99% precipitated as a phosphate upon neutralization to pH = 4.3. Any remaining HEDPA has been shown to keep some of the uranium in the supernatant solution.

Precipitation of U(IV) Phosphate

After heating to remove all of the remaining H_20_2, the solution was made 0.1 M sodium formaldehydesulfoxylate (SFS, Rongalite), and brought to pH = 4.3 with solid NaOH. The voluminous (because of ferrous ion still present) precipitate was centrifuged, but not washed. The supernatant contained only 1.7 ppm uranium (~0.1% of the total). The precipitate contained all of the uranium, 28% of the iron, 55% of the molybdenum, all of the lead, 24% of the vanadium, and 15% of the phosphorus. It also contained minor amounts of: Al (10% of total), Ca (38%), Cr

(10%), Cd (~100%), Cu (~100%), and Mg (18%). Other work has shown that all lanthanides and actinides are quantitatively included in this precipitate if sufficient carrier is present. After several days, a small amount of further precipitate was observed.

Final purification of Uranium

The uranium was then separated from all apparent impurities with a U/Teva•Spec™ extraction chromatographic column. The precipitate was dissolved with concentrated HNO_3.

Since the solution still contained phosphoric acid which interferes with the retention of uranium on the U/TEVA•Spec™ column, more nitric acid was added until the nitrate concentration was ~10 M, the H^+ was ~8 M, and the phosphorus content was 1.1 M. The concentrations of cations were: 0.015 M uranium, 0.045 M iron, 0.0075 M molybdenum, 0.0025 M vanadium, and very small amounts of Al, Cr, Cu, Cd and Pb. Subsequent to this work, it was learned that the very high acid concentration was only slightly valuable in increasing the distribution ratio between uranium and the column-material, while dilution of the H_3PO_4 is very important. The uranium occupied about one-half of the (470 mL) column during loading; this was followed with 10 free column-volumes of 10 M HNO_3. No uranium (<0.2 ppm) was found in the effluent, and all of the known cationic impurities were below detection threshold after the seventh free column volume.

The uranium was stripped with 0.02 M HNO_3, again in the reverse direction. A guard-tube containing macroporous resin was added to the top of the column to catch any bleeding solvent from the U/Teva•Spec™ column. The first four free-column-volumes contained virtually all of the uranium in dilute acid.

DISCUSSION

The unique property of Diphonix resin is its ability to extract III-, IV- and VI-valent actinides from a wide variety of acids and salt concentrations (1,5). This holds promise for large decontaminations of many solutions where the sources of contamination, and in many cases, the nature of the solutions are only approximately known.

The tenacity of the diphosphonate resin for actinides is such, that another diphosphonate, HEDPA. is required for stripping, and when that is destroyed, the resulting phosphate often interferes with subsequent procedures. The demonstration reported here did not involve valuable materials, but the test was operated as if the uranium were to be recovered. This was done successfully.

A reasonable alternative to the process shown in Figure 3 is to remove the Diphonix™ resin from the first column, clean the column and load it with fresh resin. This would then form the second column for the next batch. The cost of the fresh resin would be about $500, but this might be reduced as sufficient alternative uses for Diphonix™ are developed. The removed resin, would be dried (perhaps calcined) and discarded as dry-active waste. Such an alternative is generic for all actinides that need not be recovered.

The initial phosphate precipitate could be the starting-point for the recovery of all actinides. It is also a plausible form for disposal of highly active hazardous waste. Tetravalent and trivalent actinides and lanthanides could be recovered, if necessary, from many of the other elements, and from most of the remaining phosphate by dissolution with HNO_3 and precipitating with oxalate.

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Dr. E. H. Appelman provided research and guidance on the destruction of HEDPA. J. W. Crain provided ICP/MS measusrements, A. M. Essling gave uranium-fluorescence analyses, E. A. Huff measured many elements with ICP/AEC, and J. V. Muntean measured HEDPA with ^{31}P NMR. The work was funded by the Waste Management Office of Argonne National Laboratory.

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