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OF RADIOACTIVE LIQUID WASTE

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COMPARISON BETWEEN CMPO AND DHDECMP FOR ALPHA DECONTAMINATION OF RADIOACTIVE LIQUID WASTE

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Summary

Ion exchange is the major method used at Los Alamos to recover and purify plutonium from a variety of different contaminants. During this process, a high-acid (5-7M), low-activity stream is produced that presently is concentrated by evaporation, then cemented for long-term disposal. Our goal is to remove and concentrate the radioactive elements so that the remainder can be treated as "low-level" or regular industrial waste. Solvent extraction with neutral bifunctional extractants, such as DHDECMP and CMPO, has been chosen as the process to be developed. Experimental work has shown that both extractants effectively remove actinides to below the required limits, but that CMPO was much more difficult to strip. In addition, studies of plutonium and americium removal using a wide variety of ion exchangers and supported extractants including DHDECMP, CMPO, and TOPO will be reviewed.

1. INTRODUCTION

Numerous investigators have studied carbamoylmethylphosphoryl derivative extractants during the past decade.¹⁻⁴ Of these compounds, carbamoylmethylphosphonates and carbamoylmethylphosphine oxides appear to be the most selective structures for extracting actinide and lanthanide elements from nitric acid. Of particular significance is the high extractability of actinides in their (III), (IV), and (VI) oxidation states, a fact that often eliminates the usual need for prior oxidation state adjustment. Previous published studies have demonstrated the value of dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) for full-scale nuclear materials processes. Because no commercial suppliers of pure DHDECMP existed until recently, studies used impure or purified DHDECMP in conventional solvent extraction⁷⁻¹¹ and process-scale extraction chromatography¹² systems.

High-purity DHDECMP recently became available from a new commercial supplier who uses a patented phase-transfer catalysis process¹³ to synthesize this compound. The advent of this new commercial potential source prompted us to reevaluate DHDECMP for removing actinides from nitric acid waste streams at Los Alamos. We also elected to evaluate the performance of octylphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO), an extractant selected for the proposed TRUEX process.¹⁶ Comparative performance data for both extractants, whose structures are shown in Fig. 1, were determined over a wide range of variables that encompass the composition of typical process feed streams.

2. REAGENTS AND APPARATUS

DHDECMP, obtained from Occidental Chemical Corporation, Specialty Products Division, Niagara Falls, New York, was used without additional purification. CMPO, obtained from M&T Chemicals, Inc., Rahway, New Jersey, was purified by contact with cation exchange resin, anion exchange resin, and carbonate washing, the MIX procedure of Horwitz and Gatrone.¹⁷

Tetrachloroethylene (TCE), obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey, was used as received. Isopar H, a

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

highly purified mixture of C₉ to C₁₂ isoalkanes, was used as received from the manufacturer, Exxon Chemical Company, Houston, Texas. Reagent-grade nitric acid, sodium nitrate, and hydrofluoric acid were used as received. Extraction bottles, 1 oz., high-density polyethylene with 18 mm caps (catalog number 16054-010, were obtained from VWR Scientific, San Francisco, California. Dispensing spouts (catalog number F1263-0018) to fit the 1 oz. bottles with 18 mm caps were obtained from Bel-Art Products, Pequannock, New Jersey. A Burrell model 75 wrist-action shaker (catalog number 57040-049) was obtained from VWR Scientific, San Francisco, California.

Reagents and procedures for extraction chromatography, plutonium polymer, and membrane studies have been described earlier.^{19,20}

3. EXPERIMENTAL

General

For the comparison study, we measured all distribution coefficients for the initial contact of an aqueous solution and organic solution of the specified compositions. Neither the aqueous nor organic solution was preequilibrated. Thus, the measured distribution coefficients represent the initial solvent extraction stage rather than a later stage at which each phase has become equilibrated with the other.

Extractions

We combined 5 mL portions of each combination of extractant solution and aqueous mixture in individual 1-oz. polyethylene bottles. A 0.1 mL portion of a Pu(IV) stock solution in 7 M nitric acid was added to each bottle immediately before extraction. (All aqueous solution compositions were calculated and prepared to provide the desired acid concentrations after addition of the 0.7 millimole of nitric acid in the plutonium stock solution.) The plutonium content of the extracted solutions was always about 4 g/L; americium-241 content was about 15 microgram/L, and uranium-237 was present only at trace concentrations. The oxidation states of these three actinides immediately before extraction were Am(III), Pu(IV), and U(VI). Any significant change in oxidation state during the brief extraction period was unlikely.

We sealed the polyethylene extraction bottles that contained each aqueous/organic combination with solid Polyseal caps, and the contents were dynamically contacted for one minute (which is sufficient to establish equilibrium) using a wrist-action shaker. Each bottle and its contents then were allowed to stand for at least 5 minutes to allow the phases to separate. Following phase separation, the two phases were separated by decantation through the dispensing spout cap.

Gamma Assay Technique

We assayed the extracted aqueous portions in all cases using gamma spectrometry and compared them with an identical unextracted aqueous portion. The difference between these two measurements, for each actinide, represented the quantity extracted. Gamma spectrometric assays were based on the 59.5-keV, 129-keV, and 208-keV gamma-ray peaks of ²⁴¹Am, ²³⁹Pu, and ²³⁵U, respectively.

Computation of Distribution Coefficient (K_d) Values

We computed K_ds for each extraction using the relationship

$$K_d = \frac{\text{concentration of actinide in organic phase}}{\text{concentration of actinide in aqueous phase}}$$

The concentration of each actinide extracted into the organic phase was measured by difference.

Extractants Tested

The value of DHDECMP for extracting actinides has been recognized for many years. More recently researchers have developed and proposed CMPO as the extractant for the TRUEX process.¹⁶ CMPO is unquestionably a stronger extractant than DHDECMP; however, the higher extractability of actinides makes back-extraction from CMPO more difficult. CMPO is expected to offer superior chemical and radiolytic stability and also lower solubility in aqueous nitrate solutions. DHDECMP, on the other hand, is more selective in rejecting common impurity elements, such as iron, molybdenum, and zirconium.¹⁴

Because each extractant appears to offer unique advantages and disadvantages, we elected to evaluate both under identical conditions. The only significant difference was that CMPO solutions were 0.25 M, whereas DHDECMP solutions were 0.75 M. Despite the threefold-higher concentration of DHDECMP, the current 2.5-fold-lower price of DHDECMP made the overall costs of the two extractants roughly equal. The present prices of both extractants reflect the small current market; however, the cost of either extractant would be expected to drop substantially as a larger market develops. In any case, the cost of the extractant would be a small fraction of the overall cost of an operational facility at Los Alamos.

Diluents Tested

We evaluated tetrachloroethylene (TCE) as a diluent because researchers have proposed it as the diluent for the TRUEX process, primarily because TCE is nonflammable. The disadvantages of TCE include its propensity for forming persistent organic dispersions in the aqueous phase, its high volatility, its classification as a carcinogen, and its ability to form radiolysis products that are corrosive to stainless steel process environments. Isopar H, although flammable, has a sufficiently high flash point to make ignition unlikely. The long record of safe operation with such kerosene-type diluents within the nuclear industry attests to the adequacy of this safety margin. Moreover, Isopar H is an order of magnitude less volatile than TCE under identical conditions. It provides rapid and complete phase separation after extraction and is nontoxic. This combination of favorable properties prompted us to also evaluate Isopar H as a diluent.

Other Variables Tested

We evaluated total nitrate concentrations of 0.45 M, 1.5 M, 4.5 M, and 7.5 M. Each nitrate level was evaluated as 100% nitric acid, as 2/3 nitric acid and 1/3 sodium nitrate, and as 1/3 nitric acid and 2/3 sodium nitrate. Each of the 12 combinations of total nitrate and nitric acid/nitrate salt ratio was evaluated at fluoride concentrations of zero, 0.02 M, and 0.05 M.

Evaluation of the 36 different aqueous compositions with each of the 4 extractant/diluent combinations produced K_d values of Am(III), Pu(IV), and U(VI) for each of the 144 unique aqueous/organic combinations.

4. RESULTS AND DISCUSSION

General

Experimental distribution data usually are presented in a format that illustrates the effect of a single variable. Because this study evaluated multiple variables, we sought a format that would allow presentation of the individual and interactive effects of many variables in a single figure. A "tree" format suggested by Richard J. Beckman of the Los Alamos National Laboratory Statistics Group simultaneously illustrates the effects of total nitrate, nitrate salt/nitric acid ratio, and fluoride concentration.

Effects of Specific Variables

Extractant: CMPO consistently extracts americium, plutonium, and uranium more strongly than does DHDECMP. This fact is illustrated in Fig. 2, which shows the distribution coefficients of americium as a function of the extractant/diluent combinations from nitric acid solutions (without salt or fluoride).

The higher extraction of actinides by CMPO from medium concentrations of nitric acid can be

Fig. 2: Extraction of Am(III) into various extractant/diluent combinations as a function of nitric acid concentration.

beneficial; by contrast, high Kds from dilute nitric acid are a distinct disadvantage because they make back-extraction much more difficult. DHDECMP, however, provides adequately high Kds from medium concentrations of nitric acid, but offers Kds from dilute acid that are sufficiently low to allow americium and plutonium to readily be back-extracted.

Diluent: Investigators have proposed TCE for use in the TRUEX process not only because it is non-flammable but also because it is a reasonably good solvent for CMPO and CMPO/metal complexes. In our studies, however, TCE formed persistent organic dispersions in the aqueous phase, which were removed by scrubbing with a fresh portion of TCE. Diluents that have been used safely for many decades in the nuclear industry include certain flammable liquids such as kerosene, whose high flash points provide an adequate margin of safety. Although DHDECMP and CMPO are only slightly soluble in kerosene, the addition of tributylphosphate (TBP) makes the three components miscible.

Initial experiments with Isopar H, a kerosene-type diluent approved for use in the Los Alamos Plutonium Facility, showed much-improved phase separation, which eliminated the need to scrub the aqueous phase as done with TCE. An additional benefit of Isopar H was its ability to provide higher Kds for Am(III) using either extractant than provided by TCE (Fig. 2). The Kd enhancement with Isopar H is especially pronounced for Am(III) extraction by CMPO. Comparative data for Pu(IV) and U(VI) extraction into DHDECMP and CMPO, using TCE or Isopar H as the diluents, showed a smaller increase when using Isopar H.

Nitrate Salt/Nitric Acid Ratio: High concentrations of nitrate salts are common components of nuclear process solutions. Evaluation of the effect of nitrate in the form of nitrate salts was therefore essential. The general effect of replacing nitric acid with nitrate salt is a small increase in the distribution coefficient in all of the systems studied. This increase is attributed to the higher activity of nitrate ion that results from the more complete dissociation of nitrate salt as compared with nitric acid.

TBP/Extractant Ratio: The PUREX process has used TBP for many years to extract uranium and plutonium from various nitrate solutions. TBP, proposed as a phase modifier with CMPO in the TRUEX process, decreases the extraction of actinides from dilute acid, although it increases the extraction of actinides from medium concentrations of nitric acid when compared with extraction by only CMPO.¹⁵ Moreover, TBP increases the solubility of CMPO and CMPO/metal complexes in the organic phase.

Our preliminary study that compared 1.00 M DHDECMP/TCE and 1.00 M DHDECMP/0.35 M TBP/TCE showed that the Kds of uranium, plutonium, and americium were not significantly affected by the presence or absence of TBP. We elected to include TBP as a component of both organic extractants studied, however, (1) to be consistent with the recommended TRUEX composition when CMPO was the extractant, (2) to increase the solubility of the DHDECMP and its metal complexes when DHDECMP was the extractant, and (3) to maintain similar compositions where possible during the comparative evaluation of DHDECMP and CMPO.

A serious disadvantage of TBP is that it also extracts large quantities of nitric acid. The extracted acid subsequently back-extracts into dilute acid used to strip the actinides. Substitution of a different organic phase modifier that does not extract nitric acid would allow the number of strip stages to be minimized.

Behavior of Individual Actinide Elements

Figures 3-10 show the results of americium extraction under various conditions. Space limitations do not allow us to show the results for plutonium and uranium. The results for these elements are available elsewhere²¹ and show uranium and plutonium to be more extractable than americium. Effects by nitrate salt and fluoride concentration are discussed below.

DHDECMP/TBP/TCE. (Figs. 3 and 4) Americium extraction increases slightly with nitrate salt levels. A small but consistent decrease results from increasing fluoride when nitrate salt is absent; however, a consistent decrease results from increasing fluoride at the highest nitrate salt levels.

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

Fig. 4. Extraction of Am(III) into 0.75 M DHDECMP/1.00 M TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

DHDECMP/TBP/Isopar H. (Figs. 5 and 6) Americium extraction increases significantly with nitrate salt levels, but is essentially unaffected by fluoride. Kd values with Isopar diluent are generally double to triple those obtained with TCE diluent.

Fig. 5 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. 6 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.

CMPO/TBP/TCE. (Figs. 7 and 8) Americium extraction increases significantly with nitrate salt levels. Fluoride has no effect on americium extraction. K_d values are similar from 7.5 M nitrate, but are approximately 30 times higher from 0.45 M nitrate when compared with the DHDECMP/TBP/TCE system. Thus, CMPO offers little improvement in extraction from medium concentrations of nitric acid, but back-extraction into dilute acid is far more difficult.

Fig 7. Extraction of Am(III) into 0.25 M CMPO/1.00 M TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Fig. 8. Extraction of Am(III) into 0.25 M CMPO/1.00 M TBP/TCE as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

CMPO/TBP/Isopar H. (Figs. 9 and 10) A slight decrease in americium extraction is associated with increasing fluoride levels. K_d values with Isopar diluent are approximately four times those obtained with TCE diluent. (This difference represents the largest diluent effect of the entire study.) K_d values of this CMPO/TBP/Isopar system, when compared with the DHDECMP/TBP/Isopar system, are only double to triple from 7.5 M nitrate, but are approximately 40 times higher from 0.45 M nitrate. Again, the demonstrated increased difficulty in back-extracting americium from CMPO is a major disadvantage.

Fig. 9. Extraction of Am(III) into 0.25 M CMPO/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

Fig. 10. Extraction of Am(III) into 0.75 M CMPO/1.00 M TBP/Isopar H as a function of nitrate concentration, nitrate salt/nitric acid ratio, and fluoride concentration.

5. CONCLUSIONS

1. CMPO extracts Am(III), Pu(IV) and U(VI) more strongly from all of the aqueous compositions of nitric studied than does DHDECMP. This difference, however is much greater from low nitrate concentrations than from high nitrate concentrations. Consequently, back-extraction of these actinides by dilute acid is difficult from CMPO, but relatively easy from DHDECMP.

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

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

4. Fluoride suppresses Pu(IV) extraction 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. Persistent organic dispersions remained in the aqueous phase after extraction with TCE-diluted extractants. An additional scrub step using pure TCE was required to minimize the extracted actinides in this dispersion before the aqueous phase could be reliably assayed.

6. Phase separation was more rapid and complete when Isopar H was the diluent. Extractants diluted with Isopar H provided low-dispersion aqueous phases that required no subsequent scrub step.

7. Americium(III) K_d values were significantly higher for extractants diluted with Isopar H under all conditions tested. K_d values for Pu(IV) were generally lower for CMPO diluted with Isopar H. DHDECMP extractions of Pu(IV) were essentially unaffected by the diluent. K_d values of U(VI) for both extractants were slightly lower with Isopar H diluent.

8. DHDECMP/TBP/Isopar H offers K_d values of at least 10 for Pu(IV) and Am(III) from nitrate concentrations of 4.5 M to 7.5 M. Thus, >90% extraction of these actinides is attainable from each extraction stage.

9. DHDECMP/TBP/Isopar H offers K_d values <0.5 for Am(III) and Pu(IV) from 0.45 M nitrate/0.05 M fluoride. This result (and even lower K_d values from lower nitrate concentrations not included in this study) should allow efficient back-extraction of these two actinides.

10. TBP modifies the extraction properties of CMPO in useful ways, but serves only to increase the extractant solubility when DHDECMP is used. TBP, unfortunately, also extracts large quantities of acid, which requires many additional stripping stages to remove this acid before significant back-extraction of actinides occurs. Substitution of a diluent that dissolves DHDECMP and its metal complexes, but not nitric acid, will be explored as a means of minimizing the number of strip stages in the process eventually used. [Pilot-scale studies were performed satisfactorily with diisopropylbenzene, which does not require TBP to solubilize DHDECMP or CMPO metal complexes.]

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

6. ACKNOWLEDGMENT

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7. REVIEW OF OTHER ACTINIDE REMOVAL STUDIES

Plutonium Removal

Several solvent extractants, including DHDECMP and CMPO, supported on Amberlite XAD-4 polystyrene-divinylbenzene and anion exchange resins were evaluated for their ability to remove low concentrations of plutonium from 7 M nitric acid. Table 1 shows the results for sorption of 1 mg Pu/L solutions (4.0 L) when passed at 10 mL/min through a 50 mL column of each material.¹⁹

On the basis of low sorption, TBP and IRA-938 were eliminated as candidates for further study. On the basis of elution efficiency, the rest of the materials are roughly equivalent except for TOPO (tri-octylphosphine oxide) and CMPO. TOPO was included for further evaluation because it is possible to recover the plutonium by use of incineration or acid digestion. CMPO was eliminated because of its mediocre

Table 1. Sorption and elution of plutonium (1.0 mg/l)

Material	Pu %, in Effluent	Pu %, in Eluate*
DHDECMP	2.5	49.8
DHDECMP+TBP	4.0	75.6
TBP	32.8	46.1
TOPO	3.6	3.8
Dowex 1x4	3.5	80.0
IRA-938	6.3	50.8
OPD(IB)CMPO	1.5	23.0
OPD(IB)CMPO**	2.6	16.0

*Corrected for Pu not sorbed.

**With 0.12 g/l iron in the feed.

performance in the presence of iron(III) and because it is too expensive to destroy by oxidation to recover the plutonium.

The remaining compounds were evaluated for their capacity for plutonium by passage of 30 mg Pu/L solutions through similar 50 mL columns until 10% breakthrough or more was observed. Table 2 shows the results of this test, including a comparison of the observed capacity with the theoretical capacity of the material.

We see that TOPO has twice as much capacity for plutonium as the nearest competitor, Dowex 1-x4, making it the best candidate to sorb low concentrations of plutonium. We propose, because of its greater ease of elution, that Dowex 1-x4 (50-100 mesh) be used to recover the bulk of the plutonium and that TOPO be used to remove the last traces for recovery by resin oxidation.

In addition, TOPO has the advantage of being able to sorb hydrolytic plutonium polymer, which is a common component of plutonium waste streams,¹⁹ whereas anion exchange resins cannot. Our recent studies²² have shown that this ability is probably due to an acidic impurity in some batches of TOPO. Fortunately,

Table 2. 10% Breakthrough capacities with 30 mg/l plutonium feed

Material	10% Breakthrough Vol (l)	Pu Sorbed (g)	Capacity (mg/ml)	Theor Cap (mg/ml)	% Theor
TOPO	90	2.650	53.1	112	47.4
DHDECMP	48	1.550	31.0	115	27.0
Dowex 1x4	42	1.330	26.5	167	15.8
DHDECMP+TBP	32	0.956	19.1	115	16.6

American Cyanamid has introduced a low cost alternative to TOPO, which also extracts plutonium polymer from nitric acid.²² This material, called Cyanex 923, is a mixture of trialkylphosphine oxides and its low cost makes this scenario for recovery of plutonium much more realistic.

Americium Removal

We have also investigated a variety of techniques for removal of americium from nitric acid waste streams.²⁰ Table 3 shows the results for the transfer of americium through a hollow fiber membrane module (11.5 cm x 0.15 cm Accurel with 0.1 cm wall thickness) loaded with DHDECMP.

Only at the lowest acidity was the fraction transferred high enough to calculate a permeability. At higher acidities, nitric acid is also transported through the membrane, eventually raising the acidity of the strip solution (0.25 M oxalic acid) to the point that the net transfer of americium ceases. The 0.1 M acidity simulates the partial neutralization of a 7 M nitric acid waste stream and is therefore a realistic test of the membrane transfer system.

We have also explored the possibility of concentrating americium even further using the membrane transfer system by passing the strip solution through a cation exchange column while the experiment is in progress. Two tests of the above system with Dowex 50W-x8 showed that about 80% of the americium (initially 0.0008 g/L) in the 0.1 M/6.9 M feed was removed and that the strip solution remained below the detection limit for americium ($<4.1 \times 10^{-6}$ g/L). To avoid the possibly dangerous disposal of organic resins loaded with americium, we investigated the distribution of americium between 0.1 M nitric acid and inorganic ion

Table 3. Percentage transfer and selected permeabilities of americium(III) through a hollow fiber membrane of DHDECMP as a function of feed nitric acid concentration ([Am] = 0.1 mg/l).

$[HNO_3], M$	$[NaNO_3], M$	% Transfer	$10^{-4} \frac{P}{cm \text{ sec}^{-1}}$
7.0	0.0	61	-
5.0	2.0	64	-
3.0	4.0	76	-
1.0	6.0	90	-
0.1	6.9	94	7.2

exchangers. After 1 hr contact times, the distribution ratios were as follows: sodium titanate-3500, zirconium phosphate-1100, zirconium tungstate-800, and bone char-600.

Based on these results, we envision a membrane transfer system that removes americium from a nitrate waste stream and delivers it to a low acid strip solution. An inorganic cation exchange material, such as those tested above, removes and concentrates the americium from the strip solution. The inorganic material would then be dried and shielded to become a safe material for long term waste storage.

We have also investigated extraction chromatography for americium removal using CMPO as the selective extractant. The higher Kds for CMPO make it preferable to DHDECMP for use in the extraction chromatography mode. Our tests showed that iron(III) caused rapid breakthrough when 7 M nitric acid solutions were passed through columns of CMPO on XAD-4. Satisfactory selectivity against iron can be obtained if the feed solution is partially neutralized with sodium hydroxide and 0.20 M oxalic acid is added.²⁰ However, the acid need be neutralized to only 1-2 M, a practically achievable system. Tests of such a system showed that 6.0 L of a 1.2×10^{-3} g Am/L feed solution neutralized from 7.4 M nitric acid to 1.0 M acidity plus 0.20 M oxalic acid is reduced to $<4.1 \times 10^{-6}$ g Am/L after passing through a 50 mL column of CMPO (0.36 g/mL) at 10 mL/min, even in the presence of 0.15 g Fe/L. Work remains to develop a method to elute the americium from such a column, however.

Thus, we have shown several different methods of actinide recovery and have evaluated several candidate materials. The future looks promising for the achievement of our goal of decontaminating nitric acid waste streams.

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