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and Chelating Resins
in Polishing Actinide-
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Evaluation of Extractants and Chelating Resins in Polishing Actinide-Contaminated Waste Streams

by

S. B. Schreiber, S. L. Dunn, and S. L. Yarbrow

ABSTRACT

At the Los Alamos National Laboratory Plutonium Facility, anion exchange is used for recovering plutonium from nitric acid solutions. Although this approach recovers >99%, the trace amounts of plutonium and other actinides remaining in the effluent require additional processing. We are doing research to develop a secondary unit operation that can directly polish the effluent so that actinide levels are reduced to below the maximum allowed for facility discharge. We selected solvent extraction, the only unit operation that can meet the stringent process requirements imposed; several carbonyl and phosphoryl extractants were evaluated and their performance characterized. We also investigated various engineering approaches for solvent extraction; the most promising was a chelating resin loaded with extractant. Our research now focuses on the synthesis of malonamides, and our goal is to bond these extractants to a resin matrix.

INTRODUCTION

At the Los Alamos National Laboratory Plutonium Facility, aqueous processing methods are used to recover plutonium from various scrap materials. Currently, we apply an anion-exchange method to purify and recover plutonium dissolved in nitric acid. The plutonium is subsequently precipitated from anion-exchange eluate as an oxalate with oxalic acid. More than 99% of the Pu is recovered. The major waste streams generated are the anion-exchange effluent and oxalate filtrate, which both contain trace amounts of Pu as well as any Am or U present in the feed stream. These wastes are further processed using an evaporator that produces a low-level acid waste and a concentrated transuranic (TRU) waste. The flow scheme is presented in Fig. 1.

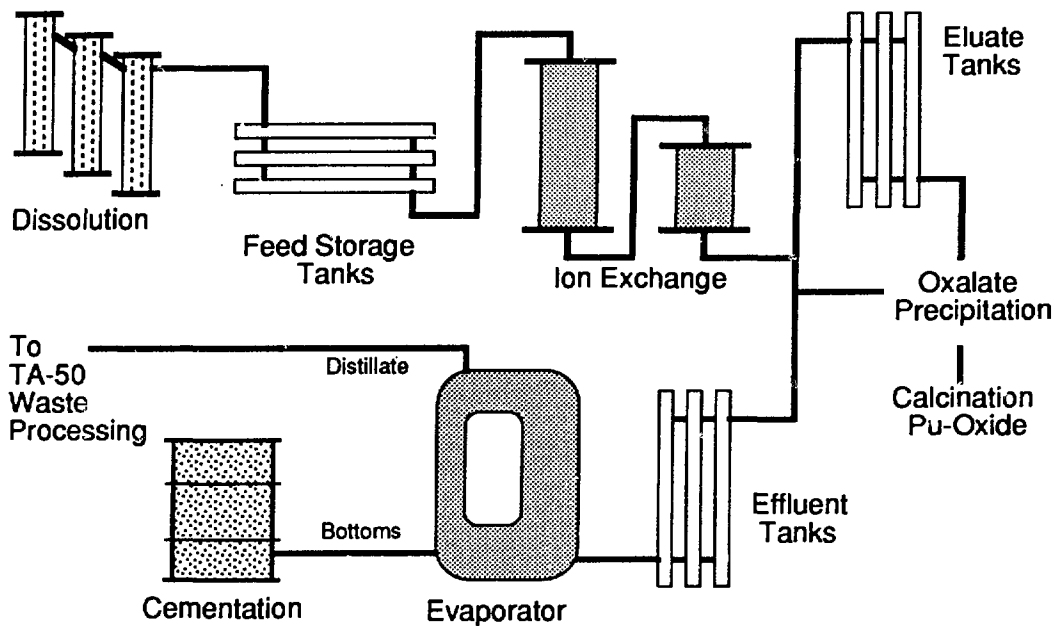


Fig. 1. Primary Aqueous Pu Recovery Flow Scheme

This low-level acid waste is sent to a separate facility where ferric hydroxide is used to precipitate any remaining actinides before discharging it to the environment. The concentrated TRU waste is cemented and placed in 55-gal. drums before it is shipped to a nuclear waste repository. Thus, subsequent processing of aqueous wastes generated by anion exchange is costly and inefficient because it improves only the form of the waste, but no additional actinides are recovered.

We are conducting an engineering evaluation of alternative secondary unit operations that could be coupled directly to the anion-exchange train and could polish the effluent to levels lower than the minimum allowed for facility discharge. A viable secondary unit operation would enhance the current approach to Pu recovery and waste disposal by minimizing the actinide content of the waste streams and would reduce the volume of solution requiring further treatment. We determined that solvent extraction was the only unit operation capable of selectively recovering actinides from large volumes of acid waste streams. Several different types of extractants have been evaluated including phosphonates, phosphine oxides, and substituted malonamides. Various methods of operation including centrifugal contactors, Scheibel columns, and loaded resins were also tested.

Figures 2 and 3 show flow schemes using this technology. Note that, in both methods, the evaporation process could be eliminated and actinide losses from the facility would be greatly reduced.

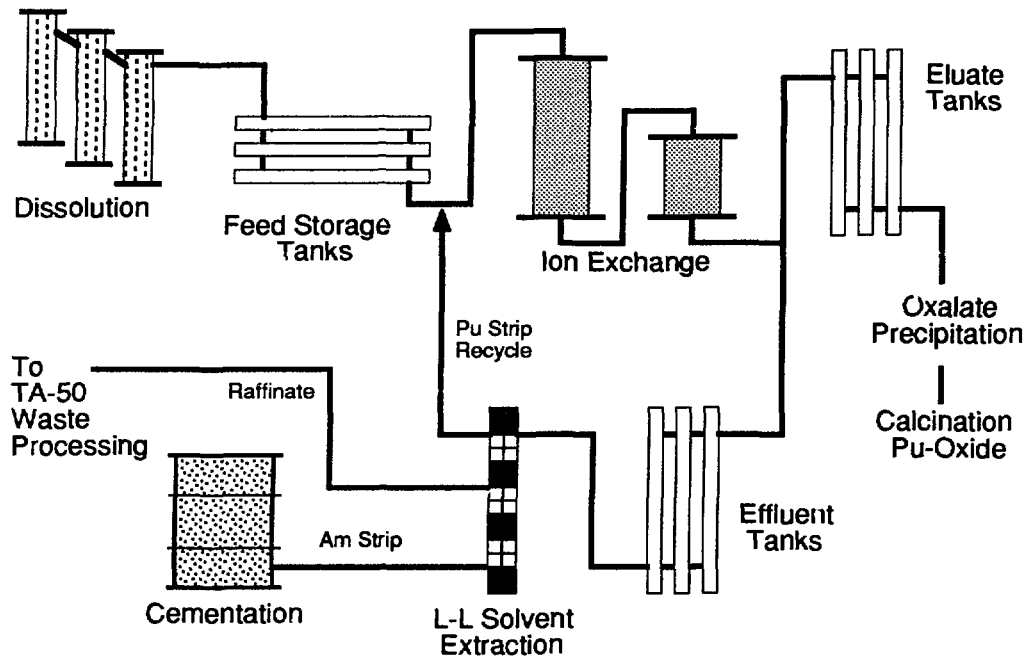


Fig. 2. Liquid-Liquid Solvent Extraction Aqueous Pu Recovery Flow Scheme

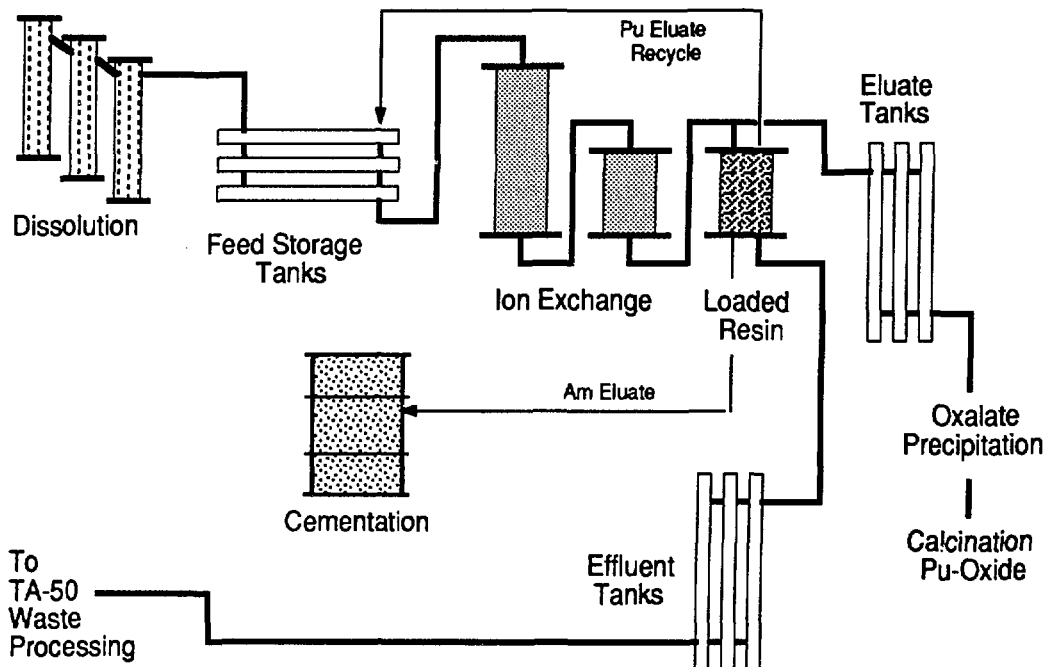


Fig. 3. Loaded Resin Solvent Extraction Aqueous Pu Recovery Flow Scheme

TRUEX EVALUATION

We chose as a baseline for comparison the highly characterized TRUEX flowsheet,¹ which we modified to fit within the glove boxes and to conform to the process flow scheme used at the Plutonium Facility. Liquid-liquid solvent extraction is a proven technology, particularly within the nuclear industry. The extractant evaluation began with two high-efficiency extractants for which a large amount of experimental data was already available: dihexyl-N, N-diethylcarbamoylmethylphosphonate (DHDECMP or CMP, manufactured by Occidental Chemical) and octylphenyl-N, N-diisobutylcarbamoylmethyl-phosphine oxide (CMPO, manufactured by M & T Chemical). The phase-contacting equipment selected had to be effective but easy to use in a glove box.

We based contactor equipment selection on cold studies performed by Yarbro,² in which the principal evaluation was between centrifugal contactors and simpler, less-expensive Scheibel columns. Initial capital costs, maintenance requirements, and the simplicity of operation and control were the main factors compared. The Scheibel columns were easier to operate consistently and their lesser stage efficiency was offset by running several columns in series. In addition, problems with entrainment and phase separation after contacting were much less severe with the columns. The operation of centrifugal contactors produced stable organic emulsions that persisted for days.

Both DHDECMP and CMPO were compared by Marsh and Yarbro³ for this type of application. Although CMPO exhibits higher K_D values for actinides than does DHDECMP, it is also more difficult to strip with dilute acid. At the time, a new synthesis method had been developed (phase transfer catalysis) that produces higher-purity DHDECMP at lower cost than previously obtainable. Because of its availability, the adequate extraction from high nitrate solutions, and its efficient stripping properties in low nitrate solutions led us to select DHDECMP for these studies.

Experimental Details

Chemicals. We selected 30 vol % DHDECMP in diisopropylbenzene as the organic phase. Initially measured volumetrically, the organic was maintained at the original concentration by monitoring its density. We took actual lean residue (LR) anion-exchange column effluent, as representative cuts from several runs as the aqueous phase. Each batch was sampled and analyzed for Pu, Am, and $[H^+]$. On the average, the effluent was between 4 and 8 M HNO_3 and contained 10 mg Am/L and 100 mg Pu/L.

Equipment. To contact the two phases on a pilot plant scale, we used a modified York-Scheibel column with 7 physical and 2.5 theoretical stages. The contactor was constructed of a 1.5-in. i.d. by 30-in.-high glass chromatography column through which a stirrer shaft extended with double propellers at 4-in. intervals. We used a design suggested by Steiner and Hartland,⁴ separating the stages by a lattice of Teflon baffles suspended on stainless steel support rods. A variable speed motor mounted on top of the column frame rotated the stirrer shaft. Magnetically driven gear pumps and 0 to 100-mL/min rotameters regulated the feed flows. The interface was maintained in the upper disengaging section by adjusting a manual needle valve on the aqueous outlet. Total flows were between 100 mL/min. and 180 mL/min. The equipment as it appeared before introduction into the glove box is presented in Fig. 4.

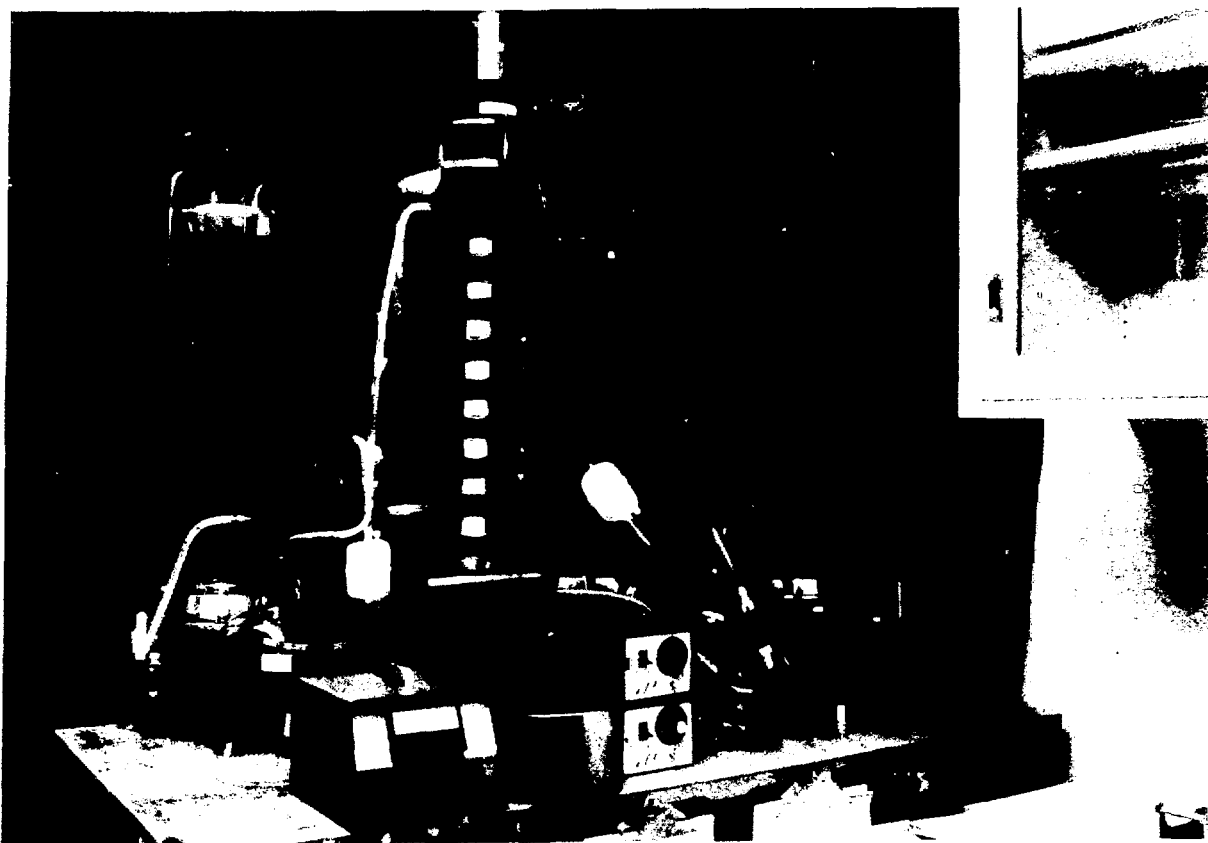


Fig. 4 York-Scheibel Column Contacting Equipment

Procedure. Organic and aqueous feeds were held in 6-in.-dia. glass tanks. To begin a run, we filled the contactor with the organic solution and then displaced it with aqueous feed. When an interface was established, both flows were brought up to their nominal values. Once a steady state was achieved, the raffinate was sampled at regular intervals throughout a run, and the samples were analyzed using radiochemistry techniques. The loaded organic was stripped using a dilute acid wash and then reacidified with 7 M HNO_3 , which prepared it for reuse on the following run.

We performed eleven 5-L to 8-L runs varying organic/aqueous (O/A) ratios, mixing rates, total flow rates, and, to a limited extent, the dispersed phase as either organic or aqueous. Samples of raffinate were taken at set intervals during the run and analyzed for Pu and Am using radiochemistry techniques. The data collected is presented in Table I.

**Experimental results using a modified York-Scheibel column, 7 stages
(21.25 in. by 1.50 in.) and 30 vol. % DHDECMP in DIPB at 25°C**

RUN	% REMOVED		PASSES	[HNO ₃]	STIRRER SPEED (rpm)	AVG. O/A	TOT. FLOW (mL/min)	DISPERSED PHASE
	Am	Pu						
A	92.6	95.8	1	4.9	350	0.35	153	Organic
B	87.8	94.7	1	6.1	300	0.45	179	Organic
C	94.3	85.9	1	3.2	300	0.35	108	Organic
D	94.5	88.8	1	7.1	300	0.54	110	Organic
E	75.0	94.6	2	7.9	300	0.44	113	Organic
F	99.4	99.5	2	7.0	400	0.65	103	Organic
G	97.0	84.9	2	7.9	450	0.49	122	Organic
H	96.0	98.8	2	6.3/5.9	400	0.50	100	Aqueous
I	89.6	95.9	3	5.8	400	0.50	171	Organic
J	94.0	92.1	2	5.7/5.6	400	0.45	166	Organic
K	96.6	-	2	3.5	400	0.36	136	Organic

Table I. Results of TRUEx Runs on IX Effluent

Results

Overall, >95% of the Pu and Am present was removed from the effluent stream and recovered, but the limits imposed on facility discharges (economic discard limits) were not consistently met. One reason for the limited extraction was thought to be the limited number of contacting stages within the Scheibel column, which we addressed by increasing the number of passes through the column to 2 and on one run to 3. We observed no additional extraction. Detailed analysis of the raffinate isolated a silicate compound that was potentially complexing with trace amounts of the actinides, thus inhibiting complete extraction.

The system was difficult to operate effectively on a pilot scale and would require extensive process control to operate on a plant scale. Additional problems that would be encountered on a plant scale are the large amounts of glove-box space required to house the storage tanks, contacting, stripping, and organic regeneration equipment. A method to dispose of large quantities of spent organics would also have to be developed. Mixed hazardous wastes are becoming more difficult to discard from a plutonium processing facility. Even the trace amounts dissolved in the raffinate stream would have to be analyzed and treated.

DHDECMP- AND CMPO-BASED SOEX EVALUATION

Another approach to deploying these extractants involves loading them onto or into a resin and using them to perform extraction chromatography. The loaded resins or solid extractants (SOEXs) offer several engineering advantages over liquid extraction methods in glove-box

applications. In particular, this approach requires little additional glove-box space and uses the same pump as the anion-exchange process. Additional process control would not be required. Disposal of the loaded resin would be the same as with current anion-exchange resins. And if the extractant could be chemically bonded to the resin, or at least tightly imbedded in the matrix, extractant losses to the effluent and other waste streams would be reduced to a manageable level.

We have evaluated and synthesized several different types of solid extractants at Los Alamos. Both CMPO and DHDECMP were loaded onto commercially available resin beads as well as incorporated into a resin during polymerization. We achieved loading of the resins by first mixing them in different solvents, causing them to swell, and then introducing the extractants. Standard styrene-divinylbenzene-based SOEXs of predominantly macroporous structure were copolymerized to incorporate the extractants.

Experimental Details

Chemicals. We synthesized resins of various properties in house from styrene or vinylbenzylchloride (VBC, manufactured by Dow Chemical) and divinylbenzene (DVB, manufactured by EM Science) using the following: benzoyl peroxide (manufactured by EM Science) as the initiator, polyvinyl alcohol (manufactured by J. T. Baker) as a dispersant, and an aliphatic hydrocarbon, such as octane, to achieve the desired structure of a macroporous resin. We evaluated Amberlite polymeric adsorbent resins (developed by Rohm and Haas) such as XAD-4, a styrene-divinylbenzene cross linked macroporous bead, and XAD-7, a polyacrylate macroporous bead. We also evaluated TRIM, based on 2-ethyl-2-(hydroxymethyl)-1,3-propanediol-triacrylate which was synthesized by Nyitray and Williams of the Polymers and Coatings Group (MST-7) in the Materials Science and Technology Division. The resins were swelled in an appropriate solvent such as toluene, chloroform, or methylene chloride to load the extractant.

Equipment. We used a standard 2-L resin kettle to synthesize the resins. It had a smooth interior to avoid accumulation in corners and included four baffles at right angles to each other. The lid was sealed with a gasket so the reactor could be filled completely to avoid vortexing. Inserted in three penetrations on the top were a thermocouple, the stirring shaft, and a vented reagent addition flask. For other resin work, we used standard glassware such as 100-mL beakers and Erlenmeyer flasks. We also used small plastic squeeze vials with disposable plastic filters to contact the resins with effluent solutions.

Procedure. The resin synthesis was a straightforward polymerization process. We measured out the reagents and kept them cool until they were mixed in a water media within the reactor and then heated to 75°C. The inhibitors were washed from the styrene or VBC and DVB using a dilute NaOH solution. By varying the amount of DVB added, we could control the cross linking. Stirring speed and polyvinyl alcohol addition controlled the bead size. The hydrocarbon modified the structure of the resin by creating voids during formation and was later removed when the resultant resin was washed several times with water and alcohol. A ratio of monomer to total organic solution of at 1 was 0.5:1 was maintained to ensure that the bead was macroporous.⁵

We used one of two ways to add extractants such as DHDECMP or tributylphosphate (TBP) to the resins. Some were placed with the reagent mixture and incorporated into the matrix during polymerization while some were loaded in afterward by swelling in an appropriate solvent. For the swelling approach, we dissolved the extractant in the solvent, added the resin, and allowed the mixture to stand for several hours or days.

Resins were evaluated for extraction by contacting 10 mL with an equal volume of prepared effluent containing a known amount of Pu (~100 mg/L) and Am (~10 mg/L) in 5-7 M HNO₃ for 5 min. We stripped the resin by contacting it with an equal volume of 0.35 M HNO₃, again for 5 min. All aqueous solutions were cleaned of residual organics by contacting them with XAD-4 adsorbent resin prior to analysis. We took 5-mL samples, analyzed them on the gamma spectrometer, and compared the results to those of the stock solution.

The effects of varying the resin properties are presented in Figs. 5, 6, and 7. Chloroform and toluene were compared as swelling solvents, different types of styrene-divinylbenzene and polyacrylate resin structures were compared, and DHDECMP and CMPO were compared as solid extractants. We evaluated the performance of the resins on the basis of extraction and stripping characteristics for Pu and Am and determined the equilibrium distribution coefficients for the SOEXs. Results are presented in Fig. 8.

	Am (III)	Pu (IV)
	% Extraction	
XAD-4 CMP w/ Toulene	23.6	87.1
XAD-4 CMP wChloroform	59.8	96.7
	% Strip	
XAD-4 CMP w/ Toulene	100.0	65.0
XAD-4 CMP wChloroform	41.1	46.8

Fig. 5. Swelling Solvent Effects

	Am (III)	Pu (IV)
	% Extraction	
PS/DVB CMP	95.3	99.3
TRIM CMP	98.0	95.5
XAD-4 CMP	23.6	87.1
XAD-7 CMP	88.9	97.5

	% Strip	
PS/DVB CMP	11.0	33.0
TRIM CMP	4.0	14.0
XAD-4 CMP	100.0	65.0
XAD-7 CMP	18.4	33.1

Fig. 6. Bead Structure Effects

	Am (III)	Pu (IV)
	% Extraction	
XAD-4 CMP	23.6	87.1
XAD-4 CMPO	41.0	92.2
XAD-7 CMP	88.9	97.5
XAD-7 CMPO	94.5	98.1

	% Strip	
XAD CMP	100.0	65.0
TRIM CMP	11.4	2.5
XAD-4 CMP	18.4	33.1
XAD-7 CMPO	0.3	0.7

Fig. 7. Extractant Effects

	Am (III)	Pu (IV)
	% Extraction	
XAD-4 CMP w/ Toulene	23.6	87.1
XAD-4 CMP wChloroform	59.8	96.7
	% Strip	
XAD-4 CMP w/ Toulene	100.0	65.0
XAD-4 CMP wChloroform	41.1	46.8

Fig. 8. Solid Extractant Distribution Coefficients

Results

Essentially, the results of the swelling solvent, bead structure, and extractant comparisons indicate that much more work would be required to optimize an effective resin. Distribution coefficients indicate that it is possible to develop a workable resin using a feasible number of stages if the loading capacity is high enough.

We demonstrated the effectiveness of this approach in a single test run. In a small column, we set up 30mL of styrene-divinylbenzene resin loaded with ~100 g DHDECMP/L. Anion-exchange effluent was then passed through the bed at a rate of 25 mL/min. Our analysis of the raffinate revealed a reduction in the gross alpha activity from 10^{10} c/m/L to 10^5 c/m/L. Thus >99.999% of the actinides present in the effluent were removed. However, breakthrough occurred after only 3 to 4 bed volumes of effluent were contacted. Thus, effective loading was ~10 mg actinides/L resin.

From these studies, several general conclusions were drawn about the SOEXs. Overall, the CMPO extracted Pu and Am more completely than DHDECMP while the DHDECMP back-stripped more thoroughly than CMPO. We have yet to thoroughly evaluate radiation and nitric acid stability but no immediate breakdown was apparent. The most serious shortcoming was that the capacity of the best SOEXs averaged only several milligrams per liter. Our calculations show that for this type of unit operation to be effective, the capacity of the resin needs to be a minimum of several grams per liter. This is, however, several orders less than standard anion-exchange resins where ~100 g/L is required to be effective. Extractant retention is also important because if it is washed from the matrix, the SOEX performance can degrade after just a few contacts. We are currently researching the effects of hydrophobic and hydrophilic matrices on extractant retention and resin capacity.

Chromatographic elution is another desirable goal because the Pu can then be collected and recycled back into the process while the Am can be segregated and disposed of in a concentrated form. The difference in Am and Pu equilibrium extraction coefficients and the subsequent use of cation exchange for Am concentration should make this possible.

We were able to draw several related conclusions on the general use of DHDECMP and CMPO. These extractants are difficult to synthesize in high purity and are expensive. Although they have extremely high equilibrium extraction coefficients, they are difficult to back-extract. It is also difficult to effectively separate Pu and Am. Once their useful lifetime has expired, they may be difficult to dispose of because incineration or other forms of thermal processing would cause the formation of phosphates and pyrophosphates in the ash. Thus, the practical application of DHDECMP and CMPO is potentially limited.

Evaluation of Malonamides

The goal of synthesizing a suitable SOEX led us to evaluate extractants other than phosphonates and phosphine oxides. A literature search revealed substantial work in the use of substituted malonamides to extract trivalent, quadrivalent, and hexavalent actinides from nitric acid solutions.⁶ There are several apparent advantages to using this type of extractant. Their synthesis is straightforward and has been performed on a small scale in the laboratory at Los Alamos. Tests indicate that these extractants possess a radiation stability similar to that of TBP and any degradation products do not appear to inhibit its extraction characteristics. The material can be disposed of by thermal processing without the formation of hazardous byproducts. Malonamides also appear to have the potential for covalent bonding to a resin matrix and yet still remain mobile enough to coordinate with actinides contacted in a solution. The major drawback to using this type of extractant is the limited amount of experimental data available to demonstrate its performance.

Experimental Details

Chemicals. Most of the chemicals that we used in the synthesis and evaluation of the malonamides were highly toxic and otherwise corrosive. The basic N,N-dimethyldibutylmalonamide (MBMA) was synthesized from malonyldichloride (manufactured by Aldrich) and methylbutylamine (manufactured by Pfaltz & Bauer) in diluents of diethylether and hexane as well as from dimethylmalonate (also manufactured by Pfaltz & Bauer) and the amine using sodium methoxide (manufactured by J. T. Baker) in methanol as a catalyst. Substitutions to the central carbon were performed using halogenated constituents such as 1-bromo-8-octanol (manufactured by Aldrich) or VBC. All chemicals were reagent grade and therefore not purified before use.

Equipment. In the synthesis of MBMA, we used a 1000-mL three-neck round bottom flask that could be immersed in a salt/ice bath contained in a 4-L flask or set in a variac-controlled heating mantle. A glass stirrer powered by a variable speed electric motor was inserted through one neck, a thermometer through another, and a vented, reagent-addition flask on the final neck. When the solutions were heated in the three-neck flask, the stirrer was replaced with a condenser and a cold trap which were tied to the facility's wet vacuum system. The substitution reactions were performed either in this apparatus or in a simple flask set on a stirrer/hot plate. We used medium or coarse glass frits as filters.

Procedures and Results. The basic malonamide has the β -diketone form presented in Fig. 9. We identified and tested two single-step synthesis routes at Los Alamos. The first uses malonyldichloride, which was reacted with a disubstituted amine to form the malonamide. We used an ice bath with the malonyl chloride diluted in ether and the amine dissolved in

hexane to perform this highly exothermic reaction. The malonyldichloride was added dropwise and the temperature maintained below 5°C. The second single-step synthesis uses the dimethylmalonate ester that was reacted with a disubstituted amine in the presence of sodium methoxide catalyst. All reagents were added to the reaction vessel and mixed at room temperature in excess of 100 hours. The product was recovered in both cases by vacuum distillation followed by recrystallization in hexane.

Results reported by Musikas⁶ indicate that the basic malonamide can be modified with different R groups to optimize extraction performance. MBMA appears to readily extract Pu(IV) and U(VI) from 4 M HNO₃ solutions in which they form anionic complexes but not Am(III), which is in a cationic form. The addition of a long chain on the central carbon appears to dramatically improve Am extraction performance.

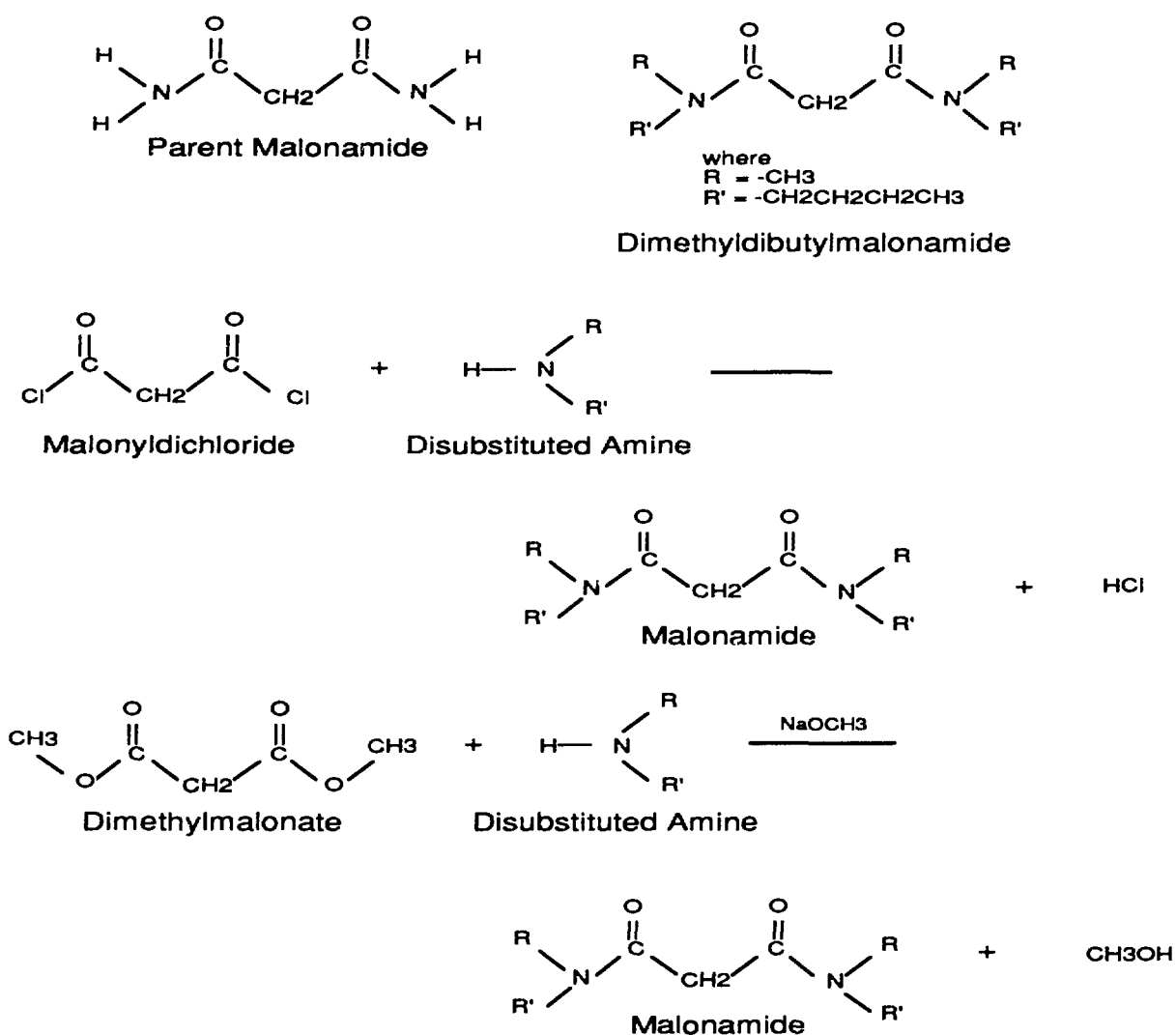
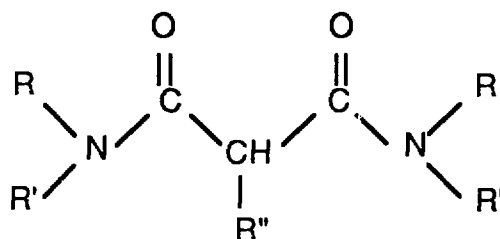


Fig. 9. Malonamide Structure and Synthesis Routes

First, we added a stoichiometric amount of sodium methoxide dissolved in methanol to the MBMA to generate an activated sodiomalonamide as an intermediate to further synthesis. The mixture was heated to 50°C until its pH changed from basic to acidic. This process replaced a hydrogen atom on the central carbon with sodium. We then added brominated octanol to the solution slowly and, after the initial reaction, distilled off the methanol. Any residual solids were filtered away from the product liquid. Using the same method, VBC was also attached to the MBMA. In both cases, the large group was attached to the central carbon in a substitution reaction by displacing the sodium and forming the halogen salt. The results compared to those of Musikas⁷ are presented in Fig. 10.



where
R = CH₃
R' = C₄H₉

Distribution Coefficients of Am(III) from 4 M HNO₃

<u>R''</u>	<u>Am(III)</u>
-H **	0.18
-C ₆ H ₁₃ *	0.615
-C ₈ H ₁₆ -OH **	0.75
-(C ₆ H ₄)-C ₂ H ₃ **	0.77
-C ₂ H ₅ -O-C ₂ H ₅ *	1.718
-C ₂ H ₄ -O-C ₆ H ₁₃ *	3.11
-C ₂ H ₄ -O-C ₂ H ₄ -O-C ₈ H ₁₇ *	5.721
-C ₂ H ₄ -O-C ₂ H ₄ -O-CH(C ₂ H ₅)-CH ₂ -(CH ₃) ₃ *	6.089
-C ₂ H ₄ -O-C ₂ H ₄ -O-C ₆ H ₁₃ *	5.65

* 0.5M MBMA in butyl benzene with 10% decanol⁴

** 0.5M MBMA in diisopropyl benzene with 10% octanol

Fig. 10. Influence of the Malonamide's Structure on Distribution Coefficients

We purchased a 500-g batch of MBMA from Poly Sciences to perform all subsequent evaluations. The MBMA equilibrium extraction coefficients were evaluated at various nitric acid concentrations to determine if changing the acid strength could be used to load and strip actinides from the extractant. The MBMA was dissolved in a diisopropylbenzene and 10%-octanol solution and evaluated for extraction by contacting 10 mL MBMA solution with an equal volume of prepared effluent containing a known amount of Pu (~100 mg/L) and Am (~10 mg/L) in HNO_3 for 5 min. We took 5-mL samples, analyzed them on the gamma spectrometer, and compared the results to those of the stock solution. Over the range of 0.1 M to 7.0 M HNO_3 , the K_D for Pu increased from 0.3 to 175. Data is presented in Fig. 11.

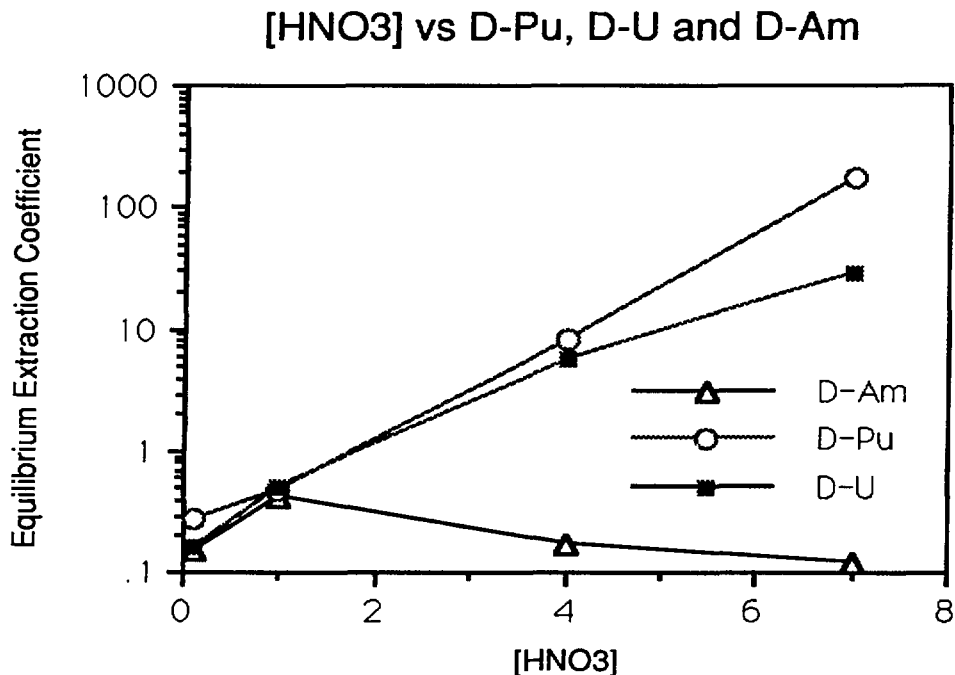


Fig. 11. MBMA Extraction from Different Acid Solutions

The next step was to determine the effective resin loading required to meet process-imposed restrictions. The design was based on a 3-ft.-tall, 6-in.-dia. glass column filled with ~15 L of resin that would process at least 500 L of anion-exchange effluent between weekly elutions. We compared MBMA concentrations with actinide K_D s. See Fig. 12, which indicates that 3 molecules of ligand coordinate in the Am complex and 2 molecules of ligand coordinate in the Pu and U complexes. For a typical effluent containing 0.1 g Pu/L, 0.01 g Am/L, and 0.001 g U/L an effective amount of 118 g MBMA would be required for a 40-hour process run. This is ~8 g effective MBMA/L of loaded resin. If only 10% of the extractant loaded into the resin is effective at removing actinides, this goal can be met with a 100 g/L extractant loading ratio, which can be realistically achieved.

[MBMA] vs D-Pu, D-U and D-Am

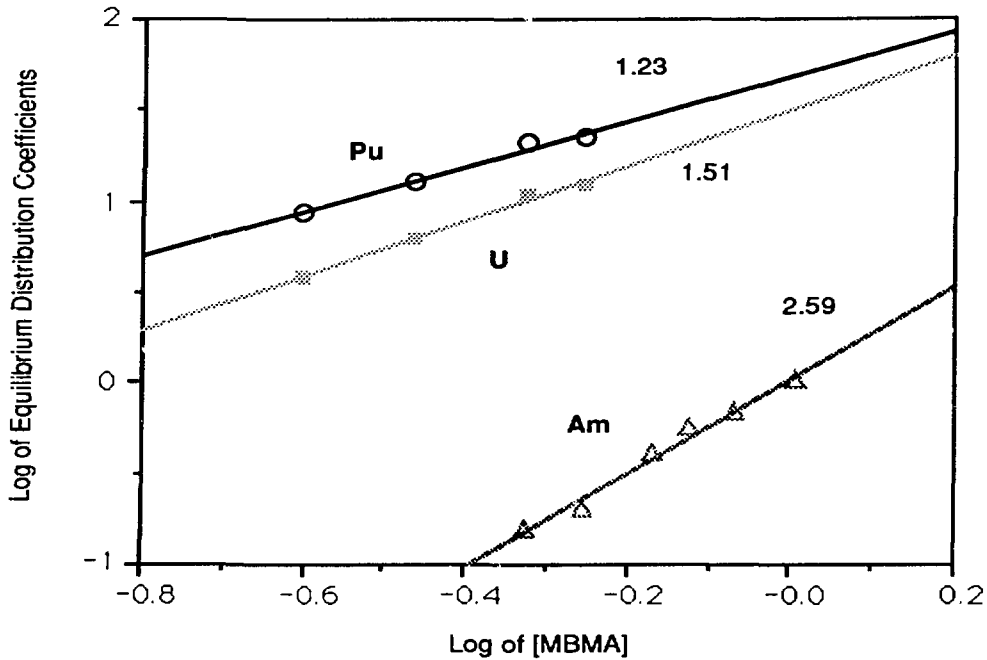


Fig. 12. MBMA Extraction at Different Concentrations

We plan to further evaluate the MBMA by attaching the basic unit to a chlorinated resin and observing the impact on extractability. This should give some indication as to whether attaching the extractant directly to a resin matrix will inhibit its effectiveness or if a long chain "stand-off" molecule will be required to maintain its mobility and flexibility to coordinate with the actinides.

Conclusions

The goal of this research has been to develop a viable secondary unit operation that can effectively and reliably remove actinides from nitric acid anion-exchange effluent. We approached the work from an engineering standpoint for use on a scale appropriate to the current glove-box operations at the Los Alamos Plutonium Facility. Liquid-liquid solvent extraction was evaluated but determined to be difficult to operate on the required scale. Several different types of extractants were also evaluated, including DHDECMP, CMPO, and MBMA with each showing particular advantages and disadvantages depending on the specific method of extraction. The major emphasis of our research has been directed at developing a chelating resin loaded with an appropriate extractant that could be readily tied to the existing anion-exchange trains. To date, our research has centered on the use of malonamides because of their numerous practical and engineering advantages over more complex bidentate extractants such as DHDECMP and CMPO.

Acknowledgements

We acknowledge the contribution of Barbara Smith of the Analytical Chemistry Group for her analysis of the solutions from our modified TRUEX evaluation and for her consultation on the possible silicate compound formation.

References

1. R. A. Leonard, G. F. Vandergrift, D. G. Kalina, D. F. Fischer, R. W. Bane, L. Burris, E. P. Horwitz, R. Chiarizia, and H. Diamond, "The Extraction and Recovery of Plutonium and Americium from Nitric Acid Waste Solutions by the TRUEX Process," Argonne National Laboratory report ANL-85-45, (September 1985).
2. S. L. Yarbrow, "Using Solvent Extraction to Process Nitrate Ion Exchange Column Effluents," Los Alamos National Laboratory report LA-11007-T (October 1987).
3. S. F. Marsh and S. L. Yarbrow, "Comparative Evaluation of DHDECMP and CMPO as Extractants for Recovering Actinides from Nitric Acid Waste Streams," Los Alamos National Laboratory report LA-11191 (February 1988).
4. L. Steiner and S. Hartland, "A New Type of Agitated Liquid/Liquid Extraction Column with Enhanced Coalescence Plates," *Separation Science and Technology* **15**(4), 907-923 (1980).
5. Sederel, W. L. and DeJong, G. J., "Styrene-Divinylbenzene Copolymers Construction of Porosity in Styrene Divinylbenzene Matrices," *Journal of Applied Polymer Science* **17**, 2835-2846 (1973).
6. C. Musikas and H. Hubert, "Extraction by N,N'-Tetraalkylmalonamides II. Extraction of Metallic Ions," *Solvent Extraction and Ion Exchange* **5**(5), 877-893 (1987).
7. C. Cuillerdier, H. Hubert, P. Hoel, C. Chachaty, and C. Musikas, "Extraction of 4f and 5f Elements with Substituted Malonamides," presentation at Commissariat a L'Energie Atomique Conference on actinides (F91191), Lausanne, Switzerland (March 1987).