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NIDE SEPARATIONS FOR ADVANCED PROCESSING OF WASTE

Report 1993

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ACTINIDE SEPARATIONS FOR ADVANCED PROCESSING OF NUCLEAR WASTE

by

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ABSTRACT

The goal of project TTP AI132009 was to develop actinide separations capabilities that could be used in an advanced-processing flow sheet, such as the "clean" option for Hanford underground storage tanks or the aqueous-based transmutation of waste. The project was composed of six subtasks:

1. Investigate the use of selective inorganic precipitation for metals (molybdenum, technetium, ruthenium, palladium, cadmium, americium, curium) to replace processes that require organic solvents.
2. Investigate the use of liquid ion exchangers as alternatives to Aliquot 336 for rapid actinide processing.
3. Investigate the use of diamides as alternatives to CMPO for removal of transuranics from aqueous wastes.
4. Develop "soft" donor extractants for trivalent actinide/lanthanide separations.
5. Investigate the use of recyclable water-soluble chelating polymers for actinide partitioning and waste stream polishing.
6. Investigate the use of microporous hollow-fiber membranes for dispersion-free liquid-liquid extraction.

This project was terminated after 7 months. Only subtasks 3 and 4 have been transferred to TTP AL121217 for continued, limited funding.

Introduction: Advanced actinide and fission product separations are needed for a variety of applications. Such applications include, for example, tank waste remediation at Hanford, decontamination and decommissioning at all Department of Energy (DOE) facilities, soil and sludge leaching, mixed waste treatment, processing for light-water reactor wastes, and transmutation of actinide waste systems. Because of the moratorium in the early 1980s on actinide reprocessing in the United States (accompanied by funding cuts), only a few US researchers have been pursuing advanced actinide separations. Thus, little "off-the-shelf" engineered technology is available to address the large variety of actinide and fission product separation problems that currently exists.

The waste streams needing treatment include aqueous acid waste, aqueous basic waste, low-level neutral wastewaters, contaminated soils, and all the materials that were and are used to handle actinides (for example, gloves, glassware, and gloveboxes). Because the waste streams are so varied, the chemistry that needs to be developed is quite broad. Thus, very few processes have reached pilot-scale, much less full-scale, testing on actinide wastes.

The work discussed in this technical task plan (TTP) addressed a variety of identified actinide separation problems. The approaches have potential application to many environmental remediation problems. For example, alternative actinide extractants for aqueous nitrate waste stream treatment must be evaluated. The only extractant system under consideration for actinide removal from Hanford tank waste is the CMPO-based TRUEX process. CMPO extraction has enough potential problems that other systems should be available that could be rapidly developed if necessary.

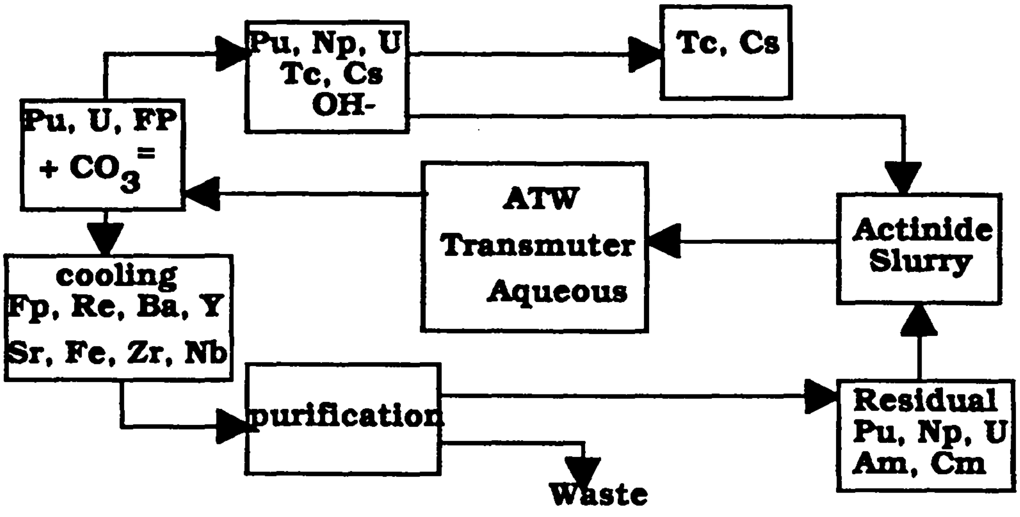
The separation system under consideration to remove actinides is liquid/liquid extraction using the TRUEX process. It is probably the most studied extraction system for the reprocessing of actinide-containing wastes. When the transuranics (TRUs) are extracted in the TRUEX process, the trivalent lanthanides are extracted simultaneously with all the actinides (likewise with malonamide extractants). Advanced trivalent actinide/lanthanide separations capabilities are needed. All the available tested methods of separating trivalent actinides and lanthanides have severe process limitations (for example, TRAMEX uses concentrated chloride salt solutions and TALSPEAK requires the addition of organics to the aqueous phase, making it difficult to control process conditions). The separation of trivalent lanthanides from trivalent actinides is one of the most difficult metal-ion separations. Several advanced extractants for this separation are under development at Los Alamos. We propose that these extractants be tested.

Alternative Applications: The proposed work has a wide application but was formulated in the context of a separation scheme for the accelerator transmutation of nuclear waste (ATW) process scheme. A baseline actinide blanket processing flow sheet for the ATW program has been developed. The preliminary baseline flow sheet was developed and collated from process steps or unit operations that had been demonstrated on actinide-containing waste streams. The baseline flow sheet can be improved, and advanced options have been suggested by Jarvinen (1991). Some of the new flow sheet options proposed here are based on the advanced concepts for actinide separations proposed in the Jarvinen report.

The first alternative flow sheet (Figure 1) is based on selective precipitation of actinide and/or lanthanide carbonate complexes. This alternative could provide a greatly simplified processing scheme for rapid separation of the bulk of the actinides (plutonium, neptunium) from the fission products without generating organic wastes. The actinides (plutonium, neptunium) are rapidly recycled back to the transmuter for further destruction. The advantages is more rapid turnaround of the processing streams without the accompanying degradation of the organic solvent by radiolysis. This scheme would reduce process inventories for the actinides in the ATW cycle, thus improving its efficiency.

Another alternative extractant to the Aliquot 336 extraction system proposed in the baseline flow sheet could have higher radiolytical and chemical stability: the pyridinium-based liquid ion exchange (LIX) series (Jarvinen 1991). These types of structures may be more stable than the Aliquot 336. Preliminary high plutonium loadings (10 W) of Aliquot 336 indicated that it would probably function for one extractive cycle before turning into a tarry material that must be discarded. Reducing the number of cycles would be advanta-

Figure 1. Proposed flow sheet based on results to date for carbonate precipitation studies.



geous for waste minimization and would improve processing conditions.

The resulting fission products and trivalent actinide (americium, curium)-containing waste streams (also containing small amounts of neptunium and plutonium) from the ATW processes would be allowed time for decay or cooldown. The waste streams thus produced could be treated with either traditional partitioning schemes (TRUEX, TALSPEAK) or other advanced schemes as we have proposed. The advanced partitioning schemes being proposed can be applied not only to ATW-type waste streams but also to other waste streams that have been produced in the DOE complex (for example, Hanford Tank Waste Remediation System [TWRS]-"clean" option) and to those that may be produced by the nuclear industry (for example, fuel reprocessing) in the future.

The goal of the flow sheet was to

- return actinides (neptunium, plutonium) to the transmuter as rapidly as possible,
- minimize TRU waste streams,
- minimize innocuous waste streams as much as possible (for example, no mixed waste), and
- develop advanced actinide separations that apply to a broad range of metal-ion separation problems (for example, all water-based reactors, TWRS).

1.0. Subtask 1

1.1. Title: Selective Inorganic (Carbonate/Hydroxide) Precipitation of Actinides and Fission Products

1.2. Investigators: R. Villarreal (CLS-1), D. Temer (CLS-1)

1.3. Objective: The objective was to complete the selective complexation/precipitation studies to determine the full potential of the inorganic precipitation approach. FY 1993 milestone: Complete precipitation study of metals (molybdenum, technetium, ruthenium, palladium, cadmium, americium, curium) that had not been previously determined and collate data. From the resulting data and literature information, define matrix and mixtures for mixed metal separations studies to start in FY 1994. (7 months) (March 1–September 31, 1993) (This subtask will not be funded for FY 1994.)

1.4. Background: We have demonstrated a variety of selective complexations/precipitations and separations of fission products from actinides by varying the inorganic reagent (Villarreal 1993). These reagents include sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), ammonium carbonate [$(NH_4)_2CO_3$], ammonium bicarbonate (NH_4HCO_3), potassium carbonate (K_2CO_3), and potassium bicarbonate ($KHCO_3$). When these bases are dissolved in water to their solubility limit, a saturated pH value is obtained as shown in Table I. Different solubilities of the salts generate different carbonate and bicarbonate concentrations. For example, K_2CO_3 yields solutions containing the highest concentration of carbonate ions and the most basic pH, whereas $NaHCO_3$ and Na_2CO_3 yield solutions of lowest carbonate concentration. The data in Table I further indicate that the precipitation of element ions would best be achieved with $NaHCO_3$ and that complexation would be favored by use of K_2CO_3.

In some cases the fission product or actinide metal ions are complexed and remain in solution; in other cases they are precipitated. From these preliminary studies, we have proposed a potential ATW flow sheet for the rapid separation of fission products from thorium, uranium, neptunium, and plutonium (Figure 1). This alternative precipitation method could provide a greatly simplified processing scheme for rapid separation of the bulk of the actinides (plutonium, neptunium) from the fission products when the actinides are present in high concentrations. The actinides (plutonium, neptunium) are rapidly recycled back to the transmuter for further destruction. The advantage is a more rapid turnaround of the processing streams with a simple one-step, on-line separation process without the accompanying degradation of the organic solvent. This method would reduce process inventories for the actinides in the ATW cycle. Other

Table I. Solubility and pH of Saturated Carbonate Solutions

Salt	**Solubility grams per100 cc H_2O**	**pH**
$NaHCO_3$	6.9	8.6
Na_2CO_3	7.1	11.4
NH_4HCO_3	11.9	8.7
$KHCO_3$	22.4	8.3
$(NH_4)_2CO_3 \cdot H_2O$	100	8.7
K_2CO_3	112	13.8

benefits include a simplified processing scheme for light-water reactor waste.

1.5. Approach: So far studies have focused on individual metal ions in solution. A few elements or fission products have carbonate solubility properties that are unknown. These elements include technetium, molybdenum, ruthenium, palladium, cadmium, americium, and curium. Studies of these elements needed to be completed. It was necessary to determine the interactive effects of mixtures of elements that would have a matrix similar to what is expected to exit from the transmuter. To extend this work to other systems, other simulated matrices would have to be studied. A series of studies were conducted with thorium, uranium, neptunium, and plutonium containing simulated fission products.

1.6. Experimental: In preparing saturated $KHCO_3$, approximately 224 g of Baker Analyzed Reagent was dissolved in a liter of deionized water. The individual metal ions used in this study (thorium, uranium, manganese, iron, cobalt, nickel, aluminum, copper, zinc, zirconium, rhodium, calcium, rhenium, molybdenum, ruthenium, palladium, cadmium, strontium, barium, chromium, lead, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, and erbium) were commercially available from NIST, SPEX, or HIGH PURITY STANDARDS. The concentration of each metal ion in solution was 10 mg/mL in 5%–10% hydrochloric acid (HCl) or nitric acid (HNO_3). We prepared plutonium(III) and neptunium(III)/(IV) stock solutions separately by dissolving 250 mg each of plutonium and neptunium metal in a 25-mL volumetric flask with HCl and diluting to volume with deionized water. The acid concentration was 10% by volume.

The tracer-level americium(III) studies were performed using the americium(III) present in the plutonium stock solution. Gamma counting of the plutonium stock solution showed the americium content to be 3.68×10^{-3} g/L. The neptunium(V) solution was obtained from personnel in the Isotope and Nuclear Chemistry Group. We prepared the plutonium(IV) by adding 4 drops of concentrated HNO_3 to 1 mL of the plutonium stock solution (10 mg of plutonium) and heating the mixture for approximately 15 min before using it. The plutonium(VI) solution was prepared as follows: Approximately 250 mg of plutonium metal was dissolved in 1 mL of concentrated HCl plus a small amount of deionized water in a 50-mL beaker covered with a watch glass. Then 0.5 mL of concentrated HNO_3 and 0.5 mL of concentrated perchloric acid ($HClO_4$) were added to the beaker. The beaker was uncovered and placed on a hot plate, and the solution was evaporated to perchloric acid fumes. The plutonium(VI) solution (faint pink) was transferred to a 25-mL volumetric flask with 1N HNO_3. The few curium(III) studies were at the tracer level. The curium(III) solution was obtained in-house and contained 9500 dpm/mL in acid.

The experiments with each metal ion were carried out two ways. In the first type of experiment, 1 mL of the metal ion (10 mg) was slowly added to the saturated $KHCO_3$ solution while it was being stirred (20 mL of $KHCO_3$ in a round-bottom centrifuge tube). It was allowed to mix for approximately 1 min and to stand for approximately 2 min before visual observations were recorded. In the second type of experiment, 1 mL of the metal ion was placed in the round-bottom centrifuge tube with 15 mL of deionized water and the saturated $KHCO_3$ solution slowly added while the mixture was being stirred; then the pH of the solution was measured. The addition of the saturated $KHCO_3$ solution was continued to excess. The data were recorded both during the addition of the saturated $KHCO_3$ (pH and visual observation) and after the addition of excess reagent. All of the tracer americium(III) and curium(III) were analyzed radiochemically, americium by gamma counting and curium by gross alpha and alpha spectroscopy.

1.7. Results and Discussion: The objective of this subtask was to separate the rare earth fission products, strontium, barium, and yttrium from the bulk thorium, uranium, neptunium, and plutonium fuel mixture. The basic approach was first to precipitate the fission products as carbonates, then to complex (keep in solution) the actinides.

Preliminary studies of the precipitation of fission product analytes with carbonates indicated that the equilibrium between carbonate precipitation and carbonate complexation depended on the carbonate concentration, the pH of the solution, the oxidation state of the cation, the size of the elemental ion, and the cationic species of carbonate added for precipitation/complexation. To enhance precipitation, we slowly added carbonate solutions to acid solutions containing the elemental ions, whereas to enhance complexation we added elemental ions to solutions saturated in the test carbonate. We have studied the effectiveness of carbonate compounds for performing carbonate precipitations. Each of these carbonate salts has different basicity and has varying degrees of applicability for precipitation of metal ions. Table I shows the solubility and pH of the carbonate solutions.

The following actinides and individual metal ions in solution were studied:

thorium
uranium
neptunium
plutonium
americium
curium
manganese
iron
cobalt
nickel
aluminum
copper
zinc
rhodium
calcium
technetium
molybdenum
ruthenium
palladium
cadmium
strontium
barium
chromium
lead
yttrium
lanthanum
other rare earth elements

In these studies, rhenium was used as a surrogate for technetium. Because of the limited availability of curium, only a few experiments were performed with that element. The results obtained from the precipitation/complexation of the above-mentioned metal ions with saturated $KHCO_3$ are discussed below. The few experiments with curium(III) were inconclusive, but its chemistry should be similar to that of americium(III), which precipitated. The results for the fission products are shown in Figure 2 in the form a of a periodic chart.

A variety of oxidation states of the actinides were tested with $KHCO_3$. Uranium(VI), plutonium(VI), neptunium(III), and neptunium(IV) all complexed and remained in solution. Neptunium(V), plutonium(III), and americium(III) precipitated.

1.8. Conclusions: We successfully separated the rare earth fission products, strontium, barium, and yttrium from mixtures of thorium, uranium, neptunium, and plutonium solutions with a single, simple precipitation by adding the actinide solutions to a saturated solution of $KHCO_3$. The method is applicable to fuel-reprocessing schemes that require removal of these fission products from actinide dissolver solutions. This method can simplify other, more complicated separation schemes using the PUREX and TRUEX technology. More work is needed to extend this unique precipitation method to americium and curium.

Study of $KHCO_3$ Precipitations

Periodic table of the elements

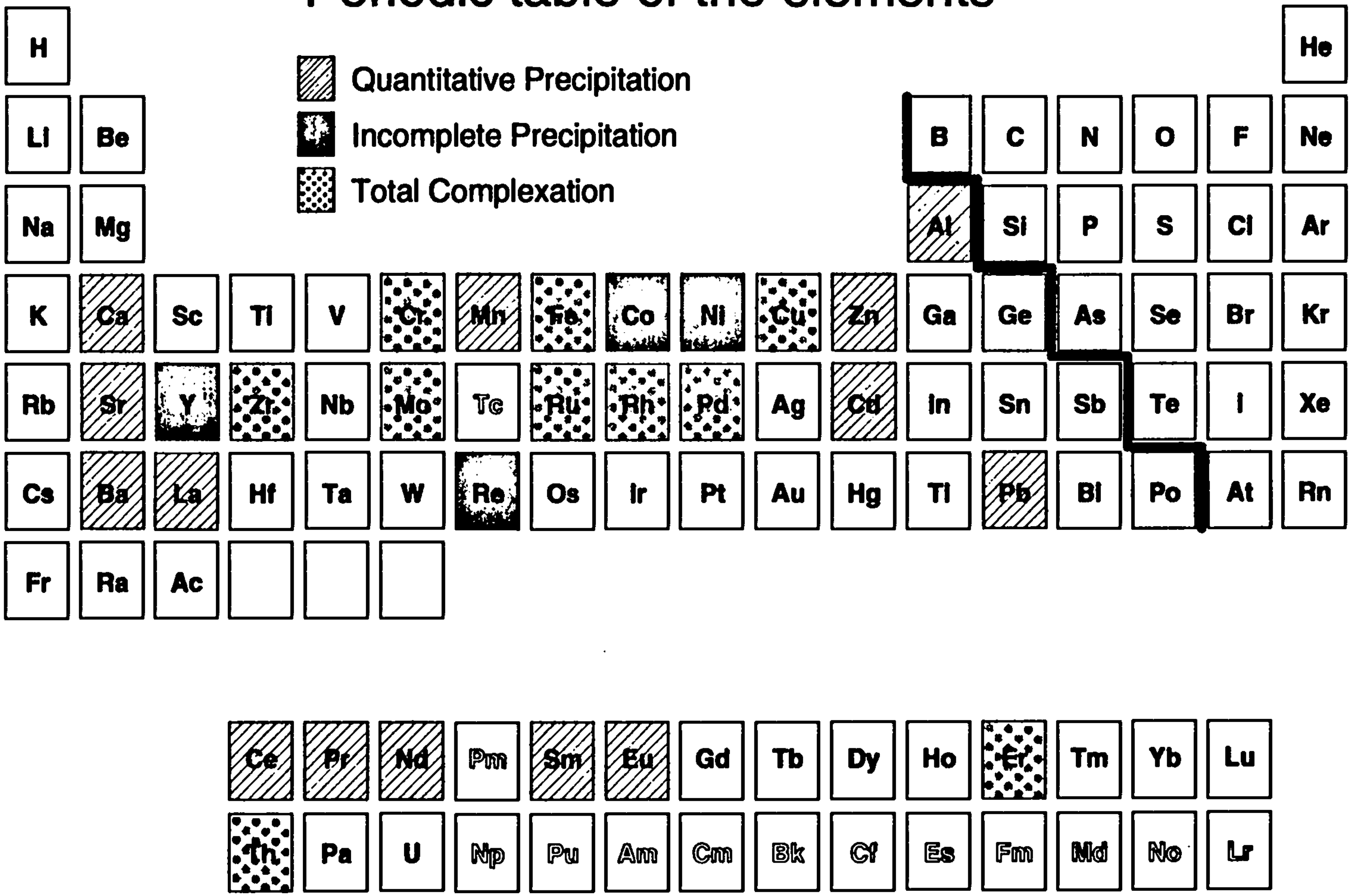


Figure 2. Periodic chart indicating the precipitation or complexation of individual metal ions.

2.0. Subtask 2

2.1. Title: Pyridinium Based-LIX Extractants as an Alternative to Aliquot 336 for Rapid Actinide Processing

2.2. Investigators: G. Jarvinen (NMT-2), B. F. Smith (CLS-1), R. Bartch (TTU), D. Ensor (TNTU)

2.3. Objective: The objective was to evaluate several pyridinium-based liquid ion exchange (LIX) agents as alternative anion exchangers for actinide separations from highly radiolytic systems. FY 1993 Milestone: Obtain commercially or synthesize several alkylated pyridinium compounds. Candidate compounds include

- 3,5-didodecylpyrinium hydrochloride,
- 1-methyl-3,5-didodecylpyrinium iodide, and
- 2,6-didodecylpyrinium hydrochloride salts.

(3 months) (July 1–September 31, 1993) (This subtask will not be funded in FY 1994.)

2.4. Background: At high HNO_3 concentrations, plutonium(IV) exists as a hexanitrato dianion. Under these conditions it is often separated from most other metal ions by anionic exchange because other metals do not form anionic complexes. Thus, plutonium(IV) can easily be purified by anion exchange resins in a column configuration. This same chemistry can be applied to a liquid-liquid extraction mode of operation making use of LIX reagents as the extractant, where the LIX is a liquid anion exchanger. A common system that has been used is Aliquat 336 (methyl tricaproylammonium chloride), a quaternary amine having long-chain aliphatic groups to give increased organic solvent solubility and decreased aqueous solubility. In the high-radiation fields present with reactor fission material or material predicted from a transmuter, Aliquot 336 degrades rapidly to a tarry material after short contact times (Jarvinen 1991). In processing highly radioactive materials, liquid-liquid extraction techniques are desirable over column approaches because the contact time between the radioactive material and the extracting agents is reduced, thus extending the ligand's useful lifetime.

For liquid anion exchangers to be useful, their stability should be greater than that of currently used materials (Aliquot 336). Work performed at Los Alamos with the development of advanced ion exchange resin materials (Marsh 1990) has shown that ion exchangers containing pyridinium rings are more stable to long-term radiation and nitration than are aliphatic ammonium-type ion exchangers.

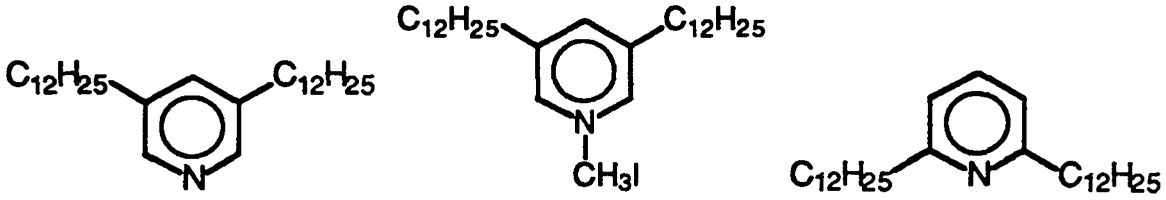
2.5. Approach: The approach was to determine whether commercially available materials—those in the pyridinium class of compounds that have low aqueous solubility and reasonable solvent solubility—would function as liquid anion exchangers. These materials would be tested, along with other actinides and selected fission products, for selectivity and back-extraction capabilities.

Because the desired materials were not commercially available, three ligands systems were synthesized. The compounds included

- 3,5-didodecylpyrdinium hydrochloride (compound [I]),
- 1-methyl-3,5-didodecylpyrdinium iodide (compound [II]), and
- 2,6-didodecylpyrdinium hydrobromide (compound [III]) salts

(Figure 3). The simple, unsubstituted pyridinium compound is water soluble, and the alkyl substituents are added to decrease water solubility and increase organic solvent solubility.

Figure 3. Structure of pyridinium-based LIX materials studied.



3,5-didodecylpyridine
Compound (I)

1-methyl-3,5-dodecylpyridinium iodide
Compound (II)

2,6-didodecylpyridine
Compound (III)

2.6. Experimental

2.6.1. Ligand Synthesis

2.6.1.1. Ni_2Cl_2 Diphenylphosphine Propane (DPPP): 1,3-Diphenylphosphine propane (DPPP) (17 g, 42 mmol) was completely dissolved in a minimum amount of hot isopropanol. We completely dissolved $NiCl_2 \cdot 6H_2O$ (10 g, 42 mmol) in a volume of hot 5:2 methanol:isopropanol that was equal to the volume of isopropanol used to dissolve DPPP. The hot solution of DPPP was added slowly to the $NiCl_2$ solution in an open flask. During the addition, the solution was heated to near boiling while being stirred. The green $NiCl_2$ solution turned brown immediately. As the addition was continued, the brown color slowly turned red, and microcrystalline Ni_2Cl_2DPPP became apparent. The red solution was heated with stirring for another hour. The solution was allowed to cool to room temperature and the Ni_2Cl_2DPPP filtered from the yellow mother liqueur as a bright red, microcrystalline solid (19.9 g, 89% yield).

2.6.1.2. 2,6-Didodecylpyridinium Hydrochloride (Compound [III]): Dodecyl bromide was distilled from P_2O_5 at a pressure of 1 mm of mercury. Diethyl ether was distilled from CaH under N_2 atmosphere. The Ni_2Cl_2DPPP catalyst was heated to 120°C at 1 mm of mercury overnight. The 2,6-dichloropyridine was stored in a vacuum desiccator (approximately 10 mm of mercury) at room temperature for 24 h. A flame-dried 1-L flask was charged with an N_2 atmosphere. 0.30 mol of Mg^0 turnings, and 600 mL of dry diethyl ether. To this was added 0.30 mol of 1-bromododecane. This reaction was at times difficult to initiate, sometimes taking hours (with occasional coaxing with trace I_2). Once the reaction started, however, it became very vigorous. It was carefully monitored and occasionally slowed with an ice bath. When initiation was achieved, the reaction was usually finished in 2 h, giving the Grignard reagent.

In a flame-dried, three-neck flask was placed 2,6-dichloropyridine (0.14 mol) and Ni_2Cl_2DPPP (3 mol%) in 100 mL of dry diethyl ether under N_2 atmosphere. The three-neck flask was fitted with a flame-dried, 1000-mL addition funnel. The Grignard reagent was cannulated into this addition funnel. The reaction vessel was cooled to 0°C, and the addition of the Grignard reagent was begun. The addition was performed over a 1-h period. This reaction was very exothermic, and care was taken to avoid vaporizing the entire volume of diethyl ether. (If the Grignard reagent and the 2,6-dichloropyridine are suspended together at 0°C and the 3% catalyst is added, the reaction will explode within 10 min.) The reaction was kept at 0°C for 2 h, allowed to warm to room temperature, stirred for three more hours while being heated to a gentle reflux. The reaction mixture was poured over ice, the organic and aqueous layers were transferred to a separatory funnel, and hexane was added. The organic phase was separated and washed three times with equivalent volumes of 1M HCl, two times with 1M NaOH, and one time with brine (in the event of partial emulsion). At times, unusually stable emulsions formed. These emulsions were not affected by addition of brine, in extreme cases, but were broken with addition of acetone. The organic phase was dried over K_2CO_3 and filtered into an open flask. Hydrogen chloride gas, generated by dropping aqueous HCl into concentrated H_2SO_4, was bubbled through the hexane solution with vigorous stirring. When the solution was saturated with gaseous HCl, the open flask was allowed to sit undisturbed at room temperature. After several hours, rapid precipitation of the 2,6-dialkylpyridinium hydrochloride ensued. Filtration yielded a white solid 32 g (57% yield) of the didodecylpyridinium hydrochloride. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.87 (t, J=6.6 Hz, 6H), 1.24 (m, 36H), 1.83 (p, J=7.6 Hz, 4H), 3.33 (t, J=7.8 Hz, 4H), 7.42 (d, J=8.0 Hz, 2H), 8.1 (t, J=8.0 Hz, 1H), 17.6 (br, s, 1H). ^{13}C NMR (200 MHz, $CDCl_3$): 14.07, 22.63, 29.01 (two peaks), 29.27 (two peaks), 29.39 (2 peaks), 29.56, 29.70, 31.85, 32.77, 123.30, 144.16, 158.61. Analysis calc. for: C,77.03, H, 12.04, N 3.10. Deter. C, 77.17, H, 12.06, N, 3.09.

2.6.1.3. 3,5-Didodecylpyridinium Hydrochloride (Compound [I]): The procedure described above was also used to make the 3,5-analog. When 3,5-dichloropyridine was used as the starting material, 30% yields were typical. The 3,5-dichloropyridine was less reactive to Ni_2Cl_2DPPP/Grignard coupling that was 2,6-dichloropyridine. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.80 (t, J=6.8 Hz, 6H), 1.19 (m, 36H), 1.61(p, J=7.0 Hz, 4H), 2.73 (t, J=8.0 Hz, 4H), 7.93 (s, 1H), 8.37 (s, 2H), 17.79 (br, s, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 13.98, 22.53, 28.79, 29.08, 29.18 (two peaks), 29.27 (two peaks), 29.45, 30.28, 31.75, 32.61, 137.43, 142.39, 145.06. Analysis calc. for: C,77.03, H, 12.04, N 3.10. Deter. C, 76.90, H, 12.16, N, 3.24.

2.6.1.4. 1-Methyl-3,5-didodecylpyridinium Iodide (Compound [II]): One gram of the dialkylpyridinium hydrochloride was dissolved in benzene and washed three times with 40 mL of 1M NaOH. The benzene layer was separated, dried over $NaHCO_3$, and concentrated on a rotary evaporator. The resulting clear oil (approximately 0.95 g) was dissolved in 30 mL of reagent-grade acetone, then 2 eq (0.64 g) of methyl iodide was added. The reaction was refluxed overnight. The reaction mixture was concentrated on a rotary evaporator and recrystallized from 10:1 ethanol:water (70°C to 0°C) to yield 0.98 g of slightly off-white crystals (82% yield). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (t, J= 5.7 Hz, 6H), 1.121 (m, 36H), 1.66 (p, unresolved, 4H), 2.80 (t, J=7.9 Hz, 4H), 4.62 (s, 3H), 7.89 (s, 1H), 8.97 (s, 2H). ^{13}C NMR (200 MHz, $CDCl_3$): δ 14.04, 22.59, 29.04, 29.24 (two peaks), 29.42 (two peaks), 29.54, 30.37, 31.81, 32.54, 49.02, 142.15, 143.46, 144.36. Analysis calc. for: C,764.61, H, 10.12, N 2.51. Deter. C, 64.68, H, 10.22, N, 2.53.

2.6.2. Ligand Solubility: We determined solubilities by adding weighed amounts of pyridinium compound to the respective solvent until no further material would dissolve.

2.6.3. Preliminary Thorium Extraction Evaluation: The solutions of compounds (I) and (II) in DIPB were equilibrated with equal volumes of HNO_3 until no further color was washed into the aqueous phase. Usually two or three washes were needed. With compound (I), a milky interface observed during the first wash disappeared after the second washing. The formation of this interface was more apparent at the lower acidities. No interfacial scum was observed at acidities of 3.0M and 5.0M for either compound.

The extractions were done by a batch method with an aqueous:organic ratio of 10 mL:5 mL. The starting concentration of the thorium(IV) in the aqueous phase was 8.4×10^{-5}. The concentrations of compounds (I) and (II) in DIPB were 0.018M and 0.034M, respectively. The organic solutions were equilibrated with a range of nitric acid concentrations for 4 h at room temperature. The thorium in the aqueous phase was measured before and after the extraction with a spectroscopic technique using Arsenazo III. The distribution was calculated from

$$D = \frac{[\mathrm{Th}]_{\mathrm{organic}}}{[\mathrm{Th}]_{\mathrm{aqueous}}} ,$$

where

$$[\mathrm{Th}]_{\mathrm{organic}} = [\mathrm{Th}]_{\mathrm{initial}} - [\mathrm{Th}]_{\mathrm{aqueous}}.$$

2.7. Results and Discussion

2.7.1. Ligand Synthesis: Because long-chain alkyl pyridinium compounds were not available commercially, we had to synthesize the materials needed for evaluation. A Grignard reaction was used to attach alkyl groups to the appropriately substituted dichloropyridine compounds.

2.7.2. Ligand Solubility: The solubility of the compounds in diisopropylbenzene (DIPB) was 0.18M for compound (I) and 0.034M for compound (II). On prolonged standing, compound (I) produced a milky phase in DIPB. The solutions of compound (II) in DIPB were clear and had a dark red color, probably from iodine formed from the iodide ion. During the prequilibration step, iodide is replaced with nitrate ion and the color-forming iodine is washed out. The solubilities of these compounds were much greater in toluene with compound (I) approaching 0.28M and compound (II) approaching 0.90M. Compound (I) in toluene also produced a milky phase upon standing overnight. These solubilities are low compared with that of Aliquot 336 in DIPB. Toluene solubilities were comparable. More solvents need to be evaluated to find one with a low flash point (170°F) for potential process application. For now, studies can be performed in toluene to determine more comparisons with Aliquot 336.

2.7.3. Preliminary Thorium Extraction Evaluation: The thorium extraction results are given in Table II. Both compounds show increasing *D*-values with increasing acid strength, which is characteristic of an anionic extraction mechanism. Although the *D*-values are similar, compound (I) is the stronger extractant because its concentration is half that of compound (II).

Table II. The Effect of the [HNO_3] on the Extraction of Thorium(IV) by Compounds (I) and (II)

Compound	[HNO_3]	D_{Th}
(I) [0.018M]	5.0	1.523
(I)	3.0	1.209
(I)	1.0	1.056
(I)	0.5	0.500
(II) [0.034M]	5.0	1.588
(II)	3.0	1.313
(II)	1.0	1.044
(II)	0.5	0.510

[Thorium(IV)] = 8.36×10^{-5}M; organic solvent = DIPB; A/O ratio = 5:10 mL.

2.8. Conclusions: The two ligands tested appear to have extraction characteristics similar to those of Aliquot 336 in its acid dependencies. The solubilities of the ligands are low in DIPB compared with that of Aliquot 336 but comparable in toluene. Further solubility and third-phase formation studies are needed to determine if better solvents than DIPB exist. Aliquot 336 has a third-phase formation problem also and often needs phase modifiers. These compounds did not appear to have this problem, but more experiments are needed for proof.

Radiolytic stability testing will have to be performed later, after suitable solvents have been identified.

3.0. Subtask 3

3.1. Title: Malonamides as Alternatives to CMPO for Removal of TRUs from Aqueous Wastes

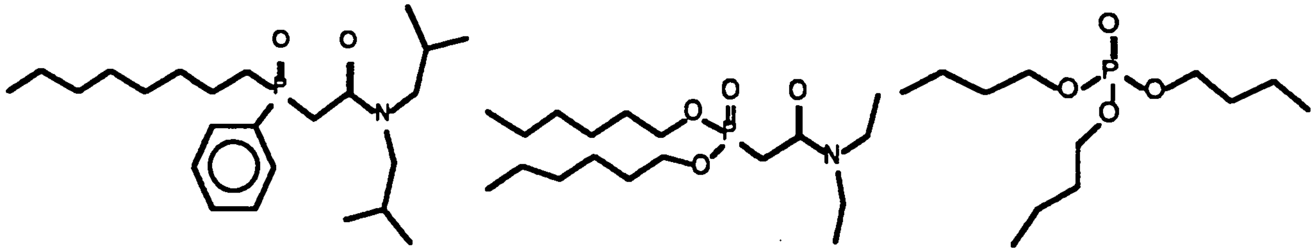
3.2. Investigators: B. F. Smith (CLS-1), G. D. Jarvinen (NMT-2), D. Kathios (NMT-2)

3.3. Objective: The objective was to evaluate several alternative, but related, liquid-liquid extractants for actinide partitioning that could substitute for the TRUEX (CMPO/TBP) process. FY 1993 Milestone: Synthesize and purify two candidate malonamides in large enough quantities for testing in FY 1994 (6 months) (April 1–September 30, 1993)

3.4. Background: To treat Hanford tank wastes for placement in their final storage form, it has been proposed that the tank wastes be redissolved and the TRUs and fission products extracted or separated from the nitric acid solutions (Morrey 1991). The extraction system under consideration is the CMPO-TRUEX process. TRUEX (CMPO/TBP) is one of the most studied extraction system for the treatment or partitioning of actinide-containing wastes (Schulz 1988) (the other is CMP-TRUEX, in which actual waste at INEL has been tested [Maxey 1980]). There are a few indications that there could be problems with phosphorous-based extractants such as CMPO and CMP (Figure 4). Because CMPO is such a good extractant, back-extracting the actinides from the organic phase has been difficult. This problem initiated the development of new water-soluble, thermally unstable (TUCS) (Gatrone 1990) compounds to aid back-extraction of the actinides. The use of these systems to aid back-extraction will only increase the expense of processing the wastes because these back-extracting agents are not recyclable and enhance waste production. The degradation products of the phosphorous-based extractants also hinder back-extraction. The other problem with phosphate-based extractants is that phosphate, a degradation product of these extractant types, interferes with the vitrification process if it is present in certain quantities (Morrey 1991).

We have proposed the comparative testing of available (literature preparation has been published) alternative extractants for TRUs that may eliminate some of the problems that have been observed with CMPO. The major class of compounds to be evaluated would be the malonamides that are being developed by the French (Cuillerdier 1990). This work would

Figure 4. Structure of CMPO and CMP and TBP extractants.



CMPO
Compound (IV)

CMP
Compound (V)

TBP
Compound (VI)

(CMPO) octyl(phenyl)-N,N-diisobutylcarbamoylmethylenephosphine oxide

(CMP) dihexyl-N,N-diethylcarbamoylmethylenephosphonate

(TBP) tri-n-butylphosphate

be performed in concert with Pacific Northwest Laboratory's (PNL's) program (TWRS) and would take advantage of the membrane extraction modules (*vide infra*) for process-scale evaluation.

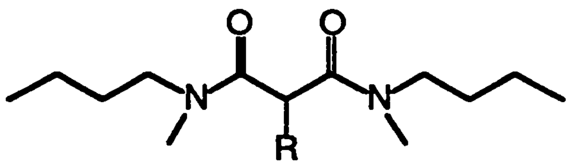
3.5. Approach: Another class of actinide extractants function well under high-nitrate conditions, as does CMPO/CMP. These extractants are the alkylmalonamides (AMAs). The malonamides are easier to handle after incineration because no phosphorous oxide ashes are produced; thus, phosphate does not enter waste streams that need to be vitrified. The degradation products do not interfere with the back-extraction of the actinide elements, and the substituted malonamides appear to have similar stability to CMPO.

Our approach would be to develop improved techniques to synthesize these materials and evaluate them using small-scale, batch-extraction techniques and the countercurrent lab pilot-scale liquid-liquid extraction (LLE) technology (*vita infra*) in concert with the PNL program (TWRS, G. Lumetta). The ligands under consideration are depicted in Figure 5. Our choice is based on the data collated by C. Musikas (Cuillerdier 1991) about the optimal substituent on both the carbonyl nitrogens and the methylene substituent. He found that an unsymmetrical pair of alkyl groups on the amide nitrogens give the best extraction. When the methylene substituent has an ether linkage gamma to the methylene carbon, americium(III) extraction is optimized. There is a tradeoff between optimizing actinide extraction and the difficulty and expense of ligand synthesis. According to the reported literature procedure, the ligand-containing oxygens in the methylene tail are very difficult and time consuming to synthesize. Improved alternative techniques and approached are required.

3.6. Experimental

3.6.1. Apparatus: Instrumentation included nuclear magnetic resonance (NMR) (Varian Model EM 390), (Varian Model Gemini 200), Fourier transform infrared (FT-IR) spectroscope (Nicolet Model 20SXB) (Mattson Model Galaxy 5020), ultraviolet-visual (UV-VIS) diode array (Hewlett-Packard Model 8451A), gas chromatograph-flame ionization detector (GC-FID) (Hewlett-Packard

Figure 5. Malonamides under consideration for synthesis.



Compound (VII) when R = H

Compound (VIII) when R = dodecyl

Compound (IX) when R = tetradecyl

Compound (X) when R = CH_2CH_2-O-dodecyl

Model 5710A, DB-1 column, 12M, 0.2-mm bore, 0.33-µm coating), and pH meter (Fisher Model 610A). Elemental analyses were performed by Galbraith Laboratories.

3.6.2. Synthesis of Dibutyldimethylmalonamide (Compound [VII]): Freshly distilled diethylmalonate (40.5 g, 0.25 mol, Aldrich)[1] and N-methylbutylamine (110.2 g, 1.26 moles, Aldrich) were mixed together in an oven-dried glass container. The container was placed in a pressure vessel, which was sealed and placed in a 105°C oven for 3 days. The pressure vessel was then removed from the oven and allowed to cool to room temperature before being opened. Excess amine and ethanol were removed under vacuum to give 60 g of crude, pale yellow product. The material was dissolved in $CHCl_3$ and washed twice with dilute HCl, once with dilute NaOH, and once with NaCl-saturated water. The organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under vacuum to give a heavy, oily material that solidified upon sitting. We recrystallized the material from petroleum ether using freezer temperatures to encourage crystallization, giving a white, crystalline material having a melting point of 48°C. Considerable material was lost in the recrystallization, but second crops were obtained. An alternative purification was distillation at 140°C per 0.3 mm, but móre than 50% of the material was lost in some degradation process.

This synthetic procedure was repeated several times (limitation on pressure vessel size) to yield more than 100 g of material for testing in the LLE apparatus.

3.6.3. Synthesis of $C_{12}H_{25}$-Substituted Diamide (Compound [VIII]): We placed NaH (3.3 g, 0.083 mol, 60% in mineral oil, Aldrich) in an oven-dried, 3-neck, round bottom flask fitted with a dry N_2 inlet and condenser. To remove the mineral oil, we washed the flask three times with small portions of hexane. Freshly distilled tetrahydrofuran (THF, 100 mL over CaH) was added and the solution cooled to 0°C in an ice bath. A solution of the dibutyldimethylmalonamide (29 g, 0.083 moles) in THF (50 mL) was added slowly over a half-hour and allowed to stir until mostly reacted. The reaction was more complete when the temperature was allowed to go to 10°C. Dodecylbromide (20.5 g, 0.083 mol, Aldrich) was added all at once and the reaction allowed to stir at room temperature for 5 h followed by refluxing for 1 h. The THF was removed under vacuum, then water was added to the reaction product and the aqueous phase extracted into hexane (the aqueous phase was basic). The organic phase was then washed with dilute HCl and NaCl-saturated water, dried over Na_2SO_4, filtered, and evaporated from the hexane to give 27 g of crude product. The material was placed on a silica gel column and eluted with hexane to remove any residual mineral oil and some by-products and starting material. The product was then eluted with 50:50 hexane:$CHCl_3$, to give 20.4 g (60%) of 98% pure oily material according to gas chromatographic (GC) analysis.

3.6.4. Synthesis of $C_{14}H_{29}$-Substituted Diamide(Compound [IX]): The procedure described above was followed for this synthesis except that bromotetradecane (22.9 g, 0.083 moles, Aldrich) was used. The crude product was 34.4 g. After silica gel clean-up, a similar yield and purity was obtained.

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[1] Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, Wisconsin 53233, USA

This procedure was scaled to prepare material for the LLE experiments.

3.7. Results and Discussion: The synthetic procedures reported in the literature for these unsubstituted malonamides gave much lower yields and required distillation of the product. The procedures were more difficult to perform because very air sensitive and caustic reagents were used (Thiollet 1989). Our synthetic approach was based on work reported by H. DuPree (private communication), who reported that he could effect the amidation of a single ethyl ester in 5 h at 60°C. The same conditions would effect only partial conversion of diethylmalonate to the diamide. After considerable experimentation, we determined that longer reaction times (3 days) and higher temperature (105°C) were required to effect the desired transformation. Because the higher temperatures were above the boiling point of the N-methylbutylamine, we had to use a pressure reactor to maintain the required temperatures. The use of the pressure vessel permitted both the use of inexpensive and noncaustic reagents in this synthesis and ready scaleup of the starting material.

The second step of the synthesis was reported in the literature (Thiollet 1989). This step used butyllithium as the base to deprotonate the malonamide, a relatively weak acid. Butyllithium is highly air sensitive and pyrophoric, making it difficult to perform large-scale reactions with this reagent. Attempts at using phase-transfer agents were reported (Charles Madic, private communication), but purification of the final product was difficult. If any transfer agent remains with the product, it interferes with the ligand's use as an extractant by acting as a surfactant.

Our approach was to use sodium hydride (NaH) as the base. The only by-product is a small amount of mineral oil that can be removed or does not interfere with the extraction process in hydrocarbon diluents. Future syntheses could use mineral-oil-free reagent to by-pass this impurity. The NaH is relatively easy to handle, simplifying scaleup.

Our final purification for these substituted diamides was by pressure chromatography on silica gel. If one had a vacuum system that allowed for very low pressures, the materials could be distilled. In general, though, a considerable amount of material is lost to degradation in the distillation process. For smaller scale purification, chromatography is the purification method of choice.

We attempted alternative approaches to the substituted malonamides. In this case, diethylmalonate was treated with sodium hydroxide for deprotonation (diethylmalonate is a stronger acid than the malonamides and can be deprotonated with a weaker base) and then alkylated with an alkylbromide to form the methylene-substituted diethylmalonate. This crude product was purified by distillation (lower boiling point than the substituted diamide). The purified substituted diethylmalonate (an oil) was then placed in the pressure vessel and reacted with N-methylbutylamine in an attempt to form the malonamide. Higher temperatures (150°C) were required to effect amide formation. At these higher temperatures, decarboxylation occurred and only monoamide was isolated. This approach has possibilities if the system can be catalyzed to cause the transformation to occur at a lower temperature. The approach has merit because NaOH is much cheaper than NaH. Unfortunately, it was discontinued because we lacked time to pursue this avenue.

Work is still in progress to obtain the oxygen-containing substituent (compound [X]). We have had little success obtaining much product by following the literature procedure (Thiollet 1989). It is a three-step procedure to obtain the alkylating group, and the yields are quite low for each step. We have identified areas where the procedure might be improved, such as the use of a high-speed stirrer to improve the mixing in the two-phase reaction. Information obtained from a meeting with the head of the French separations team indicated that the French have decided that the oxygen-containing tails are just too expensive and difficult to make. They have compromised on using the malonamide with the carbon-14 methylene substituent (compound [IX]) to continue with their studies because the extraction constants for americium(III) are still reasonable for this compound.

The second step for the scaleup of the $C_{14}H_{29}$-substituted material (compound [IX]) is still in progress because the oven needed for the first malonamide (compound [VII]) reaction step failed and because this step had to be performed several times to produce enough material for us to proceed with the second step. Because each reaction time is a minimum of 3 days, we have fallen a little behind in the scaleup of this material needed for the LLE testing. This subtask has not been terminated, so we expect this work to be completed early in FY 1994.

3.8. Conclusions: A new and better synthetic procedure has been developed for the preparation of the malomides. It has allowed us to prepare large amounts of material for testing in FY 1994.

Another problem that needs to be addressed is the prevention of third-phase formation with these diamides. Further modifications to the structures are proposed, and perhaps synergistic systems could overcome this problem. These approaches will be pursued in FY 1994.

4.0. Subtask 4

4.1. Title: Development of "Soft" Donor Extractants for Trivalent Actinide/Lanthanide Separations

4.2. Investigators: B. F. Smith (CLS-1), R. Barrans (CLS-1), G. D. Jarvinen (NMT-2), M. M Jones (CLS-1), J. Mills (TTU), S. Bowen (INC-12), Z. Svitra (INC-12)

4.3. Objective: The objective is to evaluate ligands that have demonstrated good analytical separations of the actinides/lanthanides in a process approach for the separation of the trivalent lanthanides from the trivalent actinides (americium and curium) and to evaluate several new soft donor extractants. FY 1993 Milestone: Identify and obtain two, possibly three, commercially available (in the literature) soft donor ligands that, based on previous results, have a good chance of discriminating between trivalent actinides and lanthanides. These ligands are to be tested in FY 1994. (7 months) (March 1–September 30, 1993)

4.4. Background: The separation system under consideration to remove actinides from Hanford waste streams is biphasic organic/aqueous LLE with the TRUEX process (CMPO). When the TRUs are extracted in the TRUEX process, the trivalent lanthanides are extracted simultaneously with all the actinides (likewise with the malonamides extractants). Thus, advanced trivalent actinide/lanthanide separations capabilities are needed. All the available tested methods of separating trivalent actinides and lanthanides have severe process limitations (TRAMEX [Baybarz 1963] uses concentrated salt solutions; TALSPEAK [Weaver 1968] adds organics to the aqueous phase and process conditions are difficult to control).

The Hanford waste tanks are estimated to contain between 12 and 161 kg of americium and between

32 and 80 kg of samarium (samarium-151). Morrey and Swanson (1991) have reported that double-shell tank waste contains approximately 8,000 kg of stable lanthanum, which was added as carrier during former campaigns. Considerable amounts of other early lanthanide fission products and curium also exist. The presence of the lanthanides increases the amount of waste that would have to be placed in glass logs. Up to 5000 additional logs would be required to include all the nonradioactive lanthanides in the glass (Morrey 1991).

If the number of Hanford logs is to be reduced, advanced trivalent lanthanide and lanthanide separations are needed. Lanthanide-free actinide material for entry to the transmuter are also needed to maximize the neutron efficiency of the transmuter. This need has been recognized by actinide researchers worldwide and has been given high priority in such countries as France and Japan.

4.5. Approach: The separation of trivalent lanthanides from trivalent actinides is one of the most difficult metal-ion separations. We proposed to test advanced extractants for this separation that are under development at Los Alamos or are commercially available.

Because complexes of trivalent actinides appear to have a larger covalent bonding character than those of trivalent lanthanides, "soft" donor extractants can be exploited to separate these metal ions. This approach has been recently pursued by researchers in France (Fitoussi 1984) and at Los Alamos (Smith 1987, Smith 1989, Nekimken 1992). In those studies, sulfur-containing donors (dithiophosphates, acylthiopyrazolones) have given the best separation of these metals (Figure 6). The acylthiopyrazolones have been very successful in the analytical application to trivalent actinide separation from trivalent lanthanides. The long-range plan is to further test their ability to function in a separation process in which the extractant is cycled through many extraction steps. Because sulfur compounds can be oxidized or hydrolyzed under certain process conditions, we will explore the stabilization of these types of compounds through steric and electronic effects (Figure 7) and through disulfide reduction studies.

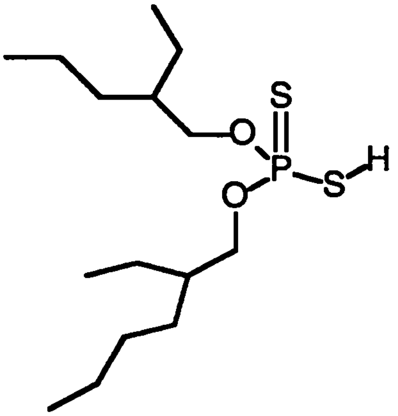
Nitrogen donor ligands are the next best types of soft donors that we would like to explore. One main class of nitrogen donor ligands (compound [XV]) has been demonstrated by the French (Bounin 1985) (Figure 8), and others are under consideration at Los Alamos by Jarvinen and Smith (Figure 9).

Pyrazolylborates, tridentate nitrogen-containing ligands, are well known for forming stable complexes with transition metals, actinides, and lanthanides (Trofimenko 1986, Stainer 1983, Bagnall 1976, Bagnall 1975). They are thus candidates for selective extraction of actinides in the presence of lanthanides. The three compounds in this class that are commercially available are depicted in Figure 9. The first, sodium tetrakis(1-imidazolyl)borate (compound [XVI]), is not strictly a member of this class because its nitrogen-containing rings are imidazoles rather than pyrazols.

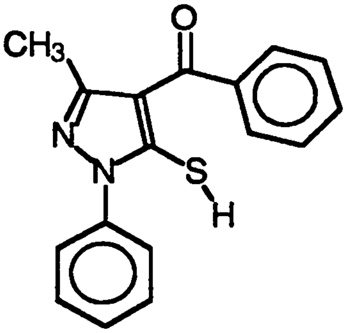
Our approach was to obtain all these soft donor ligands (or purify commercially available materials) and evaluate them for their ability to effect trivalent lanthanide/actinide separations. During this reporting period, the ligands were identified and either synthesized or purified. In addition, the synthetic procedure was improved or started.

The available processes for trivalent actinide/lanthanide separation are the not-so-desirable TRAMEX and TALSPEAK processes. The results of this work will be used to identify any alternative, practical extractant systems. The types of ligands that are developed in these

Figure 6. Structures of sulfur donor ligands that have demonstrated good separation of trivalent lanthanide from trivalent actinides.

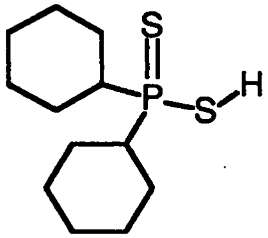


di-(2-ethylhexyl)-dithiophosphoric acid (HDEHDTP)
Compound (XI)



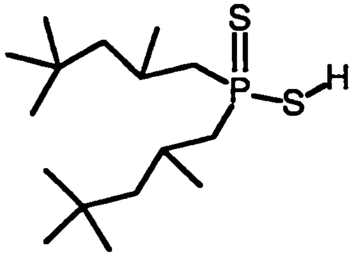
4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (HBMPPT)
Compound (XII)

Figure 7. New sulfur-containing compounds to be tested.



Dicyclohexyldithiophosphinic acid

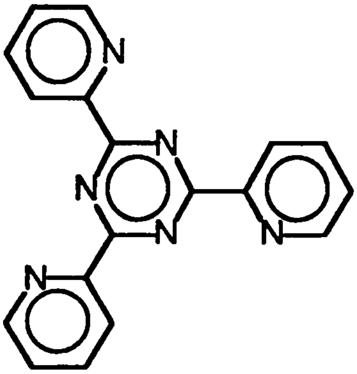
Compound (XIII)



Bis(2,4,4-trimethylpentyl)dithiophosphinic acid

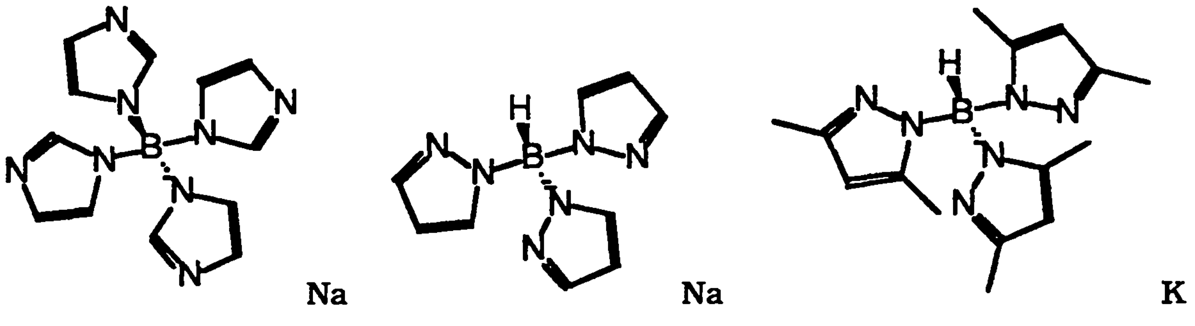
(CYANEX 301)
Compound (XIV)

Figure 8. Nitrogen-containing compound under consideration by the French for trivalent lanthanide/actinide separations.



2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ)
Compound (XV)

Figure 9. Multidentate nitrogen-containing ligands under study at LANL for trivalent lanthanide/actinide separations.



Compound (XVI) Compound (XVII) Compound (XVIII)

studies could be incorporated into water-soluble chelating polymers for more advanced separations. The separation of the trivalent lanthanides from actinides is critical to reducing the number of glass logs that will be made in the TWRS and has a clear place in both the Hanford "clean" option (Straalsund 1992) and an ATW transmutation scenario.

4.6. Experimental

4.6.1. Apparatus: Radioactivity measurements were carried out with NaI well-type scintillation counters (Packard Model 500C and Packard Model 5000). Other instrumentation included NMR (Varian Model EM 390, Varian Model Gemini 200), FT-IR (Nicolet Model 20SXB) (Mattson Model Galaxy 5020), UV-VIS diode array (Hewlett-Packard Model 8451A), GC-FID (Hewlett-Packard Model 5710A, DB-1 column, 12M, 0.2-mm bore, 0.33-µm coating) and pH meter (Fisher Model 610A). Elemental analyses were performed by Galbraith Laboratories.

4.6.2. Ligand Synthesis/Purification

4.6.2.1. Synthesis of Dicyclohexyldithiophosphinic Acid (Compound [XIII]): Compound (XII) was synthesized according to the procedure of G. Peters (1962).

4.6.2.2. Purification of Cyanex 301 (Compound [XIV]): Commercial. crude Cyanex 301 (40g, 0.12 mol), which was green, was dissolved in 200 mL of analytical-grade hexane. It was equilibrated with 200 mL of 6N H_2SO_4 for 10 min. The green color in the hexane phase became light. The mixture was then equilibrated with 170 g (0.6 mol) of $ZnSO_4$ in 400 mL of 0.1 N H_2SO_4 for 15 min. This procedure was repeated once more with fresh $ZnSO_4$ solution. A yellow zinc complex was obtained in the hexane phase. The mixture was then dried over 25 g of anhydrous Na_2SO_4 for 4 h. The resulting hexane solution was pale yellow in contrast to the darker fresh extract. The hexane was removed by rotary evaporation to obtain a pale yellow, viscous product. This product was washed three times with 150 mL of methanol, the methanol being discarded after phase separation. This step yielded a milky white product. The traces of methanol were removed by rotary evaporation in a 38°C water bath (CAUTION: higher temperatures lead to the decomposition of the zinc chelate as evidenced by the darkening of the color to deep yellow) to yield a zinc-Cyanex 301 chelate as an almost clear viscous product. The material was stored as the zinc complex because it is more stable in this form. Stripping of zinc with 6N H_2SO_4 provided a light yellow hexane solution of free ligand. Zinc could be completely removed after a single equilibration with H_2SO_4.

4.6.2.3. Synthesis of 1-Phenyl-3-methyl-4-benzoyl-5-chloropyrazole (PMBCP): PMBCP was synthesized from a literature procedure (Michaelis 1903).

4.6.2.4. Synthesis of 4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thone (HBMPPT) (Compound [XII]): BMPPT was synthesized from 1-phenyl-3-methyl-4-benzoyl-5-chloropyrazole, in a manner similar to a previously reported procedure (Smith 1987), by reaction of PMBCP (0.1 mol) and $NaSH \cdot H_2O$ (4 equivalents) in ethanol solvent (320 mL) under 5 h of reflux. The N_2-purged reaction mixture was cooled and allowed to settle. The supernatant was decanted, without disturbing the solids, by vacuum suction of the surface liquid through a Teflon tube, and the liquid volume was reduced by half under vacuum. Water (400 mL) was added and the solution (pH 9 to 10), which was extracted once with $CHCl_3$ (50 mL) to remove neutral materials. The aqueous phase was made acidic (pH 5 to 6) with HCl (25 mL concentrated diluted to 100 mL with water) and extracted three times with $CHCl_3$ (100 mL each). The three organic fractions were combined and washed with water (100 mL), and dried over Na_2SO_4. The solvent was removed under vacuum and the solid residue dissolved in hot ethanol (50 mL) and recrystallized to yield 25 g (77%) of orange crystals (melting point 111°C to 112°C), which appear to be stable indefinitely in air. ^1H NMR ($CDCl_3$-TMS): δ 2.05 (s, CH_3, 3H), 7.2-7.9 (m, Ph, NH, 11H); (DMSO-d_6-TMS): δ 2.25 (s, CH_3, 3H), 3.65 (s, SH, 1H), 7.1-7.8 (m, Ph, 10H); IR (KBr): 2400 (SH), 1600 (C=O), 1502, 1434, 1384, 1007, 765, 749, 700, 692 and 675 cm^{-1}; UV (cyclohexane) @max 247 and 277 nm; (methanol) @max 233, 274, and 354 nm.

4.6.3. Ligand Evaluation

4.6.3.1. Distribution Determinations: Carrier-free radioisotopes europium-152 and americium-241 (NIST)[2] were used. We prepared separate aqueous metal solutions by fuming the individual isotopes to dryness several times in HNO_3 and redissolving the solutions in dilute acid. We then prepared mixed isotope solutions by spiking a pre-equilibrated (with organic solvent), preadjusted (pH 0.1, $NaNO_3$), and buffered (sulfanilic acid 0.01M) solution with isotope concentrates. Concentrations of the tracer (approximately10^{-8}M) in the aqueous phases were determined directly from the gamma activity of the solution. The ligands TOPO (Eastman),[3] and TBP (Baker tech) were dissolved in the organic solvent (Baker Resid-Analyzed)[4] to give the concentration ranges needed and were pre-equilibrated with equal volumes of the corresponding aqueous acid solution. Duplicate extractions, having equal volumes of aqueous and organic phase (2 mL), were contacted for 30 min at room temperature (22°C to 24°C) in Teflon vials in a mechan-

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[2] National Institute of Standards and Technology

[3] Eastman Kodak Co., Laboratory and Research Products Division, Rochester, NY 14650

[4] J. T. Baker Chemical Co., 222 Red School Lane, Phillipsburg, NJ, 98865

ical shaker or were vortexed for 15 min followed by centrifugation for phase separation. The radioactivity was measured separately for equal aliquots (1 mL) of both phases, and the distribution ratio was calculated as activity of the organic phase divided by the activity of the aqueous phase. The pH of the aqueous phase was determined after extraction. Accountability for all extractions was 100 ± 10%.

4.6.4. Ligand Stability Studies

4.6.4.1. Stability of Dicyclohexyldithiophosphinic Acid (HDCHDTP) (Compound [XIII]): A 10-mL solution of HDCHDTP (0.4M) in toluene and a solution of TBP (0.2M) were shaken in a Teflon centrifuge tube in air while in contact with aqueous acid (1mM HNO_3, 0.1M $NaNO_3$, 0.01M sulfanilic acid). Organic-phase samples (1 mL) were removed at timed intervals and gamma-counted to determine the concentration of americium and europium. The organic material was returned to the reaction mixture and further shaken for several weeks. The pH was measured periodically.

4.6.4.2. Solubility and Stability of Pyrazolylborates by NMR: Sodium tetrakis(1-imidazolyl)borate (compound [XVI]), sodium tris(1-pyrazolyl)borohydride (compound XVII), and potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride (compound [XVIII[) were used as received from Aldrich. Toluene and heptane were obtained from EM Science.[5] Ethylacetate, dichloromethane, and isopropanol were obtained from Baker. Water was purified with a Barnsted E-pure system. A known amount of borate was placed in a scintillation vial (approximate capacity 20 mL) with 15 mL of an organic solvent. The vial was capped and shaken on a Barnell Wrist Action shaker for at least an hour. If any solid sample appeared to dissolve totally in that time, more solid was added and the shaking continued. The mixture was then forced through a Gelman Acro disc 13-mm-diam PTFE syringe-end filter, and a known volume of the filtrate was transferred to a round-bottom flask in a volumetric pipette. The solvent was removed by rotary evaporation, and the amount of residue in the flask was determined either from the weight gain of the flask or by the absorbance of an aqueous solution of the residue made to a known volume.

4.6.4.3. Hydrolysis Studies: Sodium tetrakis(1-imidazolyl)borate, sodium tris(1-pyrazolyl)borohydride, potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride, and deuterium oxide containing 1% DSS as an internal reference were purchased from Aldrich; deuterium oxide without DSS and acetonitrile-d3 containing 1% TMS were purchased from Janssen.[6] NMR chemical shifts are reported in parts per million downfield of internal DSS unless specified otherwise.

4.6.4.4. Sodium Tetrakis(1-imidazolyl)borate (Compound [XVI]): An NMR tube was charged with the borate (13.9 mg, 0.0460 mmol) and deuterium oxide containing 1% DSS (700 µL) and shaken to give a colorless solution. ^1H NMR: δ 7.330 (s, 1H), 7.086(s, 1H), 6.921 (s, 1H).

4.6.4.5. Sodium Tris(1-pyrazolyl)borohydride (Compound [XVII]): The borohydride (15.4 mg, 0.0652 mmol) was dissolved in deuterium oxide containing 1% DSS (700 µL). The solution effervesced for approximately 2 days. ^1H NMR of

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[5] EM Science, P.O. Box 70, 480 Democrat Road, Gibbstown, NJ, 08027

[6] Janssen Chimica, Spectrum Chemical Mfg. Corp., 14422 South San Pedro Street, Gardena, CA 90248

starting material: δ 7.640(d, 1H, 2 Hz), 7.387 (d, 1H, 2.12 Hz), 6.314 (t, 1H, 1.79 Hz). Hydrolysis product: δ 7.70 (d, 2H, 2 Hz), 6.41 (t, 1H, 2 Hz).

4.6.4.6. Potassium Tris(3,5-dimethyl-1-pyrazolyl)borohydride (Compound [XVIII]): A 5-mL volumetric flask was charged with the borohydride (4.3 mg, 0.0128 mmol), and deuterium oxide containing 1% DSS was added up to the mark. Approximately 700 µL was transferred to an NMR tube. ^{1}H NMR of borohydride: δ 5.874 (s, 1H), 2.117 (s, 3H), 1.837 (s, 3H). NMR of hydrolysis product: δ 5.953 (s, 1H), 2.211 (S, 6H).

4.7. Results and Discussion

4.7.1. Dicyclohexyldithiophosphinic Acid (Compound [XIII])

4.7.1.1. Musikas and coworkers (Fitoussi 1980) have evaluated extraction systems containing sulfur donors to determine their ability to discriminate between the trivalent actinides and lanthanides. The synergistic system di-2-ethylhexyl-dithiophosphoric acid (compound [XI])/tributylphosphate (compound [VI]) gave the most separation of americium(III) from europium(III). Separation factors of 10^2 to 10^3 were found at certain concentrations of aqueous acid, HDEHDTP, and TBP, apparently because the compositions of the extractant complexes are different for the two metals ions: $Am(DEHDTP)_3(TBP)$ and $Eu(DEHDTP)(NO_3)_2(TBP)$ (obtained from extraction data). Such selectivity has not been observed for the corresponding oxygen-donor systems. Note that the synergist increased the extraction coefficient to useful values (HDEHDTP alone is a poor extractant relative to its oxygen analog) and at the same time increased the selectivity. The disadvantage of these systems is their low stability, giving rise to a hydrolysis product that does not show the desired selectivity and has increased extractability of both americium and europium. In fact, hydrolysis problems have made it difficult to repeat the French experiments.

We had postulated that the dithiophosphinic acid systems would have improved stability and thus decided to synthesize or obtain several for testing (Figure 8). The synthesis of compound (XIII) had been previously reported (Tjioe 1089) Approximately 20 g of the material was obtained for testing.

A variety of pHs, concentrations, and synergist types were tested to find a parametric space where large separations factors might occur. The data are given in Table III.

This testing was followed by a study to determine the optimal ligand ratios at pH 3 using TBP as the synergist A Jobs plot is shown in Figure 10. A mole fraction in the range of 0.17 to 0.33 TBP gave the highest separation factors of 316, but the separation factor was generally high across most of the plot. Under these conditions, a pH study was performed at pH 1 to 3. No extraction occurred at pH values less than 2.

A longer term stability study of the ligand at room temperature in contact with HNO_3 (pH 3) was performed to determine if the ligand was rapidly degrading under these conditions. If hydrolysis were occurring, one would expect decreased separation factors and increased total extraction of both americium and europium. After 3 weeks, no decrease in the separation factor or increase in the total extraction was observed under the conditions of the experiment.

It will be necessary to examine the parameter space (pH, [L], [S], etc. dependencies) to determine if at high ligand concentrations we can observe extraction at lower pH values (the French studies were at 0.75M). The

Table III. Preliminary Separation Studies of Americium(III) and Europium(III) with Dicyclohexyldithiophosphinic Acid

pH	[L]	[S]	log D_{Am}	Log D_{Eu}	$SF_{Am/Eu}$
3.5	0.1	0.0	-1.54	-1.66	1.3
3.5	0.5	0.0	-0.19	-0.84	4.5
3.2	0.1	0.05(TBP)	-1.34	-2.13	6.5
3.5	0.5	0.135(TOPO)	2.40	2.02	2.7
3.5	0.5	0.1(TBP)	0.5	-2.0	250

synergist used by the French workers (Fitoussi 1980) was TBP, which also gave good results with dicyclohexyldithiophosphinic acid. One test with TOPO indicated enhanced extraction for both europium and americium. Further studies in another parameter space (for example, lower [L] and [S]) need to be performed along with testing of other synergists.

The extraction was negligible at lower pH value, indicating a very large pH dependency. Because compound (XIII) is more basic than compound (XI), protonation may occur at a higher pH value, not allowing the ligand to function at a lower pH range. This hypothesis needs further testing.

4.7.2. Cyanex 301 (Compound [XIV])

4.7.2.1. Purification of Cyanex 301 (Compound [XIV]): Cyanex 301 is commercially available from American Cyanamid Corporation,[7] but contains about 10% of an alkylphosphine oxide by-product impurity, which can also act as a synergist and can potentially cause erroneous results in extraction studies. We felt the material had to be purified. The zinc complex has been reported to be readily formed from the dithiophosphinic acid (Rickelton 1990) but not the by-product impurity. Thus, the zinc complex was readily separated from the impurity. The free ligand can then be obtained by release of the zinc ion by treatment with sulfuric acid. During purification of the Cyanex 301, the free ligand did not appear highly stable in that it easily turned darker yellow upon contact with 6M HCl or temperatures above 38°C. Further correlation studies of the observed color changes with oxidation or hydrolysis products of Cyanex 301 will have to be performed.

4.7.2.2. Extraction Studies with Unpurified Cyanex 301: We performed preliminary trivalent actinide/lanthanide studies with unpurified Cyanex 301 using americium(III) and europium(III). The results are shown in Table IV. It can be seen that there is little observed separation, and in fact europium was slightly favored over americium in most cases. No extraction occured between 1M and 0.5M nitric acid and when no synergist or only TBP was present.

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[7] American Cyanamid Co. One Cyanamid Plaza, Wayne, NJ, 07470

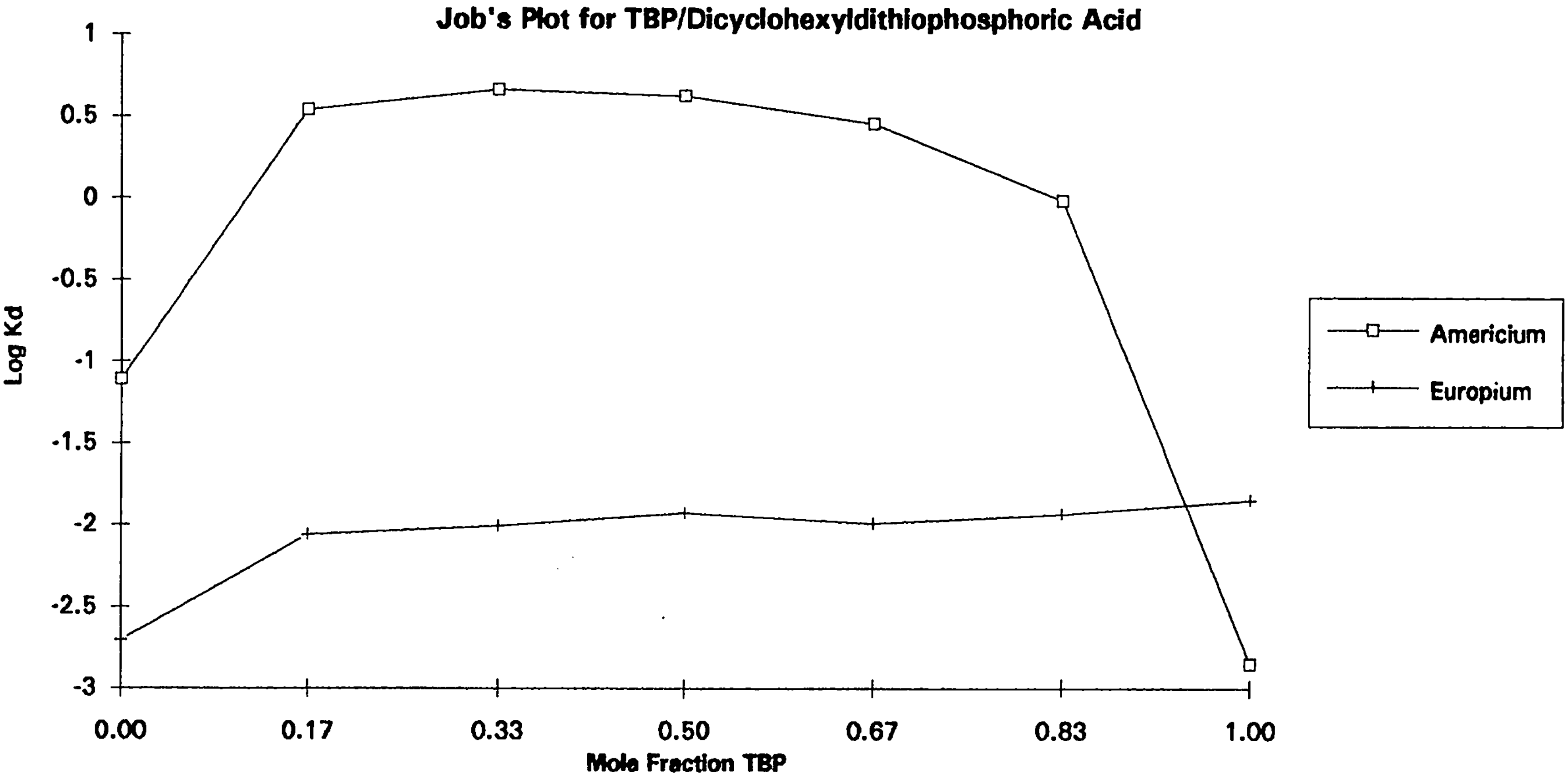


Figure 10. Jobs plot of log $D_{Am(Eu)}$ versus mole fraction of tributylphosphate with dicyclohexyldithiophosphinic acid.

Table IV. Extraction Results of Americium(III) and Europium(III) with Unpurified Cyanex 301 with Several Synergists

[H+]	[L]	[S]	Log D_{Am}	Log S_{Eu}	$SF_{Am/Eu}$
0.1	0.75	0	-0.5	-0.34	0.7
0.01	0.75	0	2.0	1.81	1.5
0.1	0.75	0.2 (TOPO)	0.67	0.81	0.7
0.01	0.75	0.2 (TOPO)	1.87	2.20	0.5
0.1	0.75	0.2 (TBP)	-0.6	-0.38	0.6
0.01	0.75	0.2 (TBP)	1.58	2.15	0.3

In toluene, = 0.1 $NaNO_3$

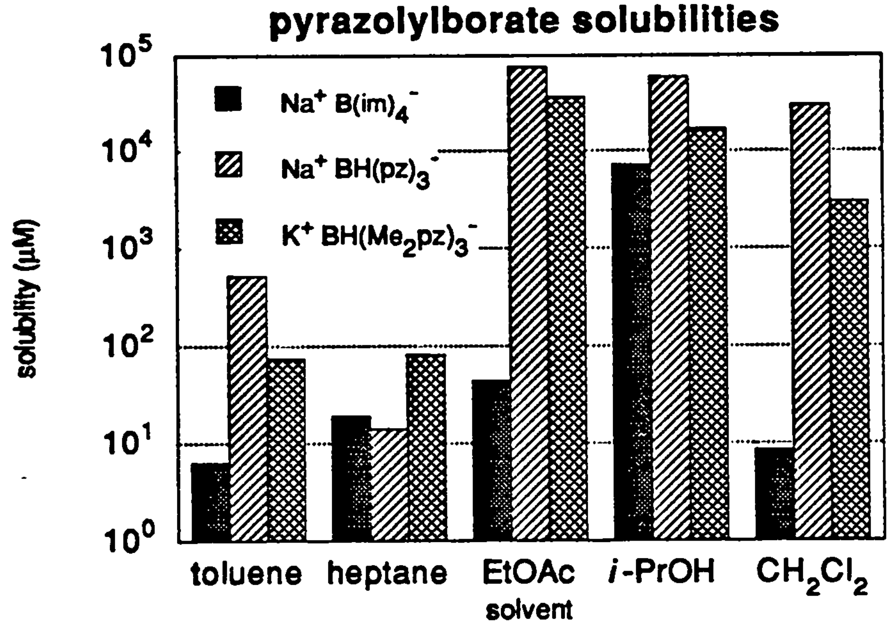
4.7.2.3. Extraction Studies with Purified Cyanex 301: These studies were not started in FY 1993 but are slated for completion in early FY 1994.

4.7.3. Pyrazolylborates: For such compounds to function as metal-ion extractants in an aqueous/organic LLE system, at a minimum they must be soluble in a water-immiscible organic solvent and be stable in the presence of water. The solubilities of these compounds in several organic solvents were therefore determined, as were their stabilities in aqueous solution. The solvents screened were heptane and toluene as representative aliphatic and aromatic hydrocarbons, ethyl acetate as a representative ester, isopropanol as a representative alcohol, and dichloromethane as a representative chlorinated hydrocarbon. The measured solubilities are reported in Figure 11. The solubilities of all three compounds in hydrocarbon solvents were too low for the compounds to be useful.

4.7.3.1. NMR Stability of Commercial Pyrazolylborates Compounds (XVI), (XVII), and (XVIII)

4.7.3.1.1. Hydrolysis Studies: In all cases, relative concentrations of starting material and product were measured by integration of their proton NMR signals. The relaxation delay between successive scans was longer than 5 times the relaxation times (*T*1) of all studied protons. The *T*1 of the protons of sodium tetrakis(1-imidazolyl)borate and sodium tris(1-pyrazolyl)borohydride and of the hydrolysis products of sodium tris(1-pyrazolyl)borohydride and potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride were determined by inversion-recovery experiments. The comparable protons of sodium tetrakis(1-imidazolyl)borate and sodium tris(1-pyrazolyl)borohydride exhibited similar *T*1, as did the comparable protons of the final hydrolysis products of sodium tris(1-pyrazolyl)-borohydride and potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride.

Figure 11. Solubilities of pyrazoylborates in selected solvents.



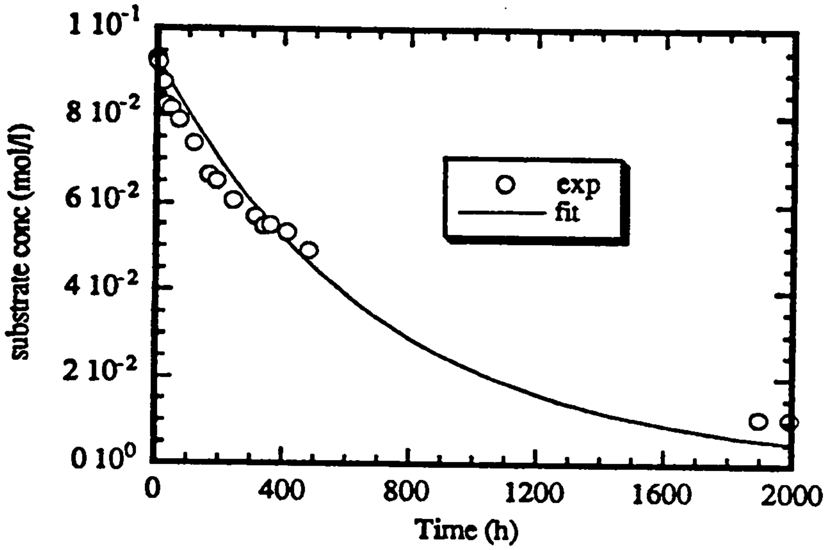
Because the *T*1-values for the hydrolysis product of sodium tris(1-pyrazolyl)borohydride were considerably longer than those for sodium tris(1-pyrazolyl)borohydride itself, the *T*1 for the protons of potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride were assumed to be shorter than those of its hydrolysis product as well.

The lifetimes of these compounds in heavy-water solution varied greatly. Sodium tetrakis(1-imidazolyl)borate (XVI) was indefinitely stable, sodium tris(1-pyrazolyl)borohydride (XVII) hydrolyzed slowly, with a half-life of 20 days (Figure 12), and potassium tris(3,5-dimethyl-1-pyrazolyl)-borohydride (XVIII) hydrolyzed rapidly, with a half-life of 45 min (Figure 13). None of these commercially available compounds meets the minimum criteria of organic solubility and hydrolytic stability.

4.7.3.2. Synthesis of Stable Pyrazolylborate Analog: To attain stability and organic solvent solubility properties within the pyrazolylborate framework, we have begun a program to synthesize alkyltris(1-pyrazolyl)-borates. Three representative examples are depicted in Figure 14. Because they possess no labile borohydride(B-H) functional group, these compounds should resist hydrolysis (Reger 1982).

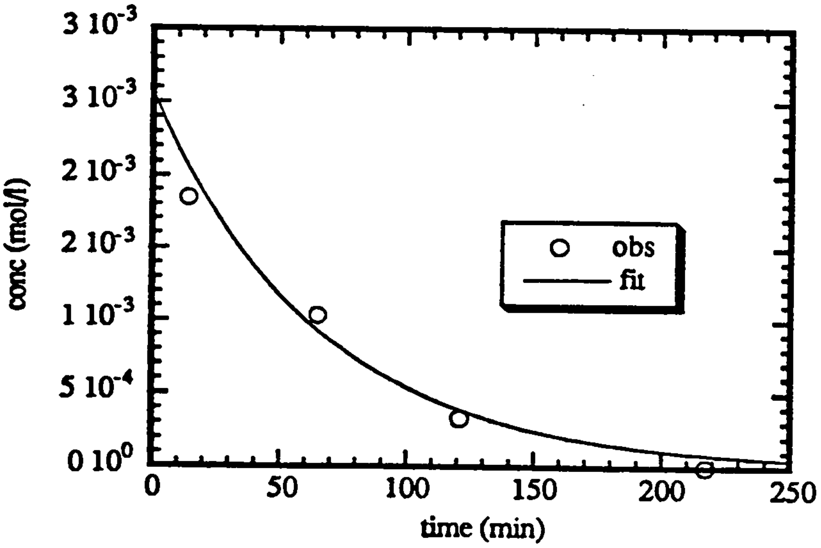
Furthermore, the organic solubility of the ligands should also be enhanced by the presence of the hydrophobic alkyl units. The general synthesis of this type of compound is shown in Figure 15 (Niedenzu 1986, Reger 1982). The reaction of an alkyl Grignard reagent with trimethyl borate followed by hydrolysis produces an alkaneboronic acid, which is transformed to an alkyltris(pyrazolyl)-borate by heating with pyrazole and

Figure 12. Hydrolysis in D_2O of sodium tris(1-pyrazolyl)borohydride.



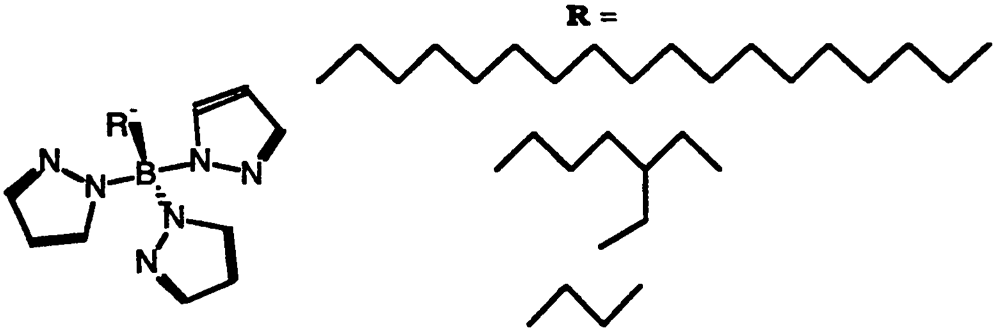
Hydrolytic data (concentration versus time) along with the best fit first-order decay curve (k = 0.00145 h^{-1}; $t_{1/2}$ = 19.9 d).

Figure 13. Hydrolysis in D_2O of potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride.



Hydrolytic data (concentration versus time) along with the best fit first-order decay curve (k = 0.0155 min^{-1}; $t_{1/2}$ = 44.5 min).

Figure 14. Three examples of potentially more stable and organic solvent soluble pyrazolylborates.



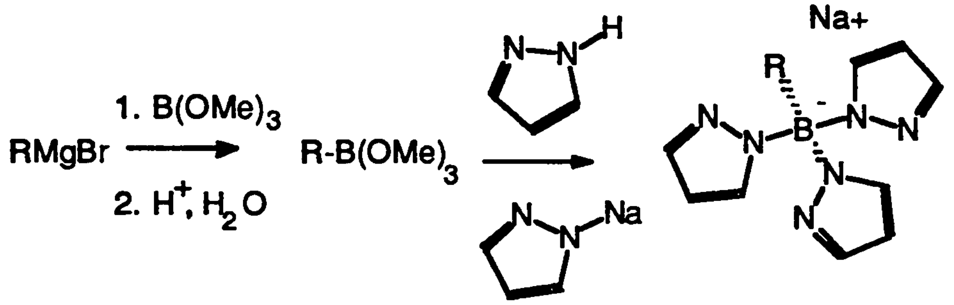
sodium pyrazolide. The more hydrophobic target compounds shown, R = n-octadecyl and R = 2-ethylhexyl, have not yet been synthesized. The third example, R = n-butyl, has been previously reported (Reger 1982). We are now attempting to synthesize this model compound to evaluate its solubility, stability, and selectivity. If it is superior to the commercially available compounds, the more hydrophobic alkyltris(pyrazolyl)borates will be further pursued in FY 1994.

4.7.3.3. Extraction Studies of Commercial Pyrazolylborates: Extractions were performed for the three commercially available materials. Because of either their instability or lack of solubility, most of the data were not easily interpretable. We attempted to improve the solubility of the salts by changing the counter ion from sodium or potassium to tetra-alkylammonium cations, which did not appear to improve the data. After further solubility studies, we determined that enough material was soluble in chloroform to perform an americium and europium extraction (the mixed waste issue was temporarily resolved, which allowed us to use $CHCl_3$ for the initial tests). A large extraction was observed, and we decided that it would be necessary to synthesize a more stable and organic-soluble analog to continue the studies.

4.7.3.4. Synthesis of Methyl-4-benzoyl-5-chloropyrazole (PMBCP) and 4-Benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thone (HBMPPT) (XI): In the past, BMPPT and PMBCP have been synthesized on the 60-g scale. It would be desirable to develop a better synthetic procedure that might lend itself to commercialization. In the first step of the synthetic procedure of PMBCP, a large amount of $POCl_3$, which is used as both reagent and solvent, must be discharged with excess sodium carbonate. This reaction is quite exothermic and results in a taffy-like solid that must be stirred until it is neutralized. The taffy material then crystalizes and is purified by a Soxlet extraction with petroleum ether. In discussions with the chemical production industry, industry representatives have said that they cannot scale up a procedure that has a taffy-like material and that it was desirable to modify the procedure to by-pass this intermediate step.

Thus, we have tried several approaches to by-pass this step. The

Figure 15. Synthetic scheme for alkyltris(1-pyrazolyl)borates.



first modification replaced several equivalents of $POCl_3$, which was the solvent, with $CHCl_3$. Therefore, less acid chloride needed to be discharged with Na_2CO_3 at the end of the reaction. The $CHCl_3$ was removed by evaporation at the end of the reaction, and the resulting residue was neutralized with Na_2CO_3. This modification required less reagent, which is an improvement, but still gave the same taffy-like material.

The second modification involved work-up of the reaction in the $CHCl_3$ solvent and avoidance of the taffy material. When this modification was attempted, and the two-phase aqueous carbonate/$CHCl_3$ mixture was in contact at room or higher temperatures, the chloreneone product, PMBCP, reverted back to the starting material. This reaction can be understood because the hydroxide ions in solution can readily replace the chloro group on the product. This approach should be attempted again keeping the temperature at 0°C and minimizing contact time. This approach will be tried in FY 1994.

4.8. Conclusions: We have obtained two pure dialkyldithiophosphinic acids, one of which was tested on a preliminary basis. A very large separation factor was observed for this compound, again demonstrating that the soft donor concept has validity. The stability study indicated that at least at pH 3 the ligand was stable for more than 3 weeks. Further stability studies in stronger acid will be needed to determine if this concept has potential for a process. The Cyanex 301 will be tested in FY 1994.

The commercial pyrazolylborates are too unstable to produce meaningful extraction results. When an alkyl pyrazoylborate, which is more stable, is synthesized, this class of compounds will be pursued further.

We have improved the synthetic procedure for HBMPPT, but further improvements are needed.

5.0. Subtask 5

5.1. Title: Actinide Partitioning and Waste Stream Polishing Using Recyclable Water-Soluble Chelating Polymers

5.2. Investigators: T. Robison (CLS-1), B. F. Smith (CLS-1), R. Barrans (CLS-1), K. Bower (CLS-1).

5.3. Objective: The objective was to develop and demonstrate actinide partitioning and waste-stream polishing using recyclable, water-soluble chelating polymers. We would like to evaluate this system as a new approach (as opposed to biphasic LLE) to complete waste treatment for actinide and fission product partitioning and separation. FY 1993 Milestone: Design a potential flow sheet for actinide waste separations based on water-soluble polymers. Suggest types of water-soluble chelating polymer donors having potential for such a scheme. (2 months) (August 1–September 30, 1993) (This subtask will not be funded in FY 1994).

5.4. Background: In the area of treating tank wastes for placement in their final storage form, it has been proposed that some tank sludges be redissolved and TRUs and fission products extracted by the TRUEX/-SREX processes. It has been proposed in Pacific Northwest Laboratory's (PNL's) "clean" option that further processing will be performed to separate out other fission products. The aqueous waste streams from these operations will probably have to be denitrated and any residual organics destroyed either before or after processing. Also, the treatment of cesium-containing supernatants will produce basic aqueous waste streams. If the final waste stream is to be discharged as liquid to the environment (as opposed to evaporation), it will have to meet stringent discharge limits, perhaps as low as the 0.05-pCi/L limits for plutonium and americium being imposed on Rocky Flats by the state of Colorado.

A new approach to actinide and fission product partitioning or removal from waste streams is being proposed. This approach uses water-soluble chelating polymers to bind with actinide and fission product metal ions for selective removal from aqueous waste streams by ultrafiltration (Novikov 1988). These chelating polymers have the advantage of being aqueous-based, like ion exchange resins, but have high throughput and rapid kinetics, like two-phase LLE systems, and do not use organic solvent-based extractants.

These water-soluble chelating polymers are being developed for the analytical application to the ultralow-level analysis of actinides in waste streams using a phosphate-based water-soluble polymer. We expect that after successful demonstration, this analytical technique can be taken the next step and expanded to waste-water treatment. Another new project involves the removal of plutonium and americium from the Plutonium Processing Facility (TA-55) waste streams using nonphosphate-based, water-soluble chelating ligands (TTP No. AL121217). Waste streams from TA-55 do not contain fission products, so the selectivity requirements are not as stringent as would be required for a fission product/actinide separation scheme as proposed here.

5.5. Approach: An ongoing research project at Los Alamos involves the development of water-soluble chelating polymers for application to the ultralow-level analysis of actinides in wastewaters. The polymers are used in the homogeneous concentration of americium and plutonium from wastewater using ultrafiltration techniques. The concentrate is then measured for its actinide content. The candidate chelating polymer (PEI-phosphate) has been synthesized and tested in high-salt, acidic (pH 4) solutions and the results reported. The polymer was compared with five commercially available and six synthetic chelating polymers.

The future approach would involve testing currently available polymers on synthetic waste streams to determine the level of actinide and fission product partitioning. Further, advanced water-soluble polymers will be synthesized and tested. The tests will include metal-ion specificity versus polymer type, pH range of optimum operation, capacity, and back-extraction studies. This work will require a series of polymer systems that could selectively separate fission products, lanthanides, and actinides. After studies with synthetic wastes have been completed, a decision will be made as to the success of the approach. If a reasonable level of success has been attained, work will progress to finalize a flow sheet.

The use of homogeneous partitioning and polishing agents eliminates two-phase organic systems, and the agent can be recovered and reused for further processing, resulting in less reagent use and less waste production. If aqueous waste streams can be polished free of residual radiological elements, then the necessity of energy-intensive evaporators would be eliminated. The retentate containing the TRU material would constitute a much smaller amount of waste after back-stripping of the polymer and would reduce the number of glass logs required. These water-soluble chelating polymers can be applyied to a variety of other waste streams such as selective soil and sludge leaching, decontaminating and decommissioning, and analysis. This technology would also lend itself to modular processing.

5.6. Experimental: In FY 1993, this study was based on ongoing projects at Los Alamos not funded by this TTP, so there is no direct experimental work. We decided to base the process flow sheet on an ATW flow sheet because it was possible to define the system, whereas the Hanford tanks remain undefined and uncharacterized. The ATW baseline flow sheet as reported by Jarvinen (1991) is not that different from Figure 1. In the baseline scenario, 400 kg of actinides is loaded into the transmuter. After 15 days residence time, material would be removed, cooled down for 5 days, and processed for neptunium and plutonium removal. We expected from the baseline process that xenon, krypton, I_2, Br_2, and RuO_4 would be collected in the off gas, and that plutonium, neptunium, technetium, and palladium would be removed in the first LIX extraction process step. The raffinate or waste stream from this first process would require treatment for trivalent actinide recovery after approximately 90 days cooldown.

The yield of fission products and neutron capture products has been calculated with ORIGEN2. This cooled waste stream would require treatment for residual actinides (plutonium, neptunium) and americium(III) and curium(III) recovery for placement into the transmuter for further destruction. The remaining metal ions would be either solidified or further separated as necessary for proper waste storage. Thus, the waste stream for treatment would be a high-nitrate stream (2M to 4M) containing the remaining fission products.

5.7. Results and Discussion: The major high-energy gamma activity from the remaining waste stream would come from strontium and cesium. Early removal of these materials would allow for future processing in lower shielded apparatus and may increase the lifetimes of materials used in subsequent processes. Because water-soluble chelating polymers may not withstand the radiation field of these materials, we suggest that cesium and strontium be removed first, perhaps with some inorganic zeolite technology. Other possibilities include crown ethers, dicarbolide, calixarenes, and resorcinol technology. If high-stability, water-soluble chelating polymers could be developed, they could contain the above-mentioned ligand types and could be used for the desired separation.

The fission product content of the waste stream is shown in Table V. The ions that would require recovery for placement into the transmuter would be the higher actinides (americium and curium) and any other trace actinides remaining from the first processing step. The goals would remain the same as in the baseline separation (Jarvinen 1992). The strategy has to overcome the same

Table V. Significant Fission Products Calculated from ORIGRN 2 to be Formed in the Transmutation of Plutonium After 10% Burnup of Plutonium-239 (After Off-Gasing and First-Stage Processing)

Monovalent(I)	**Divalent(II)**	**Trivalent(III)**	**Tetravalent(IV)**	**Penta/hexa-valent(V/VI)**
Rubidium	Strontium	Yttrium	Zirconium	Molybdenum
Cesium	Cadmium	Rhodium	Tin	Antimony
Silver	Barium	Indium	Tellurium	Niobium
		Lanthanum	Neptunium	Uranium
		Cerium	Plutonium	Selenium
		Praseodymium		
		Neodymium		
		Samarium		
		Europium		
		Gadolinium		
		Terbium		
		Dysprosium		
		Americium		
		Curium		

challenges as in the baseline case, that is, trivalent actinide separations from trivalent lanthanides. In actinide processing, high acidity or high nitrate salt concentrations are often used to enhance selectivity of the actinides over most of the fission products. The main exception is the trivalent lanthanides, which have chemistry similar to the trivalent actinide.

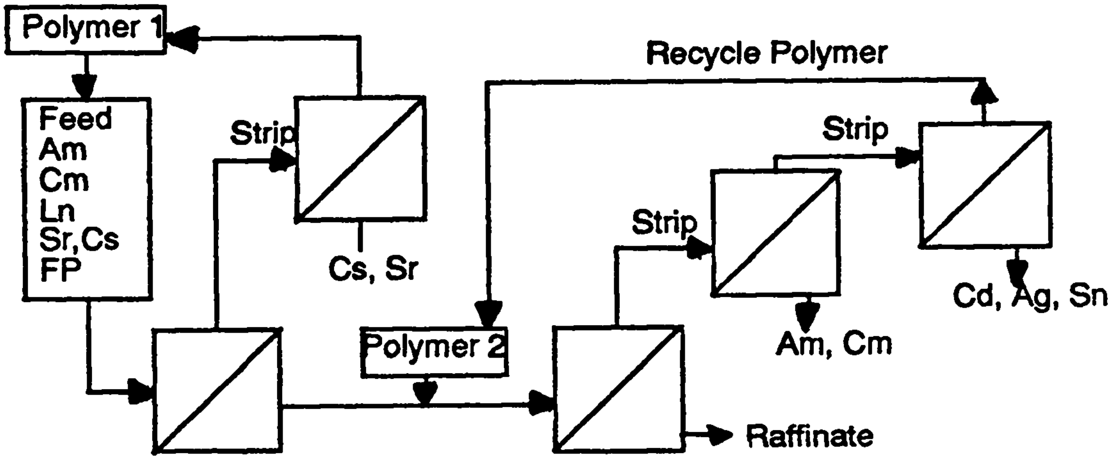
We cannot work in highly acid or basic solutions with water-soluble polymers because the ultrafiltration membranes are stable only in the range pH 1 to 13, so we may need to depend on the high nitrate salt concentration for selectivity. Another approach is separations based on valency, in which the separation order is often IV, III, II, then I for metal-ion separations. Again, the trivalent actinides and lanthanides would partition together. The hexavalent oxo-species often extract intermediate between the III and IV oxidation states, and pentavalent oxo-species often extract as monovalent or as anionic species.

Thus, separation strategies could use a system in which tetravalent ions are segregated from trivalent ions, which are in turn segregated from the lower valent ions. This strategy could be followed by some trivalent actinide/lanthanide separation step. If this strategy is followed, the capacity of the polymer would be utilized by the large amount of lanthanide ions in the waste requiring the use of extra polymer. It might be better to propose a system in which the lanthanides would not bind at all and would remain in the waste stream, or binding the smaller amount of material as opposed to the larger amount of material.

A better strategy would be to selectively bind the trivalent actinides, perhaps using water-soluble polymers containing soft donors. The disadvantage in this strategy is that most soft donor ligands will also bind the cadmium, silver, tin, and other soft transition metal ions in the waste stream. As a fraction of the waste, though, these metal ions are in lower abundance than the lanthanides, so there would be less competition for polymer capacity. Thus, we propose that this approach be studied first. Our proposed processing scheme is shown in Figure 16.

The feed for this process would come from the cooldown storage. The pH would be adjusted, and the volume would be approximately 1000 L. The polymer specific for cesium or strontium (or a zeolite, for example) would be added to the waste stream, and the solution would be ultrafiltered to an appropriate volume (concentration factor of approximately 20 times). The concentrate would be washed by a diafiltration mode to remove residual unbound ions. The raffinate stream from this process would be treated with a second polymer that would be specific for trivalent actinides (soft metals would potentially follow) and processed in a manner similar to the previous steps. To strip the metal ions from the polymer, the conditions of the concentrate would be adjusted so the metal ions of interest no longer bind to the polymer. The process of metal recovery is then diafiltration through about five cycles to recover the free metal ions. The polymer is now ready to recycle to treat another batch of waste. Depending on the strength of binding of the individual ions to the polymer, it may be possible to selectively strip the soft transition

Figure 16: Proposed flow sheet for waste stream polishing of an ATW system with water-soluble chelating polymers.



ions from the actinides. The ligand types that may be useful for these separations are ligands similar to pyrazolylborates or other soft donor ligands that are under development in subtask 4.

5.8. Conclusions: A scheme using water-soluble chelating polymers to treat transmuter waste streams has been proposed. The major separation challenge is still the trivalent lanthanide/actinide separations. Specific polymers were not suggested because these systems are still under development, but general types of ligands were suggested.

6.0. Subtask 6

6.1. Title: Modular Approach to Processing: Application of Dispersion-Free Liquid-Liquid Extraction Using Microporous Hollow-Fiber Membrane Modules

6.2. Investigators: D. Kathios (NMT-2), S. Yarbro (NMT-2), B. F. Smith (CLS-1), K. Bower (CLS-1)

6.3. Objective: The objective is to evaluate microporous, hollow-fiber membrane modules for application to processing of aqueous waste streams. The results of this study are to be used to engineer a modular approach to waste processing that is efficient and eliminates many problems that exist with conventional separation processes. FY 1993 Milestone: Purchase, install, and semiautomate the new LLE module apparatus. Obtain materials and paperwork to begin the baselining of the system with the well-studied PUREX process (uranium extraction) for comparison with other engineered separation systems (for example, pulse columns, centrifugal contactors). (6 month) (April 1–September 30, 1993) (This subtask has not been funded for FY 1994.)

6.4. Background: We proposed an advanced, membrane-based LLE modular system that could be used with any previously developed organic extraction process (for example, TRUEX with CMPO, SREX) or will be developed in the future (for example, advanced actinide/lanthanide separations).

In the area of treating the tank wastes for placement in their final storage form, it has been proposed that the solids be redissolved and the TRUs and fission products extracted or separated from the nitric acid solutions in a TRUEX/SREX-type process. If the PNL "clean" option is used, even more separation steps will be required. The proposed use of B-Plant for processing wastes is very unlikely because of its age and other maladies. Because the building of a new processing plant is expensive, the development of a modular, at-tank approach to waste processing has been encouraged by Hanford personnel.

Recent investigations have shown that microporous hollow-fiber membranes can be used to achieve an efficient separation in two-phase metal-ion separation processes (Alexander 1987). Conventional LLE processes use dispersion of one phase in another immiscible phase for efficient phase contacting. In our approach, a microporous membrane is contacted on one side with a ligand/-solvent that wets the membrane and subsequently fills its pores. If a second immiscible liquid is on the other side of the membrane, an interfacial liquid-liquid contact area is established at the membrane surface. This interface is stabilized by maintenance of a higher pressure on the nonwetting liquid than on the wetting liquid but lower than needed to displace the wetting liquid from the pores by the nonwetting liquid. An attractive feature of hollow-fiber modules is the resulting high interfacial area per unit volume that can be achieved in a dispersion-free mode. This feature allows for comparable phase contact in a small area without the subsequent phase coalescence and separation to hinder system performance as with conventional equipment.

The microporous, membrane-based separation technology has several advantages over conventional, dispersion-based devices. Dispersion in liquid-liquid systems often produces emulsions that lead to coalescence problems, especially with phases of similar density. Hollow fibers allow rapid, dispersion-free mass transfer. The rates observed in extraction are comparable to those in centrifugal contactors, but they can be achieved at a much lower equipment cost and complexity. The modules are not prone to loading, flooding, channeling, or inability to handle particles that can compromise the performance of more conventional column equipment. Flows of feed and solvent can be adjusted independently, in contrast to conventional extractors, in which flows are limited by phase disengagement. In hollow-fiber modules, the flows can be individually adjusted even when feed and solvent have similar densities. Finally, the use of the hollow-fiber geometry offers large membrane surface area per unit volume, which give large contact areas for the two phases.

6.5. Approach: The initial approach was to baseline the hollow-fiber modular system using a well-studied extraction system such as PUREX for uranium extraction. Because the PUREX system has been so extensively studied, it will provide a basis upon which to determine the boundaries of the membrane system compared with other engineered systems (for example, pulse columns, centrifugal contactors).

It will be ultimately necessary to determine the limits for the hollow-fiber extraction modules. Examples include

- radiolytic stability;
- stability with various solvents and extraction systems commonly used or under development for actinide separations (for example, TRUEX-CMPO or CMP, PUREX-TBP, malonamides, and their respective solvents); and
- stability to acids, fluorides, and reducing and oxidizing agents at some future time.

The extent to which the whole system can be automated for remote control should also be evaluated.

Because of the many advantages of hollow-fiber membrane extractors relative to conventional extractors, we evaluated them for application to actinide separations. We expect that they will play a significant role in waste treatment because their small modular design reduces the necessity of building large processing plants for waste stream treatment. Experimental results in the literature, similar to the work proposed here, show that the systems can be easily and reliably scaled up for subsequent large-scale processing if desired. These modules are made of plastic and could be disposed of by incineration, eliminating the waste disposal problems associated with metal or glass equipment.

6.6. Experimental: This study evaluated the potential of using MHF membrane modules for process-scale metal separations. In this analysis, MHF modules (Hoechst Celanese Model no. 5PCM-100) are used to extract uranyl nitrate (0.5 g/L, Aldrich) from 2M HNO_3 (Baker Reagent) by contacting it with an organic stream of 30% tributylphosphate in diisopropylbenzene (Baker technical grade). The modules also concentrated the uranyl nitrate by back-extracting it from the organic into 0.01M HNO_3. The module characteristics are given in Table VI.

The experimental setup used to conduct the experiments is illustrated

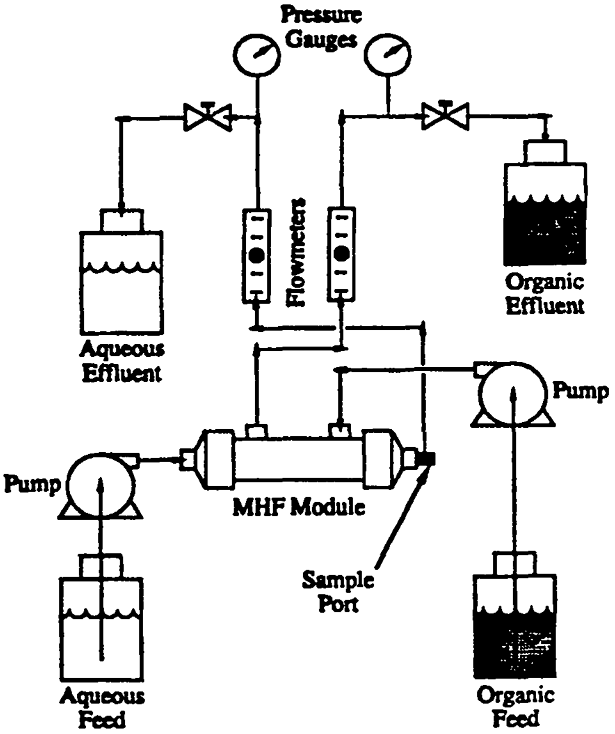
TABLE VI. Characteristics of MHF Membrane Module Used for the Uranyl Nitrate Extraction and Back-Extraction Experiments

Description	Hoechst Celanese Liqui-Cel High-Efficiency Phase Contactor Model No. 5PCM-100
Shell Characteristics	
Material:	Polypropylene
Length:	20.3 cm
Internal diameter:	2.43 cm
Outer diameter:	3.34 cm
Fiber Characteristics	
Material:	Polypropylene (Celgard X-10)
Number of fibers:	3600
Effective length:	15.9 cm
Internal diameter:	240 µm
Outer diameter:	300 µm
Effective surface area:	4300 cm^2
Effective pore size:	0.05 µm
Membrane porosity:	0.30
Membrane tortuosity:	2.6

in Figure 17. As shown in the diagram, the aqueous and the organic feed streams are pumped through the module. Here, the two phases come in intimate contact through the membrane, and mass transfer of the uranyl nitrate takes place. The two streams then exit the module and are collected in their aqueous and organic effluent reservoirs. Flow meters, valves, and pressure gauges are present to control the flow rates and to maintain the aqueous/organic pressure difference that stabilizes the membrane.

In the first half of each extraction (or back-extraction) experiment, the organic flow rate was held constant at 5 mL/min and samples were collected over a range of aqueous flow rates. In the second half, the aqueous flow rate was maintained at 8 mL/min and samples were collected over a range of organic flow rates. Conducting the experiment in this fashion made it possible to determine how changing the flow rates of aqueous and organic streams each independently affect the extraction and back-extraction processes. Once particular aqueous

Figure 17. Diagram of counter-current flow system using dispersionless extraction modules.

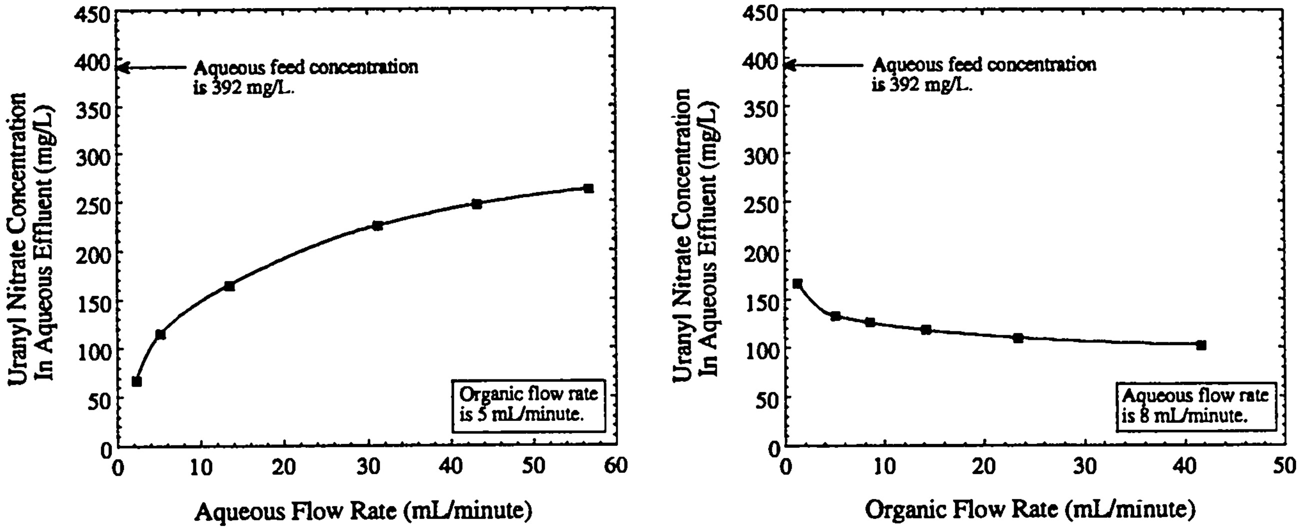


and organic flow rates were established, the system was allowed to reach steady state. Samples of the aqueous effluent were then removed from the sample port and placed in 20-mL screw-cap scintillation vials. The concentration of uranyl nitrate in these samples was determined by scintillation counting (Packard Model 500 C).

6.7. Results and Discussion: The results of these studies will be used to evaluate the module's performance over a range of aqueous and organic flow rates, to improve our understanding of how the module compares with conventional LLE technologies, and to provide a basis upon which an optimized process-scale metal-ion separation unit can be designed and constructed. The results from this preliminary analysis indicate that the modules perform quite well for the type of applications of interest to this research. The experiments were clean, easy to run, and required little supervision. In addition, all extractions and back-extractions were absolutely dispersion-free with no measurable loss of organic detected during any of the experiments.

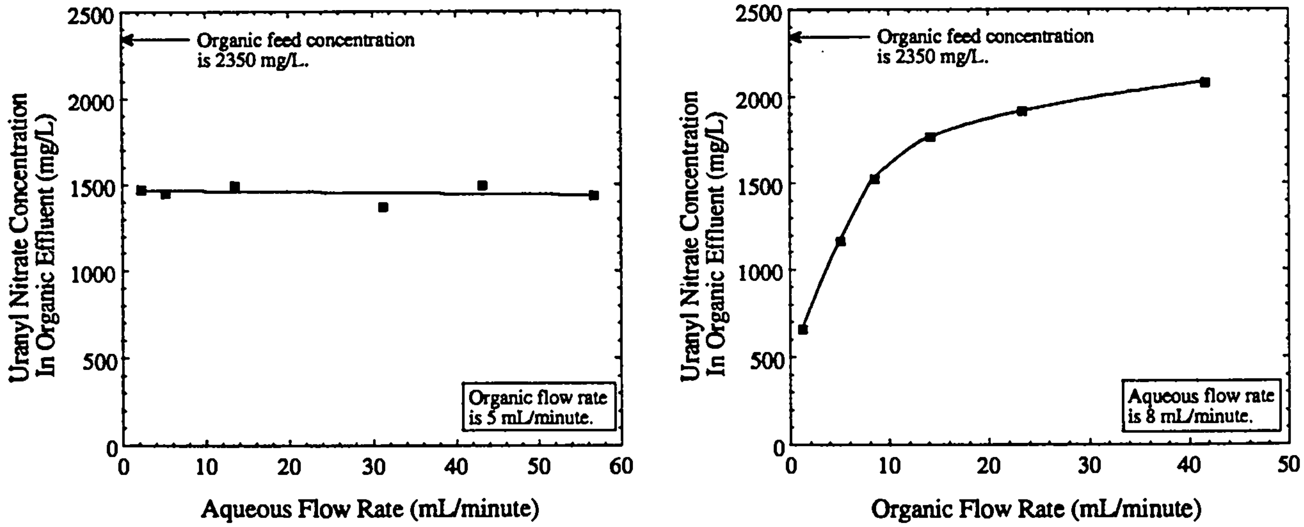
As shown in Figures 18 and 19, reasonable extractions and back-extractions were possible with the module as was demonstrated by the significant removal of uranyl nitrate from the feed streams. Superior extractions were achieved at lower aqueous flow rates and at higher organic flow rates, whereas superior back-extractions were achieved at lower organic flow rates and at higher aqueous flow rates. Apparently, the

Figure 18. Extraction of uranyl nitrate from 2M nitric acid as a function of aqueous flow rate (left) and organic flow rate (right).



Organic system is 30% tributylphosphate in diisopropylbenzene. Symbols represent experimental data.

Figure 19. Back-extraction of uranyl nitrate from 0.01M nitric acid as a function of aqueous flow rate (left) and organic flow rate (right).



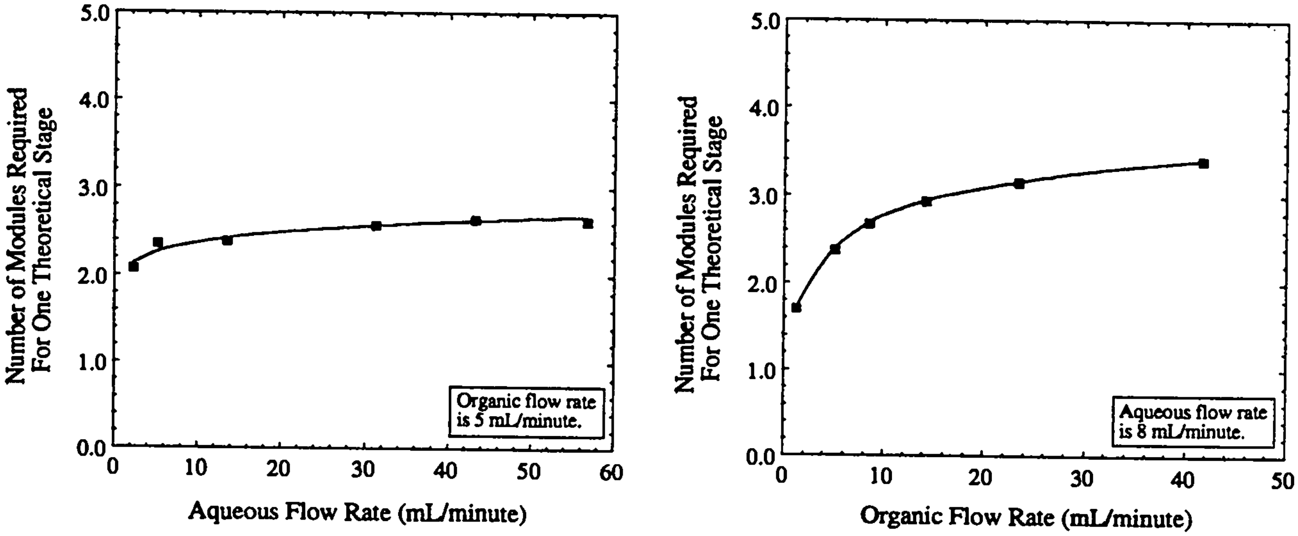
Organic system is 30% tributylphosphate in diisopropylbenzene. Symbols represent experimental data.

low flow rates of the actinide-laden streams (that is, the streams from which the uranyl nitrate is to be removed) allow for the long residence times in the module necessary for substantial mass transfer to occur. In addition, the high flow rates of the actinide-removal streams (the streams that enter the module to remove the uranyl nitrate) allow for low concentrations of uranyl nitrate to remain in those streams, thus, maximizing the concentration gradients for good mass transfer to take place.

Figures 20 and 21 show the number of modules required for a theoretical stage for the aqueous/organic system subject to analysis. A theoretical stage in an LLE process is one that first allows mass transfer of uranyl nitrate between the aqueous and organic phases to reach equilibrium, and then allows complete separation of the two phases to occur before the exit of the process. An ideal centrifugal contactor (one that does not allow aqueous/organic phase entrainment in the effluent streams) is an example of a theoretical stage. As shown in the graphs, between 2 and 4 modules were required for one theoretical stage in the extraction process, and between 3 and 18 modules were required for one theoretical stage in the back-extraction process. The number of modules required also increased with increasing aqueous and organic flow rates.

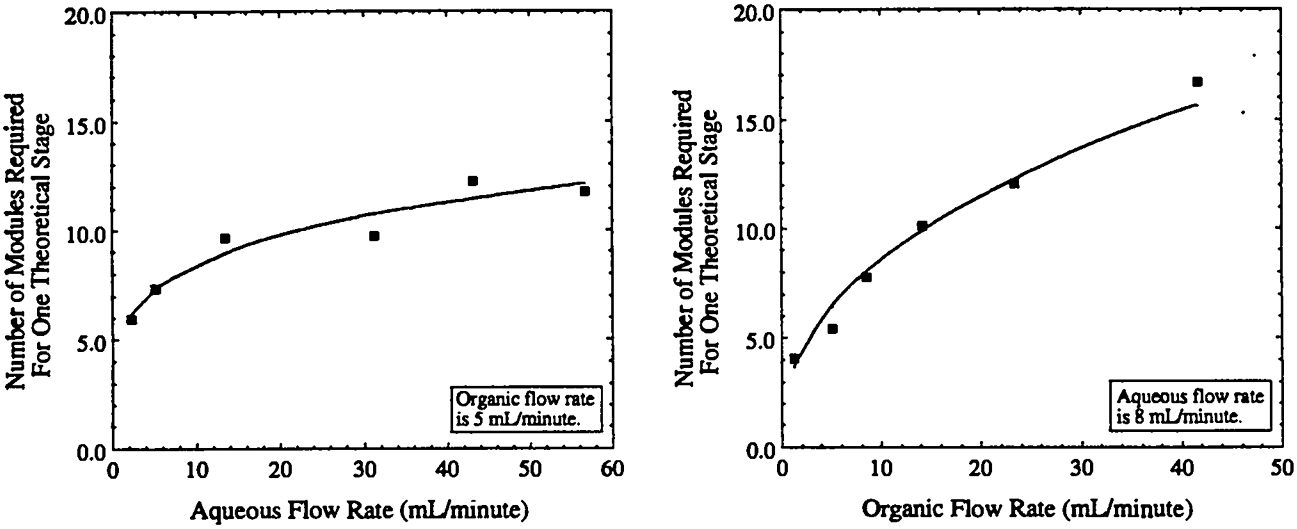
6.8. Conclusions: The preliminary results indicate the modules provide a cost-effective and convenient means of conducting the type of metal-ion separations of interest to this research. However, additional characterization work should be done before the technology is scaled up to full process-scale applications. Doing so will allow the technology to accommodate more easily the large

Figure 20. The number of modules required for one theoretical stage as a function of aqueous flow rate (left) and organic flow rate (right) for the extraction of uranyl nitrate from 2M nitric acid.



Organic system is 30% tributylphosphate in diisopropylbenzene. Symbols represent experimental data.

Figure 21. The number of modules required for one theoretical stage as a function of aqueous flow rate (left) and organic flow rate (right) for the back-extraction of uranyl nitrate from 0.01M nitric acid.



Organic system is 30% tributylphosphate in diisopropylbenzene. Symbols represent experimental data.

aqueous throughput rates normally found in such applications.

At elevated aqueous and organic flow rates, the primary resistance to actinide mass transfer occurs through the membrane wall. Reducing this resistance would significantly improve the performance of the technology and would make it possible to achieve a given separation with far fewer modules. This resistance can be reduced by either changing the organic system used in the process or by changing the material from which the membrane is fabricated.

In addition, the module used in this analysis is an early design that allows a significant portion of the membrane to be by-passed by the organic and keeps the surface area available for mass transfer from being fully utilized. Newer modules specifically designed to solve these problems are now being produced with an advanced mesh and with a shell side baffle. These modifications are expected to significantly improve the module's performance.

The results from this preliminary work will be used to construct a multiple-module experimental system designed for simultaneous extraction and back-extraction. This system is specifically designed as a predecessor for one to be built for ATLAS and will be used to test more directly the feasibility of this technology for actinide waste stream polishing.

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