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APPLICATION OF EXTRACTION CHROMATOGRAPHY TO ACTINIDE  
DECONTAMINATION OF HYDROCHLORIC ACID EFFLUENT STREAMS.

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## ABSTRACT

Extraction chromatography is under development as a method to lower actinide activity levels in hydrochloric acid (HCl) effluent streams. Successful application of this technique for radioactive liquid waste treatment would provide a low activity feed stream for HCl recycle, reduce the loss of radioactivity to the environment in aqueous effluents, and would lower the quantity and reduce the hazard of the associated solid waste.

The extraction of plutonium and americium from HCl solutions was examined for several commercial and laboratory-produced sorbed resin materials. Inert supports included silica and polymer beads of differing mesh sizes. The support material was coated with either *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (O $\Phi$ D(iBu)CMPO) or di-(4-*t*-butylphenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (D(tBu $\Phi$ )-D(iBu)CMPO) as an extractant, and using either tributyl phosphate (TBP) or diamyl amyolphosphonate (DAAP) as a diluent.

Solutions tested were effluent streams generated by ion exchange and solvent extraction recovery of plutonium. Batch volumes were typically 20-50 L of relatively concentrated (5-8 M) HCl. The chemical content of these streams includes about 90% of the total amount of HCl used, and the soluble chloride salts of alkali, alkaline earth, and most transition metals. The actinide content of the process effluent streams was usually several grams, comprised of all the americium and a small percentage of plutonium lost from solvent extraction or anion exchange operations.

A finer mesh silica support material demonstrated advantages in removal of trivalent americium in some tests, but also showed a tendency toward plugging and channeling as column sizes and flow rates were increased. Larger bead sizes showed better physical properties as the process was scaled up to removal of gram quantities of Am from large effluent volumes. The ratio of extractant to

diluent also appeared to play a role in the retention of americium. In direct comparative studies, when loaded on identical supports and diluent conditions, di-(4-*t*-butylphenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (D(tBu $\Phi$ )-D(iBu)CMPO) demonstrated better americium retention than *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (O $\Phi$ D(iBu)CMPO) from HCl process effluents.

## 1. INTRODUCTION

Minimizing the solid wastes and liquid effluents from plutonium processing and making them less hazardous are tasks of fundamental importance. Present efforts for plutonium residue processing at LANL are progressing toward the goal of environmentally benign operations. These goals can be summarized for HCl operations as follows: producing concentrated actinide residues in forms suitable for safe long-term storage, minimizing waste volumes, producing stable solid wastes with acceptable disposal routes, and releasing liquid effluents low in radioactivity and other hazards.

Aqueous processing of Pu residues produces acidic effluent waste streams that require several treatment steps before the liquids may be discharged to the environment. Effluents from hydrochloric acid (HCl) processing streams are presently routed to controlled hydroxide precipitation. The hydroxide precipitation/filtration process meets the dual requirements of reducing the dissolved actinide levels, while raising the pH to a point where corrosion of pipelines and water treatment facilities downstream is of small concern. There are several problems, however, with hydroxide precipitation as a generic effluent treatment process: 1) large amounts of caustic reagents are required; 2) many other metal hydroxides coprecipitate, creating large cakes; 3) plutonium values in the cake are of an amount that require storage as a residue, and eventual processing for recovery; 4) chloride salts can be entrained in the hydroxide matrix causing corrosion concerns for

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long-term vault storage of the hydroxide cakes; 5) many metal hydroxides are gelatinous, leading to slow filtration and associated high gamma exposure from americium ( $^{241}\text{Am}$ ) in this hands-on operation; 6) the filtrate from neutralization remains moderately high in radioactivity and requires special additional treatment downstream, producing more transuranic (TRU) solid wastes; 7) most of the soluble chloride is lost in the liquid effluent, causing concern about recommended National Pollutant Discharge Elimination System limits for chloride concentration; and 8) neutralization complicates schemes to recover and recycle HCl by evaporative techniques.

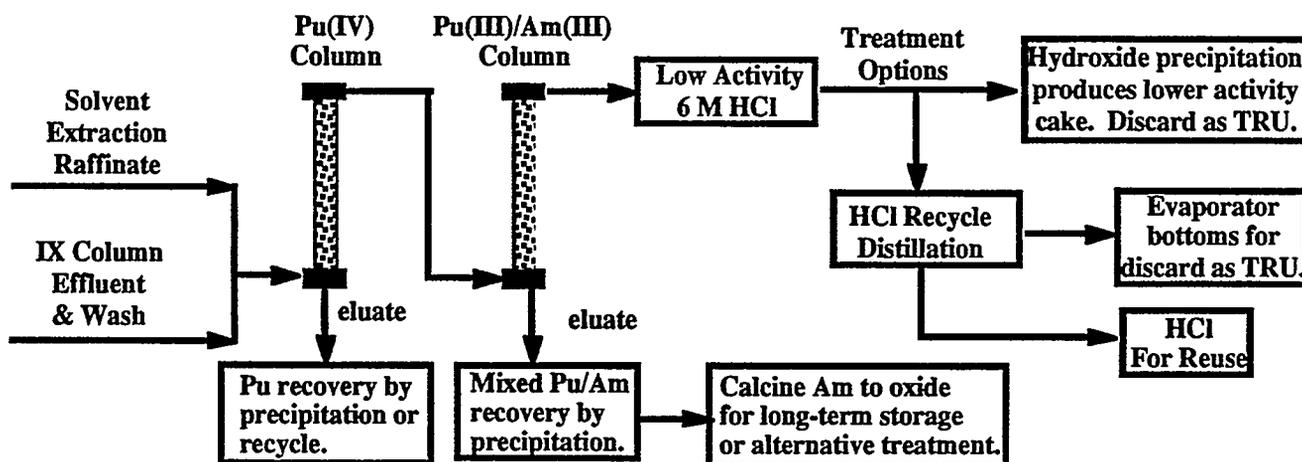
Hydroxide precipitation remains a viable choice for recovery of actinides from specific processes, but it is not the best choice as a generic treatment for all HCl effluents. Indeed, there is no single technology or unit operation that provides a panacea to resolve all of the residue, liquid and solid waste issues associated with HCl processing. The problems can be addressed by intelligently developing and applying better technologies, directed toward developing specific treatments for individual effluents. The purpose of this work is to evaluate extraction chromatography techniques and materials as one such method to selectively remove multi-gram quantities of actinides from large HCl acid volumes. Efficient recovery of the actinides in HCl effluent streams would have a large impact on wastes associated with Pu recovery from these operations.

Previous work by ourselves and others have indicated potential value in applying extraction chromatography to treatment of waste streams.<sup>1-5</sup> We performed small-scale work in HCl directed toward understanding factors of actinide distribution, loading capacity and kinetics in this specific system.<sup>1,2</sup> Results from this work indicated that a commercial resin, TRU-Spec resin from EIChroM (13%

O,Ph-CMPO/27% TBP, by weight), should effectively remove tetravalent Pu from 5–8 M HCl solutions. Efficient removal of trivalent Pu and Am from HCl media was more difficult, and required development of resins beyond those commercially available. Indications from the small-scale work were that increasing the extractant to diluent ratio increased the  $K_d$  of Am(III) on the resin.

The focus of the present report is on full-scale testing of several extraction chromatography resins to process effluent streams from HCl ion exchange and solvent extraction processes. It is our goal to develop extraction chromatography into a robust operation to efficiently decontaminate these HCl effluent streams in a single pass, and one that can be operated routinely in a process environment. The general method of applying this technology is shown in the scheme below. The 5–8 M HCl effluent stream from solvent extraction or ion exchange is routed to two columns in tandem containing extraction chromatography materials. The first column functions to remove tetravalent plutonium. The second column has the more difficult task of removing trivalent plutonium and americium to low levels. The readily available commercial resin, TRU-Spec, was selected as the leading candidate material for the first column. The second column, through necessity, required development beyond commercially available technology to lessen breakthrough of trivalent actinides under our operational conditions. For this task we selected a group of resin materials based on our small-scale results. A ratio of 30% O,Ph-CMPO/10% DAAP on a support was expected to provide sufficient retention of Am(III) and Pu(III), while preserving good loading capacity and kinetics.

Scheme 1: Proposed High HCl Effluent Stream Treatment



## II. EXPERIMENTAL

Several extraction chromatography resins were investigated in this work. In general, the resins consisted of an inert polymer or silica support of varying particle size. The support was coated with the actinide extracting ligand and a diluent. The extractive ligands studied included *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (O $\Phi$ D(iBu)CMPO) purchased from Elf Atochem and di-(4-*t*-butylphenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (D(tBu $\Phi$ )D(iBu)CMPO), which was prepared at LANL. The LANL synthesis of D(tBu $\Phi$ )D(iBu)CMPO compares favorably with synthetic approaches in the literature for symmetrical CMPO derivatives.<sup>6,7</sup> The synthesis, purification, and small scale testing of D(tBu $\Phi$ )D(iBu)CMPO will be reported in detail elsewhere.<sup>8</sup> Tributyl phosphate (TBP) or diamyl amyolphosphonate (DAAP) was used as a diluent. DAAP was purchased from Chem. Services Inc. The purity of the extractants and diluents used for LANL prepared resins were verified by <sup>1</sup>H NMR prior to use.

The resins used were purchased in bulk quantity from EICrom Industries or were prepared at Los Alamos. The resins purchased from EICrom Industries included: TRU-Spec<sup>®</sup> (13% O $\Phi$ D(iBu)CMPO, 27% TBP on amberchrom); a mixture of 30% O $\Phi$ D(iBu)CMPO/10% DAAP on a silica support; and a mixture of 30% O $\Phi$ D(iBu)CMPO/10% DAAP on a polymethacrylate support. LANL prepared resins reported in this study included 30% O $\Phi$ D(iBu)CMPO/10% DAAP on Amberlite<sup>®</sup> XAD-7 and 30% D(tBu $\Phi$ )D(iBu)CMPO/10% DAAP on Amberlite<sup>®</sup> XAD-7.

The LANL resins were prepared by methods similar to those reported in the literature.<sup>4,9</sup> The XAD-7 support was purchased from Aldrich or Arcos Chemical and washed with copious amounts of water and methanol to remove impurities. The washed support material was air dried, then dried under vacuum to constant weight on a rotary evaporator before use. The extractive ligand and diluent were mixed in the proper amounts in methanol and slurried with the polymer support. The methanol was removed by rotary evaporation until the resin reached a constant weight deposit the ligands on the support.

The resins generally were loaded into Kontes Chromaflex<sup>®</sup> glass columns equipped with PTFE or PE fittings and frits. The columns were of various sizes and shapes. The most common column used was 4.8 cm diameter and 30 cm in length (~543 mL volume). The standard Kontes 4.8 cm PTFE column endcaps were drilled and threaded for a 3/8" NPT adapter. This allowed direct attachment of a 3/8" hose barb, a significant improvement for standard operations using Tygon tubing in our glove

box environment. In general, these columns were loaded with approximately 200 g of resin material. Other column designs of varying volume capacity were also tested including a 2.5 cm by 30 cm Kontes (~147 mL volume), a tapered Kontes column that utilized 4.8 cm endcaps (~2100 mL volume), and a 3 inch diameter by 18 inch length (~2 L volume) Corning glass pipe equipped with machined KYNAR endcaps fabricated in house. The tapered Kontes column performed so poorly in regards to channeling that no results from this apparatus are included here.

The feed solution for these experiments were effluent streams from aqueous chloride solvent extraction or ion exchange processing of plutonium residues. Solutions were passed through the extraction chromatographic resins without any adjustment other than addition of 12 M HCl to raise acid molarity in a few cases. The actinide content of the process streams was usually several grams, comprised of all the americium originally present and a percentage of plutonium lost from solvent extraction or anion exchange. Volumes were typically 20-50 L per run of relatively concentrated (5-8 M) HCl. The typical chemical makeup of these streams includes about 90% of the total amount of HCl used in the processing operation, and the soluble chloride salts of alkali, alkaline earth, and most transition metals.

The columns were prepared by passing 1-2 column volumes of 8 M HCl. The solution to be decontaminated was subsequently passed through the column at rate of 1-2 L/hour. Solutions were pulled through the columns at controlled rates by the use of peristaltic or diaphragm pumps to avoid any chance of pressurization. Slight constant pressures of argon (~5 psi) were sometimes applied to tanks supplying the solution for decontamination. After the solution was passed through the columns, with an additional 2-4 column volumes of 8 M HCl was passed to wash the columns. The actinides were then eluted with 2-4 column volumes of 0.10 M HCl, sometimes containing 0.1 M hydroxylamine hydrochloride as a reducing agent to ensure more rapid and complete elution of Pu(IV). The plutonium and americium were readily stripped from the resins with small elutriant volumes, providing relatively pure solutions. The actinides were then recovered by oxalate or hydroxide precipitation and filtration, followed by calcination, to provide concentrated oxide residues suitable for long-term vault storage. The decontaminated effluent solutions from this work were neutralized prior to additional waste treatment. Lead sheets sheathed in KYNAR were wrapped around the columns to reduce gamma exposure to the operator during periods when Am-241 was loaded on the columns. Similar lead and KYNAR containers were fabricated and used as shielding for 2L polyethylene bottles

used to capture column eluates high in Am. Observations about column performance and breakthrough could often be made from the appearance of visible bands on the columns, or by holding various lengths of the loaded column near a gamma instrument to observe Am-241 bands.

A gas proportional alpha counting technique was used to quantitate total alpha content of all actinide solutions with good precision. The quantitation of plutonium (where reported) was based on the gas proportional alpha counting result, combined with gamma counting to allow subtraction of the Am-241 contribution. This approach led to increasing uncertainty in plutonium values as the ratio

of Pu/Am became smaller. A thenoyltrifluoroacetone (TTA) plutonium extraction method was utilized in some cases to better quantitate small amounts of Pu in the presence of large amounts of the higher specific activity Am-241. Acid molarity determinations were made by titration with 0.1 M KOH and a phenolphthalein indicator.

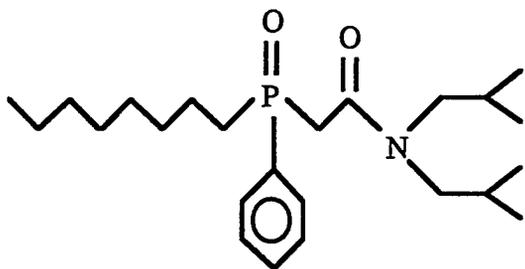
### III. SCOPE OF WORK

#### A. Extractants and Diluents

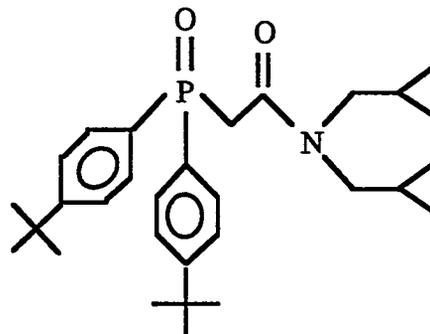
Figure 2 shows the structures, names and acronyms of the extractants and diluents used in this study.

Scheme 2: Extractants and Diluents in this Study

#### Extractants

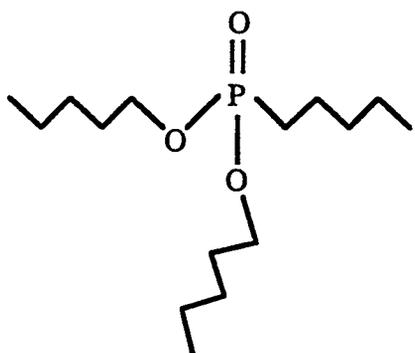


octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [OΦD(iBu)-CMPO]

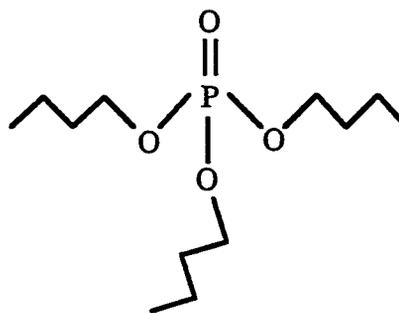


di-(4-t-butylphenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [D(t-BuΦ)D(iBu)-CMPO]

#### Diluents



diamyl amylphosphonate (DAAP)



tributyl phosphate (TBP)

n-Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (OΦD(iBu)CMPO) is one of the most widely applied and studied actinide extractants in the recent literature.<sup>10-12</sup> This extractant offers an excellent balance of properties in regards to organic solubility, acid stability, radiation stability, and a high affinity for tri-, tetra-, and hexavalent actinide in nitric acid media.<sup>10-14</sup> The affinity of OΦD(iBu)CMPO for actinides is much higher than TBP and DAAP, and is the reason that OΦD(iBu)CMPO has been proposed and utilized to decontaminated actinide solutions by several orders of magnitude. These properties have led to the use of OΦD(iBu)CMPO for a wide variety of solvent extraction and extraction chromatography uses. OΦD(iBu)CMPO has been studied as an actinide extractant in chloride media,<sup>15,16</sup> but by far the larger development efforts have been made for problems associated with nitrate processes and wastes.<sup>2-5,7,9-14</sup>

A discourse on the relationship of CMPO structure verses actinide binding strength is beyond the scope of this paper, and has been examined in detail for a large number of CMPO ligands by Horwitz and coworkers.<sup>7,17</sup> These references contain much discussion about actinide chelation by a variety of CMPO ligands, and considerable discussion about structure/activity relationships for these molecules. An intriguing result was that diphenyl-N,N-diisobutylcarbamoylmethylphosphine ligands, under some conditions, have shown enhanced actinide uptake relative to alkyl-substituted CMPO ligands. Nearly all of these comparative studies were in nitric acid, and trends may not always be directly transferable to hydrochloric acid media.

Di-(4-t-butylphenyl)-N,N-diisobutylcarbamoylmethylphosphine (D(tBuΦ)D(iBu)CMPO) is a new molecule that we have recently synthesized, purified and tested. The design logic behind D(tBuΦ)D(iBu)CMPO was to develop a ligand that mimics many of the desirable physical properties of OΦD(iBu)CMPO, while altering chemical bonding properties in a manner that may be advantageous for some actinide applications. Diphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide is known to be poorly soluble in hydrocarbon solvents, and generally requires chlorinated organic solvents to attain useful concentrations.<sup>7,17</sup> We chose to synthesize

(D(tBuΦ)D(iBu)CMPO) to increase the hydrocarbon solubility. In a simplistic argument, the two t-butyl groups in D(tBuΦ)D(iBu)CMPO might be expected to improve the solubility of diphenyl-N,N-diisobutylcarbamoylmethylphosphine oxide in hydrocarbon solvents by an amount similar to the octyl group in OΦD(iBu)CMPO. The steric bulk of the t-butyl substituents should also function to reduce the crystalline packing ability of the phenyl rings. Our observation is that the solubility of D(tBuΦ)D(iBu)CMPO is sufficient to allow liquid-liquid extraction studies in hydrocarbon solvents, and straightforward preparation of the extraction chromatography resin discussed in this paper without the use of chlorinated solvents. The synthesis, purification and properties of D(tBuΦ)D(iBu)CMPO will be reported in detail elsewhere.<sup>8</sup>

The function of the compounds referred to as "diluent" in this article, namely tributylphosphate (TBP) and diamyl amyolphosphonate (DAAP), is probably much more complex than the word diluent would imply. TBP and DAAP are well known and widely utilized extractants for tetra- and hexavalent actinides. They do not in general form strong of complexes with trivalent actinides, unlike the CMPO molecules. TBP is known to have marked and complex effects on the Am extraction by OΦD(iBu)CMPO from HNO<sub>3</sub> solutions in liquid/liquid extraction studies.<sup>18,19</sup> Molecules like TBP and DAAP would be expected to have similarly complex effects on Am extraction by CMPO ligands when they are present in extraction chromatography resins.

## B. Extraction Chromatography Materials

Table 1 shows the weight ratios of the extractants, diluents and support materials for this materials used in this study. The resin acronyms referenced in the first column are used throughout the remainder of this paper. The bead sizes ranges are those listed on the labels from various sources, and may not be precise.

Table 1: Extraction Chromatography Resins in this Study

Resin	Support	micron	Manufacturer	Ligands (weight %)
TRU-Spec	polymethacrylate	100-150	EIChrom Ind.	13 % OΦD(iBu)CMPO 27% TBP
30/10 Si	silica	100-150	EIChrom Ind.	30 % OΦD(iBu)CMPO 10 % DAAP
30/10 Amb	polymethacrylate	100-150	EIChrom Ind.	30 % OΦD(iBu)CMPO 10 % DAAP
30/10 XAD-7	Amberlite XAD-7	250-840	LANL prep.	30 % OΦD(iBu)CMPO 10 % DAAP
D(tBuΦ)D(iBu)CMPO XAD-7	Amberlite XAD-7	250-840	LANL prep.	30 % OΦD(iBu)CMPO 10 % DAAP

Table 2: Large Scale HCl Extraction Chromatography Results

Run	Pass	Vol. (L)	[H+] M	Actinide (g) Before resins	Alpha mCi/L Before resins	Alpha mCi/L After resins	% alpha Removed	Resin(s)	Resin Eluates
1	1	31.3	5.0 M	3.51 g Pu 0.251 g Am	35.040	2.964	91.50	182g TRU-Spec	5.45 g Pu 0.0057 g Am
								190g 30/10 Si	0.193 g Am
2	2	44.0	7.0 M		2.108	0.018	99.40 99.93	190g 30/10 Si	0.062 Am
2	1	10.8	6.1 M	1.35 g Pu 0.200 g Am	70.100	4.018	94.27	182g TRU-Spec	1.32 g Pu 0.0014 g Am
								190g 30/10 Si 65g 30/10 Si	0.157 g Am
3	1	2.2	7.1 M	0.062 g Pu 0.0348 g Am	53.510	0.045	99.92	190g 30/10 Si 65g 30/10 Si	0.0349 Am
4	1	33.3	8.1 M	4.64 g Pu 0.780 g Am	112.050	2.703	97.58	182g TRU-Spec	1.29 g Pu 0.0634 g Am
								190g 30/10 Si 65g 30/10 Si	2.16 g Pu 0.726 g Am
4	2	34.0		0.028 g Am	2.703	1.041	61.48 99.071	190g 30/10 Si 65g 30/10 Si	no data
5	1	25.3	8.0 M	1.47 g Pu 0.670 g Am	90.490	0.874	99.02	182g TRU-Spec	1.29 g Pu 0.066 g Am
								190g 30/10 Si 65g 30/10 Si	0.634 g Am
5	2	28.3			0.781	0.204	73.94	190g 30/10 Si 65g 30/10 Si	0.0067 g Am
5	3	32.0			0.180	0.044	75.33	190g 30/10 Si 65g 30/10 Si	0.0070 g Am
5	4	32.0			0.044	0.013	70.08 99.981	190g 30/10 Si 65g 30/10 Si	no data
6	1	37.2	7.6 M	0.614 g Pu 0.428 g Am	50.428	3.261	93.53	182g TRU-Spec	0.288 g Pu 0.0002 g Am
								190g 30/10 Si 65g 30/10 Si	0.398 g Am
7	1	17.9	6.5 M	0.703 g Am	321.710	25.369	92.11	Columns eluted together 182g TRU-Spec 600g 30/10 Amb	12.8 g Pu 0.524 g Am
7	2	22.4			20.273	0.175	99.14 99.932	190g 30/10 Si	no data
8	1	20.7	6.9 M	25.5 g Pu 1.48 g Am	331.140	126.680	61.74	600g 30/10 Amb	25.6 g Pu 0.673 g Am
9	1	31.9	3.4 M	28.0 g Pu 1.260 g Am	197.900	125.940	36.36 58.06 73.312	Columns eluted together 182g TRU-Spec 600g 30/10 Amb	34.6 g Pu 0.0288 g Am
								600g 30/10 Amb	no data
10	1	32.9	5.7 M	1.090 g Am 0.66 g Am	112.250	59.940	46.60 50.55 73.596	198g 30/10 XAD-7	no data
								198g 30/10 XAD-7	0.319 g Am
11	1	39.7	6.5 M	2.17 g Am	157.000	63.500	59.55	198g 30/10 XAD-7 198g 30/10 XAD-7	0.896g Am
11	2	42.4			59.456	24.590	58.64 83.272	198g 30/10 XAD-7 198g 30/10 XAD-7	0.481 g Am
12	1	50.0	6.5 M	0.98 g Am	63.504	40.176	36.73	198g 30/10 XAD-7 198g 30/10 XAD-7	0.203 g Am
Split into 2 portions	2	17.0		0.211 g Am	40.176	1.890	95.30 97.024	200g t-Bu CMPO XAD-7	0.167 g Am
13	2	35.5		0.440 g Am	40.176	0.460	98.86 99.276	200g t-Bu CMPO XAD-7	0.448 g Am
13	1	37.4	6.2 M	2.39 g Am	207.040	48.600	76.53	198g 30/10 XAD-7 200g t-Bu CMPO XAD-7	1.484 g Am
13	2	39.0		0.585 g Am	46.606	1.850	96.03 99.068	200g t-Bu CMPO XAD-7	0.50 g Pu 0.513 g Am
14	1	22.8	6.2 M	2.26 g Am	321.120	81.600	74.59	200g t-Bu CMPO XAD-7	2.33 g Pu 1.450 g Am
14	2	24.3		0.585 g Am	76.563	9.900	87.07 96.714	200g t-Bu CMPO XAD-7	0.829 g Pu 0.555 g Am
15	1	30.4	5.6 M	1.34 g Pu 2.07 g Am	224.250	5.350	97.61	198g 30/10 XAD-7 198g 30/10 XAD-7	0.024 g Pu 0.406 g Am
								200g t-Bu CMPO XAD-7	0.128 g Pu 1.24 g Am
16	1	18.0	7.0 M	0.63 g Pu 0.97 g Am	174.960	0.777	99.56	198g 30/10 XAD-7 198g 30/10 XAD-7	0.578 g Am 0.409 g Am
								200g t-Bu CMPO XAD-7	

## IV. RESULTS

### A. Overview of Results in Table 2

Table 2 shows a set of results from the full-scale extraction chromatography runs. The Table is necessarily complicated in order to present the large amount of data generated during both column loading and elution cycles. Columns were run in tandem for the purpose of better efficiency during decontamination of solutions, while elution of individual columns (or resin types) was usually separate to provide better data about the amounts of alpha activity and actinides removed by specific resins. Bold solid lines in the Table are used to fully distinguish data related to one individual batch of process effluent solution. Light solid lines are used to separate data for two or more successively actinide loading passes through columns for one particular effluent solution. The dotted lines separate the elution data for columns which were loaded together in tandem, but were eluted separately.

The data represented in the % alpha removed column are volume corrected for dilution from HCl additions, column preparation, and column washing. The numbers in standard text in this column are decontamination results for individual passes, while the bold numbers in this column are the summation results of actinide removal for successively actinide loading passes. A fairly wide range of acid molarities, batch volumes and actinide quantities are represented by the solutions treated. Total alpha content for the process effluent solutions prior to treatment varied from 35 mCi/L to a high of 418 mCi/L.

### B. Plutonium Removal

The quantities of Pu in the process effluent streams varied widely depending on the efficiency of the preceding processes of solvent extraction and ion exchange processes. In addition, samples were occasionally misplaced, and in some cases Pu could not be measured accurately (as discussed in the Experimental Section), leading to a few holes in the data columns reporting Pu quantities as grams. In spite of these limitations, there are a number of runs that provide useful Pu data. Plutonium quantities remaining in the effluent solutions after treatment by any of the resin materials were uniformly small, and masked by the larger amount of americium that tended to bleed through.

The amount of Pu removed from solutions by the tested resin materials was impressive in several instances (runs 1 and 7-9). We did not purposely attempt to saturate any resins with Pu to determine maximum loading levels in this work. Saturation experiments for Pu(IV) loading

on several resins have been reported in our earlier work under more carefully controlled conditions.<sup>1,2</sup>

Tetravalent plutonium is expected to be the prominent species in solution in the solutions studied here due to an excess of oxidizers used in the preceding solvent extraction and ion exchange processes. However, the ratio of trivalent and tetravalent Pu in solution was not quantitated by UV-vis or other techniques. Attempting to distinguish behavior of various oxidation states of plutonium is futile if based solely on the data presented here. In addition, it is possible that coordination by CMPO extractants may skew the mixture of Pu oxidation states in solution towards the tetravalent. Our observation is that Pu is more easily removed than Am under our process conditions by all resins tested.

### C. Americium Removal

Removal of americium closely parallels the removal of alpha in these decontamination experiments, as Am-241 is some 40 times higher specific activity for alpha than typical for the plutonium used in these experiments. Given this data and the relative ease with which we have been able to remove plutonium, it is easy to see that our problems in waste treatment simplify to a certain extent to our ability to selectively remove Am from the HCl process effluent solutions.

The entries reported in the early part of the Table (runs 1-7 and 9) utilized TRU-Spec as the first of the tandem columns. The eluate data for these runs shows that TRU-Spec resin generally removed a sizable fraction of Pu, but never removed more than a small percentage of the of Am present. This result is in agreement with our small scale studies which found that TRU-Spec resin removes Am poorly from HCl solutions.<sup>1,2</sup> Physical properties of the resin were good and few problems with plugging were noted.

There were three unique resin support materials tested for Am extraction that were loaded with the same weight ratios of 30% OΦD(iBu)CMPO, 10% DAAP, and 60% inert support material. These included two resins materials purchased from EICrom, on 100-150 micron silica or polymethacrylate supports respectively, and one resin produced at LANL on the larger bead size (250-840 micron) XAD-7 resin.

The 30/10 Si resin (30% OΦD(iBu)CMPO/10% DAAP on a silica support purchased from EICrom) is represented by several entries in the early part of the Table (runs 1-6, pass 2 of run 7) where it was used as the second column in the tandem arrangement. The solution decontaminated in run 3 was a bit of an outlier, as this originated from a hydroxide cake that had been precipitated

from an HCl process, then redissolved in a small volume of HCl. One of the advantages predicted for the 30/10 Si resin material was reduced radiation damage to the support from gamma and alpha exposure due to the loaded americium-241. The 30/10 Si material was quite successful in removing modest quantities of Am from the solutions. The disadvantage noted for the 30/10 Si material was a tendency for flow rates to decrease to slower than desired levels, sometimes to the point of a complete stop due to plugging and increased back pressure. Increasing pressure and vacuum caused tighter packing of the 30/10 Si resin material. On a couple of occasions tightly packed 30/10 Si material was loosened by removing the from the column with a spatula and refilling. In the worst case, the 30/10 Si resin material once was removed from a packed column by breaking the glass column away from the remaining monolithic core formed of tightly packed resin material.

The 30/10 amb resin (30% O $\Phi$ D(iBu)CMPO/10% DAAP on a polymethacrylate support purchased from EICrom) was tested at larger scale of ~600 g in the 3 x 18 inch Corning glass pipe (runs 7-9). Runs 8 and run 9, pass 1 were outliers from the perspective of the large amount of Pu lost from the preceding solvent extraction operation. Results were very good from the point of Pu removal, but poor from the perspective of Am and total activity decontamination. The Am removal compared particularly poorly with the very encouraging results observed for the 30/10 Si resin material. Physical properties of the resin were good and few problems with plugging were noted.

The 30/10 XAD-7 resin (30% O $\Phi$ D(iBu)CMPO/10% DAAP on Amberlite<sup>®</sup> XAD-7 support, prepared at LANL) was used in runs 10-12, 13, and 15-17. One or two columns of the standard 4.8 cm x 30 cm size were used. Results were very good from the point of Pu removal, but poor from the perspective of Am removal and total activity decontamination. The Am removal again compared poorly with the results observed for the 30/10 Si resin material. Physical properties of the resin were good and few problems with plugging were noted.

The D(tBu $\Phi$ )D(iBu)CMPO XAD-7 resin (30% D(tBu $\Phi$ )D(iBu)CMPO/10% DAAP on Amberlite<sup>®</sup> XAD-7 support, prepared at LANL) was used in runs 12-17. One column of the standard 4.8 cm x 30 cm size was used. Results were very good for removal of Am and total activity decontamination. The D(tBu $\Phi$ )D(iBu)CMPO XAD-7 resin can be compared directly with the 30/10 XAD-7 resin as the preparation method, diluent, support material and column size were identical. The D(tBu $\Phi$ )D(iBu)CMPO XAD-7 resin was clearly superior for Am removal and total activity decontamination in this

comparison. Physical properties of the resin were good and few problems with plugging were noted.

In a comparison of decontamination results for the D(tBu $\Phi$ )D(iBu)CMPO XAD-7 resin to the best runs obtained for the 30/10 Si resin, the D(tBu $\Phi$ )D(iBu)CMPO XAD-7 resin still appears favorable. Larger amounts of Am (up to 2 g) were removed efficiently in a single pass.

#### D. Elution Results

Elution of actinides was fairly facile for all resins with 0.1 M HCl at a rate of ~1 L/hour. Addition of 0.1 M hydroxylamine hydrochloride to the eluate for columns did appear to increase the rate of Pu(IV) elution and seems a prudent suggestion. When hydroxylamine hydrochloride was present in the eluate of Pu loaded resins, a very noticeable blue band (presumably due to trivalent plutonium) was observed to elute rapidly from the tan color (presumably due largely to tetravalent plutonium) of the loaded resin. Americium elution seemed complete in most cases in 2-4 column volumes, based on observations made by measuring the gamma emission of the column at various stages of elution with a hand held gamma instrument. The 30/10 Si resin appeared to have the most rapid elution kinetics.

#### E. Disposition of Solutions and Solids

During this demonstration effort, the decontaminated HCl solutions were treated by the normal process of KOH to neutralize the HCl, the precipitated hydroxides were filtered, and the filtrate sent to the LANL wastewater treatment facility. In two extraction chromatography runs, hydroxide cakes recovered by filtration were kept isolated from other residues to provide an additional demonstration of the reduced activity. The solid cakes were of too low an activity level to be counted by our normal segmented gamma scanning analysis technique.

A bit of mathematics for the activity residue recovered from run 1 in Table 2 is of interest. If we take the total alpha activity left in the solution as 0.792 mCi (44 L x 0.018 mCi/L) and divide by the weight of the (rather small) dried hydroxide cake recovered from this run (840g), we get 9.42 E -04 mCi/g or 942 nCi/g as the calculated alpha activity level for the solid waste. The criteria for LLW solid waste is 100 nCi/g or less of alpha activity (above 100 nCi/g is TRU level solid waste). We were thus within about an order of magnitude of the LLW limit on this particular run. We don't expect to be able to recover LLW from the current arrangement, which is performing these experiments in the rather high contamination environment of a Pu processing glovebox.

## V. CONCLUSIONS

Our progress in scaling extraction chromatography to our waste treatment application has been significant. The extraction chromatography columns provide a reusable method to concentrate actinides from the HCl waste effluent streams. Incorporation of extraction chromatography requires minor additional equipment. It is a simple process to run and can be integrated directly into the present plutonium recovery process flowsheet.

Pu(IV) was effectively removed at multi-gram scale from HCl effluents by several of the resins tested. TRU-Spec is an adequate choice for Pu(IV) removal, and one that is commercially available. It provides some additional separations advantages when used as the first column in a tandem arrangement and eluted separately, as it captures most of the Pu for recycle with little Am. The tandem arrangement reserves the capacity of the more esoteric resin materials for the more difficult task of americium removal. Additional anion exchange resin capacity might also fulfill a role in this application, particularly with process upsets that lose much Pu.

While the Pu quantities removed are impressive in some of the runs, Am quantities that the resins could handle before significant breakthrough are much smaller. We still have not scaled the operation large enough with the present resin materials to routinely and efficiently handle feeds with abnormally high Am-241 content (above 5 g). The problems in scaling this process somewhat larger seem solvable.

Concentrated actinide residues low in chloride content are recovered from the column eluate solutions. We expect they should be suitable for long-term vault storage or alternative disposition routes. The solids wastes generated by hydroxide treatment of the process effluents, of much lower activity than without extraction chromatography, are suitable for fixation as a TRU waste form rather than vault storage. Removal of americium from the processing stream as early and as efficiently as possible has the added benefit of reducing exposure to workers in all subsequent waste handling, treatment, and storage operations. Future plans include the option of using the decontaminated acid solution as feed for HCl recycle operations, which will further reduce activity, volume, and chloride content of liquid waste effluents. The evaporator bottoms will be of similar low activity level, and discardable as TRU waste.

Resin performance degradation by loss of extractive material, radiolysis, support failure is expected and probably does occur over time and with use. The loss in performance is poorly quantitated by this study, but it is

not so rapid as to preclude use of these materials for numerous runs. There remains room for improvement in physical properties and radiation resistance in the support materials, beyond those few tested in this report. The silica support was chosen in part due to the potential for greater radiation resistance than the polymer support. The effect of several R/hour of alpha and gamma radiation on the long-term performance of the polymer resins is of concern.

In direct comparative studies, when loaded on identical supports and diluent conditions, di-(4-t-butylphenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (D(tBuΦ)-D(iBu)CMPO) demonstrated better americium retention than n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (OΦD(iBu)CMPO) from HCl process effluents. We have small scale experiments in HCl that support this comparison. We plan to further investigate D(tBuΦ)D(iBu)CMPO to better understand the reasons why.

This process is one that would benefit greatly from on-line analytical capability to monitor breakthrough of actinides during loading, and elution curves during the strip cycle. We are exploring options in this regard.

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