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CLEANUP OF HYDROCHLORIC ACID WASTE STREAMS FROM ACTINIDE PROCESSES USING EXTRACTION CHROMATOGRAPHY.

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ABSTRACT

Extraction chromatography is under development as a method to lower actinide activity levels in hydrochloric acid (HCl) effluent steams. Successful application of this technique would allow recycle of the largest portion of HCl, while lowering the quantity and improving the form of solid waste generated.

The extraction of plutonium and americium from HCl solutions was examined for several commercial and similar laboratory-produced resins coated with n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and either tributyl phosphate (TBP), or diamyl amylphosphonate (DAAP). Distribution coefficients for Pu and Am were measured by contact studies in 1-10 M HCl, while varying REDOX conditions, actinide loading levels, and contact time intervals. Significant differences in the actinide distribution coefficients, and in the kinetics of actinide removal were observed as a function of resin formulation.

INTRODUCTION

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 usually routed to controlled hydroxide precipitation for actinide waste polishing.

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This step coprecipitates many other metal hydroxides and salts with the actinides, producing an undesirable solid cake for storage. The liquid effluent from neutralization requires further treatment to reduce activity by a flocculation process that produces additional transuranic (TRU) solid wastes.

The purpose of this work is to evaluate extraction chromatography techniques and materials as an alternative method to remove actinides from aqueous hydrochloric acid effluent streams. Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and related molecules have been examined for use in liquid-liquid extraction schemes for actinide removal mostly in nitric acid media[1], and with some efforts in hydrochloric acid[2-3]. Extraction chromatography using similar extractants has been used on an analytical scale to concentrate actinides for analysis.[4] However, testing of extraction chromatography techniques for larger-scale applications has received scant attention.[5-7] The potential advantages of applying these techniques for decontamination of radioactive aqueous effluents include generation of smaller quantities of solid residues in forms more suitable for storage, smaller quantities of TRU waste, more facile hydrochloric acid recycle, and more efficient decontamination for aqueous effluents.

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EXPERIMENTAL

A Packard 2200CA scintillation counter was utilized to measure alpha activity in the liquid samples. Aliquots of the actinide solutions were pipetted into 6 mL H_2O and 14 mL Ultima Gold XR® scintillation cocktail. Experiments in HCl used either a purified Pu stock solution of 15.3 mg/mL in 1.8 M HCl or a stock Am solution of 0.50 mg/mL in 4 M HCl. Radiochemistry analysis of the Pu stock solution was within 6 % of the value obtained by scintillation counting. Duplicate scintillation samples were counted for all experiments.

Several resins from EIChroM Industries were tested in addition to resins prepared at Los Alamos. All resins reported in this study were based on octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) diluted in tributyl phosphate (TBP), diamyl amylphosphate (DAAP), or without a diluent. EIChroM resins included TRU-Spec® (13% CMPO, 27% TBP weight percent respectively), RE-Spec® (16% CMPO, 24% TBP), 20% CMPO/20% DAAP and 30% CMPO/10% DAAP. LANL prepared resins reported in this study include 40% CMPO on Amberlite® XAD-7, and 13% CMPO/27% TBP on Amberlite® XAD-7. LANL resins were prepared by methods similar to those reported in the literature.[4,7]

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Contact experiments were run in Bio-Rad 10 mL polyethylene columns equipped with a 35 micron frit and an attached luer-lock stopcock. Columns were rotated at approx. 8 rpm. Liquid samples were removed by first draining a 1 mL portion through the frit to rinse the column tip and stopcock, followed by removing an aliquot for sampling. The typical experiment used a 5 mL solution volume, 0.5 g or 0.05 g of resin, and 0.25 M NH_2OH or $NaNO_2$ to control REDOX conditions for plutonium experiments.

Distribution coefficients (Kd values) discussed in this work are reported as actinide concentration per gram of resin divided by actinide concentration per mL of solution. A Microsoft EXCEL spreadsheet was utilized to calculate the Kd values and to correct for activity or volume changes due to reagent addition or sampling losses.

RESULTS & DISCUSSION

Very good retention of Pu(IV) is observed for several of the resins containing the CMPO ligand, as evidenced by the large distribution coefficients (Kd's) seen in the contact studies (Figure 1-4). The final equilibrium Kd for Pu(IV) does not vary dramatically at higher HCl concentrations with this series of resins (Figure 5). Slower kinetics are observed for uptake of Pu(IV) on the resins that have more CMPO, and less TBP or DAAP as a diluent. Kinetics of Pu(IV) uptake are slowest when the HCl concentrations are high, the Pu loading level is high, and the ratio of solution to resin is large (not all data shown).

Distribution coefficients for Pu(III) (Figure 6-7) and Am(III) (Figure 8-12) are much lower than observed for Pu(IV) on these resins, and are significant only at higher HCl concentrations (4 M or above). The data for Pu(III) (Figure 6-7) suggest that Pu should be recoverable from the resins at lower acid concentrations, if it can be reduced to the +3 oxidation state. For Am the resin series again shows slower kinetics for the resins containing more CMPO, and less TBP or DAAP. Final equilibrium Kd values for Am(III) are significantly higher for the resins that have more CMPO and less TBP or DAAP (Figure 13). This is a significant difference from the behavior observed for Pu(IV) where final Kd's are about 10,000 for all resins at high HCl molarity.

Figure 14 shows how the Pu(IV) Kd changed over time in a 6 M HCl contact study on TRU-Spec, as the Pu added to a set of experiments was varied over 2.5 orders of magnitude. The observed Kd's were nearly constant over the range of 3-30 mg Pu/g resin, and showed a predictable decrease as the resin loading capacity was reached at the higher loading levels. The reason for the slightly lower Kd's at the lowest loadings in this study are not well understood. The maximum amount of Pu removed in this study was 66.3 mg/g resin. Figure 15 shows a similar result for Pu(IV) loading (in mg Pu/g resin) observed for a series of resins tested at 7 M HCl. In the experiment represented by Figure 15, a relatively small fraction of the excess Pu in solution was removed by the resin.

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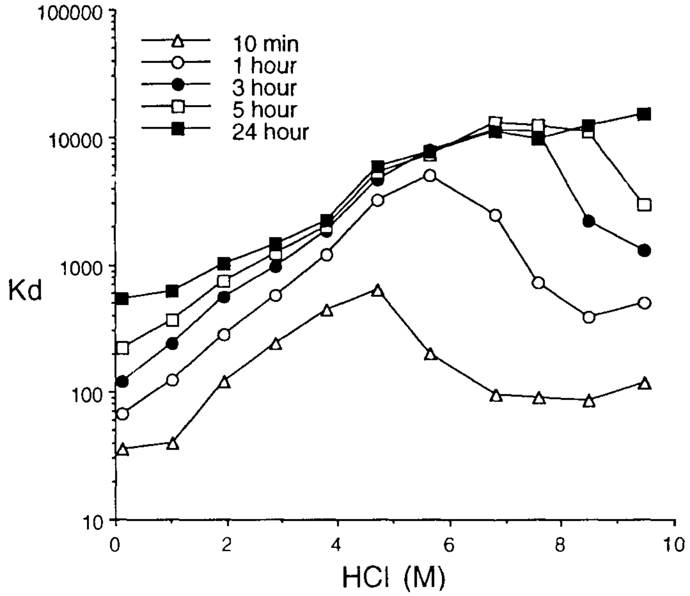

Figure 1 Pu(IV) on TRU-Spec
0.25 M NaNO2, 1.08 mg Pu, 0.05 g resin

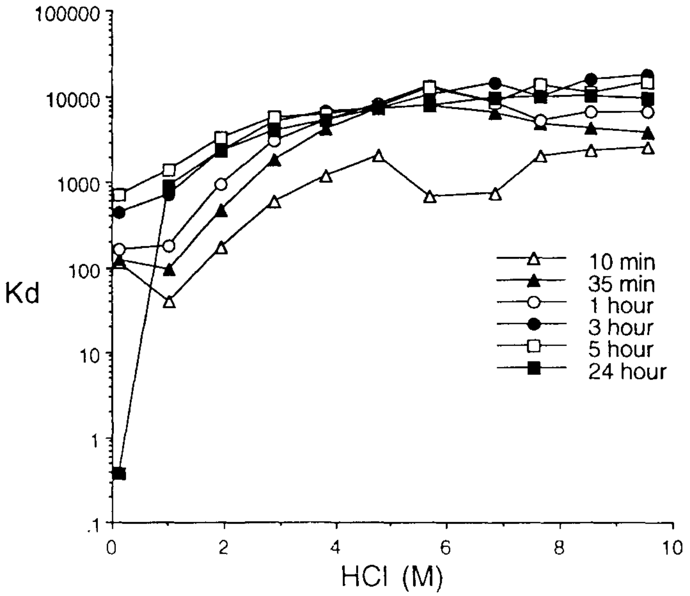

Figure 2 Pu(IV) on 20%/20% CMPO/DAAP
0.25 M NaNO2, 0.77 mg Pu, 0.05 g resin

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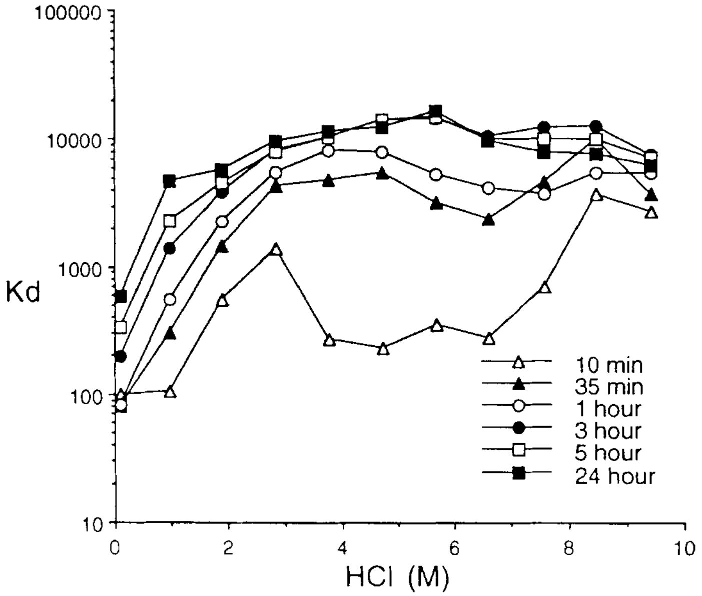

Figure 3 Pu(IV) on 30%/10% CMPO/DAAP
0.25 M NaNO2, 0.77 mg Pu, 0.05 g resin

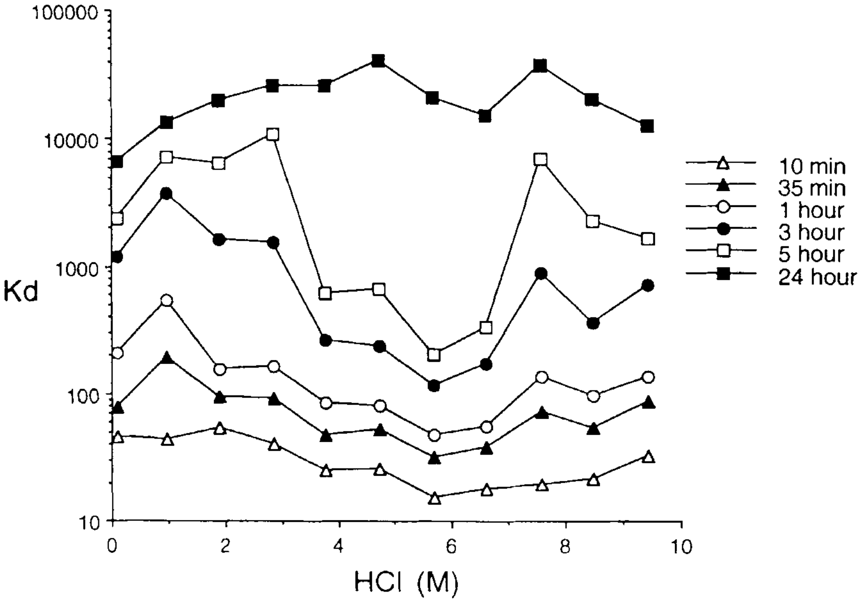

Figure 4 Pu(IV) on 40% CMPO/XAD-7
0.25 M NaNO2, 0.77 mg Pu, 0.05 g resin

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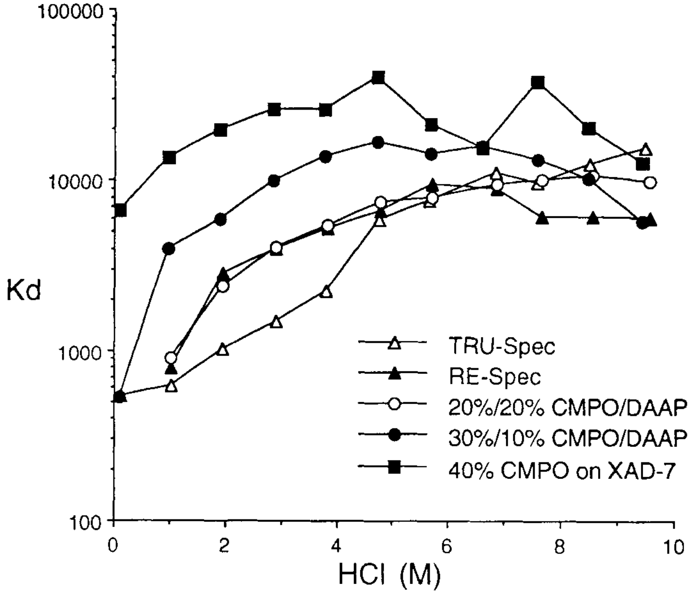

Figure 5 Pu(IV) Kd Comparison For Several Resins (24 Hour)

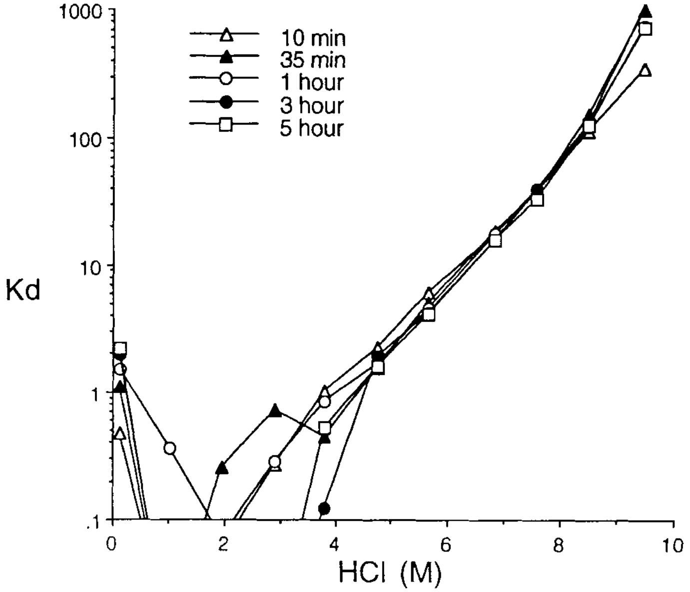

Figure 6 Pu(III) on TRU-Spec
0.25 M NH2OH, 1.08 mg Pu, 0.5 g resin

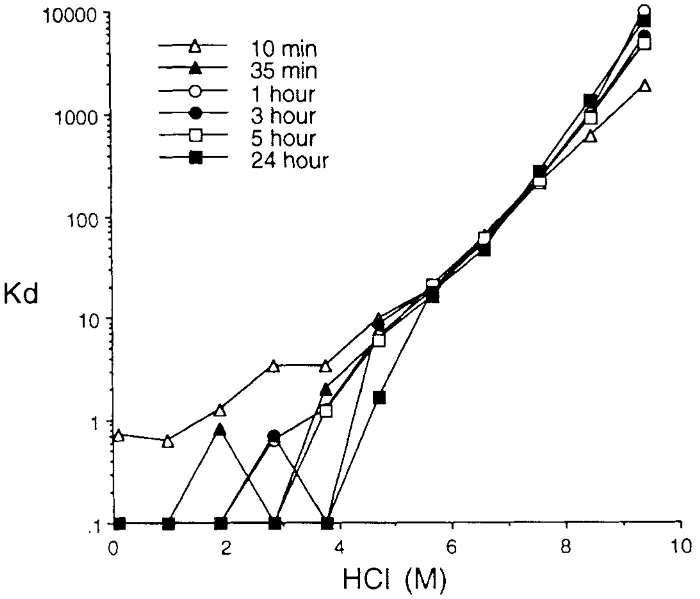

Figure 7 Pu(III) on 20/20 CMPO/DAAP
0.25 M NH2OH, 0.77 mg Pu, 0.05 g resin

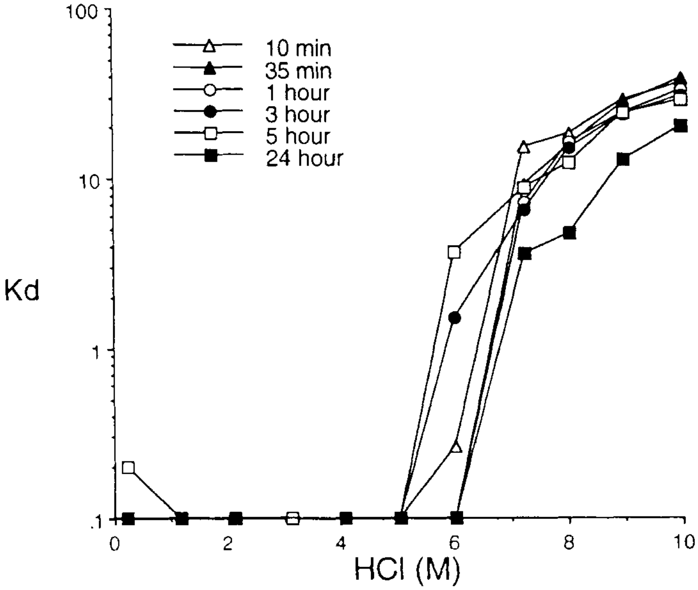

Figure 8 Am on TRU-Spec
0.05 mg Am, 0.050 g resin

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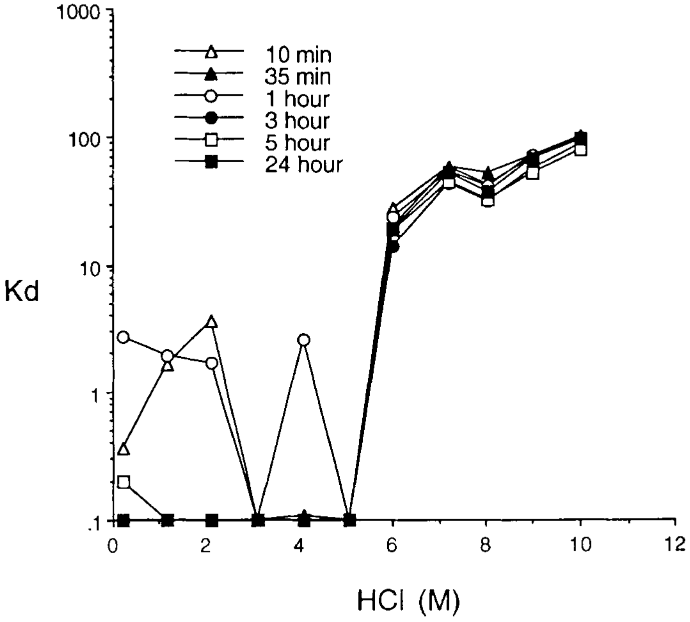

Figure 9

Am on 20%/20% CMPO/DAAP
0.05 mg Am, 0.050 g resin

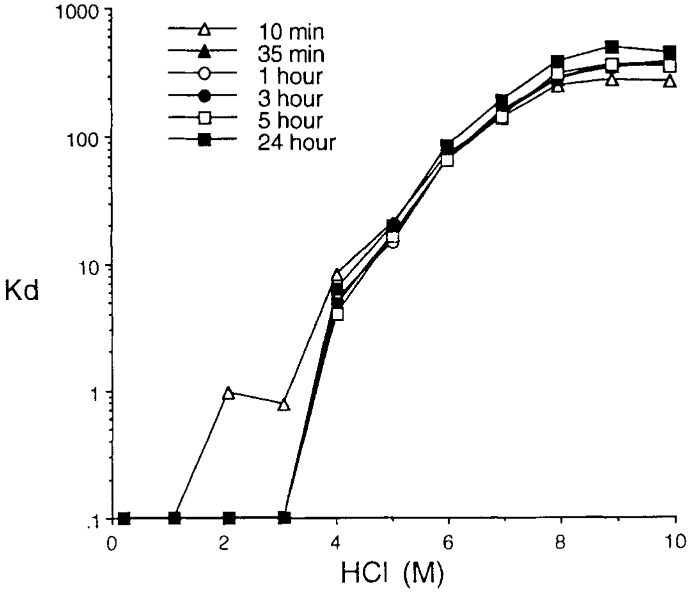

Figure 10

Am on 30%/10% CMPO/DAAP
0.05 mg Am, 0.050 g resin

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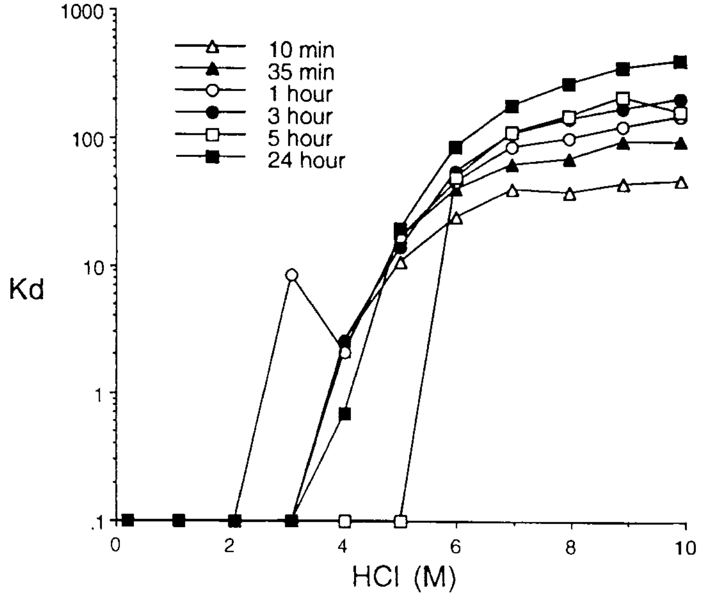

Figure 11 Am on 15%/25% CMPO/TBP/ XAD-7
0.05 mg Am, 0.050 g resin

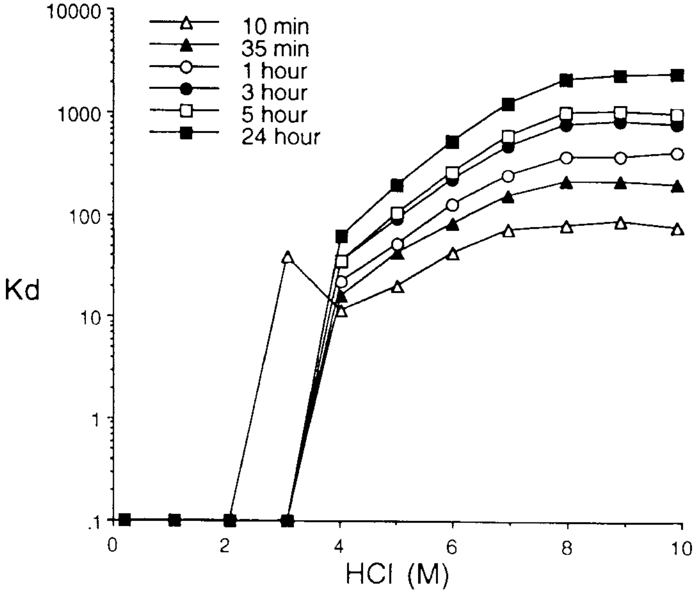

Figure 12 Am on 40% CMPO/XAD-7
0.05 mg Am, 0.050 g resin

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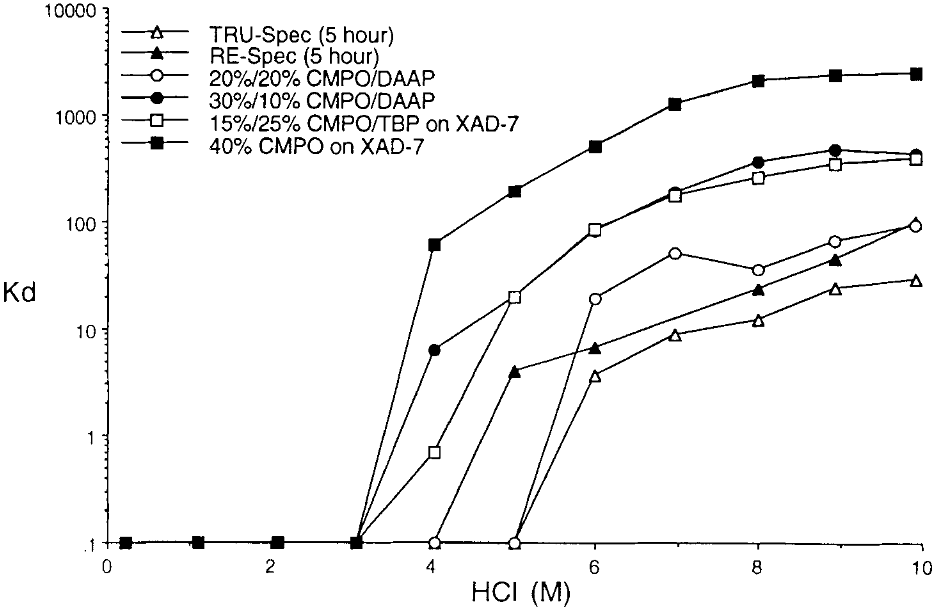

Figure 13 Am Kd Comparison For Several Resins (24 Hour)

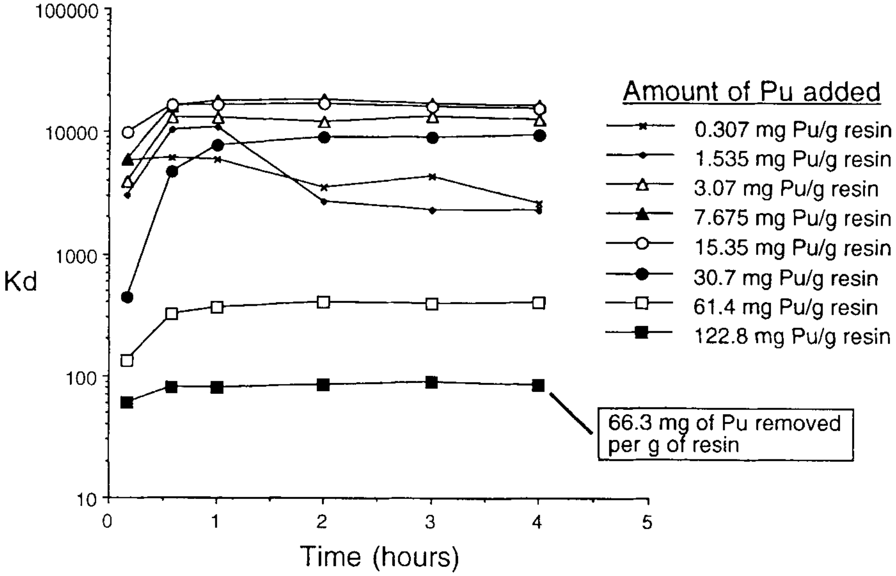

Figure 14 Pu(IV) Kd vs Loading for TRU-Spec
6M HCl, 0.25 M NaNO2, 0.05 g resin

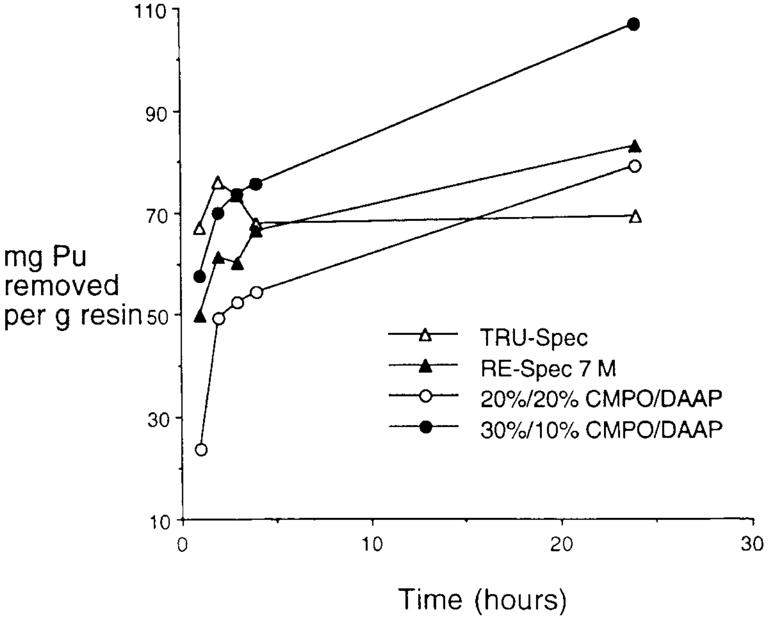

Figure 15 Maximum Pu(IV) removed from 7 M HCl for several resins

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As the loading data was calculated by measuring the Pu that remained in solution, the experiment measured small changes in large numbers, leading to greater scatter and uncertainty than for other experiments in this report. The data for the pure CMPO resin showed low loading, but also unusual scatter, and was thus excluded. The resins followed a general trend of greater Pu removal for higher CMPO content. Analysis of this data at the 24 hour timepoint (Table 1), shows that the molar ratio of CMPO to Pu is nearing 1 for TRU-Spec and is larger for the resins that contain a greater fraction of CMPO. Loading capacity of the resins is approaching one-half that of an anion exchange resin (typically ~1 mmole/g or ~240 mg actinide/g resin). Significant work has been completed on a series of complementary flow experiments which will be summarized in another report.

Table 1- Analysis of Maximum Pu(IV) removed from 7 M HCl at 24 hours.

	TRU-Spec	RE-Spec	20%/20% CMPO/DAAP	30%/10% CMPO/DAAP
mg Pu removed per g resin	69.2	82.9	79.0	106.9
Kd observed	42.7	55.6	52.0	86.0
% CMPO on resin by weight	13	16	20	30
mg Pu added to experiment	12.24	12.24	12.24	12.24
mg Pu removed	3.49	4.15	4.01	5.46
moles Pu removed	1.46E-02	1.74E-02	1.68E-02	2.29E-02
Mole ratio CMPO/Pu	1.10	1.13	1.49	1.65

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CONCLUSIONS

•Pu(IV) is effectively removed from HCl by any of several resins containing the CMPO ligand. Of the resins studied, TRU-Spec & RE-Spec offer best kinetics for Pu(IV) uptake, and most facile elution with a reducing agent. Ascorbic acid is superior to hydroxylamine in stripping Pu from these resins.

•Pu(III) and Am(III) are removed by CMPO resins only at higher HCl concentrations. The ratio of CMPO to diluent and the properties of the diluent play a large role in actinide(III) retention. More CMPO translates to higher actinide(III) Kd values.

•Kinetics of Pu(IV) uptake and elution varies more dramatically than that of Pu(III) or Am(III) with resin formulation. A larger ratio of CMPO to diluent appears to slow kinetics of uptake and elution.

•Loading studies with Pu(IV) indicate that the resins should be useful for HCl process stream decontamination.

•Of the series of resins tested, TRU-Spec appears to offer the best combination of properties for Pu(IV) decontamination from HCl. The 30%/10% CMPO/DAAP resin showed the best combination of properties for Pu(III) or Am(III) decontamination from HCl.

•Extraction chromatography may provide a method of concentration of actinides into smaller volumes of storable or treatable solid forms, decontamination of high acid stream effluents to activity levels that allow facile HCl recycle, and reduction in activity levels sent to wastewater treatment.

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