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REMOVAL OF PLUTONIUM AND AMERICIUM FROM HYDROCHLORIC ACID WASTE STREAMS 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 for radioactive liquid waste treatment would provide a low activity feedstream for HCl recycle, reduce the loss of radioactivity to the environment in aqueous effluents, and lower the quantity and improve the form of solid waste generated.

The extraction of plutonium and americium from HCl solutions was examined for several commercial and laboratory-produced sorbed resin materials. Polymer beads were 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 resin formulations. Flow experiments were run to evaluate actinide loading and elution under varied conditions. Significant differences in the actinide distribution coefficients in contact experiments, and in actinide retention in flow experiments 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. 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 large volumes of 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 historically been examined for use in liquid-liquid extraction schemes for actinide removal from nitric acid media[1], 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.[5-8] 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 efficient decontamination of aqueous effluents.

EXPERIMENTAL

A Packard 2200CA scintillation counter was utilized to measure alpha activity in 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 containing 15.3 mg/mL in 1.8 M HCl or a stock Am solution containing 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. The LANL resin was prepared by methods similar to those reported in the literature.[4,7]

Contact experiments used 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 and/or sampling losses.

Flow experiments were performed in 1 cm ID Kontes Chromaflex® glass columns equipped with PTFE fittings and frits. A Cole-Palmer Masterflex® pump using PTFE & Norprene tubing (0.8 mm ID) was used pull solutions through the columns at controlled rates. The typical experiment used 2.5 g of resin (~4.7 mL column void volume). Flow rates were set at approx. 0.35 mL/min. (~13 minutes residence time). Actinide solutions were diluted to 25 mL (5 column void volumes) acid and sometimes contained 0.25 M REDOX reagent. Following the actinide loading cycle of approx. 5 column volumes, the column was washed with 5 column volumes of HCl at the same concentration as the loading cycle, followed by elution with 10 column volumes of a more dilute acid solution. Samples for analysis were collected in 5 mL increments (approx. 1 column volume) from column flow experiments.

RESULTS & DISCUSSION

Contact Experiments

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). The final equilibrium Kd of approx. 10,000 for Pu(IV) does not vary dramatically at higher HCl concentrations (6-10 M) with this series of resins. The final equilibrium Kd at lower HCl concentrations (1-4 M) shows a trend of higher Kd for the resins that have more CMPO and less TBP or DAAP. Data for samples obtained at time intervals prior to equilibration show slower kinetics are observed for uptake of Pu(IV) on the resins that have more CMPO, and less TBP or DAAP as a diluent. The pure CMPO resin was very slow compared to the other resins, and it is not known if full equilibrium was reached for this resin even at the 24 hour timepoint. 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).[8]

Distribution coefficients for Am(III) (Figure 2) are much lower than observed for Pu(IV) on these resins, and are significant only at higher HCl concentrations (4 M or above). For Am, the resin series again shows slower kinetics for the resins containing more CMPO, and less TBP or DAAP (not all data shown). Final equilibrium Kd values for Am(III) are significantly higher for the resins that have more CMPO and less TBP or DAAP. This is significantly different from the behavior observed for Pu(IV) at high HCl molarity where final Kd's are approx. 10,000 for all resins.

Efficient use of these resins to remove actinides from process effluent streams will require a functional loading capacity significantly higher than that recommended for these resins in analytical concentration schemes (1-2 mg/ mL of resin or approx. 3-6 mg actinide/g of resin recommended for TRU-Spec). Figure 3 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 exceeded at the higher loading levels. The reasons for the slightly lower Kd's at the lowest loadings in this study are not well understood. The maximum amount of Pu removed by TRU-Spec at 6 M HCl in this study was 66.3 mg/g resin.

Figure 4 shows a similar result for Pu(IV) loading experiment conducted for a series of resins tested at 7 M HCl and 12.24 mg Pu contacted with 50 mg resin. 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 approaching 1 for TRU-Spec, and is larger for the resins that contain a greater fraction of CMPO. The measured Pu(IV) loading capacity of the resins, 107 mg/g for the 30%/10% CMPO/DAAP resin, is approaching one-half the capacity of an anion exchange resin (typically ~1 mmole/g or ~240 mg actinide/g resin).

	TRU-Spec	RE-Spec	20%/20% CMPO/DAAP	30%/10% CMPO/DAAP
% CMPO on resin (by weight)	13	16	20	30
Kd observed	42.7	55.6	52.0	86.0
mg Pu removed	3.49	4.15	4.01	5.46
mg Pu removed per g resin	69.2	82.9	79.0	106.9
Calc. mole ratio of CMPO/Pu	1.10	1.13	1.49	1.65

Table 1- Analysis of Maximum Pu(IV) removed from a 7 M HCl solution containing 0.25 M $NaNO_2$, 12.24 mg of Pu and 50 mg of resin at 24 hours.

In the loading experiments a relatively small fraction of the excess Pu in solution was removed by the resin. 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 from Table 1.

Flow Experiments

Pu(IV) retention during the loading and wash cycles of flow experiments was generally very good for either TRU-Spec or the 30%/10% CMPO/DAAP resins at 6-8 M HCl and 0.25 M $NaNO_2$. Figure 5 shows the loading and elution profiles for 2.5 g of resin loaded with 0.77 mg of Pu dissolved in 25 mL of HCl (actinide loading cycle, column fractions 1-5), followed by 25 mL of HCl (wash cycle, column fractions 6-10), and 50 mL of elutrient (column fractions 11-20). Retention of Pu on either resin under the specified conditions in Figure 5 was over 99.9% for the loading and wash cycles. Figure 5 also shows comparative data for TRU-Spec resin eluted with 0.25 M hydroxylamine or ascorbic acid (AA) in 1 M HCl. Elution of Pu(IV) loaded resins with ascorbic acid as a reducing agent was more rapid and complete than elution with hydroxylamine in this and other studies. The elution of Pu(IV) from the 30%/10% CMPO/DAAP resin proved slower than elution from TRU-Spec resin for either hydroxylamine or ascorbic acid (only the ascorbic acid elution profile is shown).

Pu(III) retention in 8 M HCl and 0.25 M NH_2OH during the loading and wash cycles varied dramatically with the resin formulation as shown in Figure 6. The best Pu(III) retention was observed for the 30%/10% CMPO/DAAP resin. TRU-Spec showed a large breakthrough by the fourth column volume, while the 40% CMPO resin showed breakthrough on the very first column volume. Experiments on TRU-Spec resin at 6 M and 10 M HCl (not shown) showed relatively minor changes in Pu(III) breakthrough from the 8 M HCl result shown in Figure 6.

Am behavior in flow experiments on three different resins is shown in Figure 7. Am retention showed a trend similar to Pu(III) during the loading and wash cycles, with the best retention observed for the 30%/10% CMPO/DAAP resin. Retention of Am on the 30%/10% CMPO/DAAP resin was over 99.99% for the loading and wash cycles. TRU-Spec showed a large breakthrough of Am by the fourth column volume.

The flow results for Pu(III) and Am(III) for the varied resins are quite similar. For flow experiments with either Pu(III) or Am(III), the superiority of 30%/10% CMPO/DAAP over TRU-Spec resin for actinide (III) retention are consistant with the large difference in Am Kd values observed in contact experiments (Figure 2) for these two resins. The poor Pu(III) retention of the 40%

CMPO resin in Figure 6 cannot be explained by the Kd comparison made in Figure 2. The reason for the rapid Pu(III) breakthough observed for the 40% CMPO resin must be due to very slow kinetics, which were also apparent in the Am contact experiments. The effect is magnified at the moderately high loading of Pu in the flow experiments (0.77 mg of Pu on 2.5 g of resin).

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 had the best kinetics for Pu(IV) uptake, and most facile elution with a reducing agent. Ascorbic acid is superior to hydroxylamine for 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.

•Contact loading studies with Pu(IV) and flow experiments indicate that the resins will function at loading levels much higher than recommended for analytical use. These observed actinide loadings make these resins an attractive option 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) and/or Am(III) decontamination from HCl.

•Elution of Pu and Am from these resins is facile at 0.1 to 1.0 M HCl concentrations, if a reagent for reduction of Pu(IV) to Pu(III) is used. At these acid concentrations phosphonic acid degradation products of CMPO, observed to hinder actinide elution in more dilute acids, should provide little interference.

•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 HCl recycle, and reduction in activity levels sent to wastewater treatment.

•The present formulation of 40% CMPO on XAD-7 showed slow kinetic uptake of actinides. This is undoubtably due in part to the absence of TBP or DAAP to function as diluent and an aid to actinide transport from the aqueous phase to the organic phase of the bead. The larger resin bead size of the XAD-7 support material may also contribute to the slower kinetic uptake.

•The stability of these resins to large volumes of acids, radioactivity and repeated use in an effluent treatment environment are important factors that will need to be determined through additional study. This work is proceeding at full scale in our laboratories removing gram quantities of actinides from actual process effluents.

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Figure 1 Pu(IV) Kd Comparison For Several Resins (24 Hour)

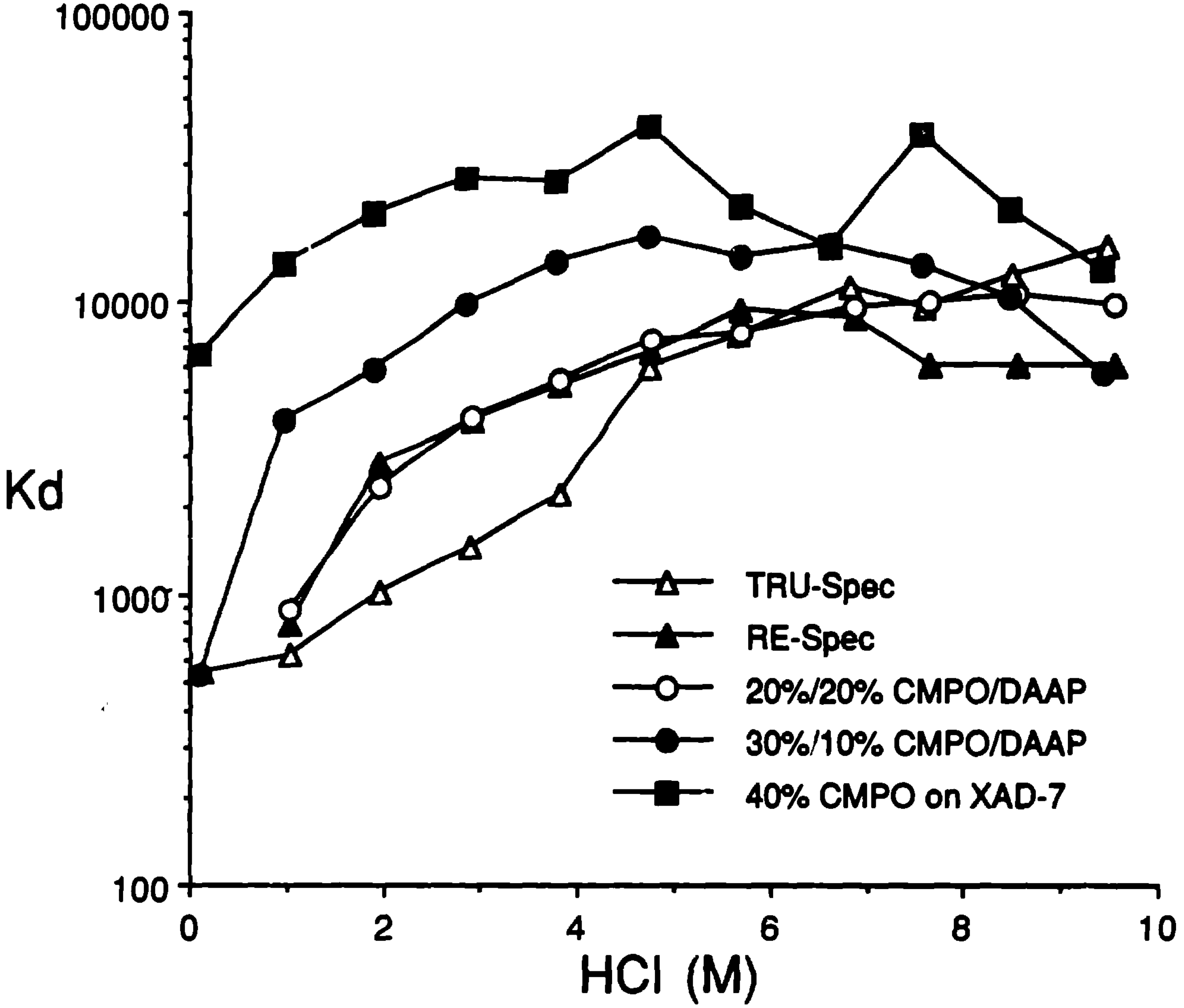

Figure 2

Am Kd Comparison For Several Resins (24 Hour)

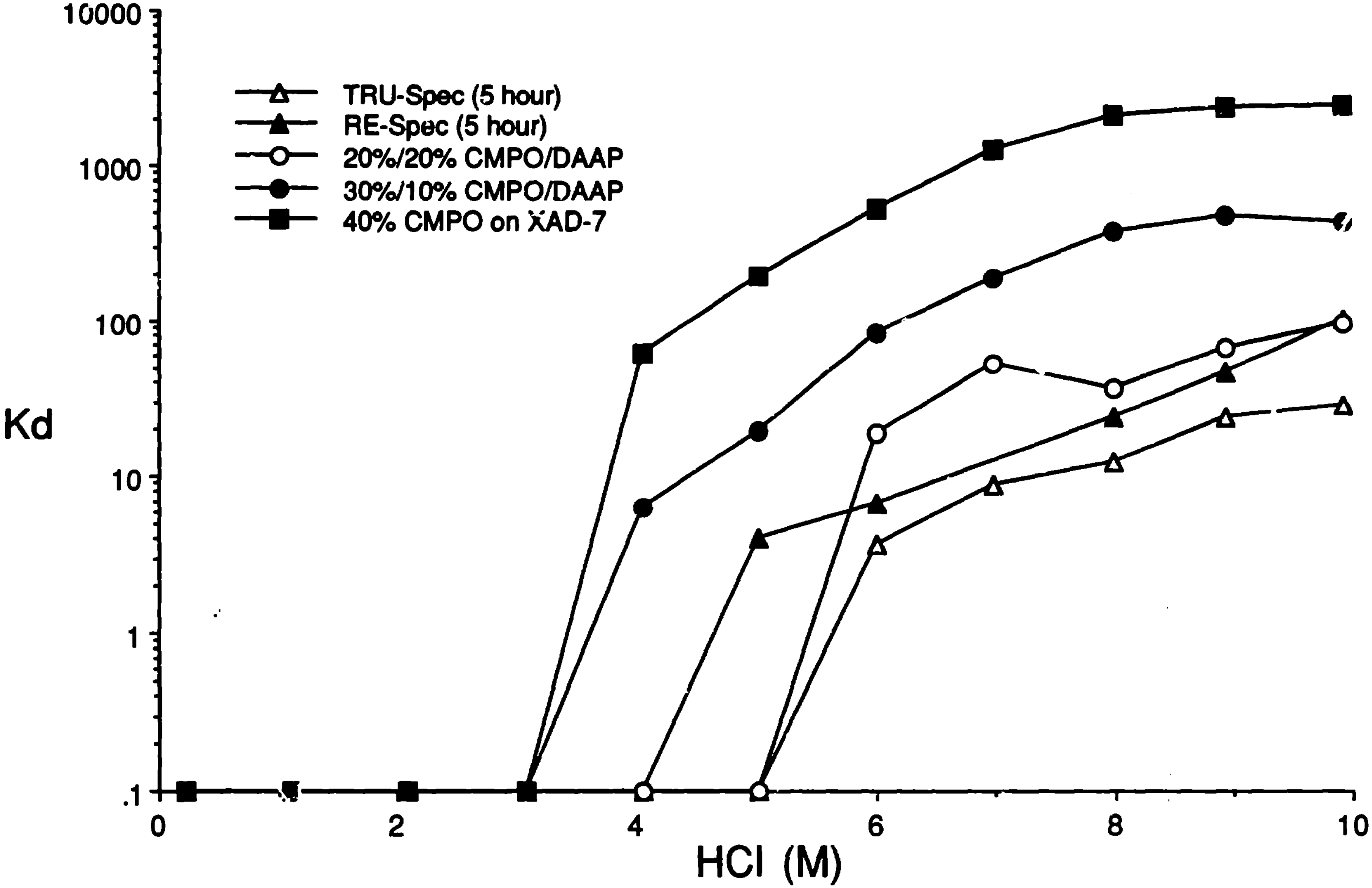

Figure 3

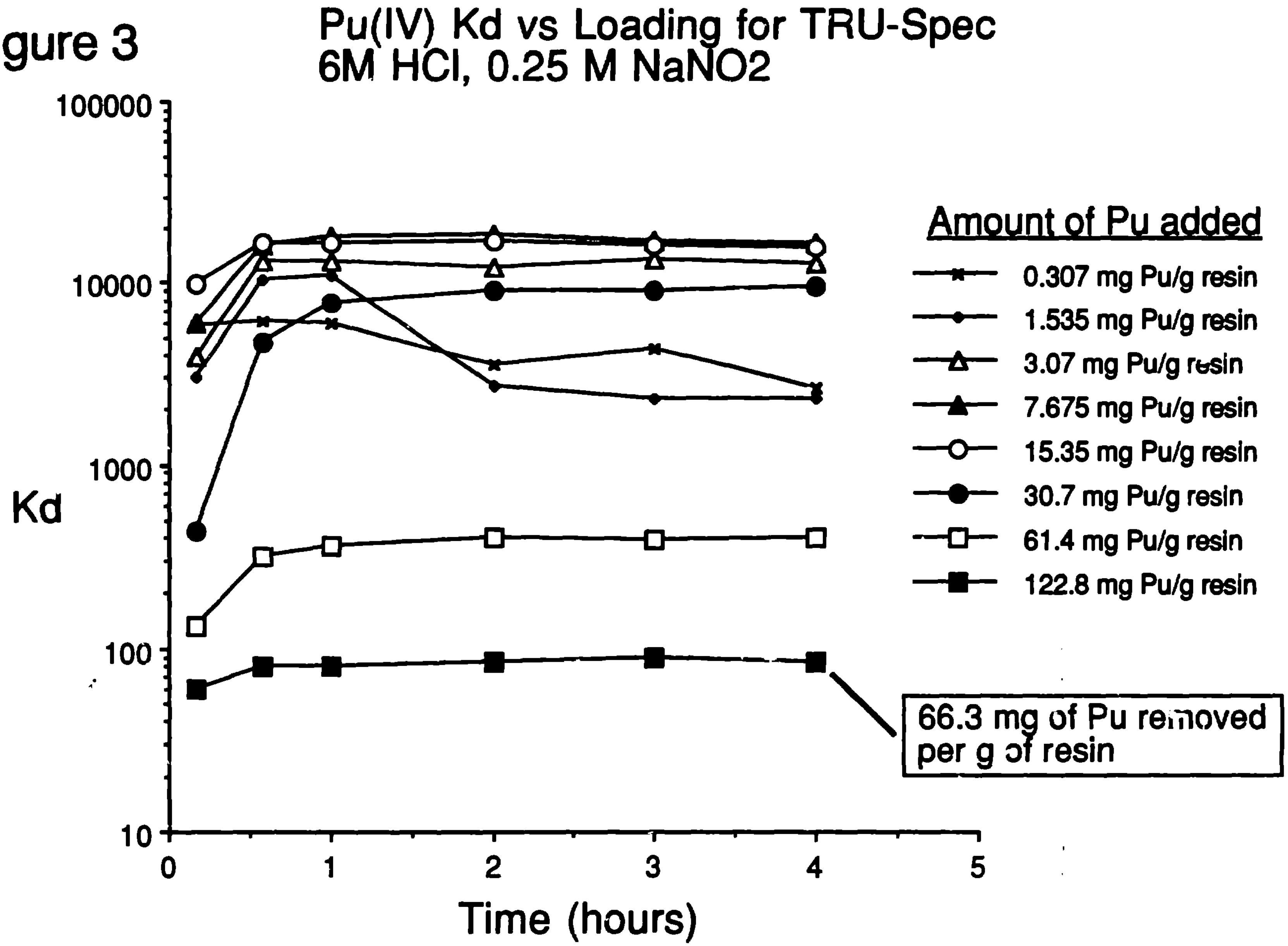
Pu(IV) Kd vs Loading for TRU-Spec
6M HCl, 0.25 M NaNO2
Kd
100000
10000
1000
100
10
0
1
2
3
4
5
Time (hours)
Amount of Pu added
0.307 mg Pu/g resin
1.535 mg Pu/g resin
3.07 mg Pu/g resin
7.675 mg Pu/g resin
15.35 mg Pu/g resin
30.7 mg Pu/g resin
61.4 mg Pu/g resin
122.8 mg Pu/g resin
66.3 mg of Pu removed per g of resin

Figure 4

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

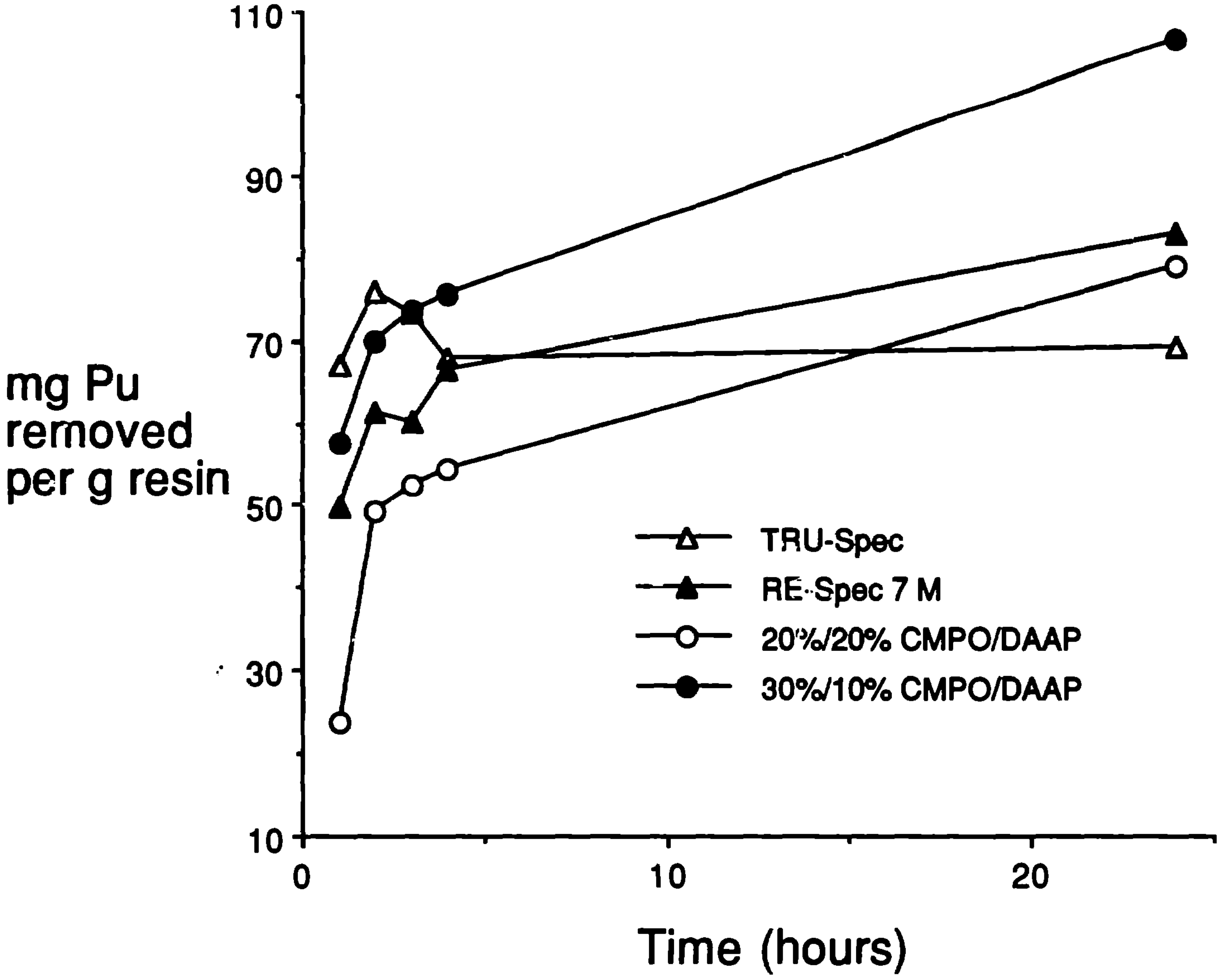

Figure 5

Pu (IV) Behavior on TRU-Spec and 30%/10% CMPO/DAAP Resins

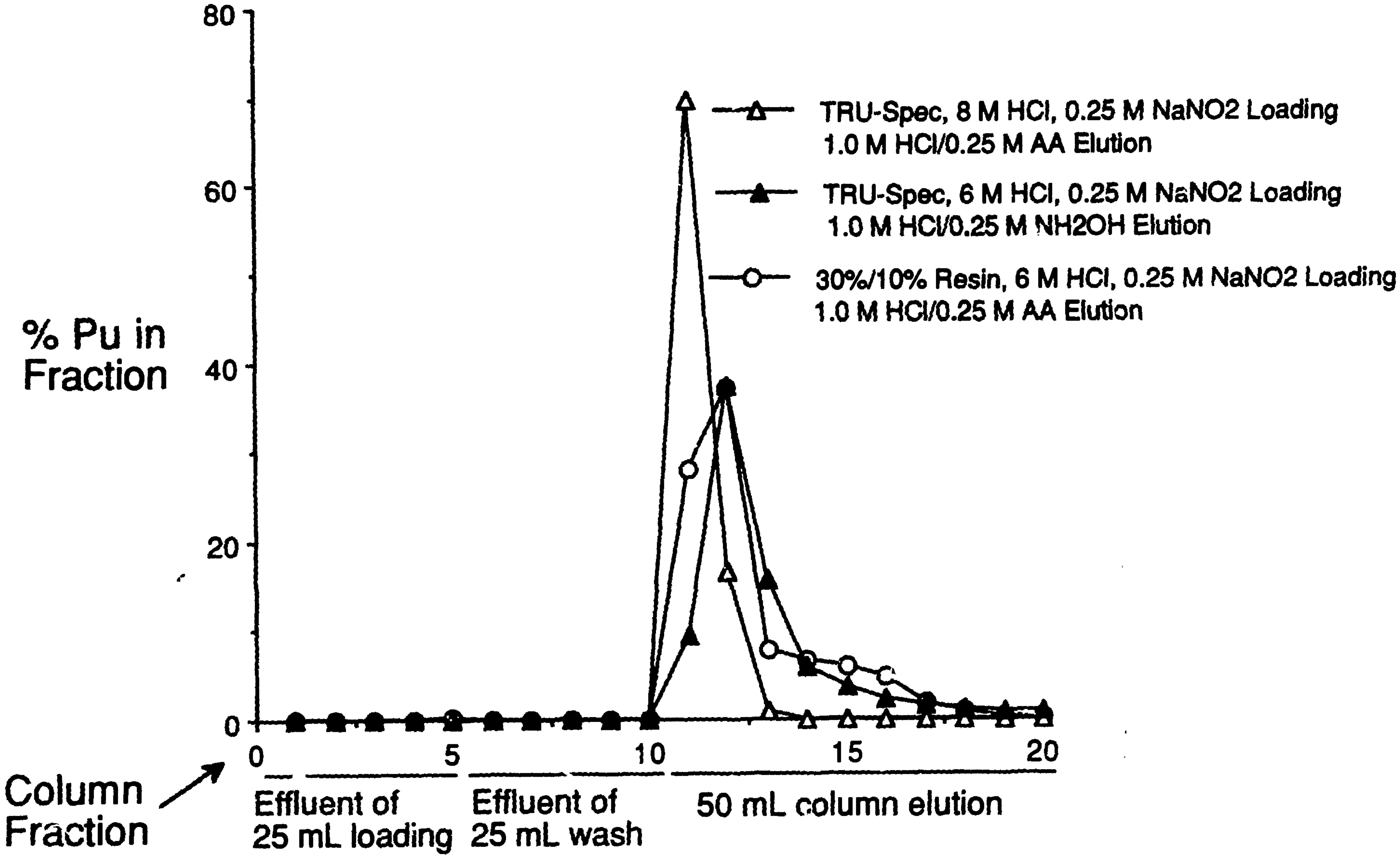

Figure 6 Pu(III) Behavior on Three Resins

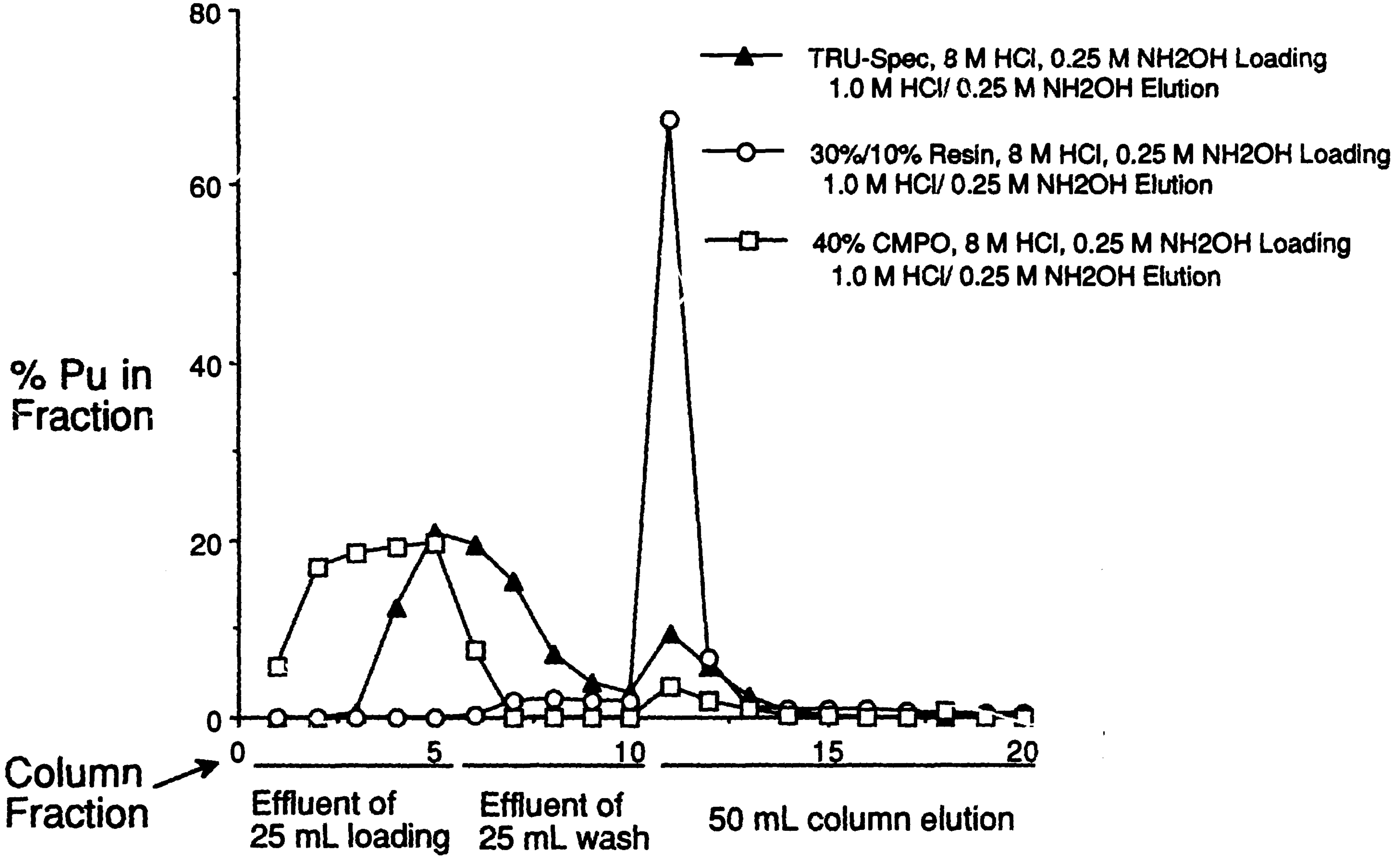

Figure 7

Am Behavior on TRU-Spec and 30%/10% CMPO/DAAP Resins