Separation of Uranium from Nitric- and Hydrochloric-Acid Solutions with Extractant-Coated Magnetic Microparticles

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ABSTRACT

The magnetically assisted chemical separation (MACS) process utilizes selective magnetic microparticle composites to separate dissolved metals from solution. In this study, MACS particles were coated with neutral and acidic organophosphorus extractants, *octyl*(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), and *bis*(2-ethyl-hexyl)phosphoric acid (D_2EHPA or HDEHP) and were evaluated for the separation of uranyl ions from nitric- and hydrochloric-acid solutions. The results suggest that a synergistic interaction between the particle surface and solvent coating may explain why the particles display, in some cases, orders of magnitude of higher partitioning coefficients than are estimated from solvent-extraction measurements. Particles coated with TBP and those coated with a combination of TOPO and D_2EHPA displayed the most desirable characteristics for removing uranium from dilute acid environments typical of contaminated groundwater. Uranium separation from moderate to highly acidic waste streams typical of Department of Energy (DOE) nuclear wastes is best accomplished using particles coated with a combination of CMPO and TBP.

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INTRODUCTION

The need for small, compact, and efficient technologies for the separation of high-level radioactive elements from process waste streams led to the development of the magnetically assisted chemical separation (MACS) process. This process utilizes magnetic microparticles coated with a selective extractant (e.g., solvent extractant or ion-exchange material) for the efficient recovery of dissolved transuranics, fission products, and hazardous species from acidic aqueous wastes. The process is well suited for separating target species from waste solutions typical of many DOE sites. The MACS process may also be used as a polishing step following the separation of target metals from concentrated solution (e.g., ore processing and other hydrometallurgy).

Major deterrents for many companies to actively practice waste reduction techniques are the inefficiency and significant associated costs of traditional recovery technologies. The development of these technologies such as solvent extraction, ion exchange, and membrane filtration has been extensive, and many industries are currently using them in successful waste-treatment programs. However, traditional separation technologies have certain limitations that preclude their universal use. For example, solvent extraction is only cost effective with concentrated waste streams (1). Also, solvent-extraction systems generate significant volumes of secondary waste (1). Ion-exchange processes suffer from lack of specificity compared to solvent extractants and from voluminous eluants (1). Precipitation techniques lack specificity and produce voluminous waste (1). Membrane-filtration technology lacks the chemical and mechanical durability necessary for many applications (1). The use of solvent-coated magnetic microparticles may bridge the gap in overcoming some of the limitations presented by current separation processes by combining specificity in extraction, simple design, durability, and increased extraction capabilities.

Previously, extractant-coated magnetic microparticles have been used for the separation of transuranics (2) and recovery of hazardous metals (3). One outstanding feature of the MACS process is the increased efficiency with which Am(III) and Pu(VI) are separated from acidic waste solutions. In such a case, the microparticles were coated with a mixture of *octyl*(phenyl)-N,N-di-isobutylcarbamoylmethylphosphine oxide (CMPO) and *tri-n*-butyl phosphate (TBP) (2). The partition coefficients were much higher than those expected from solvent extraction studies; it was conjectured that this effect was due to a synergistic interaction between the functionality of the particle surface and the coated extractant (3).

TBP has been used to extract uranium from acidic solution and TBP chemistry has been studied extensively (4). Other extractants studied for the separation of uranium include CMPO (5), *bis*(2-ethylhexyl) phosphoric acid (D_2EHPA or HDEHP) (6), and *tri-n*-octylphosphine oxide (TOPO) (7). This

paper represents an ongoing effort to investigate the capabilities and limitations of magnetic microparticles coated with selective extractants for the purification of dilute, radioactively contaminated waste streams. After a brief review of the UO_2^{2+} [or U(VI)] chemistry with respect to TOPO, D$_2$EHPA, and CMPO, experimental results from uranium partitioning onto magnetic microparticles coated with CMPO/TBP and TOPO/D$_2$EHPA will be discussed.

PARTITIONING OF URANIUM: A REVIEW

The chemistries of CMPO and the PUREX process extractant TBP have been studied extensively. This extractant combination has been implemented successively for use in the *Transuranic Extraction* (TRUEX) process developed by researchers at Argonne National Laboratory (ANL) (5). Small additions of TBP to CMPO mixtures increased the solubility and metal-nitrate-loading capacity of CMPO. These additives also improved transuranic distribution ratios (D_{TRU}) at high HNO$_3$, while decreasing those at low acidity (which facilitated stripping with dilute acid). The mechanism by which TBP interacts with CMPO is believed to be a solvent effect, and extraction of U(VI) with this combined system follows the formation of second-order complexes, $UO_2(NO_3)_2 \cdot 2CMPO$ solutions for HNO$_3$ and $UO_2Cl_2 \cdot 2CMPO$ for HCl solutions (8). At moderate nitrate concentration (3–5 M HNO$_3$) $D_{U(VI)} \approx 1000$, while uranium is stripped by using an aqueous-phase complexant.

Another example of a neutral organophosphorus extractant is TOPO. A compilation of the earlier work performed with TOPO in a solvent-extraction system was completed by White and Ross (7). From early studies with 0.1 M TOPO dissolved in cyclohexane, U(VI) was found to be extracted as the uranyl nitrate species, $UO_2(NO_3)_2$, from nitric acid. The partitioning is strong at <1 M HNO$_3$ and decreases at higher nitric-acid concentrations because of the competition for the extractant by nitric-acid concentration. The extraction kinetics are rapid, and the organic phase species is $UO_2(NO_3)_2 \cdot 2TOPO$.

A widely used acidic extractant for separation of rare earths and fission products is D$_2$EHPA (or HDEHP). It has been studied for the recovery of actinides from acidic solutions (6). Gureev et al. used 0.5 M D$_2$EHPA in isooctane to remove U(VI) from perchloric acid solutions and determined the following ion exchange reaction

$$UO_2^{2+} + 2\overline{(RO)_2POOH} \leftrightarrow \overline{UO_2[(RO)_2POO]_2} + 2H^+ \qquad (1)$$
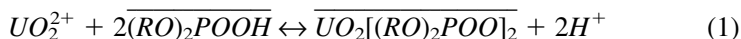
where R = 2-ethylhexyl chains. Gureev et al. also studied HNO$_3$ systems and found the extraction of U(VI) reduced systematically with increasing nitric-acid concentration, with a maximum of $D_{U(VI)} = 139$ at the most dilute acid tested (0.01 M HNO$_3$) and $D_{U(VI)} = 57$ at 8 M HNO$_3$ [organic-to-aqueous ra-

tio (O : A) of 1 : 1]. From slope analysis of $D_{U(VI)}$ as a function of acid concentration, the extraction in HNO_3 did not follow the pure ion-exchange mechanism suggested by Eq. (1), and this suggests that D_2EHPA is likely to extract $UO_2(NO_3)_2$ as a neutral extractant also.

Combining the two extractants, Hurst et al. (9) tested TOPO and D_2EHPA mixtures for uranium separation from phosphoric acid. The optimum solvent composition was 0.125 M TOPO and 0.5 M D_2EHPA dissolved in *n*-dodecane. The extraction kinetics were very rapid (<2 min) at 25°C, and extraction was highest at moderate phosphoric-acid concentration ($D_{U(VI)}$ = 180 in 2 M H_3PO_4), while effective stripping was conducted with 8 M H_3PO_4 ($D_{U(VI)}$ = 0.2).

EXPERIMENTAL

The TOPO was obtained from Cyanamid, Inc. (Cyanex 921), and the D_2EHPA and Gold label TBP were obtained from Aldrich Chemical Company. All were used without further purification. The CMPO was purified and recrystallized to greater than 99% purity (10). Nitric and hydrochloric acids were purchased as ACS grade from Baker Scientific. Experiments were conducted with tracer concentrations (~3 × 10^{-8} M) of uranium-233 obtained at ANL.

The magnetic microparticles (MagaCharc™) were purchased from Cortex Biochem, Inc. (San Leandro, CA) with a particle distribution averaging ~20 μm in diameter. The solvent-coating process has been described elsewhere (11). Typically, the particles were loaded to 3–10% by weight with the extractants (estimated by weight measurements). Test-tube experiments were conducted by contacting 3–5 mg of coated particles and 2 mL of aqueous solution, then vigorous mixing for 9–15 min as described previously (12). Aliquots were collected for alpha counting using a Packard 2200CA TRI-CARB liquid scintillation analyzer for the 4.78 MeV and 4.82 MeV alphas.

Radionuclide extraction was measured by the partitioning coefficient K_d. The partitioning coefficient was determined from the initial, c_i, and final, c_f, aqueous phase counts as

$$K_d = \frac{C_i - C_f}{C_f} \frac{V}{m} \tag{2}$$

where *V* is the volume of initial aqueous phase in milliliters and *m* is the mass of particles in grams. Typical volume-to-mass ratios were 2 mL : 0.003 g. These tests were performed in duplicate. The error associated with the data points was estimated at 10%. For solvent-extraction tests, the volume-based distribution ratio was used. The distribution ratio (D) was calculated, after preequilibration of the organic phase with the appropriate acid concentration,

from the ratio of equilibrium alpha activity

$$D = \frac{C_o}{C_a} \tag{3}$$

where C_o and C_a are the counts per minute in the organic and aqueous phases, respectively. Solvent extraction tests were conducted with single samples with periodic checks using duplicate samples. The error associated with such measurements was estimated at 5%.

To compare liquid–liquid solvent-extraction distribution coefficients and solid–liquid partition coefficients, a conversion factor was used. This conversion factor is based on transforming the partition coefficient into a dimensionless quantity by calculating the solvent volume contained on the mass of MACS particles used in an experiment. Specifically, the equivalent distribution ratio, D, is expressed as (units given in brackets)

$$D = K_d\left[\frac{mL}{g}\right] \times \frac{w_{tot}[g]}{w_x[g]} \times \rho\left[\frac{g}{mL}\right] = K_d\left[\frac{mL}{g}\right] \times \frac{100}{wt\%} \times \rho\left[\frac{g}{mL}\right] \tag{4}$$

where w_{tot} is the total mass of the prepared particles, w_x is the mass of the solvent coated onto the particles, and ρ is the density of the solvent. The ratio w_{tot} to w_x is the inverse of the fractional loading of the solvent and can be expressed in terms of mass percentage. The solvents are typically slightly less dense than water. Solvent loading onto the MACS particles is typically 3–15 wt% and most often <10 wt% based on mass gained by the particles following loading. This translates to a D value 3–30 times the partitioning coefficient value (in contrast, solvent-impregnated resins are conventionally loaded to greater than 25 wt%).

Uncoated particles were tested for U(VI) sorption from 0.1 to 8 M HNO$_3$ and HCl solutions. The K_d values were small in all cases (<15 mL/g).

The Generic TRUEX Model (GTM) (13) was used to calculate the hydrogen-ion mean activity coefficients based on the extended Debye-Huckel formulation of Bromley (14) and extensive experimental data.

RESULTS AND DISCUSSION

Nitric-Acid Solutions

TOPO-Solvent

A number of MACS particles were prepared with varying concentrations of TOPO dissolved in dodecane. The partitioning results for U(VI) are displayed in Fig. 1. The trend is apparent; the highest K_d values are obtained for the highest extractant concentration (1 M TOPO). At all extractant concentrations, the K_d rises slightly to a maximum at 1 M HNO$_3$ then decreases presumably be-
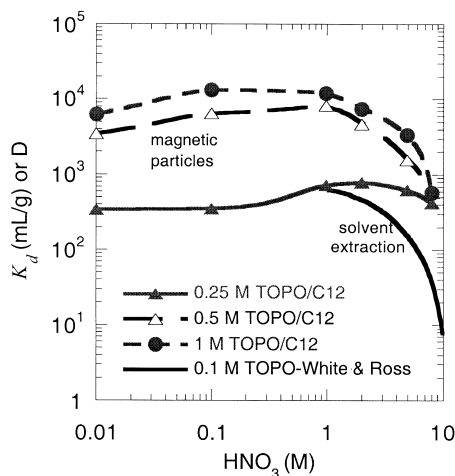
FIG. 1   Uranium(VI) partitioning as a function of nitric-acid concentration for particles coated with TOPO in dodecane (C12). Solvent extraction D values (7) were determined with 0.1 M TOPO in cyclohexane at room temperature, phase ratio of 1, and 10-minute mixing time.

cause of the co-extraction of nitric acid as determined by solvent extraction (7). The separation of U(VI) by MACS follows similar chemistry to solvent-extraction measurements (7).

D_2EHPA-Solvent

The effect of the D_2EHPA solvent was assessed by coating particles with 0.5 M D_2EHPA in dodecane and comparing the results to solvent-extraction measurements (Fig. 2). Compared to the solvent-extraction results, the K_d values for the MACS particles display a greater sensitivity to the nitric-acid concentration, dropping two orders of magnitude, from 64,000 to 514 mL/g, over the nitric-acid range studied. At low nitric-acid concentration, the pH dependence on extraction should follow Eq (1) with a slope of two on a K_d versus pH plot. The pH was calculated based on the activity of nitric acid using the GTM model. According to this exercise, the curve for MACS particles displays a slope of 0.7, indicating a departure of the measurements from theory. However, this is not completely unexpected. Similar results were described in solvent extraction studies (6) and are evident by the slight pH dependence shown in Fig. 2 for solvent-extraction data obtained here and by Gureev et al. (6).

TOPO/D_2EHPA-Solvent

Figure 3 shows the partitioning of U(VI) from 0.01 M HNO$_3$ with particles coated with various concentrations of TOPO and 0.5 M D_2EHPA dissolved in
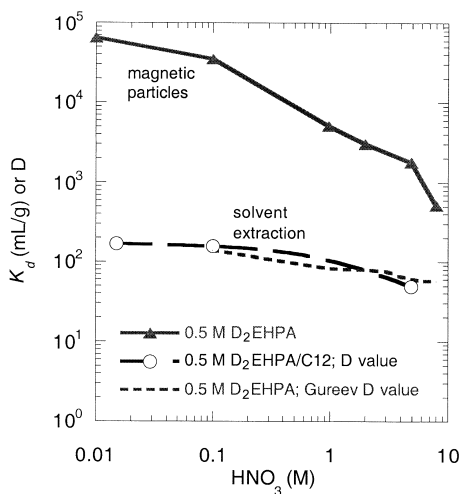
FIG. 2   Uranium(VI) partitioning as a function of nitric acid at 25°C for particles coated with 0.5 M D_2EHPA. Solvent extraction measurements from Gureev et al. (6) were conducted with 0.5 M D_2EHPA in isooctane at 20°C and a phase ratio of 1. Solvent extraction measurements were conducted with 0.5 M D_2EHPA in dodecane (C12) at 25°C.

FIG. 3   Partitioning of U(VI) as a function of TOPO concentration in 0.1 M HNO_3 at 25°C. Particles were coated with TOPO and 0.5 M D_2EHPA (solid circles). Data modified from Fig. 1 shows the trend when D_2EHPA is absent (open circles).
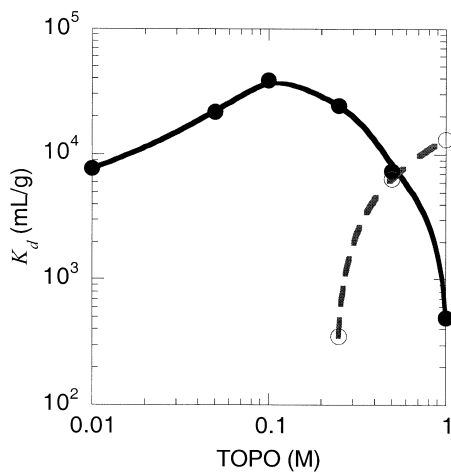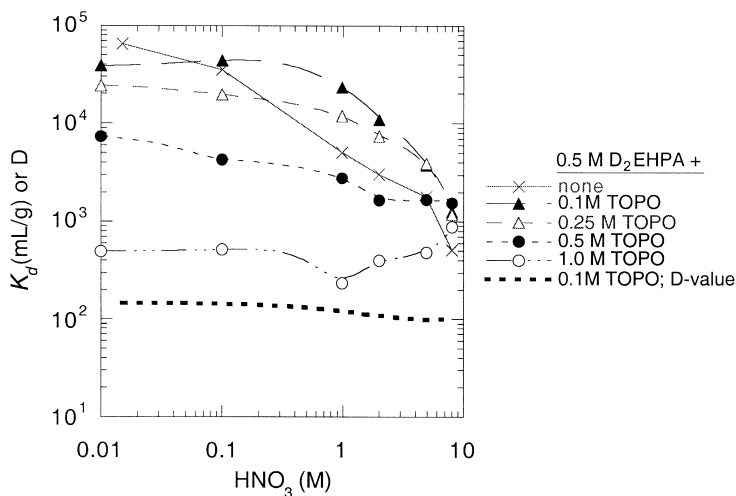
FIG. 4   Uranium(VI) partitioning as a function of nitric-acid concentration at 25°C for particles coated with TOPO and 0.5 M D$_2$EHPA. The data from MACS particles coated with 0.5 M D$_2$EHPA alone are provided for comparison. We also conducted solvent extraction experiments (D values) with 0.1 M TOPO and 0.5 M D$_2$EHPA in dodecane (O : A = 1 : 1).

dodecane. The highest extractions obtained with the MACS particles are with 0.1 M TOPO and 0.5 M D$_2$EHPA.

Figure 4 displays the partitioning of uranium as a function of the nitric-acid concentration for particles coated with 0 to 1.0 M TOPO and 0.5 M D$_2$EHPA. The lack of nitric-acid dependence is clear for particles coated with the most concentrated extractant solution (1.0 M TOPO/0.5 M D$_2$EHPA). At low nitric-acid concentration, the effect of the TOPO is measurable. The particles coated with the more dilute TOPO concentration displayed the highest extraction of U(VI), with the curves showing a progressive decrease in extraction efficiency with increasing acidity.

To compare this trend more directly, we conducted solvent extraction measurements. The solvent extraction measurements using 0.1 M TOPO and 0.5 M D$_2$EHPA in dodecane did not show a drop in partitioning at high nitric acid. This drop at high acid concentration had been reported previously with TOPO (7, 15) and had been attributed to the co-extraction of the mineral acid by TOPO. Instead, solvent extraction using a combination of TOPO and D$_2$EHPA shows that the extraction of U(VI) is nearly constant throughout the acid range, similar to the solvent–particle trend for the highest solvent loading (1.0 and 0.5 M TOPO/0.5 M D$_2$EHPA). Also, the solvent extraction with the 0.1 M TOPO/0.5 M D$_2$EHPA mixture offers D values similar to those for the 0.5 M D$_2$EHPA solvent extraction system alone (see Fig. 2). This similarity

in extraction behavior between the two systems is unresolved but may be due to a combination of D_2EHPA extraction at high acidity, to diluent effects, or to the solvation of TOPO by D_2EHPA.

The use of MACS particles with a combination of TOPO and D_2EHPA produced interesting effects. The partitioning of U(VI) was reduced at low acidity and augmented at high acidity compared to D_2EHPA-coated particles alone. The coated magnetic-particle system displayed a synergism *between the sorbed extractants* TOPO and D_2EHPA at high nitric-acid concentrations. For 0.1 M TOPO : 0.5 M D_2EHPA the synergism occurs at > 0.1 M HNO_3, whereas for 0.25 M TOPO : 0.5 M D_2EHPA it occurred at > 0.3 M HNO_3. At dilute nitric-acid concentrations (0.015 M), the particles coated with D_2EHPA extracted more efficiently. Thus, the addition of TOPO has an important effect in that it reduces the acid dependence on extraction at low acidity, even with small additions of TOPO. At an acid concentration of almost 10 M there appears to be little difference between any of the systems tested.

An attempt was made to quantify this synergism between TOPO and D_2EHPA, which is dependent on the HNO_3 concentration. The approach is based on the following relationship (16):

$$S = \frac{K_{d,TOPO+D_2EHPA}}{K_{d,TOPO} + K_{d,D_2EHPA}} \tag{5}$$

where $S > 1$ indicates a synergistic effect, and $S < 1$ is indicative of an antagonistic effect. Table 1 displays the values of this synergistic contribution for particles coated with 0.1 to 1.0 M TOPO and 0.5 M D_2EHPA. Only in small amounts (0.1 and 0.25 M TOPO) and in moderately acidic solution (>0.1 and >1.0 M HNO_3, respectively) does the addition of TOPO increase the uranium extraction capabilities significantly. The greatest synergism occurs with 0.1 M TOPO-coated particles at 0.98 M HNO_3 ($S = 4.6$). The an-

TABLE 1
Synergistic Factors for TOPO and 0.5 M D_2EHPA for the Extraction of U(VI) with MACS Particles

| HNO$_3$ (M) | S values at different TOPO concentrations | | | |
	0.1 M	0.25 M	0.5 M	1.0 M
0.01	0.6	0.37	0.11	0.01
0.1	1.3	0.55	0.10	0.01
0.98	4.6	2.0	0.21	0.01
2.0	3.6	1.9	0.21	0.04
4.9	2.1	1.6	0.50	0.09
8.0	2.4	1.3	1.4	0.81

tagonistic effect is most marked in dilute acid and high concentrations of TOPO. With 1.0 M TOPO the antagonism is strong throughout the nitric-acid concentration range.

TBP and CMPO System

Figure 5 shows the partitioning data for MACS particles coated with 0.5 M TBP dissolved in dodecane and for various solvent-impregnated support materials. In general, the trends for Levextrel-TBP resins (17), 48 wt% TBP in dichloroethylene (DCE) (18), and macroporous styrene divinylbenzene resins with 17.8 wt% TBP (18) are similar but have different magnitudes. Partitioning of U(VI) onto these systems is highlighted by a second-order dependence on nitric-acid concentration, the D value reaching a broad peak in separation at ~8 M HNO$_3$. The MACS particles coated with 0.5 M TBP in dodecane demonstrated a small acid dependence on partitioning below 2 M HNO$_3$. At higher concentrations of nitric acid, the extraction is lowered with increasing concentration. In comparing the MACS particles to the other systems, we found the MACS particles partition greater than an order of magnitude higher

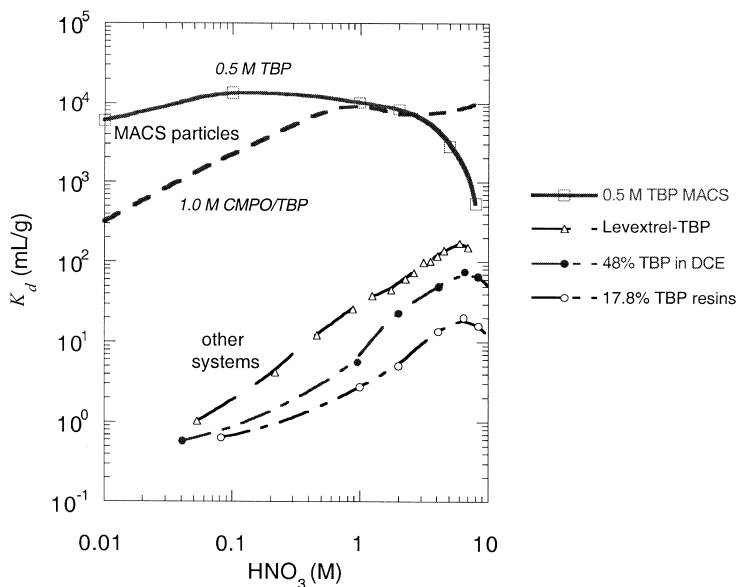FIG. 5   Uranium partitioning as a function of nitric acid for magnetic particles coated with 0.5 M TBP at 25°C. The trend with magnetic particles coated with 1.0 M CMPO/TBP is shown for comparative purposes. Experimental data were obtained from Levextrel-TBP resins (17), solvent extraction using 48 wt% TBP in dichloroethane (DCE) (18), and resins with 17.8 wt% sorbed TBP on styrene divinylbenzene copolymer (18).
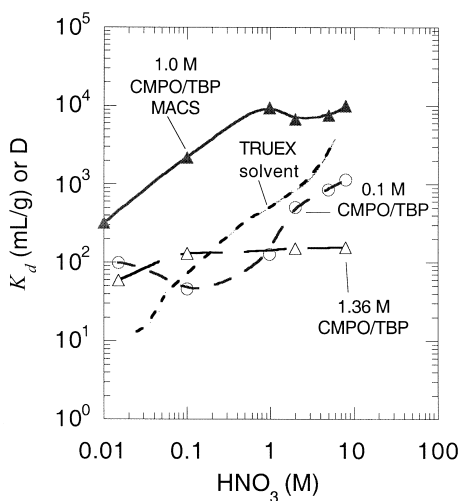
FIG. 6   Partitioning of U(VI) onto magnetic particles coated with CMPO/TBP at 25°C. Solvent extraction experimental data were obtained with the TRUEX solvent, 0.2 M CMPO–1.2 M TBP-dodecane (20), and 1.36 M CMPO in TBP at 25°C.

at 4.9 M HNO_3 and greater than four orders of magnitude higher at 0.1 M HNO_3. This is an extraordinary finding, considering that blank tests with un-coated particles displayed low separation capabilities, $K_d = 14$ mL/g at 1 M HNO_3, and $K_d = 7$ mL/g at 8 M HNO_3.

The effect of CMPO additions to TBP-coated particles is similar to that determined by solvent extraction data (19). At low nitric-acid concentration, the partitioning of U(VI) onto the particles coated with 1.0 M CMPO : TBP is reduced, and partitioning is increased at high nitric-acid concentrations (>2 M) compared to particles coated with 0.5 M TBP alone (see Fig. 5). A portion of these data is displayed in Fig. 6 along with data from additional experiments. With only 0.1 M CMPO dissolved in TBP, the partitioning of U(VI) was dramatically reduced except at the most concentrated nitric acid tested, when compared to the TBP-particle data presented in Fig. 5. The particles coated with 1.0 M CMPO : TBP demonstrate similar extraction trends, at low nitric-acid concentrations, to the TRUEX solvent. Analysis of K_d versus CMPO concentration reveals a slope of 0.74 but, in this instance, this may not be an accurate method of analysis. Horwitz et al. (19, 20) found that at concentrations above 0.1 M, CMPO begins to aggregate as a result of intermolecular hydrogen bonding and possibly dipole–dipole interaction, thereby reducing its activity coefficient. At >1 M HNO_3 the acid dependency is lost. This loss of sensitivity is also demonstrated by solvent extraction with 1.36 M CMPO dis-

solved in TBP. This may be explained by the coextraction of the mineral acid by the CMPO as found by others (7).

Hydrochloric-Acid Solutions

TOPO/D$_2$EHPA Solvent

The partitioning behavior of U(VI) in hydrochloric acid has been studied. Figure 7 summarizes the results. The partitioning of U(VI) as a function of hydrochloric-acid concentration for particles coated with varying concentrations of TOPO (0.1–1.0 M) and 0.5 M D$_2$EHPA is shown. The curves have a shape similar to that for the separation of U(VI) from nitric-acid solutions, where a dependence on the hydrochloric-acid concentration is only apparent at high concentrations and low TOPO concentrations. Particles coated with 0.1 M TOPO : 0.5 M D$_2$EHPA extracted most strongly. The K_d ranged from a high of 67,000 mL/g at 0.01 M HCl and a low of 380 mL/g at 4.9 M HCl, a decrease by greater than two orders of magnitude. At 5 M HCl, the K_d was 390 mL/g and independent of the TOPO concentration for 0.1, 0.25, and 0.5 M TOPO. The MACS particles coated with 1.0 M TOPO : 0.5 M D$_2$EHPA displayed low partitioning, <200 mL/g for all acidity.

Solvent extraction measurements are displayed in Fig. 7 as well and are expressed with distribution ratios. The experimental data are presented to com-
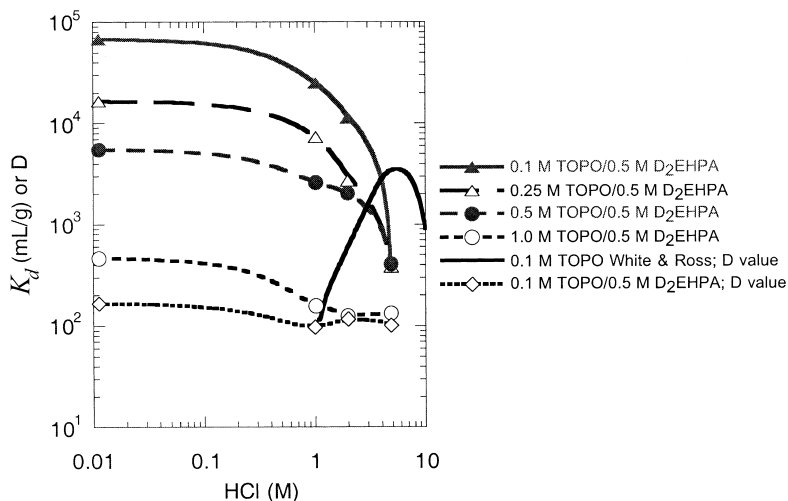

FIG. 7   Uranium(VI) partitioning as a function of hydrochloric-acid concentration for particles coated with TOPO and 0.5 M D$_2$EHPA. Solvent extraction measurements were conducted with 0.1 M TOPO and 0.5 M D$_2$EHPA in dodecane at 25°C, phase ratio of 1, and 9-minute mixing time. Solvent extraction reported by White and Ross (7) was conducted at 25°C.

TABLE 2
Partitioning of U(VI) onto Particles Coated with
1.2 M CMPO in TBP from Hydrochloric-Acid
Solution

HCl (M)	K_d	D^a
0.01	700	—
1.0	4160	700
2.0	7680	5100
4.9	4190	34260

[a] Distribution ratios are for 0.5 M CMPO in TCE (8).

pare the effect of adding D_2EHPA to TOPO-coated MACS particles. The solvent-extraction data of White and Ross (7), using 0.1 M TOPO in cyclohexane, show that the distribution ratio has a second-order dependence on the hydrochloric-acid concentration, suggesting the extraction of the neutral dichloride salt of uranium until high acidity, where co-extraction of the acid becomes important. The optimum concentration for extraction is 5–7 M HCl where D = 3800. However, our distribution ratio measurements do not show the hydrochloric-acid dependence reported by White and Ross, which indicates the effect of D_2EHPA or dodecane diluent on extraction. The lack of hydrochloric-acid dependence for the TOPO/D_2EHPA solvent extraction measurements in hydrochloric acid is similar to previous results on nitric-acid systems (see Fig. 4).

CMPO/TBP Solvent

The partitioning of U(VI) from hydrochloric acid solutions was evaluated with particles coated with 1.2 M CMPO diluted in TBP. The results are presented in Table 2 and are compared to the results of the TRUEX-Chloride process, which uses 0.5 M CMPO solution in tetrachloroethylene (8). The magnetic particles separate U(VI) with increasing efficiency up to a maximum at about 2 M, where K_d = 7680 mL/g. At higher nitric-acid concentrations, the partitioning is decreased. This behavior contrasts with that of the TRUEX-Chloride process where D_U increases as the hydrochloric-acid concentration increases up to 4.9 M in HCl.

CONCLUSIONS

This synopsis of the HNO_3 and HCl-acid dependence on U(VI) extraction reveals that MACS particles function similarly to expected solvent extraction

chemistry at first glance. The MACS particles display similar general trends in extraction but at somewhat different acid dependency (i.e., slopes on a K_d versus acidity plot). Figure 5 is a pronounced indication of this as acid dependency below 1 M HNO_3 is depressed in the MACS particles coated with TBP as opposed to other TBP resins. This dissimilarity suggests a significant interaction between the particle surface and the sorbed extractant. This interaction results in an increase in the partitioning of U(VI) onto the particles beyond what is calculated by purely solvent extraction chemistry of the extractants. Table 3 provides a comparison of the data. The table gives the equivalent distribution ratios, D_{eq}, from the partition-coefficient measurements at selected acid concentrations and the solvent extraction distribution values, D_{sx}. Using the solvent concentration, the conversion factor (100/wt%·ρ) is experimentally estimated as 10 g/mL for 0.1 M TOPO : 0.5 M D_2EHPA systems and 3 g/mL for 1.0 M CMPO/TBP systems. The D_{eq} values are much higher than those of D_{SX} by up to three orders of magnitude.

Although this synergistic interaction cannot be fully explained, it may be a result of the activation or participation of the acrylamide polymer of the particle surface with the sorbed extractants. This type of synergistic interaction, a result of the different functionality of the particle surface material and the sorbed extractant, has been studied previously (21, 24). Further evidence is provided from previous experiments (22) where solvent loaded styrene-divinylbenzene, dextran, and polyacrolein-based particles displayed poor K_d for Am(III) ($K_d < 100$ mL/g) compared to what the polyacrylamide particles

TABLE 3
Summary of Partitioning Data and Equivalent Distribution Ratios for Systems Presented in this Paper

Acid	Particle coating	K_d	D_{eq}	D_{sx}
0.01 M HNO_3	0.1 M TOPO/0.5 M D_2EHPA	38,700	387,000	145[b]
8.0 M HNO_3	0.1 M TOPO/0.5 M D_2EHPA	1,260	12,600	101[b]
0.01 M HNO_3	0.5 M D_2EHPA	64,400	644,000	170
4.9 M HNO_3	0.5 M D_2EHPA	1,790	17,900	49
1.0 M HCl	0.1 M TOPO/0.5 M D_2EHPA	24,900	249,000	115[a]
				97[b]
4.9 M HCl	0.1 M TOPO/0.5 M D_2EHPA	380	3,800	3,500[a]
				101[b]
1.0 M HNO_3	1.0 M CMPO/TBP	9,440	28,320	530[c]
4.9 M HNO_3	1.0 M CMPO/TBP	7,600	22,800	2,450[c]

[a] Using 0.1 M TOPO in cyclohexane (7).
[b] From our experiments using the solvent mixture in dodecane.
[c] From Schulz and Horwitz (20).

have shown ($K_d > 3000$ mL/g). The implications are that less particle material is necessary to obtain a better separation or recovery than is possible with solvent extraction with these extractants at the low concentrations of uranium present, as is the case for many DOE waste streams and contaminated waters, such as tailings runoff or contaminated groundwater.

In an engineering system, the large K_d values translate into lower particle-to-volume ratios, while achieving desired extraction efficiency over solvent extraction for contaminated feeds such as groundwaters, DOE liquid radioactive wastes, or in "polishing" industrial effluents for free release. The challenge with the behavior demonstrated by the magnetic particles is the requirement for more aggressive stripping techniques. Although there is very little doubt that the diphosphonic acids (e.g., 1-hydroxyethane-1,1-diphosphonic acid) would function very effectively as stripping agents (23), additional alternatives are being investigated. In preliminary experiments, a combination of sodium carbonate and oxalic acid recovered 82% of the uranium in the strip, for a volume reduction of a factor of 100 over the original feed. Over 99% recovery of actinides from particles coated with CMPO/TBP by stripping with ethanol has also been achieved, essentially by dissolving the extractant coating off the particles. However, this type of stripping is economically questionable for practical application. Ongoing work is addressing the stripping methodology and loading capacity for these MACS systems.

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