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SORPTION CAPACITY OF FERROMAGNETIC MICROPARTICLES COATED WITH CMPO

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ABSTRACT

Magnetically assisted chemical separation (MACS) was developed at Argonne National Laboratory as a compact process for reducing the volume of high-level aqueous waste streams that exist at many U.S. Department of Energy sites. In the MACS process, ferromagnetic particles coated with solvent extractants are used to selectively separate transuranic nuclides and heavy metals from aqueous wastes. The contaminant-loaded particles are recovered from the waste stream by using a magnet. For the recovery of transuranic species the extractant used is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP). To better understand the extraction chemistry of this solvent/particle system, europium was used to monitor the sorption capacity of the MACS particles for lanthanides and actinides. Europium concentrations varying from $10^{-7}\underline{M}$ to $10^{-1}\underline{M}$ were prepared with $3\underline{M}$ $NaNO_3$ in $0.1\underline{M}$ HNO_3. Neutron activation analysis was used to measure the concentration of europium. The sorption capacity was evaluated, along with the sorption isotherms to simulate multiple contact stages. The maximum absorption capacities obtained was 0.62 mmol/g. The adsorption models of Langmuir and Freundlich and the extended Langmuir model of Brunauer, Emmett, and Teller (BET) were fitted to the data. The best correlations were obtained from the Langmuir and BET models, a result that supports a monolayer adsorption mechanism. The Langmuir and BET models suggested a loading capacity of 0.33 mmol/g and 0.25 mmol/g, respectively. The Freundlich model results support favorable metal loading with a 1/n value of 0.3.

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INTRODUCTION

Argonne National Laboratory (ANL) has been involved in developing processes for the treatment of a variety of radioactive and hazardous tank sludge or supernatant. Transuranic (TRU) waste is of considerable concern, because of the long half-lives of its TRU constituents.

Nuclear fuel reprocessing and nuclear weapons production have generated waste solutions containing low concentrations of long-lived radioisotopes such as the TRU elements in high-level liquid waste (HLW). Removing the TRU elements from these wastes would greatly reduce the volume of HLW requiring disposal, thus reducing disposal costs. The U.S. Department of Energy was interested in developing compact, efficient processes for removing low concentrations of TRU species. The Magnetically Assisted Chemical Separation (MACS) Program was initiated to address this need.

The MACS process utilizes the selectivity afforded by solvent extractants and magnetic separation to provide more efficient chemical separation of TRU radionuclides and heavy metals. Ferromagnetic microparticles are coated with octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) dissolved in tri-n-butyl phosphate (TBP). These coatings, by their chemical nature, selectively separate TRU nuclides onto the particles. The contaminant-loaded particles are recovered from the waste stream by using a magnet. The advantages of the MACS process are the simplicity of its design, its fast reaction kinetics, and the availability of copious amounts of data on CMPO-based extraction systems (i.e., the TRUEX process)(1).

The MACS process has been evaluated for recovery of low concentrations of TRU species from nitric and hydrochloric acid solutions and from various simulant waste solutions. This early work revealed that the extraction of TRU species was much higher than would be expected from traditional solvent extraction (i.e., from a TRUEX process for similar CMPO concentrations). The partitioning coefficients were consistently large for a variety of acid systems and simulant solutions. This was especially apparent considering the extremely low equivalent organic-to-aqueous O/A ratios of the process (2).

The unexpected partitioning results of the earlier MACS studies initiated research into the extraction chemistry of the process. The focus of this study was to investigate the CMPO/TBP sorption mechanism of the MACS process for TRU removal. The emphasis was specifically directed at performing loading experiments to determine the sorption isotherms and sorption capacity of the microparticles for TRU species. Neutron activation analysis (NAA) was chosen as the analysis technique because it offers low detection limits with reliable precision.

MACS Process Description and Design

The MACS process is detailed in previous studies (2). The design goals were compact equipment, modular operation, and a minimum of mechanical features (to reduce maintenance). The result was a magnetically fluidized bed design. Magnetically stabilized fluidized beds have been used in chromatographic separations (3,4). For the MACS process the fluidized bed (currently a preliminary design, awaiting construction for hot testing) will be used to contact extractant-coated ferromagnetic particles with actinide radioisotopes in solution. Figure 1 shows the magnetically fluidized bed designed for laboratory studies that has a hold-up volume of 10 L. The bed would operate in a countercurrent fashion, with the waste solution entering the column from the bottom and the magnetic microparticles entering from the top. The particles can be pulsed as they descend through the column to promote mixing. The actinide elements are extracted by the CMPO/TBP sorbed on the magnetic microparticles. Waste solution can be pumped into the bottom of the column to disperse and fluidize the MACS particles.

Extensive research and development was done to optimize the MACS process (2). Extraction behavior was measured for many particle types and a variety of acid and simulant waste solutions. The chemical and radiolytic durabilities of the particles were also tested, as well as the stripping efficiency (5). The partitioning coefficient (K_d) was measured for various concentrations of nitric acid. The K_d values for Am and Pu increase slowly with increasing HNO_3 concentration, reaching peaks of 1,500 mL/g at 2$\underline{M}$ HNO_3 for Am and 13,000 mL/g at 5$\underline{M}$ HNO_3 (2). Temperature-dependence tests showed that K_d was affected negligibly between 10 and 50° C.

Partitioning Behavior for Simulated Waste Streams

In that earlier work, the MACS particles were tested for efficiency of extraction from acid solutions and simulant waste streams from Plutonium Finishing Plant (PFP), Idaho Chemical Processing Plant (ICPP), Hanford single shell tank (SST), and Cs-bearing Hanford SST (Table 1).

The partitioning coefficients suggest that the MACS process can effectively treat a wide variety of waste streams. The extraction of TRU from nitric acid systems is well documented (1). Also, for solutions with high Cl^- activity a large K_d was obtained, as in previous studies of the TRUEX solvent (6). For PFP waste simulants, the extraction of plutonium was high (K_d = 18,000 mL/g). Results were excellent for the Cs-bearing SST waste and for the SST supernatant. Although many waste streams were effectively treated, certain waste streams that contained significant concentrations of rare earth salts, such as the ICPP and SST dissolved sludge presented problems in efficient extraction.

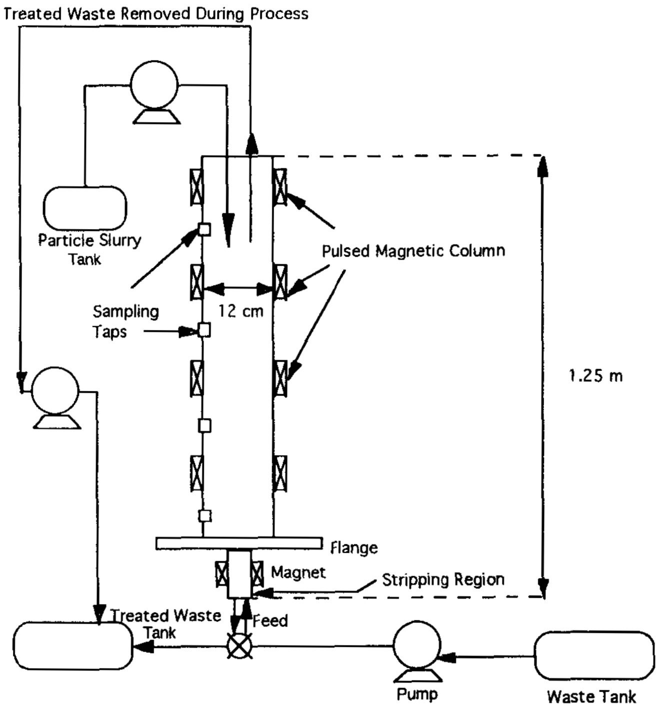

FIGURE 1. Process diagram for MACS fluidized bed.

This study focuses on the loading capacity of the coated microparticles for multiple extraction stages. This is important since the process conceptual design offers the option of multiple contacts using a semicontinuous countercurrent flow system. A series of tests have been completed using various concentrations of contaminant in a high-salt solution to promote loading. Europium was chosen as the contaminant to simulate the extraction behavior of all rare earths and americium and because of its extremely low detection limits using NAA.

EXPERIMENTAL

Reagents and Equipment

The nitric acid used was ULTREX® II Ultra pure reagent nitric acid. Deionized water was obtained from the laboratory supply. The salts used were reagent-grade sodium nitrate and

TABLE 1. PARTITIONING COEFFICIENTS (K_d) AND DISTRIBUTION RATIOS (D) FOR ACTINIDE SEPARATION IN ACID AND SIMULANT WASTE SOLUTION

Tracer	Particle Coating	HLW Simulant	K_d, mL/g	D[a]
Am	1.2M CMPO	2M HNO_3	4000-5000	1700
Pu	1.2M CMPO	2M HNO_3	65,000	-
Pu	1.0M CMPO	2.0M HCl	10	-
Pu	1.0M CMPO	5.0M HCl	560	-
Pu	1.0M CMPO	8.0M HCl	26,000	1600
Pu	1.0M CMPO	PFP	18,000	1400
Am	0.58M CMPO	ICPP	<6	-
Pu	1.2M CMPO	SST Cs Supernatant	20,000	-
Am	1.5M CMPO	SST Dissolved Sludge	2	-
Pu	1.0M CMPO	SST Dissolved Sludge	2400	-
Pu	0.58M CMPO	SST Supernatant	14,000-40,000	8800

[a] Distribution ratio at 1:1 O:A at same CMPO concentration.

99.99% europium(III) nitrate hexahydrate. Solutions were pipetted using a calibrated Gilson Pipetman. Deionized water and reagent-grade ethanol were filtered through a Anatop 0.02 μm filter prior to use. The CMPO was purified and recrystallized to greater than 99% purity (7). Aldrich Chemical Company Gold label TBP was used.

Solution Preparation

Solutions prepared were 3M $NaNO_3$ and $Eu(NO_3)_3$ in 0.1M HNO_3. The europium concentrations were 0.1, 10^{-3}, 10^{-5}, and 10^{-7}M. The europium concentrations for all samples were determined using neutron activation analysis. The CMPO was dissolved in TBP to a concentration of 1.2M.

Particle Preparation

The MACS particles have an average diameter of 25 μm and consist of 1:1:1 cross-linked N,N-methylene bis-acylamide, iron oxide, and charcoal (Cortex Biochem, Inc.). The particles were washed with deionized water several times to eliminate preservatives and additives, then dried and weighed. Next, ethanol was used to disperse the particles and act as a volatile diluent for the coating. For every 1 g of particles, 4 mL of 1.2M CMPO/TBP solvent was added. The particles were dispersed using an ultrasonic bath, dried in a rotoevaporator at 80-100°C, and heat-treated at 120°C for 39 h. During the heat treatment, it was evident that not all the solvent was coated onto the particles. The data indicated a mass gain of less than 0.8 g from the addition of 4 mL of solvent and subsequent heat treatment.

Neutron Activation Analysis

Instrumental neutron activation analysis is a well-accepted technique capable of determining 30 to 40 elements. This technique can also determine major elements such as sodium, chlorine, and potassium, as well as many rare earth elements. Activation analysis measures the total amount of an element in a material without regard to chemical or physical form. It has the following advantages: (1) samples can be liquids, solids or powders; (2) it is nondestructive, and since no prechemistry is required, reagent-introduced contaminants are completely avoided; (3) it is a multielemental analytical technique in which many elements can be readily analyzed simultaneously; and (4) it is sensitive to trace elements. These factors have reduced the detection limits of most elements of interest to very low levels, not readily achievable by other analytical techniques. Neutron activation analysis is also totally unaffected by the presence of organic material in the sample, a significant problem in many types of conventional chemical methods.

For greatest sensitivity, the monitoring of europium is usually performed using the 841.6 keV photon from ^{152m}Eu with a 9.35 hour half-life. However, the high sodium content in the samples used in this study forced the use of long-lived counting. Therefore, the 1407.5 keV photon from ^{152}Eu with a 12.2 year half-life was used for these experiments. The activation reaction of natural ^{151}Eu follows from the absorption of a thermal neutron,

$$^{151}Eu + n \rightarrow {}^{152}Eu + \gamma \qquad \text{(Eq. 1)}$$

with a cross-section of 5900 barns.

Irradiations. Irradiations were performed at the University of Illinois 1.5 MW TRIGA Reactor, and all counting was done in the NAA laboratory at the UIUC. The solutions were irradiated for periods from 15 seconds (for the 10^{-1} M Eu tests) to 9 hours (for the 10^{-7} M Eu tests). Samples were allowed to decay at least two weeks prior to counting.

Detection System. The γ-ray detection system utilizes a high-purity germanium detector in conjunction with an ORTEC ADCAM PC based multichannel analyzer. The detector has an 18% relative efficiency with an energy resolution of 1.9 keV for a 1332-keV photopeak of ^{60}Co. For all counting times the 1408-keV background levels were below detection limits. This type of counting system has been used with much success (8).

Quality Control. Europium elemental calibrations were established using the NIST-certified single-element solution with a europium concentration of 10.00±0.03 mg/mL and diluted when appropriate. Flux monitors were included with all samples. For quality control, NIST SRM 1632a and 1632b (trace elements in coal) were placed into each batch of samples.

Sorption and Loading Procedure

A constant weight of 3 mg of dried microparticles was tested in triplicate[1]. First, 2 mL of europium stock solution was pipetted into each test tube. The tubes were placed in an ultrasonic bath to promote particle dispersion. The samples were mixed vigorously, centrifuged, and placed on a magnetic rack. With the particles drawn to one side of the tube by the magnet, the supernatant was withdrawn, irradiated, and gamma counted. These steps constituted one contact stage. Next, 2 mL of fresh stock solution was added to the previously contacted particles to initiate the second contact stage. Twenty stages were completed for the $10^{-5}\underline{M}$ europium solutions and 10 stages each for the, 10^{-7}, 10^{-3}, and $10^{-1}\underline{M}$ europium solutions.

Adsorption Models

Adsorption isotherms were determined for the solutions tested, and three models were applied to the curves: the Freundlich model, the Langmuir model, and the extension of the Langmuir model developed by Brunauer, Emmett, and Teller (BET) (9). The Freundlich model is an empirical formulation while the Langmuir and BET models are derived mechanistically.

The Freundlich equation (Eq. 2) is expressed as

$$a_e = K_F C_e^{1/n} \qquad \text{(Eq. 2)}$$

where a_e is the amount of solute adsorbed per unit weight of adsorbent, C_e is the residual liquid phase concentration, and K_f and 1/n are characteristic constants which are determined. The quantity K_f is the relative indicator of adsorption capacity. The quantity 1/n represents the intensity of the reaction, with a value less than one indicating favorable adsorption.

The Langmuir model is a theoretical approach that was originally applied to gas adsorption onto solids but which can also be related to the K_d relationship. This model assumes that adsorption energy is constant independent of surface coverage, that adsorption occurs at local

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[1] Stages 10-20 for the $10^{-5}\underline{M}$ Eu tests were conducted in duplicate. The $10^{-7}\underline{M}$ Eu tests were conducted with single samples.

sites without interaction between adsorbate molecules, and that a monolayer of adsorbate cover produces the maximum adsorption. This model is expressed as:

$$a_e = \frac{Q^\circ b C_e}{1 + bC_e} \qquad \text{(Eq. 3)}$$

where Q° is the limiting adsorption capacity and b is related to the enthalpy of adsorption.

The Langmuir model was extended to include multilayer adsorption by Brunauer, Emmett, and Teller. The BET equation (Eq. 4) is expressed as

$$a_e = \frac{BC_eQ^\circ}{(C_e - C_s)\left[1 + (B-1)\left(\frac{C_e}{C_s}\right)\right]} \qquad \text{(Eq. 4)}$$

where C_S is the solubility limit of the solute and B is related to the energy of adsorption. The premise for this formulation was that the first layer need not be covered before sites in additional layers are occupied.

RESULTS AND DISCUSSION

The extraction efficiency was monitored using K_d, a ratio of the amount of the contaminant on the particles per unit mass of particles to the amount of contaminant per total volume of contact solution. Equation 5 was used to calculate K_d values:

$$K_d = \left(\frac{C_i - C_f}{C_f}\right) \times \frac{V}{m} \qquad \text{(Eq. 5)}$$

where C_i is the initial activity per mL of solution prior to treatment, C_f is the final activity per mL of solution after treatment, V is the volume of solution in mL used in the contact, and m is the mass of particles in grams.

The data from the 10^{-1}M Eu tests was widely scattered among the triplicate samples. This suggested that the solubility limit had been exceeded and colloids had formed. Therefore, the sorption data for the 10^{-1}M Eu tests were unreliable and were excluded.

For the remaining tests, the raw data were averaged within each triplicate or duplicate set. The reproducibility was reliable for all stages. The averaged data are provided in Figure 2. For the 10^{-3}M Eu tests the first stage loaded the particles appreciably. Therefore, europium loading was nearly constant, as indicated by the lack of variation in the residual europium concentration. The 10^{-5}M Eu data are markedly different. The loading decreased steadily without showing any evidence of complete loading even after 20 stages. The data for the 10^{-7}M Eu tests show constant

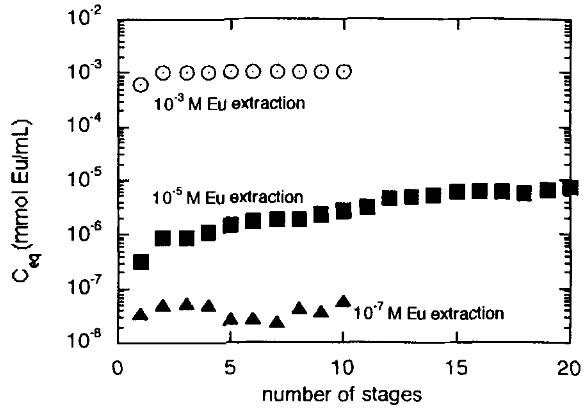

FIGURE 2. Europium residual solution concentration (C_{eq}) for contact stage extraction.

loading over 10 stages. Also, an error of approximately 15% was associated with the 10^{-7}M Eu data points, making subtle trends impossible to discern.

Figure 3 shows the partitioning coefficients for europium, along with results of multiple-stage tests conducted previously with americium tracer in 1M HNO_3. The figure shows that extraction was nearly constant for the 10^{-3}M Eu tests after the first stage. The K_d values dropped from 520 mL/g for the initial stage to approximately 35 mL/g for the additional stages. For the 10^{-5}M Eu tests, the K_d values dropped from an initial value of 25,000 mL/g to a final value of 400 mL/g. The K_d values for the 10^{-7}M Eu experiments were consistently between 1000 and 3000 mL/g. For comparison, the K_d values for americium ranged from 3500 to 250 mL/g.

These results show that in a batch system, the MACS particles would remain efficient in treating many stages for low concentrations of contaminant, but would be saturated quickly at high contaminant levels.

The sorption isotherms are displayed in Figure 4. The sorption capacity from the data appears to be about 0.62 mmol/g. This follows from the strong extraction in the first stage of the 10^{-3}M Eu test followed by the constant extraction for the next 9 stages. This constant extraction could be the phenomena of multilayer adsorption for the nearly loaded particles but, as yet, is unconfirmed. The best fits are produced from the Langmuir and BET formulations (the curves coincide with each other and are indistinguishable in the figure). This suggests that monolayer adsorption is the prevalent mechanism. Both models account well for the extraction behavior at

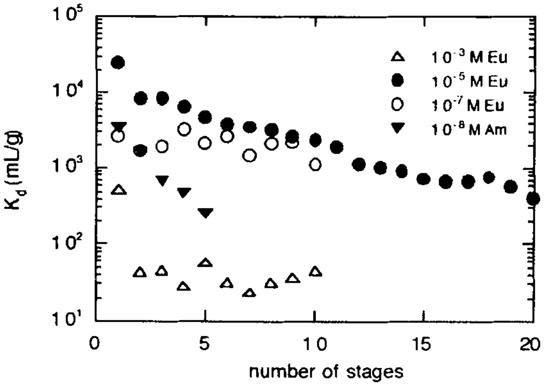

FIGURE 3. Contact stage partitioning coefficient (K_d) for europium.

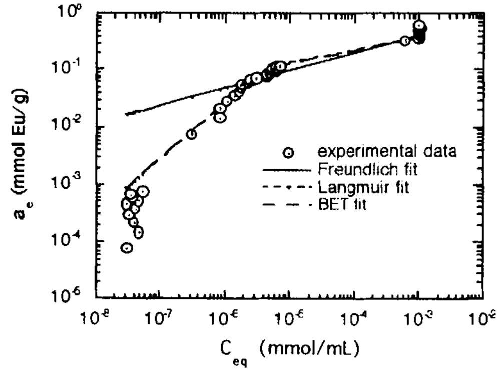

FIGURE 4. Sorption model isotherms for equilibrated loading experiments.

low concentrations, while predicting nearly identical sorption capacities, Q°. The constants for each model are provided in Table 2.

The Langmuir and BET models predict a loading capacity of 0.33 and 0.25 mmol/g, respectively. Additionally, the BET model predicts that the solubility limit for europium is 0.0028 mmol/mL, which is consistent with the difficulties observed for the 10^{-1}M Eu tests. The Freundlich equation suggests favorable loading with a 1/n value of 0.31.

TABLE 2. MODEL CONSTANTS FOR EXTRACTION DATA

Langmuir	Freundlich	BET
$b = 8.24 \times 10^4$ mL/mmol	$K_f = 3.3$	$B = 308$
$Q^\circ = 0.33$ mmol/g	$1/n = 0.31$	$C_s = 0.0028$ mmol/mL
		$Q^\circ = 0.25$ mmol/g

CONCLUSION

The isotherms generated from the extraction tests closely follow the Langmuir formulations well. This supports the mechanism of monolayer adsorption. The sorption capacity obtained from the data was 0.62 mmol/g compared to the Langmuir and BET model fits of 0.33 and 0.25 mmol/g, respectively. This is comparable to ion-exchange resins currently available. The MACS particles demonstrated large partitioning coefficients for systems containing low concentrations of europium, which will permit efficient multiple-stage contacts. Further concentration-dependent studies will have to be performed on this CMPO/TBP system to clarify the mechanism of extraction and how it may differ from the TRUEX process. This study also showed that NAA is a useful analytical tool for this type of investigation.

REFERENCES

1. G. F. Vandegrift, D. B. Chamberlain, R. A. Leonard, J. C. Hutter, D. G. Wygmans, C. Conner, J. Sedlet, L. Nuñez, J. M. Copple, J. A. Dow, B. Srinivasan, M. C. Regalbuto, S. Weber, and L. Everson, "Development and Demonstration of the TRUEX Solvent Extraction Process," Proc. of the 19th Annual Nuclear Waste Symp., Waste Management '93, Tucson, AZ, February 28-March, 1993, *2*, 1045 (1993).

2. L. Nuñez, B. A. Buchholz, and G. F. Vandegrift, Separation Science and Technology, *30*, 1455 (1995).

3. G. Dupré, J. Pirkle, and J. Siegell, *Chromatographic Separations in a Crossflow Magnetically Stabilized Bed*, Exxon Research and Engineering Company, Florham Park, NJ, 1986.

4. M. Burns and D. Putnam, *A Microscopic Study of Particle Filtration in a Magnetically Stabilized Fluidized Bed*, University of Michigan, Ann Arbor, MI, 1992.

5. B. A. Buchholz, L. Nuñez, and G. F. Vandegrift, Separation Science and Technology, in press.

6. E. P. Horwitz, H. Diamond, K. A. Martin, Solvent Extraction and Ion Exchange, *5*, 447 (1987).

7. P.-K. Tse and G. F. Vandegrift, Development of Supercritical Fluid Chromatography for Analysis of TRUEX Process Solvents, Report ANL-89-21, Argonne National Laboratory, Argonne, Illinois, 1989.

8. S. Landsberger, S. Larson, and D. Wu, Anal. Chem. *65*, 1506 (1993).

9. F. Slejko, *Adsorption Technology: A Step-by-Step Approach to Process Evaluation and Application*, Chemical Industries, 19, Marcell Dekker, Inc., (1985).