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Transuranic Separation Using Organophosphorus Extractants Adsorbed Onto Superparamagnetic Carriers

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Abstract

Polymeric coated ferromagnetic carriers with an absorbed layer of octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) diluted by tributyl phosphate (TBP) are being evaluated for application in the separation and the recovery of low concentrations of americium, plutonium, and uranium from nuclear waste solutions. Due to their chemical nature, these extractants selectively complex americium and plutonium contaminants onto the particles and the complexed particles can be recovered from the solution using a magnet. Physical and chemical characterization of the extractant-absorbed particles were performed by gamma and liquid scintillation counting, scanning electron microscopic (SEM) micrograph, and other physical measurements. Plutonium, americium, and uranium separations have been performed at various HNO_3 and HCl concentrations. Parameters were studied to determine the limitations and capacity of the process. The status of the chemistry and application of the process to Department of Energy (DOE) remediation efforts for actinide decontamination are discussed.

Keywords

Solvent extraction, Ion exchange, synergism, transuranic separation

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Introduction

The Magnetically Assisted Chemical Separation (MACS) process provides an effective and cost-effective way of removing transuranics from nuclear waste streams.

In-tank or near-tank separation of radionuclides (e.g., Am, Pu, U) using the MACS process is a new approach to the critical problem of waste treatment at U. S. Department of Energy, and Department of Defense sites [1-7]. For sites with waste streams containing low concentrations of transuranic elements and large volumes of water, decontamination of those waste streams to acceptable health and disposal levels required by states and federal agencies can be very difficult and expensive.

Ion exchange and solvent extraction are the two primary technologies currently used for the separation of transuranic elements from process or waste solutions. Both are complex processes involving, in some cases expensive, bulky equipment and large chemical inventories, and both are inefficient for low concentrations of contaminants. Furthermore, they generate significant amounts of secondary waste.

MACS process

The MACS process has the advantages of (1) less complex equipment, compared with solvent extraction and ion exchange and (2) simplicity that will facilitate scale-up. Tiny, superparamagnetic magnetic carriers (30 nm to 25 μm) provide a simple way to remove these contaminants from solutions under a wide range of chemical conditions. The magnetic carriers are coated with a material (an extractant) that has affinity for the targeted transuranic elements. Figure 1 shows a diagram of the MACS concept. These magnetic carriers are poured into a tank containing a contaminated solution, where they complex the contaminants. In this concept, the slurry or aqueous stream is added to a treatment tank, which can also be used for the stripping stage. To maintain magnetic carrier suspension, the tank contents can be mixed by mechanical stirring, magnetic fluidization, or other methods. The magnetic carriers and their complex radionuclides are removed after extraction. The magnetic carriers are magnetically separated by one of three methods: (1) placing a magnetic field around the treatment tank, (2) pumping the solution through a magnetic

filter (e.g., commercially available high gradient magnetic separation units), or (3) introducing a magnet into the tank. The contaminant-laden coating is removed by using a small volume of stripping agent. The magnetic carriers are then regenerated. The concentrated solution containing the contaminant can either be disposed of or treated further to recover the radionuclides.

The process can be tailored for many specific applications for which solvent extraction or ion exchange processes are already developed. The magnetic carriers are composed of rare earths or superparamagnetic materials embedded in a polymeric matrix. The surface of the polymeric materials are treated to retain selective chemical extractants (e.g., octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide [CMPO], trioctyl phosphine oxide [TOPO], diethylhexyl phosphoric acid [D₂EHPA], tributyl phosphate [TBP], amines, phosphinic acid, crown ethers, cryptands, polyethylene glycols, polyethylene imine, silicotitanates). The MACS process can be used at any tank or location, including situations where remote operation is necessary. Unlike ion exchange processes, MACS does not require preliminary filtration of the solution since it is not hindered by very fine particles. The effectiveness of the process has been demonstrated at bench scale for uranium, americium, and plutonium at Argonne National Laboratory.

In development of a magnetic carrier separation process, various parameters and variables must be studied to determine the limitations of the process and suitability for radioactive waste treatment. Some of the variables include the selection of particles, extraction, stripping, loading, kinetics, radiation damage, sorption, and temperature dependency of the extractions. Combined, the physical and chemical parameters allow an understanding of the separation system and better determine the requirements for scale-up of the process. Some of these process variables will be discussed in the following sections.

Magnetic Carrier Selection

The capacity of the particles to adsorb extractants (e.g., organophosphorous) and maintain physical integrity under chemical (acid) and physical (gamma irradiation) [2] conditions was examined using Transmission Electron Microscopic (TEM). The combination of the TEM results,

radionuclide partitioning (K_d values), gamma irradiation, and other physical measurements was used to select a suitable magnetic carrier type for MACS applications specifically for radionuclide separation. However, the primary factor for the magnetic carrier selection was radionuclide partitioning onto the carrier. The K_d values are determined by Eq (1).

$$K_d = \left(\frac{C_i - C_f}{C_f} \right) \times \frac{V}{m} \quad (1)$$

where

V = contact volume of transuranic element (TRU) solution in mL

m = mass of particles in grams

C_i = initial stock solution counts before contact

C_f = final solution counts after contact

An important criteria for selecting a magnetic carrier is a radionuclide metals loading ability. This requirement was not an original design feature for which the magnetic carriers were developed. For biochemical assay applications, maximizing absorption is unnecessary. Loading capacity is obviously an important concern for the task of recovering a particular component of a nuclear waste streams. Commercially available magnetic carriers that were judged as best for the MACS process were chosen.

Another important consideration for applications of the MACS particles is the absorption or binding strengths exhibited between (1) the magnetite core and the polymeric coating and (2) the polymeric coating and the absorbed extractants. Loss of interfacial integrity in either case under radioactive contaminant conditions is undesirable. The chemical durability of the magnetite core is also required for separation. The pretreated waste streams can be either a harsh acidic or alkaline environment, and dissolution of the magnetite would behave in a similar manner to physical separation of the magnetite and polymer. The durability of the magnetic carriers was studied in an acidic environment using the K_d values combined with the information obtained by TEM and other experiments. A K_d value of 1000 was estimated as a practical threshold value for a batch process to operate efficiently using CMPO and TBP as extractants.

Five magnetic carriers samples were selected for radionuclide separation (Table 1) four of which were examined by TEM (Fig. 2).

Table 1. Magnetic Carriers Evaluated for Radionuclide Separation

Sample	Description	Diameter, μm	Manufacturer
1	DVB ^a /acrylic acid (58%) bound to magnetite core (35%)	0.68	Bang Laboratories
2	Magnetite particles bound to polyacrolein core	1-10	Cortex Biochem, Inc.
3	Charcoal poly bis-acrylamide coated magnetite particles	1-25	Cortex Biochem, Inc.
4	Magnetite particles embedded in S/DVB ^b	12	Bang Laboratories
5	Acrylamide-based magnetite particles with charcoal-dextran coating	12	Cortex Biochem, Inc.

^aDVB = divinylbenzene.

^bS = styrene.

All the magnetic carriers were tested in 2 M nitric acid solutions. Typically, large partition values are obtained with 2M HNO₃ in solvent extraction processes when using CMPO/TBP as the extractants [5]. Sample 1, the divinylbenzene polymer, demonstrated low sorption of the CMPO/TBP extractants, with $K_d \leq 100$ for Am. Sample 2, polyacrolein-magnetite particles, is pictured in Figure 2b. The magnetite inclusions on the particles are extremely small (<1 nm) and the magnetite is attached to the outer surface of the polymer rather than being located in the core. The magnetite particles obstruct access of the CMPO/TBP solution to the absorbent polymer core. The effective surface area of the particle is dramatically reduced and absorption is limited by how quickly the solution can percolate or diffuse through the narrow spaces between the magnetite particles. Table 2 shows the surface areas determined by BET measurements for uncoated and coated magnetic carriers. The nonporous polyacrolein polymer demonstrated insignificant sorption of the CMPO/TBP extractants, with $K_d \leq 10$ for Am in 2 M nitric acid. Sample 4, styrene/divinylbenzene-magnetite particles, pictured in Figure 2c, showed low sorption of the CMPO/TBP extractants, with $K_d \leq 100$ for Am in 2 M nitric acid. Sample 5, acrylamide-based magnetite particles, is shown in Figure 2d. The particles are randomly shaped, and the distribution of magnetite inclusions is also irregular. Some particles appear to be a mass of magnetite, while

others have very little magnetite attached. It is possible that a significant number of carriers would not be magnetically separable because few magnetite particles are present. The charcoal/dextran polymer showed low sorption of the CMPO/TBP extractants, with $K_d \geq 100$ for Am in 2 M nitric acid, but the polymer combination of charcoal in a cross-linked N, N-methylene bis-acrylamide gave $K_d \geq 4000$ for Am in 2 M nitric acid solution. This high partition coefficient was attributed to the chemical affinity of the polymer and charcoal, and the large surface area of the particles.

The surface area of the magnetic carriers and their differences were followed by nitrogen adsorption at 78 K (BET). The charcoal in a cross-linked N, N-methylene bis-acrylamide magnetic carrier shows larger surface area than other magnetic carriers (Table 2) and commercial zeolite-supported catalysts (5.5 m²/g). Table 2 shows a direct relationship between the surface area loss and extractant coating. The effective surface area can be approximated by the surface area loss which is shown in Table 2, by subtracting the original available surface area of the particles. Between 33 and 98% of total surface area is coated by the extractants. The TEM and BET analyses were used to select the charcoal in a cross-linked N, N-methylene bis-acrylamide magnetic carrier type as the magnetic carriers for the MACS process.

Table 2. Magnetic Carrier* Surface Area Determinations of Different Types of Magnetic Particles

Size, μm	Magnetic	Extractant Coating	BET , Surface Area, m ² /g	BET , Surface Area Loss, m ² /g
25	Magacell CM	None	4.89	-
10	Bang S/V-COOH	None	5.0	-
44	Fe ₂ O ₃	None	5.64	-
25	Magacell Cellulose	None	7.61	-
0.88	Charcoal poly bis-acrylamide	None	89.3	-
0.88	0.25 M Cyanex 272	0.5MD ₂ EHPA	2.02	87.28
0.88		0.1M CMPO/TBP	29.79	59.51

^aDVB = divinylbenzene.

^bS = styrene.

*Only the charcoal poly bis-acrylamide (Sample 3 in Table 1) is used for the extractant coated particles

Radionuclide Extraction

Studies with charcoal poly bis-acrylamide magnetic particles [6] using 0.75 M CMPO in undiluted TBP gave a partition coefficient, K_d of 3000-5000 mL/g for americium. In contrast, the same concentration of extractants for a solvent extraction system (with aqueous to organic ratio=1) yielded a distribution ratio of 240 which is equivalent to a partitioning coefficient of only about 80 mL/g. A similar behavior was observed for plutonium with partitioning coefficients for the magnetic carrier separation that were much higher than predicted by solvent extraction measurements (5000-10,000 mL/g and 3000, respectively). The nitric acid dependency of the MACS process is important for applications of this process to radioactive waste streams having a wide range of acidities. The partition coefficients for various coatings were monitored using ^{241}Am , ^{233}U , and ^{238}Pu tracers. Samples were tested in nitric acid solutions with CMPO concentrations of 1.2 M. The results are presented in Figure 3. Figure 3 shows that the three curves have similar shapes. The K_d values for Am and Pu increase slowly with HNO_3 concentration, reaching peaks at 2 M and 5 M HNO_3 , respectively. Uncertainty for actinide K_d measurements are ± 25 .

These results suggest that the process can be applied in a batch mode for a wide range of nitric acid concentrations without a large loss in extraction capabilities. The magnetic separation process is up to 100 times more efficient than current separation systems using the same extractant [3].

Typical organic species involved in solvent extraction processes are $\text{Pu}(\text{NO}_3)_4(\text{CMPO})_2$ and $\text{Am}(\text{NO}_3)_3(\text{CMPO})_3$. Although the precise chemical equilibrium constants are not determined for the magnetic carrier system, the K_d values obtained are much larger than partitioning values obtained in a solvent extraction process. Increases in K_d may be a result of a synergistic effect between CMPO/TBP and the polymer on the particle in the absence of a diluent, (such as normal paraffinic hydrocarbons (NPH) or trichloro-ethylene (TCE)). Although CMPO/TBP systems have been extensively investigated, the current studies without a standard diluent (e.g., dodecane, NPH, TCE) and with high concentrations of CMPO/TBP without third phase formation are unique. The

MACS process shows promise in using more efficiently the standard organophosphorous extractants such as CMPO and TBP for transuranic separation applications.

Figure 4 shows the separation of low concentrations (0.01M) of uranium in acidic solutions which has potential applications for metallurgical and mine tailing effluents. The separation of the uranium from acid solutions using TOPO and D₂EHPA (coated in a similar fashion as CMPO), [6], are three orders of magnitude higher than in traditional solvent extraction techniques. The separation is maximum at low acid concentrations (0.01 M) and decreases at high acid concentration (up to 8 M). Since D₂EHPA is present as a dimer in hydrocarbon solutions species such as $\text{UO}_2(\text{NO}_3)_2\text{R}_4\text{H}_2$ are suggested as the extracted complex where R is the alkylphosphate anion.

Uranium extracts with TOPO as follows:



where the K for the reaction is about 1.25×10^5 [8]. The partitioning of uranium as a function of increased TOPO concentration exhibit a slope of two which is indicative of two TOPO molecules in the uranium complex.

Conclusion

Extractant coated magnetic carriers can efficiently separate radionuclides such as plutonium, americium and uranium from acidic solutions. The large surface area and the proper carrier morphology allows optimization for reactions to occur on magnetic carrier. Furthermore, the magnetic carrier have shown increased partitioning suggesting a synergism between the magnetic carrier surface and the extractants that improve the separation efficiency over more traditional separation techniques. Scale up of the process is currently underway to demonstrate the process under industrial processing conditions.

References

- [1] M. D. Kaminski, L. Nuñez, and A. Visser, Separation Science and Technology, "Tenth Symposium on Separation Science and Technology for Energy Applications," Gatlinburg, Tennessee, (1997a).
- [2] B. A. Buchholz, L. Nuñez, and G. F. Vandegrift, Separation Science and Technology, 31, (1996), 1933.
- [3] M. Kaminski, S. Landsberger, L. Nuñez, and G. F. Vandegrift, Separation Science and Technology, 32, (1997b), 115.
- [4] L. Nuñez, B. A. Buchholz, M. Ziemer, G. Dyrkacz, M. Kaminski, G. F. Vandegrift, K. J. Atkins, F. M. Bos, G. R. Elder, and C. A. Swift, Argonne National Laboratory Report ANL-94/47, Argonne, IL, (1994).
- [5] L. Nuñez, B. A. Buchholz, and G. F. Vandegrift, Separation Science and Technology, 30, (1995a), 1455.
- [6] L. Nuñez, M. Kaminski, C. Bradley, B. A. Buchholz, S. Landsberger, S. B. Aase, H. E. Tuazon, and G. F. Vandegrift, Argonne National Laboratory Report ANL-95/1, Argonne, IL, (1995b).
- [7] L. Nuñez, B. A. Buchholz, M. Kaminski, S. B. Aase, N. R. Brown, and G. F. Vandegrift, Separation Science and Technology, 31, (1996), 1393.
- [8] J. C. White and W. J. Ross, Nuclear Science Series, U.S. Atomic Energy Commission, NAS-NS 3102, (1961).

Figure Captions

Figure 1. Concept Diagram of MACS Process for Radioactive Waste Streams

Figure 2a. TEM Micrographs. Sample 1, which is comprised of large, irregular-shaped magnetite particles ($0.2\ \mu\text{m}$) with polymer randomly bonded to surface core. **2b.** Brightfield Image of sample 2 (polyacrolein) embedded in Araldite. Magnetite particles are small ($<10\ \text{nm}$) and attached to the outer surface of the particles. **2c.** Mag-encapsulated particles. The magnetite particles are small ($\sim 10\ \text{nm}$) and are embedded as agglomerates within the polymer. **2d.** Dextran-coated particles are shown here. Polymer particles are randomly shaped, with a non-uniform polymer coating. In most cases, it does not appear that the magnetite and polymer are tightly bound.

Figure 3. K_d vs. Nitric Acid Concentration for Am, U, and Pu for $1.2\ \text{M}$ CMPO/TBP Coatings on Magnetic Particles at 25°C

Figure 4. K_d vs. Hydrochloric Acid Concentration for U for $0.1\ \text{M}$ TOPO/ $0.5\ \text{M}$ D₂EHPA Coatings on Magnetic Particles at 25°C

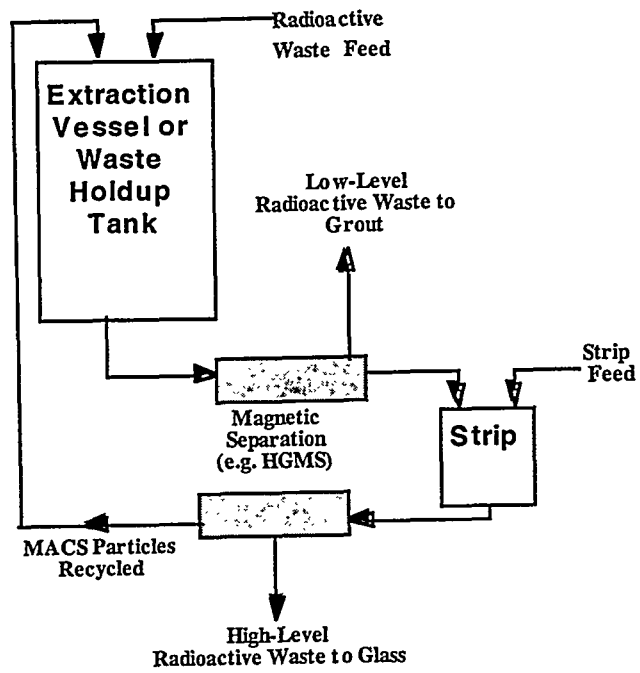


Figure 1 – Nuñez, Luis – “magmeet98”

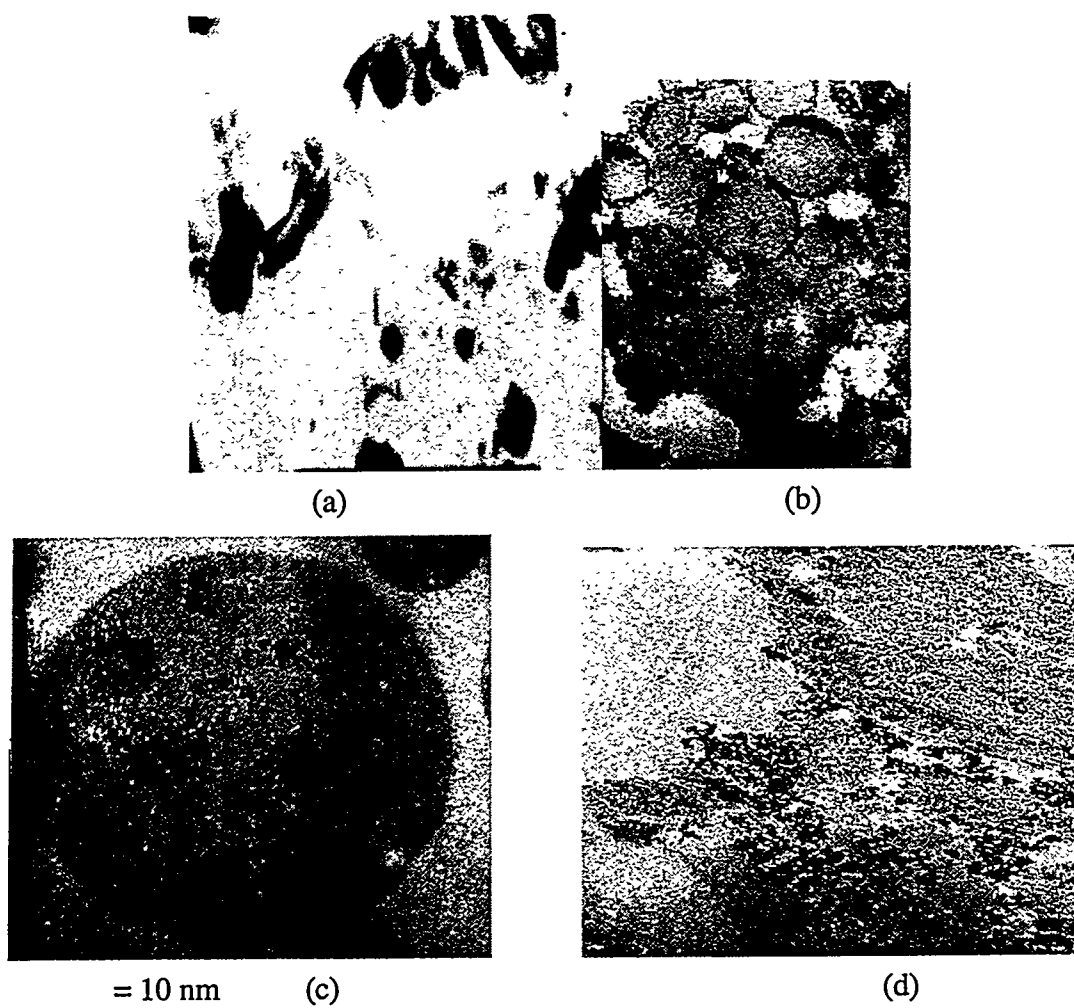


Figure 2a – Nuñez, Luis – “magneet98”

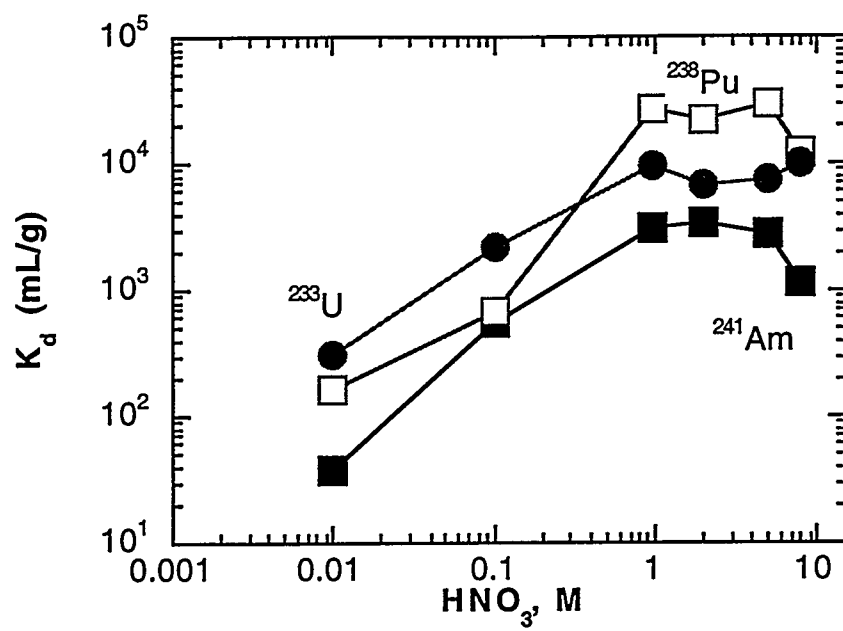


Figure 3 – Nuñez, Luis – “magmeet98”

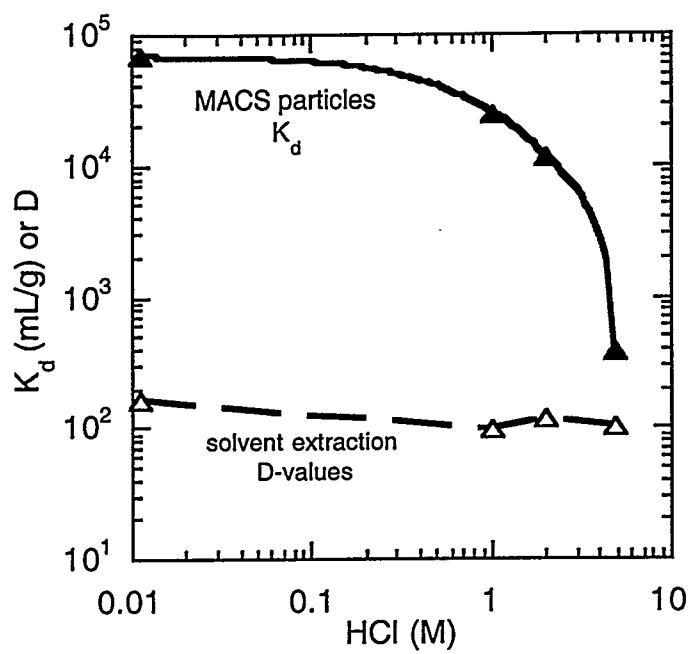


Figure 4 – Nuñez, Luis – “magneet98”