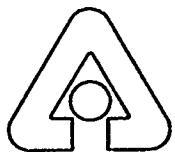


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Review and Evaluation of Extractants for Strontium Removal Using Magnetically Assisted Chemical Separation

by C. B. Bauer, R. D. Rogers, L. Nuñez,
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REVIEW AND EVALUATION OF EXTRACTANTS FOR STRONTIUM REMOVAL USING
MAGNETICALLY ASSISTED CHEMICAL SEPARATION

by

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ABSTRACT

A literature review on extractants for strontium removal was initially performed at Northern Illinois University to assess their potential in magnetically assisted chemical separation. A series of potential strontium extractants was systematically evaluated there using radioanalytical methods. Initial experiments were designed to test the uptake of strontium from nitric acid using several samples of magnetic extractant particles that were coated with various crown ether ligands. High partition coefficient (K_d) values for simulant tank waste were obtained. Further studies demonstrated that the large partitioning was due to uncoated particles.

I. INTRODUCTION

New methods need to be developed to selectively separate strontium from other metal ions. Radiostrontium is a problem in a wide variety of areas ranging from environmental systems (such as rivers, lakes, subterranean aquifers, and streams) to ecological systems (such as contaminated cow's milk in the former Soviet Union). The main problem in the United States with radiostrontium, however, is its presence in large quantities in certain nuclear wastes. The major thermal and radiological hazards in the highly alkaline underground storage tanks at the Westinghouse Hanford site are believed to be due to the presence of strontium and cesium [KUPFER]. The high heat-load generated by ^{90}Sr and ^{137}Cs excluded these isotopes from low-level grout formation in remediation efforts at Hanford. Unfortunately, the separation of these two metal ions is problematic, especially from highly basic systems.

In order to more fully understand the solution behavior of strontium and possible selective separation methods, a comprehensive review of the recent literature was undertaken. This review covers all methods for the selective separation of strontium published during 1988-1993.

This report evaluates the choice of extractant and optimization of strontium separation for the Magnetically Assisted Chemical Separation (MACS) process being developed with funding from the Efficient Separations and Processing Integrated Program (ESPIP) for Hanford and other DOE sites.

The MACS program is developing processes to treat a variety of radioactive and hazardous tank sludges and/or supernatants [NÚÑEZ-1993, -1994A]. Transuranic (TRU) waste is of considerable concern because of its long half-life constituents.

Many Department of Energy (DOE) sites have aqueous radioactive, mixed, and hazardous wastes stored in tanks awaiting treatment and ultimate disposal. Sludge and supernatants in the underground storage tanks (USTs) at Hanford contain Cs, Sr, and, in some cases, low concentrations of TRU elements that must be removed to dispose of this stream as low-level waste (grout). For the remediation efforts at Hanford and other DOE sites, this project will develop compact, economic, in-tank or near-tank processes to remove contaminants from solution.

The innovative processes use magnetic beads coated with either (1) a selective ion-exchange material (e.g., silicotitanates, resorcinol), (2) an organic complexant-containing solvent for Cs and Sr, or (3) solvents for selective separation of TRU elements (e.g., TRUEX solvent). The beads are formed from iron or another magnetic material and coated with either organic polymer or ion-exchange resin. The ion-exchange resin is attached by an adhesive or by direct bonding. Organic solvents can be adsorbed onto the polymeric surface by contacting the beads with a solution of the solvent in a volatile diluent and then evaporating off the diluent. By their chemical nature, these coatings selectively separate the contaminants onto the beads, which can be recovered from the tank using a magnet [NÚÑEZ-1994B, -1994C].

Once the contaminants have been removed, they can either be (1) left on the loaded beads and added to the glass feed slurry or (2) stripped into a small volume of solution to regenerate the extracting beads. The greatest benefits of the technology are the simple separation of radionuclides from waste by a cost-efficient and compact process without producing large waste streams and the application of this process to many DOE liquid TRU wastes.

This process can compete with more traditional solvent extraction and ion-exchange techniques only if the K_d values are at least 1000 for the batch separation. If the K_d values are lower than 1000, other techniques would probably be more suitable for the separation.

II. SUMMARY

The MACS program is seeking to develop an efficient separation method for Sr, Cs, TRU elements, and other contaminants. In this project, the literature was first evaluated to find suitable strontium extractants. After the review, di-tert-butyl-dicyclohexyl-18-crown-6 was selected as a suitable selective extractant for strontium separation under high acid conditions. The extractant was evaluated and found to separate strontium from acid solutions with low K_d values (~ 10 mL/g at $2M$ HNO_3), similar to the distribution ratios (D values) obtained by liquid/liquid extraction systems. The results in basic and simulant waste solutions indicated higher K_d values (> 7200 mL/g at $1M$ $NaOH$) than solvent extraction techniques. Further studies showed that the high partition coefficients were due to the uncoated MACS particles and not due to the crown ether coating.

III. REVIEW OF LITERATURE ON STRONTIUM SEPARATION

A. Separation of Strontium by Extraction in Liquid/Liquid Systems

1. Traditional Systems

In a liquid/liquid extraction system, strontium is extracted by a strontium-specific hydrophobic ligand in an organic diluent. A stable neutral complex incorporating the metal ion is formed; this complex partitions to the organic phase. A variety of extractants featuring a range of functionalities have been investigated. Specific details for each type of extractant are presented below.

2. Crown Ethers

Because crown ethers offer multiple oxygen donors and a well-established size selectivity, they have been extensively investigated as possible strontium extraction agents. Simple crown ethers with no additional functionalities or lipophilic groups (such as 12-crown-4, 15-crown-5, and 18-crown-6) are readily available via several commercial sources and have been used as extractants in these systems [TAKEDA-1989A, SUKHAN, MIKULAJ, TAKEDA-1991, LIU, UMETANI-1993]. The extraction of metal picrates with these ligands has been reported from a variety of systems including picric acid/benzene, picric acid/chloroform [TAKEDA-1991], and water/dichloromethane [LIU]. In general, these simple crown ethers enhance the extraction of strontium, but they tend to be rather unselective. The distribution coefficient for strontium in a picric acid/benzene system at 25°C is 0.397, using 18-crown-6 as the extractant. At room temperature, 15-crown-5 had a D value of 8.27 in a picric acid/chloroform system. The process is further hindered by the fact that these ligands have an affinity for the aqueous phase, not the organic phase. Despite these problems in terms of successful extraction, a number of useful thermodynamic studies have been performed using these simple crown ether ligands [TAKEDA-1991, LIU]. Uses for these ligands for purposes other than as the primary extractant have also been developed, most notably as masking agents. Masking agents are used to enhance the extraction of alkaline earth metal ions [UMETANI-1993] when used with extractants such as tri-N-octylphosphine oxide (TOPO) and 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (MPMBP).

The partitioning of the crown ether ligand to the organic phase, and hence the improvement of metal ion extraction, can be greatly enhanced by the addition of lipophilic groups. The most common are the benzo- and dibenzo- crown ethers. The extraction of strontium picrates using these ligands has been well investigated [MATEL, YAKSHIN-1992, MAMEDOVA, TAKEDA-1989B]. In general, strontium is extracted more favorably by using these ligands rather than the simple crowns. Selectivity is again an issue in these systems, as other cations (e.g., Pb^{2+} and Group 1 cations) are often more favorably extracted than is strontium. A mixture of dibenzo-21-crown-7 and cyclohexyl-18-crown-6 ligands in a nitric acid system ($\sim 2M$ HNO_3) at 25°C was investigated [YAKSHIN-1992]. Strontium (95% recovery) and cesium (99% recovery) were effectively separated from a soil-leaching simulant. The effectiveness of these lipophilic crowns (e.g., dicyclohexyl-18-crown-6, dibenzo-18-crown-6, dibenzo-24-crown-8, 18-crown-6, benzo-15-crown-5) as extractants for strontium after gamma irradiation was also studied [MATEL]. A significant decrease in strontium partitioning from a chloroform system was observed after gamma irradiation (range of dose between 10 to 70 Gy), but no radiolytic degradation of the crown ether was observed.

The crown ethers that have shown the most promise for the extraction of strontium are those which contain cyclohexyl and substituted cyclohexyl groups. The most well-developed technique that uses these ligands is the strontium extraction (SREX) process [HORWITZ-1990A,

-1990B, -1991A]. Di-tert-butyl-dicyclohexyl-18-crown-6 is the extractant in normal hydrocarbon solvents from nitric acid solutions in this process, which offers a number of advantages including radiolytic stability, ease of stripping, and excellent selectivity for strontium. (Ba and Pb are the only other metals which exhibit a distribution ratio greater than unity.) Other recent studies use cyclohexyl-substituted crown ethers and determine: the effects of anions on strontium partitioning (overall efficiency decreases in the order: $\text{ClO}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^-$) [OLSHER]; the co-extraction of strontium with uranium from nitric acid [YAKSHIN-1993]; the extraction of strontium from natural waters and nitrate salt solution [YAKSHIN-1989]; and the extraction of strontium from nuclear power plant wastes [MAMAKIN]. Concentrations of dicyclohexyl-18-crown-6 (0.1-0.2M) were used to separate strontium from nuclear power plant waste without any precipitate formation in the chloroform phase at 25°C. Additional studies involving the extraction of strontium with picrate and Orange II anions [NAZARENKO] have also been reported with strontium D values of 24.8 in chloroform from ~3.3M HNO_3 .

Another class of crown ether ligands being evaluated as possible strontium extractants have functional groups that affect the ligand-binding characteristics. Perhaps the most notable members of this class of compounds have oxyacetic acid side chains that are attached to some portion of the crown (e.g., acylpyrazolones, crown phosphoric acid monoesters) [CZECH, BARTSCH, WOOD, HE, BUKOWSKY-1990A,-1990B,-1992, INOUE]. These ligands are unique in that the added functionalities allow them to act as both metal ion coordinators and cation exchangers. In addition, these functionalities allow the extractants to act in a bifunctional manner in some cases. Promising extraction data for the strontium cation from chloroform involving a variety of aqueous phases have been reported [UHLEMANN].

Several other classes of crown ethers have been sporadically investigated as strontium extractants. Those which incorporate mixed donor atoms (usually N) in the crown (e.g., 10,19-dibenzyl-1-1,4,13,16-tetraoxa-7,10,19,22-tetraza-cyclotetradecane, 4,16-dibenzyl-1,10-dioxa-4,7,13,16-tetrazacyclooctadecane) [ZINIC, PIGOT, KIDO] offer the advantage of the ready addition of sidearms to the N atom in the ring. Other types of crown ethers studied have dyes incorporated [KATAYAMA] or have polyaromatic portions and/or multiple macrocyclic rings [WEBER] incorporated into their structures.

3. Dicarbollides

Dicarbollides, specifically chlorinated cobalt(III) dicarbollides, have recently been investigated as extractants or synergists for the separation of both strontium and cesium [SPIVAKOV, VANURA, KOROLEV-1990, KOROLEV-1988, SELUCKY]. In general, acidic nitrate solutions were the aqueous phase with which different organic phases were tested (e.g., nitrobenzene, 1,2-dichloroethane). In one system, strontium and cesium were separated out by adding a crown ether to the system [SPIVAKOV]. Some of the best results are obtained in a nitrobenzene system that yields D values ≥ 1 for 0.3M HNO_3 [KOROLEV-1990]. A review of cobalt(III) dicarbollide as a potential extraction agent for ^{137}Cs and ^{90}Sr waste points out some drawbacks in extractive properties and recycling possibilities [REILLY].

4. Phosphine Oxide-Based Extractants

Although they are most well known as actinide extractants, phosphine oxide-based bidentate ligands have recently gained some attention as strontium extractants [e.g., (2-ethylhexyl)-2-ethylhexyl phosphonic acid and tetra-phenyl-diphosphine-P,P'-dioxide [LEE, TSIVADZE, SUN, OGURA, KOMATSU-1991A, TURANOV, UMETANI-1992, BUKOWSKI-1990A, BJORNSTAD,

KIM]. They have been shown to be promising extractants from a variety of acidic systems. Unfortunately, these ligands tend to be rather unselective for strontium, less selective than previously investigated crown ethers in similar systems [TSIVADZE].

5. Calixarenes

Calixarenes are a relatively new class of macrocyclic molecules that consist of phenolic units joined by $-CH_2-$ bridges. These molecules were investigated because of their interesting structural features and their ability to form inclusion complexes with a variety of different molecules. These molecules are easily modified, and several variations have recently gained attention as possible extractants for a number of different metal ions including the alkaline earths. Certain amide-based calixarenes (e.g., diethylamide, pyrrolidine amide) have also been shown to extract calcium and strontium better than the other alkali and alkaline earth metals. A formation constant of $\geq 10^8$ for the strontium complex was obtained in both diethylamide and pyrrolidine amide-based systems. Other dialkylated [BRUNINK] and carboxylated [NOMURA] calixarenes have been shown to be potential alkaline earth extractants in dichloromethane solvent systems.

6. Cryptands

Cryptands, like crown ethers, have a rigid cavity size and thus offer the potential of size selectivity for metal ions of different sizes. As a result, some of these ligands, specifically 4,7,13,16,21,24,-hexaoxa-1,10-diazabicyclo-8,8,8-hexacosane (commonly known as crypt-2.2.2), have been studied as strontium complexants. The extraction of strontium in chloroform solvent systems was studied [ANDREAS, GOMIS-1989A]. Strontium was found to be extractable with large anions such as eosinate. Several applications have been reported involving this ligand to separate strontium as a model for nobelium behavior [HUSSONNOIS]. For example, Hussonnois found the formation of a 1:1 complex of $[Sr(2.2.2)] [picrate]_2$ was obtained with $\log K_d$ equal to 7.3 ± 0.1 at a pH of 11 in an $8.3 \times 10^{-3}M$ lithium picrate/chloroform solution. The determination of the strontium levels in sugar [GOMIS-1989B] and in calcium-rich materials has also been reported [JUSKOWIAK].

7. Pyrazolyl Borates

These ligands (e.g., hydrotris-pyrazolyl-borate) have recently been investigated as alkaline earth chelators and extractants [KOKUSEN, SOHRIN]. They tend to form stable, six-membered chelate rings with a number of different metal ions. Interestingly, the selectivity of the ligands can often be modified by changing the steric characteristics and hence the "bite-size" of the chelator. Selectivity is again a problem when dealing with strontium, as it has been reported that calcium, magnesium, and beryllium are extracted more efficiently than strontium with a number of these pyrazolyl-borates in a chloroform-based system [SOHRIN].

8. Amido Podands

Certain amido podands (e.g., open chain ether dicarboxylic acid diamides, ether dicarboxylic monoamido acids, and N-alkyl imino diacetic diamides) have been shown to be effective in separating strontium and calcium from the alkali metals [KUVAEVA, STEPHAN-1991A, STEPHAN-1991B]. In the case of a dicarboxylic acid diamide in toluene, distribution ratios in the range of 0.1-10 were obtained as a function of ligand concentration (at a pH of 5.2). The extraction chemistry analysis showed a strontium complex with a metal:ligand ratio of 1:2 [STEPHAN-1991B]. In this system, Na^+ and K^+ were not extracted (distribution ratios less than 0.01). Other amido

podands were examined for the extraction of strontium with the addition of phosphonic acid [POPOVA].

9. Non-Traditional Liquid/Liquid Extraction Systems

One class of non-traditional, liquid/liquid extraction systems has been used to investigate the extraction behavior of a number of metal ions including strontium. They are aqueous biphasic systems formed by adding an inorganic salt to a water-soluble polymer (such as polyethylene glycol). The resulting system consists of two aqueous immiscible layers (one phase polymer-rich, the other salt-rich). The extraction of strontium has been investigated using crown ether ligands from both basic [ROGERS-1993] and acidic [ROGERS-1995] media. It has been demonstrated that molecular recognition is possible in these systems. For example, distribution ratios as a function of extractant concentrations are ≥ 1 for Ba, Rb, and Ca and ≤ 1 for Sr in the 18-crown-6 2M NaNO₃/20% NaOH/40% PEG-2000 system (w/w/w). Unfortunately, no ligands that are selective for strontium in the aqueous biphasic systems have been found to date.

B. Separation of Strontium in Liquid/Solid Systems

The other major category of strontium separation methods are liquid/solid techniques. Among them are extraction chromatography, ion exchange, and use of solid sorbents. As in the liquid/liquid techniques discussed previously, crown ethers are among the most frequently studied extraction agents in liquid/solid systems. Therefore, crown ether methods will be presented first followed by other techniques.

1. Crown Ethers

These ligands have been used extensively and quite successfully for the selective extraction of strontium in column-based systems. The most developed of these methods is the so-called "Sr-Spec" process, which is the adaptation of the previously mentioned SREX process to an extraction chromatographic system [CHIARIZIA, HORWITZ-1992, HORWITZ-1991B]. Here, di-tert-butyl-dicyclohexyl-18-crown-6 in 1-octanol is impregnated on a resin. Specific applications for this material include a method to determine strontium levels in urine [DIETZ], removal of strontium from synthetic nuclear wastes [HORWITZ-1991B], and the separation of strontium from calcium [HORWITZ-1991C]. A similar material that is prepared using a styrene-divinylbenzene copolymer has also been reported [KREMLYAKOVA]. Kinetics for these liquid/solid systems are fast, and metal loading is the only limitation of the chromatographic resin.

Another popular method is the use of silica gel-bound crown ethers. In these systems, the macrocycle is chemically bound to the silica-gel through covalent bonds [IZATT, BASYUK]. Again, these systems have similar kinetics compared to the solvent extraction system, but strontium loading is low. These materials have shown promise for the selective extraction of strontium. A class of commercially available materials called SuperLig is now available with specific application for strontium [ARNAUD-NEU, CAMAIONI, BRADSHAW].

Several other liquid/solid techniques have been utilized, including the use of supported liquid membranes that contain crown ether extractants [RAMADAN, CHO, AKABORI, DELLOYE]. The selectivity for strontium over cesium has been demonstrated in one case [RAMADAN]. One other miscellaneous technique which has been used is that of sorbing strontium/crown complexes onto various media, including papers [WAI], synthetic polymers [MASLOVA], and graphite [LE BERRE].

2. Other Methods

Several other liquid/solid methods that do not involve crown ethers have been investigated. Sorption of strontium onto zeolites (e.g., mordenite, clinoptilolite, erionite, Na-chabazite) from salt solutions has received attention [CHERNYAVSKAYA, LITVINENKO]. Selective strontium removal has been reported with certain zeolites; for example, K-chabazite, K-G(13), has a K_d of $1.2 (\pm 0.3) \times 10^4$ mL/g for 5M NaCl and for 5×10^{-5} M strontium that decreases to $6.0 (\pm 1.5) \times 10^3$ mL/g in 9M NaCl. This sorption of strontium required 7-14 days to establish equilibrium. Sorption onto other supports such as aluminosilicates [HOYLE] and silico-polymethylsiloxane [STRELKO] has also been reported.

A variety of ion-exchange resins have been tested as possible strontium extractants. The simplest resin involves the use of EDTA and its derivatives as the extractant [SINGH]. This method presents an efficient means of separating strontium from large amounts of calcium. Other ion exchangers which have been examined include dihydrogen tetratitanite fibers [KOMATSU-1991B], P₅₀₇ resin [MA], acrylic-based resins [NIKOLAEV], and naphthalenesulfonic acid-based exchangers [KUVAEVA].

One other liquid/solid method is worth noting. It involves the extraction of strontium with a liquid membrane in the presence of a cobalt(III) dicarbollide [EL SAID]. This technique allows the preconcentration of strontium, cesium, and the lanthanide(III) ions. Selectivity is again the major problem with this method in terms of strontium-specific applications. For practical purposes, kinetics and stability of the majority of the methods described in this section would require future investigation for nuclear process development.

C. Miscellaneous Methods

A number of other techniques for strontium removal exist which cannot be classified in the previous two categories. One example involves the precipitation of strontium species from milk samples [RAURET]. Good selectivity was reported using this method. Other methods include a capillary electrophoresis-based method that uses EDTA as a chelator [MOTOMIZU], a high-temperature fluorination method [KAWASE], and an electrochemical-based extraction process [YOSHIDA]. A foam separation method has also been developed for the flotation of an insoluble strontium tracer complex [SHAKIR].

D. Conclusions

A review of the literature has revealed that there is a need for the effective separation of strontium from a variety of different systems. Unfortunately, the majority of the work that has been published consists of a series of sporadic probes with very few well-developed processes that have actually been implemented. Key issues for process development such as kinetics, loading, and strippability have been extensively studied in only a few systems.

IV. EVALUATION OF EXTRACTANTS FOR STRONTIUM REMOVAL USING MAGNETICALLY ASSISTED CHEMICAL SEPARATION

A. Experimental

The following general experimental procedure was followed for the measurement of all metal ion uptake experiments. A small amount (0.001-0.01 g) of the desired sorbent particle sample (magnetic particles uncoated or coated with extractant [NÚÑEZ-1993]) was weighed into a test tube. A 1.2-mL sample of the desired aqueous solution was measured into a shell vial. This solution was then spiked with a tracer quantity of ^{85}Sr (the stock solution was prepared and stored as the $\text{Sr}(\text{NO}_3)_2$ form in 0.02M nitric acid). A 100-mL aliquot of this spiked solution was removed and counted radiometrically (Packard-Cobra II Auto-Gamma counter) to obtain an initial activity (A_i). One milliliter of the spiked solution was added to the MACS particles in the test tube. The solution was vortexed for 2 h with frequent (every 15 min) centrifugation to ensure that all of the particles were in uniform contact with the solution. The tube was then placed in a magnetic separator, and the solution was separated from the particles. A 100- μL aliquot of the solution was removed for radiometric counting to obtain a final activity (A_f). The partition coefficient K_d is then calculated from this equation:

$$K_d = \frac{A_i - A_f}{A_f} \times \frac{\text{mL solution}}{\text{g of beads}} \quad (\text{IV-1})$$

B. Results

The first extractant samples that were evaluated were particles that had been coated with a dicyclohexyl-18-crown-dissolved in tributyl phosphate (TBP). The uptake of strontium was measured over a range of nitric acid concentrations. These results were disappointing, as there was essentially no uptake of strontium by the particles. The extraction data are reported in Table 1.

Table 1. Strontium Extraction Data for 2 mL/g of 0.2M Dicyclohexyl-18-crown-6/TBP on Charcoal Bis-acrylamide Particles at 25°C as a Function of Nitric Acid Concentration

[HNO ₃], M	Mass Particles, g	A _i , cpm ^a	A _f , cpm ^a	K _d , mL/g ^b
0.001	0.0023	2149	2236	-18
0.01	0.0027	2162	2203	-6.6
0.1	0.0031	2152	2167	-2.2
1.0	0.0031	2097	2089	1.2
2.0	0.0038	2255	2221	4.0

^aA 0.1-mL aliquot was used for gamma counting and 1 mL of spiked solution was used for K_d measurement.

^bNegative values are attributed to errors in mass balance assumptions.

After these results were obtained, two new samples of extractant particles were evaluated, one coated with 0.05M and the other with 0.3M crown ether (di-tert-butyl-dicyclohexyl-18-crown), both

diluted in TBP. Again, a nitric acid dependency revealed disappointing strontium uptake from the entire range of concentrations (Table 2). In addition, a synthetic Hanford tank supernatant waste simulant spiked with strontium (waste composition given in Table 3) was also evaluated. Uptake of strontium from the waste simulant was, however, much higher than observed from the nitric acid solutions (Table 4). The K_d values for the two simulant waste samples were 490 and 200 for the 0.05M and 0.3M crown ether samples, respectively.

Table 2. Strontium Extraction Data^a for ~ 5 mL/g of 0.05 and 0.3M Crown Ether^b in TBP on Charcoal/Bis-acrylamide Particle Samples from HNO₃ at 25°C

Bead Material Crown Ether/TBP, <u>M</u>	[HNO ₃], <u>M</u>	Mass Particles, g	A _i , cpm ^c	A _f , cpm ^c	K _d , mL/g ^d
0.05	0.001	0.0018	15,139	15,242	-3.8
0.05	0.01	0.0049	15,639	14,713	13
0.05	0.1	0.0029	15,614	15,985	-8.0
0.05	1.0	0.0027	15,654	15,676	-0.52
0.05	2.0	0.0028	15,821	16,044	-5.0
0.3	0.001	0.0065	15,274	15,037	2.4
0.3	0.01	0.0033	15,339	15,240	1.8
0.3	0.1	0.0056	15,095	15,255	-1.9
0.3	1.0	0.0062	15,495	15,756	-2.7
0.3	2.0	0.0066	15,738	15,868	-1.2

^aA 1-mL sample was used for K_d measurement.

^bDi-tert-butyl-dicyclohexyl-18-crown-6.

^cA 0.1-mL aliquot was used for gamma counting.

^dNegative values are attributed to error in mass balance assumptions.

Table 3. Recipe for Hanford Simulant Waste Stream^a

Major Components	Component Charge	Concentration, <u>M</u>
Na	1	8.83
K	1	9.35 x 10 ⁻²
Cs	1	4.88 x 10 ⁻⁵
OH	-1	6.54
NO ₃	-1	1.09
NO ₂	-1	8.09 x 10 ⁻¹
Al(OH) ₄	-1	2.06 x 10 ⁻²
CO ₃	-2	2.22 x 10 ⁻¹
CrO ₄	-2	4.37 x 10 ⁻³
PO ₄	-3	8.00 x 10 ⁻⁴

^aA ⁸⁵Sr tracer was spiked into this solution.

Table 4. Strontium Extraction Data^a for ~5 mL/g of 0.05 and 0.3M Crown Ether^b in TBP on Charcoal/Bis-acrylamide Particles from Simulated Hanford Tank Supernatant Simulant

Bead Material Crown Ether/TBP, M	Mass Particles, g	A _i , cpm ^c	A _f , cpm ^c	K _d , mL/g
0.05	0.0020	13,857	7012	490
0.3	0.0055	15,018	7241	200

^aA 1-mL sample was used for K_d measurement.

^btert-Butyl-dicyclohexyl-18-crown-6.

^cA 0.1-mL aliquot was used for gamma counting.

The successful uptake of strontium from the waste solution was both encouraging and confusing. The waste simulant is basic, with a substantial quantity of hydroxide (6.54M) and carbonate ions (0.22M) present. Because of the lack of partitioning from nitric acid, it was possible that the acidic media hindered extraction. In this case, successful extraction using the nitrate anion from neutral solutions was still a possibility. To test it, the nitrate ion dependency was determined for aqueous aluminum nitrate solutions and the 0.3M and 0.05M crown ether particle samples. Extraction data from these systems are reported in Table 5.

Table 5. Dependency^a of [Al(NO₃)₃] on Strontium Uptake from Aqueous Solutions Using Crown Ether-Coated Charcoal/Bis-acrylamide Particles at 25°C

Bead Material Crown Ether/TBP, M	[Al(NO ₃) ₃], M	Mass Particles, g	A _i , cpm ^b	A _f , cpm ^b	K _d , mL/g
0.05	0.001	0.0021	7302	7351	-3.2 ^c
0.05	0.01	0.0025	7635	7614	7.1
0.05	0.1	0.0046	7147	7132	0.46
0.05	1.0	0.0046	8019	7507	15
0.3	0.001	0.0131	7515	7428	0.89
0.3	0.01	0.0091	7564	7506	0.89
0.3	0.1	0.0092	7683	7577	2.5
0.3	1.0	0.0086	7438	7508	-1.1 ^c

^aA 1-mL aliquot of solution was used for K_d measurement.

^bA 0.1-mL aliquot was used for gamma counting.

^cNegative values are attributed to error in mass balance assumptions.

Again, there is essentially no uptake of strontium from these solutions, indicating that the favorable uptake results from the waste simulant were due to alkaline conditions. As a result, it was decided that all further uptake studies would be done with a 6M NaOH solution because the 6M concentration approximates the hydroxide concentration present in the Hanford waste simulant.

Sodium is present in relatively high concentration in the Hanford waste simulant as well as in the 6M NaOH solution. As a result, it may interfere with strontium uptake. One experiment was performed to test the uptake of strontium in the presence of the 6M NaOH solution with and without added nitrate present.

The uptake of strontium from the 6M NaOH solution (Table 6) is virtually unchanged by the presence of 1M NaNO₃. The presence of sodium, therefore, presents no problem in terms of strontium extraction efficiency.

Table 6. Uptake^a of Strontium from 6M NaOH with and without NaNO₃ Present Using ~5 mL/g Crown Ether-Coated Charcoal/Bis-acrylamide Particles at 25°C

Bead Material Crown Ether/TBP, M	Mass Particles, g	[NaNO ₃], M	A _i , cpm ^b	A _f , cpm ^b	K _d , mL/g
0.05	0.0038	0	9238	1117	1900
0.05	0.0020	1M	10,139	2068	2000
0.3	0.0145	0	8532	436	1300
0.3	0.0108	1M	11,565	780	1300

^aA 1-mL aliquot of solution was used for K_d measurement.

^bA 0.1-mL aliquot was used for gamma counting.

Strontium nitrate is known to form stable complexes with crown ethers. Because of the lack of any nitrate effect on strontium uptake with these coated particles, however, an alternative explanation of the observed behavior was sought. The first step was to study the uptake of strontium from basic solution in the presence of magnetic particles that were composed of a magnetite charcoal and bis-acrylamide mixture but were not coated with any crown ether. These data are presented in Table 7. A hydroxide dependency reveals a linear decrease in the strontium uptake with increasing hydroxide concentration over the range of 0.5-6M. It is interesting to note that there is essentially no uptake from an aqueous solution without NaOH. Very high distribution ratios are observed at low NaOH concentrations.

After these results were obtained, the next step was to determine which component of the bead was responsible for extracting strontium. The plain magnetite particles are encapsulated with a bis-acrylamide/charcoal mixture, which may cause strontium uptake. Again, NaOH dependencies were performed using both plain magnetite (Fe₃O₄ >10 μm particles) and magnetite encapsulated with the polymeric material polyacrolein. The extraction data are presented in Table 7. A plot of K_d(Sr) vs. NaOH concentration for the two samples is presented in Fig. 1. It is clear that both samples cause appreciable strontium uptake, although the plain magnetite particles display higher K_d(Sr) values at all [OH⁻] concentrations.

Table 7. Uptake^a of Strontium with Uncoated Charcoal/
Bis-acrylamide Extractant Particles from NaOH
Solutions at 25°C

NaOH, <u>M</u>	Mass of Particles, g	A _i , cpm ^b	A _f , cpm ^b	K _d , mL/g
0	0.0015	6205	6291	---
1.0	0.0024	4800	107	18,000
2.0	0.0012	6050	441	11,000
3.0	0.0017	5125	539	5000
4.0	0.0024	5857	402	5700
5.0	0.0017	5043	972	2500
6.0	0.0015	6902	1198	3200

^aA 1-mL aliquot of solution was used for K_d measurement.

^bA 0.1-mL aliquot was used for gamma counting.

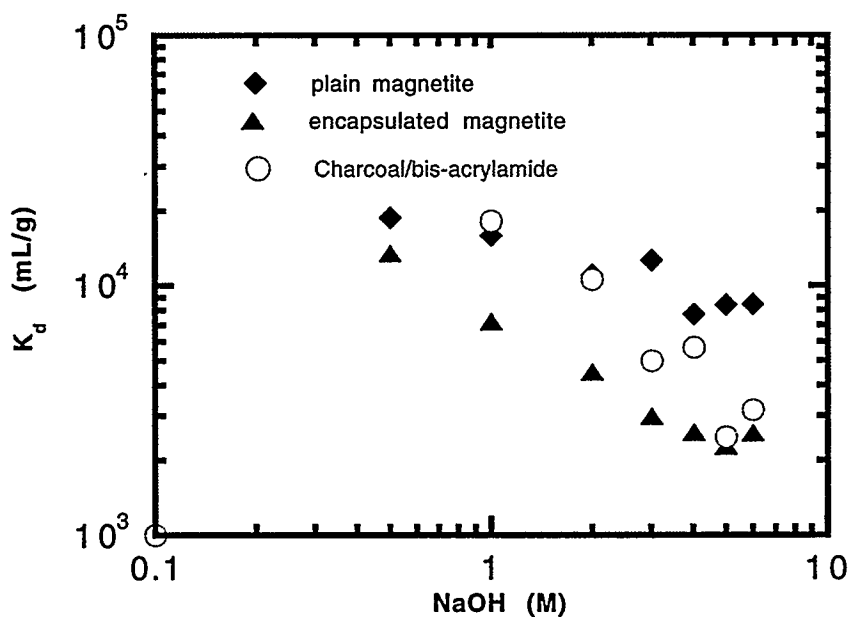


Fig. 1. Strontium K_d at 25°C vs. [NaOH] with Uncoated Charcoal/Bis-acrylamide Magnetite and Encapsulated Magnetite/Polyacrolein Particles

C. Comparison of Partitioning Coefficients and Distribution Ratios

Additional data from solvent extraction provides evidence that the magnetic particles are involved in strontium separation in basic solutions. Table 8 shows partitioning coefficients for strontium that are orders of magnitude lower than the magnetic particles (Table 9) at the same hydroxide concentration. For the solvent extraction system with TBP and 1-octanol as diluent, the

Table 8. Uptake^a of Strontium by Various Types of Commercially Available Magnetite Particles as a Function of NaOH Concentration at 25°C

[NaOH], <u>M</u>	Mass of Particles, g	Particle Type	A _i , cpm ^b	A _f , cpm ^b	K _d , mL/g
0	0.0014	plain	4796	4772	3.6
0.5	0.0015	plain	3789	130	19,000
1.0	0.0017	plain	4661	166	16,000
2.0	0.0025	plain	4366	152	11,000
3.0	0.0016	plain	4603	216	13,000
4.0	0.0025	plain	4530	224	7700
5.0	0.0018	plain	4797	298	8400
6.0	0.0019	plain	4548	266	8500
0	0.0018	encapsulated	4635	4815	---
0.5	0.0014	encapsulated	4294	216	13,000
1.0	0.0018	encapsulated	4844	347	7200
2.0	0.0024	encapsulated	3695	312	4500
3.0	0.0017	encapsulated	4171	685	3000
4.0	0.0015	encapsulated	4891	1005	2600
5.0	0.0022	encapsulated	5090	849	2300
6.0	0.0024	encapsulated	5120	716	2600

^aA 1-mL aliquot of solution was used for K_d measurement.

^bA 0.1-mL aliquot was used for gamma counting.

D values are <1 in 6M NaOH. On the other hand the D values in 2M HNO₃ solution were 5.7 in TBP and 7.1 in 1-octanol (Table 9).

The 2M HNO₃ D values (Table 9) are only slightly lower than the K_d values obtained with magnetic particles in Table 10; thus, the separation with traditional solvent extraction technique would be more favorable in acid solution than in basic. In basic solution, the uncoated particle would permit the MACS process to be a viable solution to the removal of strontium from Hanford tank supernatant.

Table 9. Distribution Ratios for Strontium Extraction with 0.2M tert-Butyl-dicyclohexyl-18-crown-6 in TBP or Octanol for 6M NaOH and 2M HNO₃ at 25°C

Diluent ^a	Phase	Stock, cpm ^b	Background, cpm ^b	cpm	D value
<u>Strontium Extraction in 6M NaOH</u>					
0.2M/TBP	aqueous	9925	28	8505	0.0143
	organic	9925	28	149	
0.2M/1-oct 0.2M	aqueous	9925	28	8225	0.0109
	organic	9925	28	117	
<u>Strontium Extraction in 2M HNO₃</u>					
0.2M/TBP	aqueous	8314	28	1245	5.73
	organic	8314	28	7000	
0.2M/1-oct 0.2M	aqueous	8314	28	1022	7.06
	organic	8314	28	7041	

^aApproximately 5 mL/g of the crown ether was used.

^bA 0.1-mL aliquot was used for organic- and aqueous-phase gamma counting.

Table 10. Strontium K_d Values for ~5 mL/g Coated 0.2M Crown Ether on Charcoal Particles at 2M HNO₃

Particle Type	Particle Mass, g	Average Count, cpm	Average K _d , mL/g	Uncrt +/-
Charcoal	0.01185	7324	11.0	1.2
Charcoal	0.01075	7320	12.1	1.3

Notes: Stock solution activity: 8336 cpm/0.1-mL. Background solution activity: 20 cpm. A 1-mL aliquot of solution was used for K_d measurement. A 0.1-mL aliquot was used for gamma counting.

D. Conclusions

This work has demonstrated that magnetically assisted chemical separation particles can selectively extract strontium from alkaline solutions. The low K_d values obtained in neutral and acidic solutions show that strontium can be stripped. Although no extraction dependence on the crown ether coatings was demonstrated, extraction could be accomplished with the uncoated particles. Even though the mechanism that governs this extraction is still not fully understood, the lack of any expensive added organic extractants in this system offers a unique possibility for the selective separation and recovery of strontium under basic conditions.

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