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CESIUM EXTRACTION FROM A NOVEL CHEMICAL DECONTAMINATION PROCESS SOLVENT USING MAGNETIC MICROPARTICLES*

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ABSTRACT

The chemical, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), has been the subject of recent publications and patents regarding decontamination and decommissioning applications, and its superiority as a decontamination agent has been highlighted in various field demonstrations. To recycle the aqueous HEDPA solvent and/or facilitate waste formation, it would be advantageous to remove dissolved radionuclides that originated from the contaminated surfaces. Cesium isotopes ($^{137,\ 135}$Cs) comprise

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the vast majority of radioactivity found in potential applications at nuclear power facilities.

The present study evaluated magnetic microparticles containing embedded silicotitanate powders for uptake of ^{137}Cs from HEDPA solution. Results indicate that the kinetics are rapid, reaching ~95% of equilibrium within 10 min. The distribution coefficient (K_d) was between 3000 and 10,000 mL/g (90–98% ^{137}Cs removed) depending on particle mass-to-solution volume ratios. The excellent sorption of ^{137}Cs indicates that particle batches may be reused many times without a reduction in extraction efficiency. However, particle degradation and magnetic susceptibility reduction may be a problem due to the dissolution of the magnetite component by the diphosphonic acid. This may be overcome by substituting the magnetite component with other ferromagnetic materials such as Ni or Co alloys.

Key Words: Cesium extraction; Magnetic microparticles; Silicotitanates; HEDPA

INTRODUCTION

In recent years, organic diphosphonic acids have been studied as chemical agents for the decontamination of ferrous metal surfaces. In particular, 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) has been the subject of recent publications and patents[1–3] regarding decontamination and decommissioning (D&D) applications, and its superiority as a decontamination agent has been highlighted in various field demonstrations.[4,5] In large-scale deployment of a D&D process, it would be advantageous to remove radionuclides so that the HEDPA solution can be recycled and/or waste formation facilitated. An example process schematic is represented in Fig. 1. In this example, a fraction of the contaminated HEDPA solution is removed and cleaned by the magnetically assisted separation process studied previously (see Refs. [6,7] and references therein). The magnetic particles used in this process are composed of magnetite, polymer, charcoal, and chemical extractant. These particle composites are small ($< 50\,\mu$m) and are added to a waste tank or mixing chamber ($< 1\%$ by mass) and agitated. Because the particles are magnetic, they can be recovered from solution easily using magnetic separators (e.g., high gradient magnetic separators) and they can be fabricated smaller to offer higher specific surface areas for complexation and added directly to the waste tank (small particles cannot be used in an extraction column because of prohibitive pressure drops). This system may offer distinct advantages over traditional separation techniques (e.g., ion

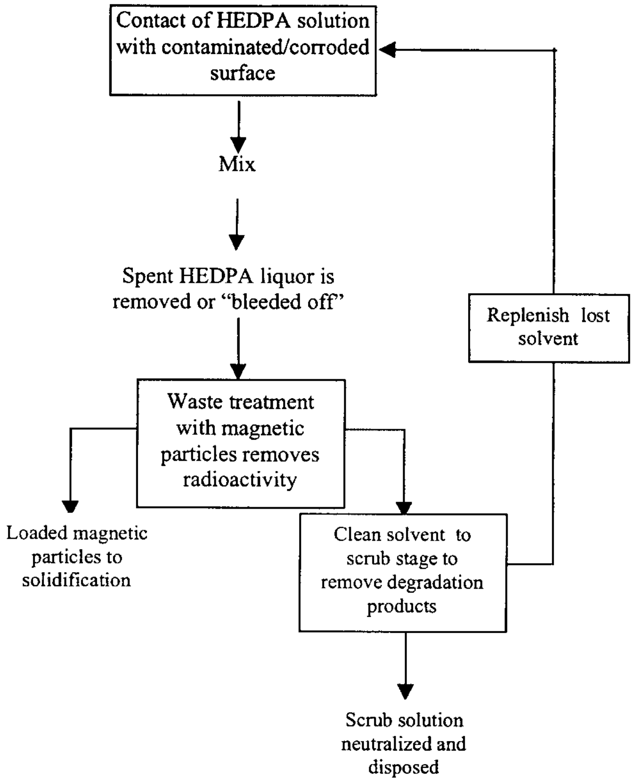

Figure 1. Process schematic of a decontamination process based on HEDPA and solvent treatment with magnetic particles.

exchange, solvent extraction), such as low capital investment, low space requirement, in-tank processing, and high extraction efficiencies (see Ref. [8]). The particles may be recycled if the loading of radionuclides on the particles per contact stage is small and this condition is expected in D&D applications based on the low concentrations of radionuclides typically found in nuclear reactor effluents. Once the microparticles have become loaded with radioactivity, they can be consolidated for disposal. The clean HEDPA solvent may require scrubbing to remove solvent degradation products (e.g., phosphates, acetic acid) before being adjusted for lost solvent and recycled.

For nuclear utilities, radioactive cesium ($^{137,\ 135}$Cs) and cobalt ($^{60,\ 58}$Co) comprise the great majority of radioactivity found in evaporators, holding tanks, tools, and general reactor effluents. Before a process flowsheet can be developed, some basic chemical and physical properties of the magnetic microparticle–

HEDPA system have to be determined. The HEDPA solution does not form strong complexes with cesium, or with monovalent cations in general, and the cesium may be removed with inorganic ion exchangers or silicotitanates. Several studies[9–11] have demonstrated the excellent affinity ($K_d = 10^3 - 10^9$ mL/g) of silicotitanate material for cesium in various alkaline aqueous wastes. In this article, we report cesium uptake kinetics onto magnetic composite microparticles containing embedded crystalline silicotitanate powders, cesium extraction dependence on solution concentrations, and the microparticle degradation rates.

EXPERIMENTAL

The HEDPA (Rhoda Inc., Cranbury, NJ, USA) was diluted with deionized water to 0.01, 0.1, 0.5, and 1.0 *M*. Stock solutions of the appropriate HEDPA concentrations were spiked with ^{137}Cs (from a concentrated stock containing 20 μCi/mL) to produce a stock solution containing 50–60 μCi/L. The magnetic particles were prepared by Cortex Biochem, Inc. (San Leandro, CA) under the trade name MagAcryl™-CST with a 1:1:1 ratio of magnetite, crystalline silicotitanate (CST), and polyacrolein. The particles were washed repeatedly with deionized water and 0.1 *M* NaOH, followed by washing with deionized water alone and drying prior to use. The geometry of the particles was irregular (size range, 5–50 μm) as indicated in Fig. 2. X-ray spectra and images were collected with a Topcon ABT60 scanning electron microscope (Cleaner Image, Indianapolis, IN, USA) with a Noran energy dispersive spectroscopy (EDS) (Thermo Noran, Middleton, WI, USA) system for compositional analysis. The

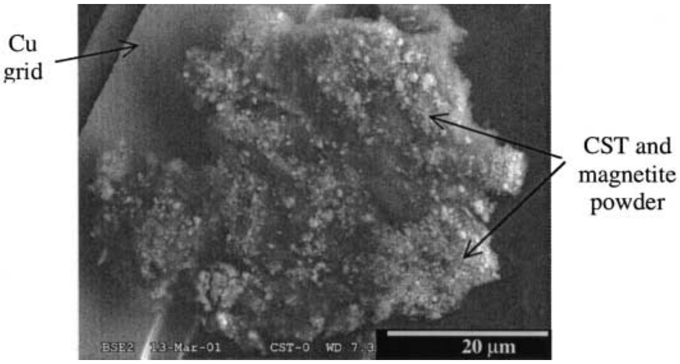

Figure 2. Scanning electron micrograph of a washed MagAcryl-CST particle. The white specks are superparamagnetic magnetite nanocrystals and CST (particle diameter approximately 40 μm).

surfaces of the CST magnetic particles were examined after mounting the particles on double-sided carbon sticky tape.

To determine ^{137}Cs uptake kinetics, 40 mL of 0.1 M HEDPA was added to 258 mg of MagAcryl-CST in a 50-mL glass test tube. Moistened air was sparged through the test tube to mix the contents thoroughly. Periodically, the air sparging was discontinued, and the test tube was placed against a magnetic test tube rack (BioMag® rare earth magnet, Polysciences, Inc., Warrington, PA, USA) for <1 min to separate the magnetic particles to one side of the tube. Aliquots of 50 μL were withdrawn in duplicate and each diluted to 200 μL with water in a round bottom gamma counting tube. Most other experiments were performed in batch mode during which 3 mL of HEDPA solution was added to 20 mg of MagAcryl-CST in a polypropylene test tube. For experiments in which the mass/volume ratio was varied, we used 2–33 mL of HEDPA stock solution. For all experiments, no measurable sorption of cesium onto the walls of the tubes was observed. Relative ^{137}Cs concentrations were determined by gamma counting (662 keV of ^{137}Cs) using a Minaxi AutoGamma 5000 Series analyzer (Packard Instrument Company, Downers Grove, IL, USA) with a 3.5-in. NaI scintillating crystal. The partitioning coefficient, K_d (mL/g), was determined from the initial, c_i, and final, c_f, solution counts as follows:

$$K_d = \frac{c_i - c_f}{c_f}\frac{V}{m} \tag{1}$$

where V is the volume of solution used in the experiment in milliliters and m is the mass of CST particles in grams. This relationship describes the equilibrium concentration of cesium on the particles (activity/g) relative to its equilibrium concentration in solution (activity/mL). Because equilibrium was never achieved, a “practical” K_d was computed based on 30-min mixing times. All experiments were conducted at room temperature.

RESULTS AND DISCUSSION

Uptake Kinetics

The extraction of ^{137}Cs from solution at 6.45 g CST/L, as shown in Fig. 3, was rapid. The solution activity was reduced from 6600 to 490 cpm after 10 min of mixing. The activity dropped by an additional factor of 2.3 after an additional 182 min of mixing. Two mechanisms appear to be prevalent. In the initial stage, the rate is fast up to about 20 min. Cesium sorption is slowed in the next stage where moderate increases in uptake are realized over long mixing periods. Gu et al.[12] used linear and Langmuir isotherms to model exchange kinetics within CST powders and granules. Powders like that entrapped in the MagAcryl-CST

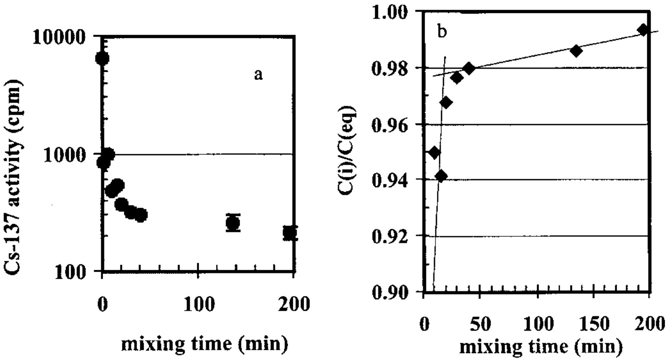

Figure 3. ^{137}CS activity in solution displayed in terms of (a) residual solution activity in 0.1 *M* HEDPA and (b) fraction of equilibrium attained. The lines in (b) are illustrative only and highlight the change in slopes.

were found to be best described using a single-phase diffusion model to produce intracrystalline diffusivities in the order of 10^{-19} m^2/sec.[12] In granules $>10\,\mu$m, a heterogeneous model was used to describe macropore diffusion in addition to intracrystalline diffusion. The values of macropore diffusivity was 10^{-10} m^2/sec making intracrystalline diffusion rate limiting.[12] The MagAcryl-CST magnetic microparticles would likely display relatively large macropore diffusivities where the macropore is defined as the region occupied by polymer since the polymer material can sorb water well.

Figure 3 shows that 95% of equilibrium is achieved within 10 min and 98% after 30 min. The magnetic microparticle separation process is designed to run in semi-continuous or in batch mode, where mixing times will be limited. For this reason, aliquots were not withdrawn after 192 min and this data point was used to represent equilibrium. Equilibrium was arbitrarily chosen as 80% of the solution count rate at 192 min. Thirty minutes was chosen as a practical mixing time for the remainder of experiments, and the solution count rate at this time was used to compute K_d with the understanding that equilibrium has not been achieved.

Mass/Volume Ratio Dependence

In the next set of experiments, the particle mass-to-solution volume ratio was varied. The results, shown in Fig. 4, reflect a thermodynamic advantage in using low mass-to-volume ratios. At 6.4–9.7 g/L the partitioning coefficient is 4100–4300 mL/g, while 2 and 0.6 g/L produced a higher partitioning coefficient of 12,000 and 14,000, respectively. The absolute removal of ^{137}Cs naturally

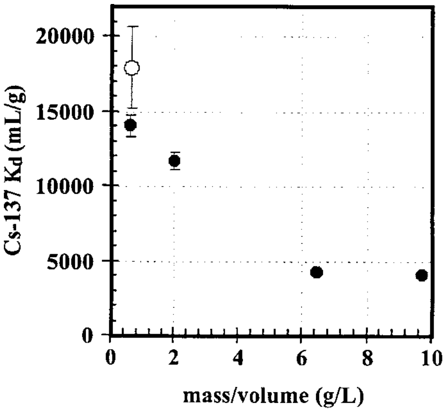

Figure 4. ^{137}Cs extraction as a function of the ratio between magnetic particle mass and solution volume in 0.1 *M* HEDPA. The relative uncertainty in the measurement is provided.

follows the opposite trend, where 89.5% is removed at 0.6 g/L and 97.5% at 9.7 g/L. The open circle in Fig. 4 at 0.6 g/L represents the K_d determined by contacting the same solution twice (two-stage extraction). The K_d increases in the second extraction.

Cesium Loading

Since the cesium concentrations are low in power reactor effluents, the magnetic particles may be reused often without regeneration. To confirm this, a single batch of particles was contacted repeatedly with fresh HEDPA solution spiked with ^{137}Cs. Specifically, a batch of particles was mixed with a volume of 0.1 *M* HEDPA solution (6.7 g/L) containing 2.9 μCi/mL ^{137}Cs (contact 1). The supernatant was removed and an equal volume of HEDPA–Cs solution was added to the same particles (contact 2). This was repeated for eight more contacts. The ninth and tenth contacts were made with a solution concentration of 67 μCi/mL to increase the loading of Cs^+. The partitioning data presented in Fig. 5 indicate a strong affinity of CST for ^{137}Cs at these concentrations. Even after the same particles had reacted with 10 successive contacts of fresh solution, the K_d per contact was constant (the overall K_d increases because the system is never in equilibrium). The anomalously high K_d from the seventh contact is not understood.

Taking this result with the results of the previous section, we conclude that the particles perform well during reuse at the low concentrations of ^{137}Cs tested, which are higher than those typically found in nuclear power effluents.

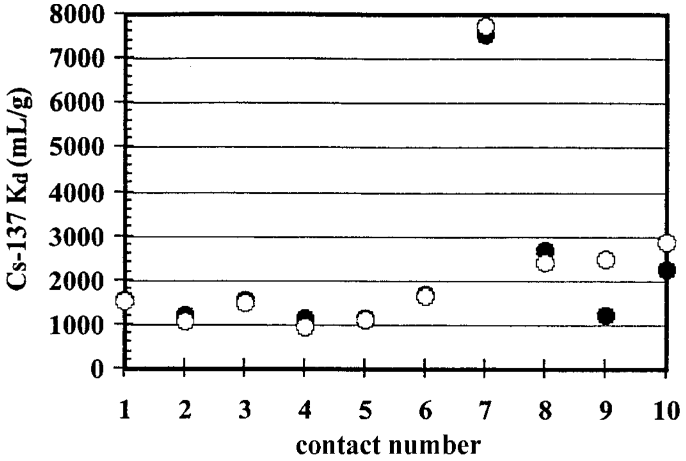

Figure 5. ^{137}Cs partitioning coefficient as a function of the number of contacts with fresh stock solution containing 2.9 or 67 μCi/L ^{137}Cs and 0.1 M HEDPA (duplicate data sets shown).

When plotted as an isotherm, the slope is nearly vertical. Thus, the particles are highly undersaturated (0.016 mmol Cs/g particles) with respect to exchange capacity (~0.5 mmol/g) and are operating at the lower end of Langmuir isotherm (see Fig. 4 of Ref. [13]), where the partitioning coefficient will change little with each successive contact.

HEDPA and Na Concentration Dependence

We also investigated the effect of HEDPA concentration and interfering components that might be found in wastewaters on Cs extraction. These effects are reported in Fig. 6. The HEDPA range is representative of typical concentrations proposed for actual decontamination processes.[1] The extraction dependence favors higher HEDPA concentration. The Na/Cs ratio was varied at 10^5–10^8 and the effect suggests a reduction in partitioning coefficient although the reduction is modest compared to the 1000-fold increase in Na concentration.

MagAcryl-CST Acid Hydrolysis

Since the magnetic component is exposed to solution, a primary concern is the dissolution of magnetite in HEDPA and loss of the particles' magnetic

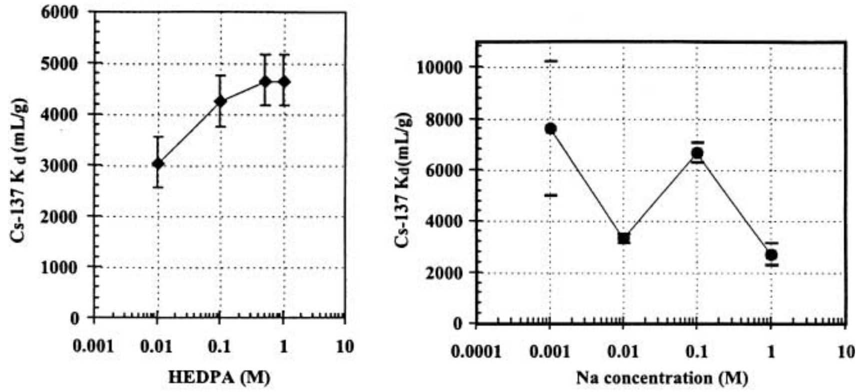

Figure 6. Dependence of the ^{137}Cs K_d on HEDPA and Na concentration (fixed Cs concentration). Relative uncertainties in the individual measurements are shown.

character. Previous kinetic experiments with HEDPA[1] showed that the dissolution of magnetite followed first-order kinetics with a half-life of $t_{1/2} = 14$ min (0.5 *M* HEDPA at 50°C). The question arises as to whether room temperature processing, short contact times, and the polymeric matrix will be sufficient to protect the magnetite from dissolution. Or, will particles containing only encapsulated magnetite be necessary? To answer these questions, the particles were mixed for various periods in 0.1 *M* HEDPA solution at room temperature, tested for magnetic separability, and examined by microscopy.

Figure 7 shows how the exposed and encapsulated magnetite is removed from the surface at various mixing intervals. After 40 min of contact, the magnetite is only sparsely populated on the surface. The magnetic susceptibility of the particles is sufficient for our magnetic separation, with no apparent increase in the time required to attract the magnetite to one side of the test tube. After 2 hr the surface is almost completely removed of magnetite. Isolated regions on the surface still contain magnetite, and the embedded magnetite is still intact. But, magnetic filtration functions as initially observed. Between 2 and 4 hr, the magnetic character was slowly degrading. After 4 hr a portion of the particles lost their black color, and the resulting white powder settled to the bottom of the test tube despite the presence of the magnetic field gradient. After 24 hr no iron was detectable by energy dispersive x-ray analysis (accelerating voltage = 20 kV) on the surface or within the polymer. Only white powder remained in the tube, and there was no attraction of this powder to the magnet. From this information, we expect the particles to endure less than 2 hr of contact with

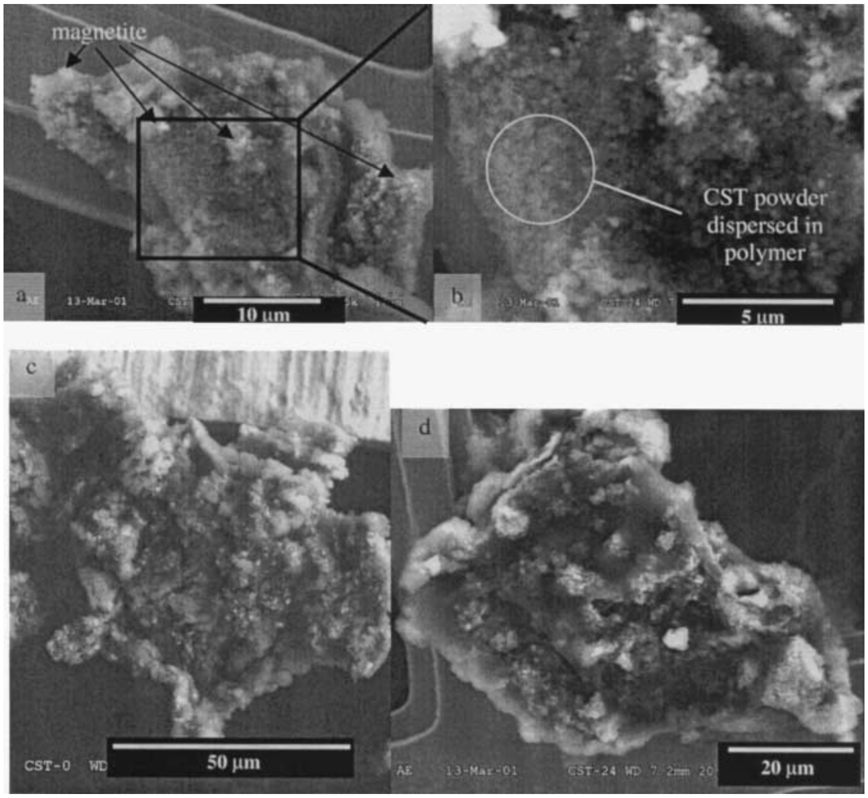

Figure 7. View of (a) MagAcryl-CST before contact and after (b) 40 min, (c) 2 hr, and (d) 24 hr of contact with 0.1 *M* HEDPA at 25°C.

the 0.1 *M* HEDPA solution and shorter times for higher HEDPA concentrations or higher temperatures.

SUMMARY

MagAcryl-CST offers good kinetics (~95% equilibrium in 10 min) for sorption of ^{137}Cs from HEDPA solution at a wide range of concentrations and dissolved sodium. Loading of ^{137}Cs suggests that particles may be reused many times for typical applications, although the total contact times are limited to approximately 2 hr for magnetic filtration to be effective. With 10 min mixing times the particles can endure 12 cycles approximately. Pretreating the particles to remove surface magnetite or use of a magnetite-encapsulated particle is not recommended* since it is clear that the HEDPA freely diffuses within the particle and dissolves the encapsulated matrix. For an HEDPA system we suggest that other superparamagnetic materials be examined as the magnetic component of the microparticles. It is known that the dissolution of Ni metal and Ni alloys is slow in HEDPA[1] and would greatly increase the useful life of the magnetic particles.

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*Unless a less porous polymeric matrix is used. The hydrophobic nature of such a matrix might have adverse effects on the quality of mixing between the solid and liquid phase.

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