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MAGNETIC SEPARATION FOR ENVIRONMENTAL REMEDIATION

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INTRODUCTION

Magnetic separation is a physical separation process that segregates materials on the basis of magnetic susceptibility. High Gradient Magnetic Separation (HGMS) is a form of magnetic separation used to separate solids from other solids, liquids or gases. HGMS uses large magnetic field gradients to separate ferromagnetic and paramagnetic particles from diamagnetic host materials. The technology relies only on physical properties, and therefore separations can be achieved while producing a minimum of secondary waste.

Actinide and fission product wastes within the DOE weapons complex pose challenging problems for environmental remediation. Because the majority of actinide complexes and many fission products are paramagnetic, while most host materials are diamagnetic, HGMS can be used to concentrate the contaminants into a low volume waste stream. We are currently developing HGMS for applications to soil decontamination, liquid waste treatment, underground storage tank waste treatment, and actinide chemical processing residue concentration.¹ In 1992 Los Alamos National Laboratory entered into a Cooperative Research and Development Agreement (CRADA) with Lockheed Environmental Systems & Technologies Company to develop High Gradient Magnetic Separation technology for soil decontamination.

Application of HGMS usually involves passing a slurry of the contaminated mixture through a magnetized volume. A diagram of the method is shown in Figure 1. Field gradients are produced in the magnetized volume by a ferromagnetic matrix material, such as steel wool, expanded metal, iron shot, or nickel foam. The matrix fibers become trapping sites for ferromagnetic and paramagnetic particles in the host material. The particles with a positive susceptibility (paramagnetic) are attracted toward an increasing magnetic field gradient and can be extracted from particles with a negative susceptibility (diamagnetic), which react in the opposite direction, moving away from the areas of high field gradients. Table 1 lists several contaminants and host materials and indicates the magnetic susceptibility of each. The extracted paramagnetic contaminants are flushed from the matrix

fibers when the magnetic field is reduced to zero or when the matrix canister is removed from the magnetic field. The actinide-containing concentrate can be processed for disposal.

Figure 1. Schematic diagram of High Gradient Magnetic Separation.

Because only a fraction of the original bulk requires disposal, significant cost savings can be achieved.

Table 1. Volume Magnetic Susceptibility of Selected Compounds

Compound/Element	Susceptibility x 10 ⁶ (SI)
FeO	7178
Fe ₂ O ₃	1479
UO ₂	1204
Cr ₂ O ₃	844
Am	707
Pu	636
U	411
PuO ₂	384
Th	84
UO ₃	41
TbO ₂	-7.5
ZrO ₂	-8.0
H ₂ O	-9.0
MgO	-11.4
CaCO ₃	-13.0
SiO ₂	-13.6
Graphite	-14.0
Al ₂ O ₃	-18.0

EXPERIMENTAL

The production of both high magnetic fields (>4 tesla) and large field gradients using superconducting magnet technology now makes it possible to separate small ($>0.1\mu\text{m}$) paramagnetic particles. Our current HGMS equipment includes one conventional-coil separator and three superconducting high gradient magnetic separators. The conventional coil (one inch bore diameter) and one three inch bore superconducting magnet are installed on a vent hood in the plutonium facility at Los Alamos. This treatability lab is used to handle low-level radioactive samples such as contaminated soils and uranium and plutonium spiked experiments. A second three inch bore superconducting magnet is currently installed at the Los Alamos waste treatment facility where it is being used for experiments with applications of HGMS to waste water treatment. This magnet will soon be moved and interfaced with a glove box in the plutonium facility to investigate applications of HGMS to plutonium chemical processing residues. Finally, a six-inch bore superconducting magnet is being used in a non-radioactive area for non-radioactive and surrogate tests and for prototype development for soil decontamination applications through the CRADA.

The conventional coil magnet is a Pacific Electric Motor Co. crossfield electromagnet with a maximum field intensity of 2.0 tesla. All three superconducting magnets were built by Cryomagnetics, Inc. with maximum field strengths of 8 tesla. The field is axial with respect to the flow through the matrix.

Feed samples, effluents and backflushes are collected and analyzed for each HGMS experiment. Samples are analyzed for uranium or plutonium concentration using alpha spectroscopy (Controls for Environmental Pollution, Santa Fe, NM), gamma spectroscopy (LESAT, Las Vegas, NV) and Instrumental Neutron Activation Analysis, INAA (Activation Laboratories, LTD, Ancaster, Ontario, Canada). HGMS experiments are conducted using both the conventional and superconducting magnets, with magnetic fields orientations both parallel and perpendicular to the slurry flow.

HIGH GRADIENT MAGNETIC SEPARATION ANALYTICAL MODEL

More than ten variables independently affect the HGMS process (*vida infra.*); an analytical model for the process was needed to select appropriate bench-scale experiments and to effectively analyze the resulting data. In addition, a validated analytical model supports prototype design and process scaleup. The behavior of the paramagnetic particles as they interact with the magnetized matrix has been investigated through modeling studies in the past.²⁻⁸ Areas investigated include the dynamic effect of particle trajectories in homogeneous materials, the influence of particle build-up on the matrix elements, and the effects of particles on the flow field. These studies, though requiring simplifying assumptions, identify appropriate independent variables that form the basis for this investigation.

The matrix materials currently used for HGMS are inhomogeneous and have a complex cross section. In addition, the paramagnetic particles are nonspherical and include a range of particle sizes. All of these factors preclude precise analytical treatment. If the particles are physically liberated from the host material and are not electrically charged, the principle forces governing their behavior are magnetic, viscous, and gravitational.

The performance of the magnetic separator is modeled using a static force balance on an individual paramagnetic particle in the immediate vicinity of a matrix element, as shown in Figure. 2. The model assumes that if the magnetic capture forces are greater than the

competing viscous drag and gravity forces, the particle is captured and removed from the flow stream.

Figure 2. Force balance on a paramagnetic particle in the vicinity of a matrix element.

We propose a rate model for this process that depends on a separation coefficient, which we define in terms of a capture cross section and a potential function defined by the force balance on the particle. A series of tests was performed to evaluate separator performance as a function of the independent variables in the separation process. The results were used to determine the separation coefficient in the proposed rate model and were correlated using physically meaningful, dimensionless groups.

We assume that there exists for each matrix element a capture height, wherein each magnetic particle entering the window defined by the capture height and the matrix element diameter will be captured by the matrix element. We then define a capture cross section for a matrix element to be the ratio of the capture height to the matrix element diameter, as shown in Figure 3. The separation coefficient is related to the capture cross section, and if the capture cross section is known, the separation efficiency can be calculated.

Figure 3. The matrix capture cross section defined as the ratio of capture height to matrix element diameter.

HIGH GRADIENT MAGNETIC SEPARATION DATA CORRELATION

A comprehensive series of experiments was performed to determine the capture cross section as a function of the independent variables. Table 2 lists the variables investigated and their range. For convenience, the list has been divided into material characteristics and separator parameters. A total of 120 experiments were conducted; 76 involved water/contaminant mixtures and 44 involved water/soil/contaminant mixtures. The capture cross section for each test was based on the measured feed and effluent concentrations, the particle force balance, the matrix geometry, and the contaminant particle size.

The capture cross section is significantly less than 1.0, which implies that particles are swept around the matrix elements by the fluid flow even if the particles enter the region defined by the projected frontal area of the matrix element. In addition, the capture cross

section is proportional to the magnetic force and the contaminant particle diameter and inversely proportional to the matrix element diameter and the matrix element spacing. These results are consistent with our observations. The cross section 1 is inversely proportional to the superficial velocity, which is the ratio of the separator length and the slurry residence time in the matrix. Intuitively, one expects to have to maximize both the separator length and the matrix residence time for optimum performance; however, only their ratio has to be considered, and this fact makes superficial velocity the more fundamental parameter.

Table 2. Variables in Separator Performance.

MATERIAL CHARACTERISTICS	SEPARATOR PARAMETERS
Particle Size: Solids and Impurity	Matrix Element Size and Spacing
Impurity Concentration	Matrix Material/Orientation
Solids Concentration	Magnetic Field Strength
Solids Type	Matrix Residence Time/Flow Velocity
Magnetic Susceptibility	Matrix Volume/Temperature
	Surfactant, pH

RESULTS AND DISCUSSION

We have completed a comprehensive series of HGMS experiments with nonradioactive surrogates, as discussed above, and have progressed to tests with radioactive material. The results to date are very promising and are summarized below.

Contaminated Soils

After completion of the work with surrogate systems, work on radioactive samples was started. One of the biggest contamination problems within the DOE Defense Complex is contaminated soils. To address the feasibility of using HGMS for these problems, preliminary tests using uranium and plutonium spiked systems were investigated. Much of the original radioactive work was performed using the 2.0 tesla electromagnet.

Uranium. Figure 4 shows the results of an HGMS experiment to extract UO_3 from water. The efficiency of separation was expected to be only approximately 70%, based on model calculations, due to the low magnetic susceptibility of UO_3 ($\chi_{\text{vol}} = 41 \times 10^{-6}$ (SI)). The results show much better separation than expected. The UO_3 had an equivalent Stoke's diameter of 2-5 μm and the experiment was conducted at 2.0 tesla at pHs of 7 and 12. One other variable that was investigated was the addition of magnetite to the UO_3 slurry. The use of magnetite as a plutonium and americium waste treatment process was reported by Kochen and Navratil in 1987.⁹ The process works by adsorption of the actinide to the ferrite surface, followed by magnetic separation. Magnetite is ferromagnetic and is easily extracted using magnetic separation.

Our results show that with only one pass through the magnetic separator at 2.0 tesla and pH 7, 91.7% of the uranium can be removed from the flow stream with the addition of magnetite. Also encouraging was that even without the addition of magnetite, >85% of the uranium was removed on two passes through the separator at pH 7. These results were very encouraging as we anticipated moving toward experiments with authentic uranium contaminated soils.

Figure 4. Extraction of UO_3 from Water. Variables: pH, Fe_3O_4 ; Field Strength = 2 tesla; UO_3 Particle Size = 2-5 μm .

PuO_2 Spiked Soils. Many sets of experiments have been performed on PuO_2 -spiked clay and SiO_2 slurries. Variables that been investigated include pH, soil particle size, PuO_2 particle size, and field strength. In general, for 2-5 μm PuO_2 particles, >90% of the plutonium can be removed from the influent flow stream during an HGMS experiment. This number is calculated as the difference in the influent activity and the effluent activity ($\text{Ci-Co}/\text{Ci}$)(100). Typically, final plutonium concentrations are between 20 and 80 pCi/g.

Figure 5 shows the results of a typical HGMS experiment to extract PuO_2 from SiO_2 . A 10 weight percent slurry was pumped through the separator at two different pH values. From the graph it is clear that there is little difference in the separation efficiency for removal of PuO_2 from SiO_2 at pH 7 and pH 10. About 98.5% of the plutonium activity is removed from the PuO_2 -spiked mixture at both pH 7 and pH 10. Similar results were seen for PuO_2 -spiked clay slurries, however we observed *ca.* 10-15% better extraction of the PuO_2 at pH 10 than at pH 7.

Figure 5. HGMS Extraction of PuO_2 from SiO_2 : Effect of pH. Field Strength = 6.5 tesla; PuO_2 Size = 2-5mm; SiO_2 size = 10-45mm; 10% solids; 0.2% Hexametaphosphate.

The variable that had the most effect on the extraction of PuO_2 from SiO_2 was the solids particle size. When 10-45 μm SiO_2 was used the extraction efficiency was only about 85%. With the <10 μm SiO_2 the extraction efficiency was >95%. This is probably due to the bigger SiO_2 particles knocking the smaller PuO_2 particles off of the matrix. This was not observed in the clay experiments because typically the clay has very few particles >20 μm in size.

Authentic Soils. At the Fernald Environmental Management Project (FEMP) near Cincinnati, Ohio, there are an estimated 2,000,000 to 4,000,000 m^3 of soil contaminated with uranium. The source of the uranium contamination is from the deposition of airborne particulates from incinerator stacks, aqueous uranium wastes from chemical processing, and solid uranium product spills. The target clean-up for the soils is 30 ppm. Current technologies for remediation of the soil include 1) excavation and transportation of the soil to a repository, 2) immobilization of the uranium in place, 3) physical separation and removal of the highly contaminated soil fractions from the balance of the soil, and 4) soil washing. The incinerator areas, as mentioned above contain soil with uranium contamination in the form of particulates. This makes HGMS a strong candidate for partitioning of the uranium from the soil.

Figure 6 shows the results of an HGMS test run on an incinerator area soil from Fernald. The soil was dry sieved to <53 μm and a 10 weight % slurry was run through the magnetic separator at 2.0 tesla and at three different pH values. The incinerator area soil contains about 500 ppm uranium. Spectroscopic characterization indicates that the uranium is ca. 75% U(VI) and 25% U(IV).

Figure 6. HGMS of Uranium from Fernald Soil. Field Strength = 2 tesla; 10% solids; 0.2% Hexametaphosphate.

From the data it is clear that the separation did not work well at pH 10. However, pH 8 and pH 4 both show promising results. At pH 4 ca. 58% of the uranium was concentrated in 14% of the bulk mass. At pH 8 ca. 47% of the uranium was concentrated in only 3% of the bulk mass. Both of these results represent reasonable separation efficiencies for only one pass through the separator and at only 2.0 tesla field strength. However, in neither test run were we able to reach the 52 ppm uranium target. A second series of tests is planned with test variables of pH and field strength. Also planned are experiments involving reducing agents. If the U(VI), which has a low magnetic susceptibility, can be reduced to U(IV), ($\chi > 1000 \times 10^{-6}(\text{SI})$) we have a much better chance at removing it by magnetic separation. Also planned are tests with magnetite seeding due to the success as had employing this technique with UO_3 in water.

The second DOE soil we have tested using HGMS is from the Nevada Test Site. The soil is a residue from Lockheed Environmental Systems & Technologies. The residue we received were the fines (<100 μ m) from the soil that had been processed through a centrifugal jig and a screw classifier. Again, the residue was sieved to <53 μ m and two passes of a 10 weight % slurry were passed through the magnetic separator at pH 8 and pH 10. The results from the first pass are shown in Figure 7. The first pass was performed at only 0.25 Tesla. At both pH values 83-84% of the plutonium was removed from the flow stream. However, *ca.* 30% of the soil mass was also caught in the separator.

Figure 7. HMGS of plutonium from NTS Residue: LESAT Thickener Underflow Residue. Effect of pH. Field Strength: Pass 1 = 0.25 tesla; 10% solids; 0.2% Hexametaphosphate.

On pass 2 at 0.5 tesla another 24% and 32% of the mass was collected at pH 8 and pH 10, respectively. These results indicate that the NTS residue is highly magnetic and the activity is probably tied up with the magnetic minerals. We are exploring other pretreatment options to try and liberate the plutonium from the soil. A second series of tests has been scheduled.

Soil Results Summary. We have conducted more than 100 HGMS experiments on paramagnetic surrogate materials in water and simulated soils. We have shown that >95% of the paramagnetic contaminant can be extracted from the surrogates. HGMS tests have begun on authentic contaminated soils. Preliminary tests have been performed on Fernald soil and NTS residue. Information from these tests is being used to determine test parameters and pretreatment steps. Future soils to be investigated include samples from Rocky Flats Plant, Johnston Atoll, Hanford, INEL, Mound and Los Alamos.

Waste Water Treatment

High Gradient Magnetic Separation (HGMS) is also being investigated for applications to waste water treatment. Los Alamos National Laboratory Waste Treatment Facility has an average annual influent of 20 million liters with an average gross alpha activity of 70nCi/L from isotopes of plutonium and americium.¹⁰ The contaminants are in the form of particulates, colloids, polymerized colloids and dissolved ions. Another important characteristic of the waste is that most of the activity is associated with particles in the 1-20 μ m size range.

Current DOE regulations for the radioactive levels in the effluent allow 30pCi/L gross alpha for plutonium and americium combined. Current treatment at the waste facility results

in an effluent activity of *ca.* 50pCi/L. Another major concern with the current treatment process is the large volume of low level radioactive sludge that is generated. Annually, 200 55-gal. drums of sludge are produced in the process. New technologies are being sought that can achieve the desired effluent activity levels while producing a minimum of secondary sludge waste. Because the contaminants are in the form of particulates or colloids in the 1-20 μ m size range, HGMS is a strong candidate to address the problems at the LANL Waste Treatment Facility. HGMS also has the advantage of producing a minimum of secondary waste.

One of the 3-inch bore, 8 tesla superconducting magnets was set up at the waste treatment facility to perform treatability tests on plant influents. The first test was performed on influent that had been in a holding tank for *ca.* six months. The pH was adjusted to pH 8. Three different concentrations of magnetite were added to the influent to aid in the separator performance and address the problem of the dissolved ions. The test was performed at a field strength of 7.5 tesla and the results are shown in Figure 8. In each run, over three orders of magnitude of reduction in plutonium activity were achieved. It appears that the addition of magnetite is not necessary to achieve these separation efficiencies. Activity levels below 10pCi/L were achieved, well below the 30pCi/L required by the DOE, with or without magnetite seeding.

Figure 8. HGMS of LANL Waste Treatment Facility influent. Field Strength = 7.5 tesla; pH 8

Future HGMS tests are planned on raw waste treatment facility influent, (i.e. influent that has not been stored in a holding tank.) The question has been raised as to whether the influent is changing with time in the holding tank.

CONCLUSIONS AND DEVELOPMENT PLANS

We have demonstrated that HGMS can be used to concentrate actinides in waste residues and contaminated soils. One of the major benefits of this technology is that it partitions the existing waste volume, creating a low volume, high contaminant concentration component and a high volume, low contaminant concentration component. If the separation efficiency is high, the high volume component can be discarded and the low volume component can be processed further or packaged for disposal. Concentration of the actinides from extraneous materials before further processing can result in more efficient recovery or treatment operations.

We plan to continue to utilize our magnetic separators for surrogate and authentic contaminated soils, residues and waste streams to determine operational parameters. The

experimental results will continue to be used to develop a performance-based HGMS model. We hope to demonstrate the application of HGMS to the separation of actual residues, waste streams and contaminated soils and to develop HGMS for new applications. Results from the CRADA tests are being used to support LESAT's prototype separator design effort.

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$$\lambda = \frac{\text{Capture height}}{\text{Element diameter}}$$

$$D_m = \text{Matrix Element Diameter}$$