REMEDIATION OF HANFORD TANK WASTE USING MAGNETIC SEPARATION

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ABSTRACT

Large volumes of high-level radioactive waste are stored at the Department of Energy's Hanford site. Magnetic separation, a physical separation process, can be used to segregate actinides and certain fission products from the waste. High gradient magnetic separation (HGMS) tests have been performed successfully using a simulated, nonradioactive underground storage tank (UST) waste. Variations in HGMS test parameters included separator matrix material, magnetic field strength, slurry surfactant, and slurry solids loading. Cerium was added to the simulated tank waste to act as a uranium surrogate. Our results show that over 77% of the uranium surrogate can be captured and concentrated from the original bulk with a simple procedure. The results of these tests and the feasibility of magnetic separation for pretreatment of UST waste will be discussed.

INTRODUCTION

High-level radioactive waste (HLW) has been stored in large underground storage tanks (UST) at the U.S. Department of Energy's Hanford Site since 1944. More than 253,000 m^3 of waste have been accumulated in 177 tanks. These wastes consist of many different chemicals and are in the form of liquids, slurries, salt cakes and sludges. The Department of Energy Office of Environmental Restoration and Waste Management is funding an Underground Storage Tank-Integrated Demonstration (UST-ID) to address the UST wastes. A small magnetic separation effort at Los Alamos National Laboratory was funded through the UST-ID to explore the use of high-gradient magnetic separation for tank waste segregation. The concept is to concentrate into a low volume waste stream, all or most of the magnetic components, which include actinide compounds, most of the fission products and precious metals.

Magnetic separation is a physical separation process that can be used to segregate materials in a mixture on the basis of magnetic susceptibility. HGMS is a form of magnetic separation that can be applied to the separation of solids from other solids, liquids, or gases. (1) Because the technology relies on physical processes, little or no secondary waste is generated. HGMS, in some respects, is a mature technology being applied industrially on the sixty ton per hour scale to purify kaolin clay.

When a paramagnetic particle encounters a non-uniform magnetic field, the particle moves in the direction of increasing field gradient. Diamagnetic particles react in the opposite sense. This serves as a basis for separation. When the field gradient is of sufficiently high intensity, the paramagnetic particles can be captured and separated from diamagnetic materials. Table I illustrates several species identified in tank waste that can be separated and concentrated with magnetic separation. The compounds with a positive magnetic susceptibility are attracted towards an increasing magnetic field gradient and can be separated from compounds with a negative susceptibility that react in the opposite direction. Thus, HGMS can be looked upon as a high rate selective filter. Our initial tests show that HGMS is a suitable technology for concentrating paramagnetic material found in the UST.

The production of both high magnetic fields (>4 tesla) and large field gradients using superconducting magnet technology have helped make magnetic separation of small (<0.1 μm) paramagnetic particles achievable. Actinides, selected fission products, precious metals, and other paramagnetic contaminants can be extracted and concentrated using this technology. The sludge/slurry mixtures in the UST have been found to contain the majority of the radioactivity. The sludges consist of small particles and colloids in the form of hydrated metal oxides and hydroxides and is, therefore, ideally suited for the application of magnetic separation. Magnetic separation should provide a head-end separation and concentration of many radioactive components of UST waste. This will reduce the volume of tank waste that ultimately goes to the vitrification unit while reducing the chemical processing capacity needed for other unit operations such as TRUEX. (2) With volume reduction a commensurate cost reduction should result. HGMS can be made portable, making field operation practical.

Application of HGMS usually involves passing a slurry of the contaminated mixture through a magnetized volume. The magnetized volume is filled with a porous magnetizable matrix material, such as steel wool or expanded nickel foam, that generates high field gradients in the magnetized working volume. Ferromagnetic and paramagnetic particles of the mixture are captured on the matrix. In this way, the bulk of the sludge or slurry is decontaminated by removing actinide compounds, and the paramagnetic fission products. Thus, at sufficiently high separation efficiency, the separation process converts the bulk sludge to low level waste for low cost treatment and disposal. The extracted magnetic components are retrieved by removing the magnetic field. The concentrated contaminate can then be processed for vitrification.

The UST Magnetic Separation work is a portion of the magnetic separation effort at Los Alamos. Other current areas of investigation include the use of magnetic separation methods to enhance the chemical processing of plutonium and uranium residues. HGMS is also being evaluated as a soil decontamination technology. In this area, a Cooperative Research and Development Agreement (CRADA) was signed

TABLE I
Volume Magnetic Susceptibility of Selected UST Elements and Compounds

Compound or Element	Susceptibility x 10^6 (SI)
FeO	7178.0
CoO	5300.0
Fe_2O_3	1479.0
Ce	1463.0
UO_2	1204.0
Cr_2O_3	844.0
Pd	805.0
NiO	740.0
Am	707.0
Pu	636.0
U	411.0
PuO_2	384.0
CuO	242.0
RuO_2	107.0
UO_3	41.0
MoO_3	26.0
Al	21.0
Ca	19.0
Si	-0.3
CaO	-1.0
ZrO_2	-7.8
MgO	-11.0
KCl	-13.0
$CaCl_2$	-13.0
NaCl	-14.0
SiO_2	-14.0
Al_2O_3	-18.0
$BiPO_4$	-20.1

early in 1992 between Los Alamos and Lockheed Environmental Systems and Technology Company.

RESULTS/DISCUSSION

The Hanford UST waste contains radioactive constituents, making tests with actual waste difficult and expensive. Therefore, a nonradioactive waste simulate was provided by Pacific Northwest Laboratory (3) for use in developing the HGMS waste treatment process. The composition of the waste is shown in Table II, with the paramagnetic components indicated in bold-faced text. The simulated waste is a complex heterogeneous mixture including a sludge composed of metal oxides and hydroxides, and a supernate composed of dissolved salts and metal complexes. The particulate paramagnetic species in the mixture could be separated and concentrated by HGMS. For this particular simulant the targeted components for HGMS are compounds of iron, chromium, nickel, manganese and cerium (a surrogate for uranium).

TABLE II
Single Shell Tank Waste Simulant Composition[a,b]
in Bold-faced Text Chemicals are Paramagnetic

Chemical	Dry Weight %
Aluminum oxide/hydroxide	16.8
Bismuth (phosphate below)	3.30
Calcium oxide/hydroxide	0.49
Cerium Oxide (Uranium Simulate)	0.76
Chromium oxide/hydroxide	0.49
Copper oxide/hydroxide	0.03
Fluorine	0.42
Iron oxide/hydroxide	4.64
Lanthanum oxide	0.32
Lead oxide	0.17
Magnesium oxide/hydroxide	0.11
Nickel oxide/hydroxide	0.08
Manganese oxide/hydroxide	0.23
Phosphate	8.50
SiO_2	7.09
Silver oxide	0.02
Sodium	17.8
Strontium Oxide	0.03
Zinc oxide/hydroxide	0.03
Zirconium (phosphate above)	0.12
Nitrate	27.5
TOC (citrate/EDTA)	0.21
Nitrite	1.53
Sulfate	0.73
Carbonate	1.50
Total	90.68%[c]

a. Single Shell Tank Simulate provided by M. Elmore of Pacific Northwest Laboratory.
b. Sample contains ~80% H_2O, pH ~ 11. Composition determined by inductively coupled plasma spectroscopy and ion chromatography. The results and sample were provided by M. Elmore, Pacific Northwest Laboratories.
c. Other 10% is accounted for by waters of hydrations.

The HGMS process involves at least nine distinct parameters that are important to a separation. Separation design parameters that are controllable include matrix residence time (flow velocity), matrix volume, matrix element size and spacing, matrix material, magnetic field strength, and type of surfactant. Non-controllable parameters that are dictated by the sample include particle size, contaminant concentration, and magnetic susceptibility of the paramagnetic particles. An analytical model of the separation process using these parameters has been developed and verified with the experimental

results from HGMS bench-scale tests. With the analytical model, a variety of waste processing and remediation problems can be analyzed. In the UST application, the appropriate HGMS process parameters and specification of test protocols were determined with the model.

The model was derived from a multi-component force balance, which governs the physical separation of discrete particles involved in the HGMS process. The separation efficiency predicted by the analytical model is proportional to this force balance. When the feed stream is passed through a high magnetic field interlaced with high field gradients the magnetic forces on the particles are proportional to the applied magnetic field, the resulting field gradient, and the relative magnetic susceptibility between the particles and the bulk slurry. Particle motion within the separator is governed by inertial, frictional, and gravitational forces. Also, attractive or repulsive interparticle forces become significant as particle size decreases. These forces combine to act differently for each particle system or feed material treated.

A typical HGMS experiment consisted of pumping a 200 ml slurry of the Hanford simulate through a 5 cm^3 ferromagnetic filter element contained in a cylindrical matrix canister. The canister was positioned in the bore of either a Cyromagnetics, Inc. superconducting magnet or a Pacific Electric Motor (PEM), Inc. electromagnet. The slurry was pumped through the matrix and a sample of the effluent was obtained for analysis. Two or three repetitive passes were made with sample collection from the effluent of each pass. After testing was completed, the matrix canister was removed from the magnetic field and rinsed with distilled-deionized water to collect the paramagnetic particles that were trapped in the filter. The concentration of the paramagnetic components (Fe, Cr, Mn, Ni, Ce) was determined by inductively coupled plasma-mass spectrometry (ICP-MS) or atomic emission spectroscopy.

Three sets of experiments were performed on the Hanford UST waste simulate. Separator design parameters that were varied in the investigation were matrix type (nickel foam, stainless steel felt metal, and stainless steel wool) and magnetic field strength. In addition, the type of surfactant added to the slurry and sonication of the slurry before processing were also investigated. The results are shown in Tables III, IV and V.

In the first set of experiments (Table III) the matrix material was nickel foam. Two slurries were prepared: one with $Na_4P_2O_7$ surfactant (0.5 wt%) and one without surfactant. The slurries were pumped through the matrix canister at a flow rate of 1 ml/s. Three passes were made at increasing field strengths of 0.1, 0.5 and 2.0 tesla (T). Between each pass, the magnetic field was reduced to 0 T and the matrix was washed with distilled-deionized water. The purpose of the increasing field strengths was to initially scavenge ferromagnetic iron compounds at a low field to prevent clogging of the matrix during later high field extractions. It is interesting to note that only 20% of the total iron was removed during the 0.1 T pass. This indicates that in the total bulk solution (4.64% iron, see Table II), less than 1% of the iron compounds are ferromagnetic. With a low ferromagnetic iron content the possibility of the matrix plugging on subsequent passes is reduced. The results also show that a higher separation efficiency is achieved when surfactants are added. The uranium surrogate (cerium) results are striking. Over 77% of the cerium was captured and concentrated from the original bulk.

The second series of experiments (Table IV) was done with a felt metal screen matrix in a parallel plate configuration. Previous experiments had indicated a surprisingly high performance with the felt metal matrix. (4) Three slurries were prepared: one without surfactant, one with 0.5 wt% $Na_4P_2O_7$, and a third with a non-phosphate containing surfactant, Triton CF-10 (0.4 wt%). To further disperse and de-agglomerate the particles, the slurries were sonicated before the separation test. Two passes at a flow rate of 2.7 ml/s were made through the matrix canister. An initial ferromagnetic scavenge pass at 0.1 T was followed by a pass at 2 T. This experiment again showed that a higher separation efficiency was achieved when surfactants were used. The performance of the two surfactants were similar indicating that using a non-phosphate surfactant is possible. With the felt metal matrix, the extraction of the paramagnetic particles was not as high as with the nickel foam matrix. Possible explanations include the following: 1) The sonication pretreatment broke the particles into nanometer or molecular sized species. The effective particle size range for proficient HGMS, as described earlier, is between 70 and 0.1 μm. 2) The shorter residence time, relative to the first experiment, fell below some critical value resulting in poor separation. 3) Channel flow within the matrix allowed the slurry to flow along the inside walls of the canister instead of passing through the matrix. Previous experiments with a simple water mixture spiked with characterized paramagnetic particles identified this as a problem. A new matrix has been designed to prevent channel flow. However, this modified parallel plate matrix was not tested with the Hanford simulant waste.

A third series of experiments was designed to answer questions that were raised in the earlier separation tests. The results are shown in Table V. The matrix material was medium stainless steel wool pads. This matrix has proven to be an effective filter for paramagnetics in clays. (4) Two slurries were prepared, both with 0.4 wt% Triton CF-10; one slurry included a sonication pretreatment. Two passes were made through the matrix canister at 7.5 T and a flow rate of 2.7 ml/s. The results show that sonication pretreatment reduces the extraction efficiency. The particles apparently are broken into sub-micron species, which are not extracted effectively by HGMS. The results also show that even at 7.5 T, the paramagnetic extraction efficiency was lower compared to the experiment with the nickel foam matrix (Table III), only 30% of the cerium was extracted versus 77% in the first experiment.

Despite the complexity of the problem and the limited number of experiments performed several important results were obtained as follows: 1) Surfactant is necessary for slurry dispersion as shown by comparing runs 1 and 2. Of the two surfactants investigated, both produced similar results (runs 4 and 5). 2) Sonication reduced the separation efficiency probably because it breaks particles into sub-micron species making separation more difficult. 3) The residence time of the slurry within the matrix is an important parameter for an efficient separation. 4) Slurry simulant aging seems to have a significant, adverse effect on separation efficiency. The results from two separations (runs 2 and 7) were compared with the results from the model. A plot of separation effectiveness versus particle size is shown in Fig. 1. The plot shows two curves. The open circles plot the predictive cerium extraction curve for run 2 (nickel foam matrix). The measured cerium extraction of 77% is shown on the curve. The closed circles indicate the expected cerium extraction for run 7 (medium

TABLE III

HGMS Results for Hanford Single Shell Tank Waste Simulate

Experiment 1 Conditions: Nickel Foam Matrix, 95% Void; 10% Solids; Slury Flow Velocity - 1ml/sec; Ambient Temperture

Run	Conditions	Field Strength (Tesla)	Pass	Effluent Concentration[a]									
				Ce (ppm)	Ce (Total eff.)[b]	Cr (ppm)	Cr (Total eff.)	Fe (ppm)	Fe (Total eff.)	Mn (ppm)	Mn (Total eff.)	Ni (ppm)	Ni (Total eff.)
1	no surfactant	0	0	650		203		2750		118		53	
		0.1	1	625		205	-0.01	2750	0.00	118	0.00	50	0.057
		0.5	2	600	0.077	188	0.074	2500	0.091	105	0.110	45	0.151
		2.0	3	425	0.346	135	0.335	1875	0.318	75	0.364	30	0.434
2	0.5 wt% $Na_4P_2O_7$	0	0	700		220		2750		125		52	
		0.1	1	475	0.321	170	0.227	2200	0.200	95	0.240	43	0.173
		0.5	2	450	0.357	158	0.282	2050	0.255	88	0.296	40	0.231
		2.0	3	160	0.771	120	0.455	1550	0.436	65	0.48	25	0.519

a. Experimental error in the effluent concentrations is ±10%. Negative numbers fall within the ±10% error.

b. Total effectiveness detrmined by $(n_o - n_i/n_o)$ where n_o is the initial feed concentration and n_i is the concentration of the pass effluent.

TABLE IV

HGMS Results for Hanford Single Shell Tank Waste Simulate

Experiment 2 Conditions: Felt Metal Matrix, Papallel Plate Configuration; 10% Solids; 4 min. Pre-sonication; Slurry Flow Velocity - 2.7 ml/sec; Ambient Temperature

Run	Conditions	Field Strength (Tesla)	Pass	Effluent Concentrationa									
				Ce (ppm)	Ce (Total eff.)[b]	Cr (ppm)	Cr (total eff.)	Fe (ppm)	Fe (Total eff)	Mn (ppm)	Mn (Total eff.)	Ni (ppm)	Ni (total eff.)
3	no surfactant	0	0	640		160		2000		84		39	
	sonicated	0.1	1	640	0.000	170	-0.06	2300	-0.15	93	-0.11	43	-0.10
		2.0	2	610	0.047	180	-0.13	2300	-0.15	93	-0.11	40	-0.03
4	0.5 wt% $Na_4P_2O_7$	0	0	680		190		2600		100		44	
	sonicated	0.1	1	690	-0.02	160	0.158	2000	0.231	83	0.170	34	0.227
		2.0	2	610	0.103	150	0.211	2000	0.231	77	0.230	31	0.295
5	0.5 wt% Triton CF-10	0	0	640		190	2600		100		50		
	sonicated	0.1	1	620	0.031	180	0.053	2400	0.077	96	0.040	44	0.120
		2.0	2	600	0.063	140	0.263	1800	0.308	73	0.270	35	0.300

a. Experimental error in the effluent concentrations is ±10%. Negative numbers fall within the ±10% error.

b. Total effectiveness determined by $(n_o - n_i/n_o)$ where n_o is the initial feed concentration and n_i is the concentration of the pass effluent.

TABLE V

HGMS Results for Hanford Single Shell Tank Waste Simulate
Experiment 3 Conditions: Medium Stainless Steel Wool Matrix, 92% Void Fractions; 5% Solids; 0.5 Weight% Triton CF-10; Slurry Flow Velocity - 2.7 ml/sec; Ambient Temperature.

Run	Conditions	Field Strength (Tesla)	Pass	Effluent Concentration									
				Ce (ppm)	Ce (Total eff.)[b]	Cr (ppm)	Cr (Total eff.)	Fe (ppm)	Fe (Total eff.)	Mn (ppm)	Mn (Total eff.)	Ni (ppm)	Ni (Total eff.)
6	0.5 wt% Triton CF-10	0	0	200		72		990		42		17	
	sonicated	7.5	1	210	-.05	72	0.000	980	0.010	38	0.095	18	-0.06
		7.5	2	180	0.10	68	0.056	930	0.061	36	0.143	15	0.12
7	0.5 wt% Triton CF-10	0	0	200		71		980		41		17	
	no sonication	7.5	1	180	0.100	66	0.070	890	0.092	35	0.146	14	0.176
		7.5	2	140	0.300	51	0.282	700	0.286	27	0.341	11	0.353

a. Experimental error in the effluent concentrations ±10%. Negative numbers fall within the ±10% error.

b. Total effectiveness determined by $(n_o - n_i/n_o)$ where n_o is the initial feed concentration and n_i is the concentration of the pass effluent.

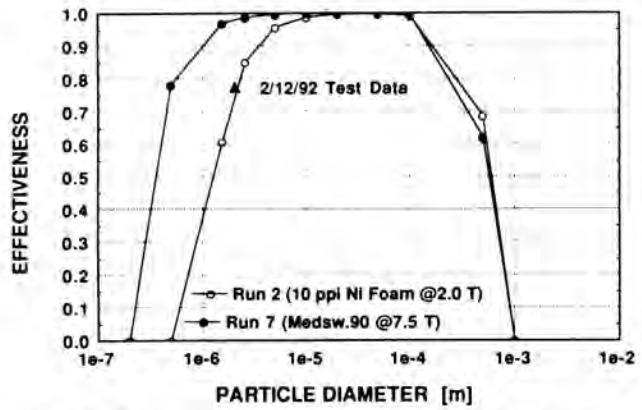

Fig. 1. Separator performance: Hanford simulant.

stainless steel wool matrix). Using the measured data from run 2, the particle size of the cerium in the slurry was determined to be ~2 μm. Assuming the same 2μm particle size for run 7 and considering the improved performance for the medium stainless steel wool matrix, ~98% of the cerium was expected to be extracted in run 7. This value is much higher that the measured 30% value of cerium extraction in run 7. Because run 7 was made six months after run 2, it appears that simulant aging had a significant effect on separation performance. Further tests are planned to verify the high extraction efficiency predicted by the analytical model in conjunction with the earlier tests. Future tests will be conducted to identify the behavior of individual compounds of interest such as iron oxides, actinide oxides and hydroxides, as well as non-radioactive fission product surrogates.

Application of HGMS to headend UST processing can offer several benefits. Assuming some type of chemical processing will ultimately be used to separate the radioactive elements from the bulk of the waste, our preliminary results show that HGMS can be used to extract and concentrate the ferromagnetic and paramagnetic components. Removal of the bulk of the radionuclides will result in a significant simplification and cost reduction of process chemicals used downstream. A reduced processing capacity will also be realized downstream.

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