Superconducting Open-Gradient Magnetic Separation for the Pretreatment of Radioactive or Mixed Waste Vitrification Feeds

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Vitrification has been selected as a final waste form technology in the U.S. for long-term storage of high-level radioactive wastes (HLW). However, a foreseeable problem during vitrification in some waste feed streams lies in the presence of elements (e.g., transition metals) in the HLW that may cause instabilities in the final glass product. The formation of spinel compounds, such as Fe_3O_4 and $FeCrO_4$, results in glass phase separation and reduces vitrifier lifetime, and durability of the final waste form. A superconducting open gradient magnetic separation (OGMS) system maybe suitable for the removal of the deleterious transition elements (e.g. Fe, Co, and Ni) and other elements (lanthanides) from vitrification feed streams due to their ferromagnetic or paramagnetic nature. The OGMS systems are designed to deflect and collect paramagnetic minerals as they interact with a magnetic field gradient. This system has the potential to reduce the volume of HLW for vitrification and ensure a stable product. In order to design efficient OGMS and High gradient magnetic separation (HGMS) processes, a fundamental understanding of the physical and chemical properties of the waste feed streams is required. Using HLW simulant and radioactive fly ash and sludge samples from the Savannah River Technology Center, Rocky Flats site, and the Hanford reservation, several techniques were used to characterize and predict the separation capability for a superconducting OGMS system.

INTRODUCTION

Open-gradient magnetic separation (OGMS) can pretreat and separate deleterious elements from radioactive and mixed waste streams prior to vitrification to reduce cost, increase glass durability, and maximize vitrifier lifetime. Additionally, this potentially low-cost physical separation process may serve DOE by reducing the large quantities of the high-level waste (HLW) from defense-related activities currently targeted for glass production, as well as low-level waste (LLW) streams. Many HLW and LLW waste streams include constituents deleterious to the durability of borosilicate glass and possess paramagnetism. For example, Fe, Cr, Ni, and other transition metals may limit the

waste loading and affect the durability of the glass by forming spine1 phases at the high operating temperature used in vitrification. Some magnetic spine1 phases observed are magnetite (Fe_3O_4), chromite ($FeCrO_4$), and other spine1 phases [(Fe, Ni, Mg, Zn, Mn)(Al,Fe, Ti,Cr)O_4] as described elsewhere. Stable spine1 phases can cause segregation between the glass and the crystalline phases. As a consequence of the difference in density the spine1 phases tend to accumulate at the bottom of the glass melter. This accumulation decreases the conductivity and melter lifetime, as well as the durability of the resulting glass. Optimization of an OGMS system involves identifying the heterogeneous mineral phases present in the waste and the sorption behavior of target radionuclides onto the mineral phases. This program addresses feasibility and optimization of an OGMS system for separating paramagnetic constituents (spinel-based and other minerals) from DOE waste streams targeted for vitrification.

Tests will focuses on the Savannah River Technology Center (SRTC) waste streams which is initiating vitrification for HLW glass production at the Defense Waste Processing Facility (DWPF). Surrogate wastes streams from the Savannah River site will be the initial subject of this study. However, other DOE waste streams will be evaluated in the near future. In order to determine the feasibility of OGMS we are investigating (1) the mineral composition and the chemical state of the constituents present, (2) methods for liberating the deleterious constituents from the matrix and characterizing them, (3) component magnetic susceptibility, (4) the separation of these materials effectively to reduce both the quantity of deleterious waste constituents (e.g., iron, chromium, nickel) that hamper production of borosilicate glass, and (5) the final disposition of radionuclides. Pretreatment of waste with OGMS will reduce the feed stream to a vitrifier (and drastically reduce cost) while diverting the bulk as a LLW.

Open Gradient Magnetic Separation

Open gradient magnetic separation is based on a particle behavior while in the presence of a magnetic field. Paramagnetic particles (e.g., U, Pu, fly ash, ferrite, pyrite) are deflected when free falling in an applied magnetic field and attracted toward the bore wall of the magnet. Diamagnetic particles (e.g., clay, alkali and Al salts) are repulsed from the magnetic field toward the center of the bore. Using magnetic field gradients generated by a superconducting magnet spatial separations of different &actions are achieved in a short distance. For example, coal ash has been used to demonstrate the separation of pyrite (FeS_2) from the rest of the coal components with size distribution between 50-150 µm. At Argonne National Laboratory (ANL) a l-m long 3.6 T superconducting quadruple magnet with a highly uniform gradient of 60 Wb/m^3 is used for OGMS. Previous OGMS systems used to separate plutonium and uranium waste streams had magnetic fields up to 2 T. The ANL OGMS system has various advantages over physical and chemical separation techniques when applied to radioactive and hazardous waste streams: (1) the separation has minimal mechanical parts, (2) no chemical additives required, (3) effective with solid or liquid waste, (4) continuous processing, (5) the magnetic field in the separator space is not limited by saturation properties of iron ($B_0 \sim 2T$), (6) high feed throughput, and (7) low power cost.

OGMS Apparatus

Figure 1 shows the dimensions of the OGMS apparatus where the magnetic field axis (z) is vertical, and the gradient is constant in the radial direction from the bore center to the wall and the magnetic field is isotropic in the angular *(6)* axis. In a cylindrical bore a uniform magnetic field gradient can be produced with a quadruple superconducting magnet (length=0.68 m diameter=0.064 m). It operates at liquid He temperatures and generates intense magnetic field gradients with very low power consumption ~l/5 conventional separator costs). Once the magnet is energized the electricity consumption is minimal. A waste stream is metered into the system through an AccuRate screw feeder capable of feeding-solid waste at 0-20 Kg/hr. Waste continuously spills into a vertical pipe that permits 1.83 m of free falling before passing through an annulus of 3.18 to 4.13 cm and entering the magnetic field zone. The magnetic field gradient in the center bore

is characterized by a high field at the bore wall and zero field at the center. This design is amenable to both dry and wet processing.

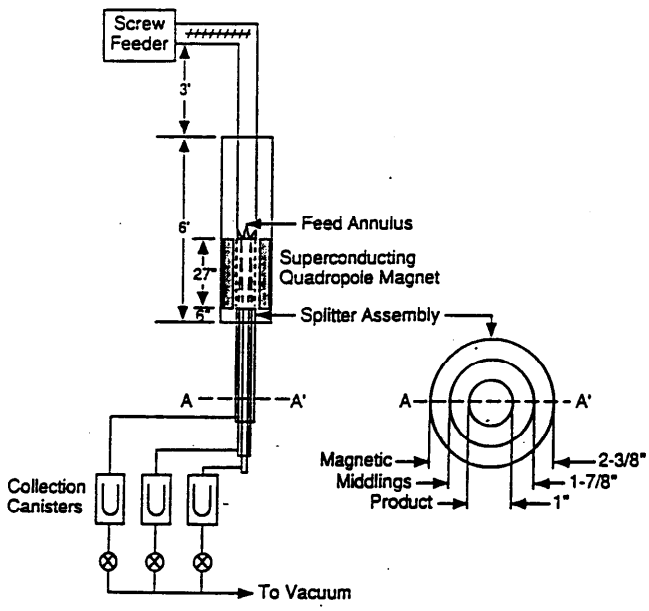

Figure 1. ANL Superconducting Open Gradient Magnetic Separator.

Extensive experimental and theoretical work has been performed on OGMS and HGMS systems for coal beneficiation and other mineral separations. Both OGMS and HGMS techniques have advantages and disadvantages for specific waste streams. Superconducting magnetic separation is being used commercially to remove Fe_2O_3 and TiO_2 impurities from Kaolin clay in the paper industry. Magnetic separation of uranium from MgF_2 has shown potential in wet and dry systems. Aven et al. showed that for an OGMS system separation of Pu from graphite, bomb reduction, sand, slag, and crucible were possible obtaining Pu rich and lean fractions. Other waste streams such as electrorefining pyrochemical salts and direct oxide reduction were less suitable for conventional OGMS systems due to the high concentration of Pu obtained in the lean fraction. The high gradient field possible with the ANL superconducting OGMS system may potentially reduce the Pu in the lean fraction. Other waste streams studied containing Pu are selected Rocky Flat incinerator ash which. produced identical lean and rich fractions of Pu.

However, for a particular Pu ash waste stream a good segregation was obtained with OGMS and it is important to reevaluate the feasibility of magnetic separation with a higher field gradient system. However, before attempting to segregate radioactive waste streams, chemical and physical characterization is performed to model the magnetic separation process.

Theory

As in HGMS, the major forces acting on the particles in the open gradient magnetic separator are magnetic, fluid drag, gravitational, and inertial forces. Theoretical modeling must take these forces into consideration including the method used to introduce the waste into the separator.

Magnetic Force

The magnetic force (F_m) acting on a weakly magnetic particle is proportional to the gradient of the magnetic field (∇B), the particle dimension (D_p), the magnetic susceptibility (χ) of the particle, and the induced magnetic moment of the particle (μ).

$$F_m = \frac{\pi}{6} D_p^3 \chi \frac{\bar{B}}{\mu_o} \nabla \bar{B} \qquad (1)$$

For angular motion, the field gradient for the quadrupole magnet is constant for a given θ value. For radial motion this magnet has a constant r-gradient (60 T/m) at the field maximum which leads to $\bar{F} \frac{dB}{dr} r$ for the geometry of this magnet

$$F_m = \frac{\pi}{6} D_p^3 \chi \frac{\bar{B}}{\mu_o} \frac{dB}{dr} = \frac{\pi}{6} D_p^3 \chi \left(\frac{dB}{dr}\right)^2 r \tag{2}$$

Fluid-Drag Forces

The fluid-drag force (Fd) acting on a particle will be determined by the relative motion of the waste particle with respect to the gas carrier fluid (e.g., air, water). Low Reynolds number is (Re<O.3) expected for the radial motion of the waste particle and Stoke's law can be used. Where η viscosity, and V_p V_f are the volumes of the particle and the fluid media.

$$F_d = 3\pi\eta D_p(V_p - V_f) \tag{3}$$

For those region where Reynolds number is greater than 0.3 but less than 1000, F_d is defined as

$$F_d = \frac{\pi}{8} C_d D_p^2 (V_p - V_f)^2 \tag{4}$$

Newton's law for drag would apply for Reynolds numbers greater than 1000. Variations in Reynolds number will be discussed in a future paper.

Gravitational Force

The waste particles will experience gravitational effects (F_g) while entrained in the carrier fluid. Thus F_g is defined as:

$$F_g = g \frac{\pi}{6} D_p^3 (\rho_p - \rho_f) \tag{5}$$

Due to the radial magnetic force being the driver of the magnetic separation and this magnetic force is smaller than the gravitational force, the magnetic is arrange such that the two forces are orthogonal or the magnetic bore is parallel to the gravitational force.

Inertial Force

The inertial force (F_i) is the rate of change in velocity for the waste particle:

$$F_i = \rho_p \frac{\pi D_p^3}{6} \frac{d^2 r}{dt^2} \tag{6}$$

Radial Motion of Particles

The force balance in the radial direction is

$$F_i = F_m + F_d \tag{7}$$

Initially the fluid will have no inertial velocity component in the r direction. The assumption that the magnet is vertical and the radius is orthogonal to gravity is the reason no gravitational force terms appears in Equation 7.

For Stoke's law in low flow region (Re<0.3) equation 7 becomes:

$$\rho_p \frac{\pi D_p^3}{6} \frac{d^2 r}{dt^2} = \frac{\pi D_p^3}{6\mu_o} \left(\frac{dB}{dr}\right)^2 r - 3\pi\eta D_p \frac{dr}{dt} \tag{8}$$

Equation 8 can be converted into a second-order linear differential equation with the solution being

$$r(t) = r_o \frac{[\exp(\lambda_1 t) - \exp(\lambda_2 t)\frac{\lambda_1}{\lambda_2}]}{(1 - \frac{\lambda_1}{\lambda_2})} \tag{9}$$

where :

$$\lambda_{1,2} = \frac{9\eta}{\rho_p D_p^2} \pm \frac{1}{2}\left[\left(\frac{18\eta}{\rho_p D_p^2}\right)^2 + \frac{4\chi\left(\frac{dB}{dr}\right)^2}{\rho_p \mu_o}\right]^{1/2} \tag{10}$$

For the vertical motion of particle (z-direction) equation 11 is solved

$$F_{zi} = F_{g} + F_{d} + F_{z(0)} \quad (11)$$

and results in equation 12

$$z = \frac{gDp^2\rho_p}{18\eta}\left(t + \left[\frac{Dp^2\rho_p}{18\eta} - \frac{V_0}{g}\right]\left[\exp\left(\frac{18\eta t}{Dp^2\rho_p}\right) - 1\right]\right) \quad (12)$$

This solution is for low Reynolds number.

Magnetic Susceptibility

The magnetic susceptibility is a vital physical property for the magnetic separation of materials from the feed waste streams. In coal (χ = -3.1x10^{-6}) using HGMS up to 50 µm, ash and pyrite (19x10-6) are liberated and separated effectively with OGMS. However, coal is not as chemically complex as the radionuclide and hazardous waste streams considered for magnetic separation. As shown from magnetic separation studies the susceptibilities for the major phases must be determined. The magnetic susceptibility of a pure PuO_2 phase is $910x10^{-6}$ however the variation in oxygen stoichiometry of the oxide in the ash waste causes the lowering of the pure phase susceptibility. The particle size distribution and composition will determine the extent of constituent liberation and size range to apply magnetic separation. For example, the simulant from the Hanford C-103 tank sludge simulant contains various particles sizes of colloidal SiO_2, gibbsite $Al(OH)_3$, boehmite $AlOOH$, $Ca_{10}(OH)_2(PO_4)_6$, $Fe(NO_3)_3\ 9H_2O$ as initially prepared. After heat treatment and storage these particle sizes are expected to vary significantly; simulant of ash and other waste streams will have similar problems. However, due to the high susceptibility of the transition metals and the micron particle size range these constituents can be separated with an OGMS system if sufficient particle liberation exist.

Waste Streams

A wide variety of waste streams are expected to be evaluated. However, this section concentrates on potential ash and sludge waste streams. The Hanford C-103 sludge tank was selected due to the availability of the sludge and the high concentration of Fe in the waste stream. Iron precipitation has been used to concentrate the transuranic in some DOE tank waste streams, this study intend to determine which tanks are easier to segregate with magnetic separation without blending of the sludge a labor intensive task. The high Fe concentration is typical in sludge waste streams. Treatment of sludge requires careful characterization of radionuclides. ANL has obtained one radioactive, and two fly ash simulant. In the case of the STRC fly ash from the Consolidated Incineration Facility (CIF) a simulant was available and we are studying the potential to reduce the hazardous and low level materials that need to be process. Although this fly ash waste stream has been targeted for cementation, separations are needed to reduce the volume of RCRA-permitted vault space. The Pu ash came from the Rocky Flat site.

EXPERIMENTAL

Waste Stream Preparation

A 55 gallon drum of the C-103 Hanford sludge simulant (8%wt) was prepared by Pacific Northwest National Laboratory and sent to ANL. The specific sludge preparation procedure follows: add 24.532 Kg of Fe $(NO_3)_3\ 9\ H_2O$ to 73 liter of deionized (DI) water and stir until dissolved. Sufficient 5M NaOH was added to obtain a pH of 7.5. Approximately 36.472 liters of NaOH was required. The last 7.294 liters of the NaOH solution was added slowly to reach the desired pH. The solution was stirred for 30 minutes and 13.026 Kg of 50%wt colloidal SiO_2 (0.1 microns, Nyacol silicasol 9950) was added and sitr. Then 1.411 Kg of gibbsite (0.25 micron, Alcoa SpaceRite S-11), 0.44 Kg boehmite (20 nm, Vista Catapal) and $Ca_{10}(OH)_2(PO_4)_8$- 2.605 kg was added to solution and allowed to sit, 5 M HNO_3 was added slowly and stirred until pH 12 and stir vigorously for 24 hours. Then 5 M NaOH was slowly added and stirred until pH 10 was reached. Sufficient DI water was added such that the volume of the simulant reaches 200 liters and stirred for three hours. Compositional

analysis of the sludge and incinerator ash are provided in Table 1. The STRC and Rocky Flat incinerator ash were obtained from the sites. Specific details of their composition are obtainable elsewhere.

Physical and Chemical Measurements

Samples were examined in an ATOPON ABT-60 scanning electron microscope (SEM) at 20 kV. Samples that were suitable for electron dispersive spectroscopic (EDS) and backscattering analyses and experiments were performed in tandem using a NORAN ultrathin window system in the horizontal port of the ABT-60. Furthermore, particle size distribution were obtained using the National Institute of Health image program with SEM micrographs. Waste particle samples were prepared for electron microscopy by drying, embedding them in epoxy, and sectioning with an ultramicrotome. Sections produced were approximately 500 and 1000 Å thick. Samples were then examined in a JEOL 2000FXII transmission electron microscope (TEM) at 200kV. The chemical analysis of cations and anions of the sludge and fly ash were determined using atomic absorption spectroscopy and inductively coupled plasma (ICP-AES). The magnetic properties of the materials were characterized with a Superconducting Quantum Interference Device (SQUID) magnetometer. The simulant fly ash waste stream was separated using commercially available ASTM sieves with a shaking time of 30 minutes.

RESULTS AND DISCUSSION

Physical Characterization

Hanford C-103 Sludge Simulant

SEM micrographs obtained for Hanford C-103 tank sludge samples show a wide variety of particle shapes and sizes. The EDS spectrum (not shown) confirms the presence of prepared components and a large concentration of crystalline NaCl. The majority of particles appear to have rough edges and lengths between 30 and 100µm. Judging by the appearance of the particles and their morphology, an inhomogeneous composition and distribution is present. Asymmetrical particles are predominant, while others are long and narrow with a layered appearance. The average particle size is about 50-60µm, with some near 100µm. Back scattering micrographs (not shown) illustrate regions of high density in the particles. The iron nitrate phase is one with the highest magnetic susceptibility and can be easily separated from the diamagnetic components and observed with backscatter analysis of the large particles.

SRTC Fly Ash

Micrograph of fly ash particles reveal a narrow particle size distribution. Most particles are less than 25µm long, but range as high as 100µm. Figure 1 shows a large portion of a simulant fly ash sample.

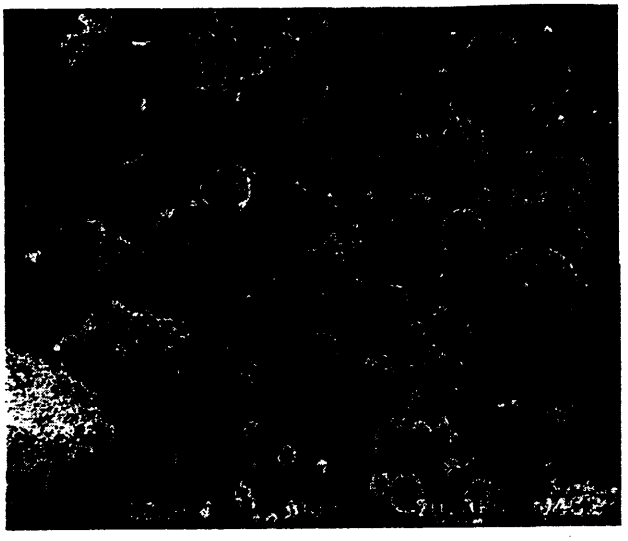

Figure 1. SEM Micrograph of CIF fly ash

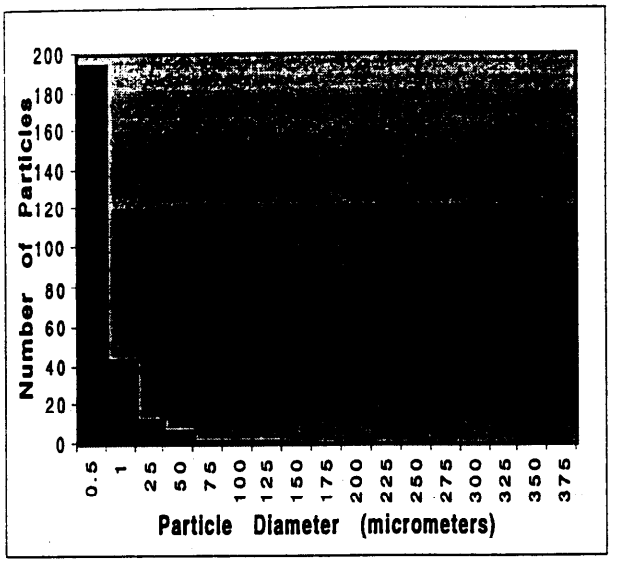

Figure 2. Particle size distribution for fly ash

Several large particles in Figure 1 appear to be agglomerations of smaller particles. That could provide some necessary insight about the separation scheme for OGMS. Characterization of the fly ash with TEM has identified Al-Si rich phases 10-50 nm in size that are embedded in the fly ash. EDS spectra for different spherical particles show a high percentage of Si and Al. However, additional metals are present, such as Fe, K, Ti, Ca, and Mg. In the same sample, an EDS spectrum of a particle shows different composition; S, Cl, and more Ca than in other particles. Figure 2 shows the particle size distribution for the SEM micrograph and excludes agglomerations greater than 50 µm. This high distribution of particles less than a micron in size will have an negative effect on the magnetic separation due to the competing forces (e.g., electrostatic, gravity).

Chemical Characterization

Chemical composition of simulants are tabulated in Table 1. The fly ash shows high concentration of Ti, Mg, Al, Fe and the sludge displays a high concentration of Al, Fe , Si. The high concentration of Fe in both the fly ash and sludge are indicative of various Fe phases that have high susceptibility and are favorable for magnetic separation.

Table 1. Elemental Composition of Simulant Waste Stream and Fractionated Fly Ash

	SRL	C-103			Fly Ash Fractionation		
Element	Fly Ash	Sludge	Microns	75	45	38	Bottoms
Cs	114	41.5	%	11.35	48.3	7.12	33.23
K	4630	5.5	Units	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
Li	52.6	<1.0	Elements				
Ti	1800	60	Fe	16990	26390	29790	33590
Mn	77.2	<3.0	Ca	5760	6840	6860	6380
Co	20.1	<8.0	Na	417	585	629	845
Ca	71	<3.0	Zn	49	63	83	103
Mg	1510	22.2	Cr	40.5	54.7	55.3	73.1
Fe	26300	12500	Ba	364	488	404	536
Hg	<1.0	<0.1	Pb	32	44	28	72
Cd	1.4	<1.2	Ni	31.4	42.6	47.4	54.6
Al	32900	2475	Ag	<3.2	<3.2	<3.2	<3.2
Sr	287	<5.0	K	3148	4260	4824	6616
Gd	20	*	Li	36	45.2	49.6	66.4
Zr	20	*	Ti	1121	1517	1603	1861
B	52	*	Mn	57.6	72.8	77.2	86.8
Si	275	1400	Co	17.7	30.5	34.5	35.9
Nd	20	*	Cu	47.5	61.7	70.3	91.9
Pr	25	*	Mg	1230	1570	1670	2150
			Hg	<0.1	<0.1	<0.1	<0.1

The step fractionation of the simulant fly ash shows that over 33% was smaller than 38µm (or bottoms). The highest fraction was found in the 45-75µm range and the lowest fraction in the 38-45 µm. In all four fractions there are large concentration of Fe, Ti, Cr, Ni, and other transition metals which are potentially candidates for magnetic separation. In addition, the magnetic susceptibility suggest there is a difference between the mineral present for a specific size fraction. The bottoms are enriched in all elements except for Ca and elements not detected. Table 2 also shows that the particle distribution by fractionation is higher than the distribution determined by the SEM micrograph analysis due to the exclusion of the agglomerated particles in the analysis.

The evaluation of various radioactive fly ash from Rocky Flat site shows that the percent of transition metals can vary from 2-25wt% while the PuO_2 content is between 0.3-0.8%. The step fractionation shows that for mesh size >45 many of the fly ash waste streams are between 43-61% wt PuO_2 and between 45-170 mesh is the next highest fraction of PuO_2. This range would indicate that magnetic separation can indeed affect the segregation. Furthermore, the TEM study used to characterizes the waste streams show Pu oxide particles size of 0.5 µm and greater. Larger particles (5 µm) where observed by SEM analysis with Pu rich and Pu lean fractions (Figure 3). Nonmagnetic phases in Pu ash where observed such as aluminosilicate phase, $CaAlSiO_x$ possibly amorthite, SiO_2-quartz, $CaMgSiO_x$, Zirconia (artifact from grinding) and $SiTiO_x$ with magnetic susceptibility in the range of -1 to -30 x 10^{-6} (Figure 4). The only ferromagnetic phase is Fe0 (χ = 7100 x 10^{-6}) that can be easily separated from the paramagnetic PuO_2 (χ = 910 x10^{-6}). The magnetic susceptibility of Pu will potentially decrease due to the presence of Pu_4O_7 and PuO_{2-x} phases in the ash. This would suggest that a Pu rich fraction can be obtained similar to what Aven et al. has shown in their magnetic separation study. Figure 3 shows SEM with Pu rich and Pu lean particles illustrated by backscattering measurements. Figure 4 shows the TEM and EDS used to identify various mineral phases in the radioactive fly ash.

Figure 3. Backscattering Image of Ash Showing Pu Rich (bright Spots) and Pu Lean Particles

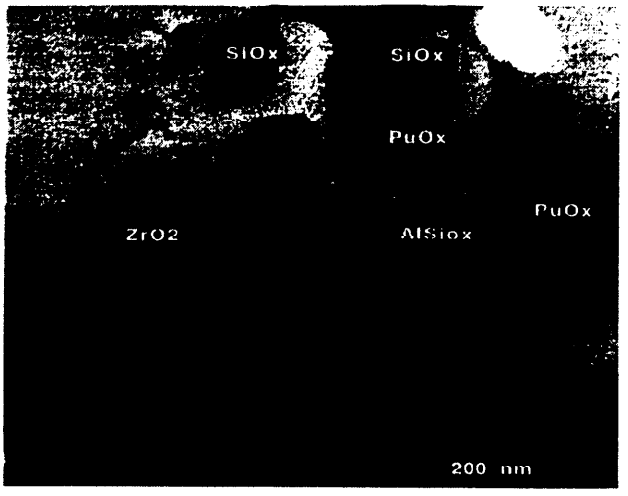

Figure 4. TEM of Pu Ash with the Various Mineral Phases

Magnetic Characterization

The magnetic susceptibility of the simulant sludge and fly ash are shown in Figure 5. In Figure 5 the plot of reciprocal susceptibility vs. temperature shows a rapid increase as temperatures increases between 4 and 50K. At temperature above 50K, the plot assume a more linear shape (Curie-Weiss law) for the sludge and slightly parabolic for the simulant ash. The magnetic susceptibility value was calculated to be 3.47 $\mathbf{x10^{-6}\ m^3/Kg}$ at 25°C for the simulant fly ash. The shape of the susceptibility curve can be due to the inhomogeneity and the mixture of magnetic phases in the simulant fly ash. While this values is low in comparison with other iron containing compound. The calculated value for the bulk magnetic susceptibility is $\mathbf{2.08x10^{-7}}$ m^3/kg at **25°C** for the simulant sludge. Figure 6 shows the magnetic susceptibility as a function of fractionation size and illustrates the highest susceptibility for the 38-45µm fraction. Table 2 show the diamagnetic and paramagnetic susceptibilities of the simulant materials and are compared with pure mineral phase susceptibility. One interesting point to note is the higher magnetic susceptibility for the simulant ash than the sludge and agrees with the chemical composition. This may be due to the inhomogeneity of the sludge and large difference between the suspended and aqueous phase distribution.

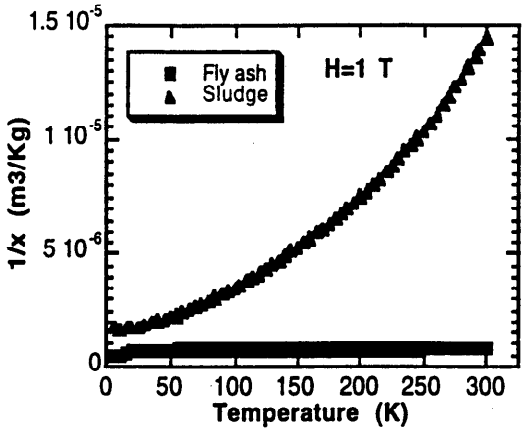

Figure 5. Magnetic Susceptibility as a Function of Temperature for Waste Streams.

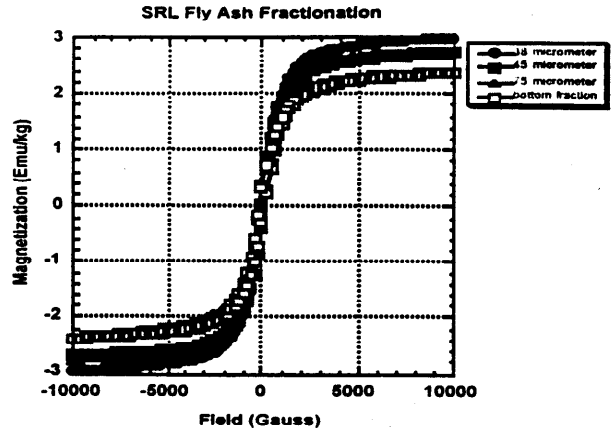

Figure 6. Magnetic Measurement of Fly Ash Fraction.

Table 2. Magnetic Susceptibility of Waste Components

Compound	Susceptibility ($x10^6$) m^3/kg
FeO	7178.0
Fe_2O_3	1479.0
NiO	740.0
UO_3	41.0
Fly Ash	3.465
Sludge	0.208
Al_2O_3	-18.0

Savannah River Site Activities

The Savannah River Technology Center (SRTC) Vitrification Technology Section (VTS) is currently supporting or pursuing several vitrification programs, including vitrification of radioactive and/or hazardous wastes and stabilization of excess nuclear materials.

The SRTC has recognized expertise in the vitrification field because of the more than 25 years experience in research and development of vitrification technology. Currently, the VTS of SRTC provides technical support to the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS). The DWPF is the United States' largest working plant for the vitrification of liquid High Level Wastes (HLW). To date, more than 200 canisters of HLW have been vitrified in this facility. It is expected that the DWPF will continue treating HLW for the next 20 years. Additionally, the VTS is supporting the start-up and operation of the SRTC designed Transportable Vitrification System (TVS). The TVS was designed to demonstrate the treatment of Low-Level Mixed Wastes (LLMW), but can be used to treat small waste streams in their entirety. The TVS is currently located at Oak Ridge Reservation and is scheduled to commence treatment of actual wastes in September 1997. The SRTC is also involved in many other vitrification programs to support vitrification of radioactive wastes for the Tanks and Mixed Waste Focus Areas of the Office of

Science and Technology Development and the disposition of excess/surplus weapons materials (94-l materials) for the Department of Energy (DOE).

The ANL, on the other hand, has expertise in the field of magnetic separation. They are pursuing the use of Superconducting OGMS as a pre-treatment method for vitrification streams because it has the potential to separate some of the more difficult to vitrify species from the waste streams. For example, many of the DOE waste streams contain iron which impedes the waste loading possible in the glass because of the potential for formation of spinel crystals. By using magnetic separation as a pre-treatment step, the potential is increased for obtaining higher waste loadings with amorphous products that do not present a problem during processing. In addition, the separation process has the potential to reduce the volume of waste that needs to be vitrified. It is anticipated that the material that is separated will be considered Low-Level Waste (LLW) so it would not have to be treated to the same extent as the original HLW.

Through an Intra-DOE Work Order (IWO) between SRTC and ANL, SRTC will provide vitrification technical expertise to the program. They will also help direct the activities of ANL so they are beneficial to vitrification programs. The long-term goal is for SRTC to provide a waste stream amenable to the separation process, for ANL to perform the separation process on the stream and provide the pre-treated stream to SRTC, and for SRTC to vitrify the stream in a pilot-scale melter. The benefits of the pre-treatment method can then be determined as compared to direct vitrification methods.

In fiscal year 1997, the main focus of SRTC's efforts involved the identification and characterization of the candidate waste streams. Characterization included determination of chemical composition, radionuclide content, particle size distribution, and phase identification.

A kick-off meeting was held in November at ANL with all interested parties. This meeting defined the roles of the individual sites and researchers involved in this program. During the meeting, several waste streams were discussed which would have applicability to the Superconducting OGMS process. The three different waste matrices selected were sludges, ashes, and soils.

After this meeting, some background research was performed at SRTC and then a meeting was held in July at the SRTC. At the meeting at the SRTC, specific streams and wastes to be tested were determined. SRTC's progress to date with characterizing and obtaining the necessary surrogate and actual waste samples will be discussed below.

SLUDGES

The SRTC is supporting vitrification treatment of HLW sludges at the SRS and at the Hanford Reservation and LLMW sludges at the Oak Ridge Reservation and other DOE sites. Some of these sludges contain significant amounts of iron, and other transition metal compounds. These compounds limit waste loading because of the crystalline species that can form upon cooling or during melter temperature excursions. Therefore, if these compounds can be separated from the wastes, higher waste loadings can be obtained in the glass wasteform and potentially a smaller volume of waste can be treated. Higher waste loadings and smaller volumes of waste to be treated lead to less production time and fewer packages of final waste, which both correspond to cost savings for DOE and the operational facility.

HLW Sludges

The SRTC has performed several demonstrations using different SRS HLW compositions to show the feasibility of vitrification treatment. In the process, characterization of several tanks of waste have been performed so representative compositions could be determined. Table 3 gives the results of an early elemental characterization of three SRS HLW tanks. This table also shows an oxide composition range that was determined from the analyses of several SRS HLW tanks.

TABLE 3 - MAJOR SPECIES OF SRS HLW SLUDGE (WI%)

Element	Tank 5[1]	Tank 13[1]	Tank 15[1]	Oxide	Range[2]
Fe	27.5	27.9	3.1	Fe_2O_3	4.5 - 46.9
Al	1.5	7.1	33.5	Al2O3	2.8 - 63.3
Mn	10.8	8.8	2.3	MnO_2	2.7 - 17.1
U	15.4	4.0	0.9	U_3O_8	0 - 18.5
Na	6.1	3.1	1.2	Na_2O	1.3 - 8.2
Ni	5.1	0.5	0.5	NiO	0.4 - 8.0
Ca	0.6	2.3	0.2	CaO	0.3 - 4.1
Hg	0.1	2.1	0.9	HgO	0.1 - 3.0
				SiO_2	0.4 - 6.8
				Nd_2O_3	0.3 - 1.2

Table 4 lists the radionuclides contained in the samples taken from the three tanks listed in Table 3.

TABLE 4 - TYPICAL RADIONUCLIDES IN SRS HLW SLUDGE (mCi/g)[1]

Radionuclide	Tank 5	Tank 13	Tank 15
^{90}Sr	74.7	15.5	25.6
^{144}Ce	4.8	2.0	16.9
^{106}Ru	2.7	0.4	1.7
^{154}Eu	0.5	0.3	1.2
^{137}Cs	1.3	0.3	0.1
^{125}Sb	0.4	0.1	1.3
Total a	0:1	0.3	0.1

More recent analyses of the tanks at SRS have resulted in the determination of a representative sludge composition and radionuclide content. The representative sludge components are shown in Table 5, while the representative radionuclides are shown in Table 6.

Most of the vitrification demonstrations that have been performed have been on surrogates formulated from the waste characterizations. Four drums of surrogate from pilot-scale demonstrations were located at the SRTC, with each drum representing a different SRS HLW composition. Characterization of the drums is currently being performed to quantify and qualify the contents. The major species of the drums are shown in Table 7.

TABLE 5 - CURRENT REPRESENTATIVE SRS HLW SLUDGE COMPOSITION3

Component	Wt%	Component	Wt%
$Al(OH)_3$	13.7	MnO_2	2.0
AlO(OH)	5.2	$NaNO_3$	1.1
$CaCO_3$	1.5	NaOH	1.3
CaC_2O_4	0.2	$Ni(OH)_2$	0.8
$CaSO_4$	0.2	SiO_2	0.2
$Ce(OH)_3$	0.2	ThO_2	1.8
$Cr(OH)_3$	0.2	$UO_2(OH)_2$	1.3
$Fe(OH)_3$	11.8	$ZrO(OH)_2$	0.2
HgO	0.4	Zeolite	1.5
$Mg(OH)_2$	0.2	Others	1.2
		Water	55.0

TABLE 6 - REPRESENTATIVE RADIONUCLIDES IN SRS HLW SLUDGES

Radionuclide	Amount (Ci)	Radionuclide	Amount (Ci)
^{90}Sr	1.24E+08	^{147}Pm	2.32E+07
^{90}Y	1.24E+08	^{233}U	2.60E-01
^{99}Tc	2.11E+04	^{235}U	2.80E-01
^{106}Ru	3.98E+05	^{238}U	2.20E+01
^{106}Rh	3.98E+05	^{238}Pu	1.60E+06
^{125}Sb	2.12E+05	^{239}Pu	2.30E+04
^{137}Cs	1.14E+07	^{240}Pu	1.00E+04
^{137}Ba	1.05E+07	^{241}Pu	1.40E+06
^{144}Ce	2.46E+06	^{242}Pu	1.70E+01
^{144}Pr	2.46E+06	^{244}Cm	1.40E+04

TABLE 7 - MAJOR SPECIES IN DRUMS OF SRS HLW SURROGATE SLUDGES (WT%)

Species	Drum 2	Drum 4	Drum 7	Drum 9
Ag	0.015	0.016	0.023	0.019
Al	2.330	4.514	1.504	1.734
B	2.305	0.168	1.962	3.069
Ba	0.032	0.004	0.113	0.031
Ca	0.460	2.160	0.950	0.671
Cd	0.016	0.002	0.002	0.002
Cr	0.041	0.214	0.091	0.035
Cu	0.126	0.208	0.325	0.115
Fe	3.986	23.073	10.647	10.721
Hg	0.047	0.001	0.086	0.039
K	5.549	0.356	3.233	0.996
Li	0.834	0.068	0.789	1.542
Mg	0.164	0.063	0.383	0.600
Mn	1.110	4.213	1.923	0.767
Na	11.739	8.494	9.734	6.927
Ni	0.246	2.144	1.213	0.705
P	0.022	0.044	0.022	0.023
Pb	0.051	0.052	0.137	0.052
Si	5.964	3.620	10.830	19.160
Sr	0.087	0.097	0.020	0.006
Ti	0.126	0.090	0.166	0.097
Zn	0.041	0.025	0.176	0.069
Zr	0.148	0.078	1.465	0.518

These drums are being packaged for shipment to the ANL in September 1997. The SRTC will continue to characterize the simulated sludges for particle size distribution.

The phases contained in the sludges were also identified using X-Ray Diffraction (XRD). These are shown in Table 8.

TABLE 8 - PHASES IN SIMULATED SRS HLW SLUDGE

ID	Phases Identified
Drum 2	$NaNO_3$, $Al(OH)_3$, SiO_2, KNO_3
Drum 4	$NaNO_3$, $Al(OH)_3$, $FeO(OH)$, SiO_2
Drum 7	$NaNO_3$, $Al(OH)_3$, SiO_2, KNO_3
Drum 9	Fe_2O_3, Al_2O_3, $CaCO_3$

A portion of the original samples taken from the SRS HLW tanks for characterization still remains in the Shielded Cells facility at SRTC. Initial chemical characterization of the wastes was performed several years ago. However, in order to ensure that the sample was homogeneous and to determine how much of the radioactivity remains and what compounds are present, the SRTC will perform additional characterization. If the samples are still representative of the contents of the SRS HLW tanks, representative samples will be shipped to the ANL for verification of the pre-treatment process on HLW.

Like the SRS, Hanford Reservation is also planning to vitrify their HLW. A pilot-scale melter demonstration with representative Hanford HLW sludge was performed by the SRTC in 1994. The sludge used in this demonstration represented the Hanford Neutralization Current Acid Waste

(NCAW). The composition used to formulate the surrogate is shown in Table 9, along with the chemical compounds used to make the surrogate.

TABLE 9 - HANFORD NCAW SLUDGE SIMULANT[4]

Component Wt%	Compound	Component Wt%	Compound
0.0843% Ag	$AgNO_3$	0.0061% Nb	Nb_2O_5
3.6306% Al	$Al(OH)_3$	2.2637% Nd	Nd_2O_3
0.0013% B	HBO_3	1.3700% Ni	$Ni(OH)_2$
0.1190% Ba	$Ba(OH)_2$	0.0193% P	Na_3PO_4
4.6205% CO_3^{2-}	Several	0.4597% Pb	$Pb(NO_3)_2$
0.4276% Ca	$Ca(OH)_2$	0.0793% Pd	$Pd(NO_3)_2$
2.0032% Cd	$Cd(OH)_2$	0.0991% Pr	$Pr(NO_3)_2$
0.3964% Ce	$Ce(OH)_4$	0.0340% Rb	$Rb(NO_3)_2$
0.2279% Cl^-	NaCl,LiCl	0.0636% Rh	$Rh(NO_3)_2$
0.1355% Cr	$Cr(NO_3)_2$	0.2310% Ru	$RuNO(OH)_3$
0.4286% Cs	$CsNO_3$	0.4582% SO_4^{2-}	$NaSO_4$
0.1483% Cu	$CuSO_4$	0.0085% Se	SeO_2
0.0735% F^-	NaF	1.4266% Si	SiO_2
13.8482% Fe	$Fe(OH)_3$	0.0494% Sm	$Sm(NO_3)_3$
0.1236% K	KNO_3	0.0070% Sn	SnO
0.4218% La	La_2O_3	0.1089% Sr	$SrCO_3$
0.1663% Mg	$Mg(OH)_2$	0.0021% Ta	Ta_2O_5
0.5128% Mn	MnO_2	0.0601% Te	TeO_2
0.2820% Mo	MoO_3	0.2961% Ti	TiO_2
12.1564% NO_2^-	Several	0.0477% Y	$Y(NO_3)3$
4.3590% NO_3^-	Several	0.2033% Zn	$Zn(NO_3)_2$
12.0396% Na	Na_2CO_3,NaC_2O_4,NaI $NaNO_2$,$NaNO_3$,NaOH	8.4594% Zr	$Zr(OH)_4$

A drum of the Hanford surrogate material has been located for the joint work with ANL. A verification of the chemical composition and a determination of the particle size distribution are now being performed. This sludge will also be shipped to ANL so the viability of pre-treatment can be determined.

LLMW Sludges

The DOE has begun to determine a path forward for treatment of its large inventory of LLMW. The SRTC has been funded to pursue vitrification treatment of LLMW and has designed and built a TVS to demonstrate the vitrification process. The TVS was designed for the treatment of LLMW sludges and soils. Oak Ridge Reservation wastes will be the first wastes treated in the TVS. The wastes to be treated are wastewater treatment sludges which contain some amount of iron and transition metals. One waste stream in particular, the Central Neutralization Facility (CNF) sludge, can contain up to twenty weight percent iron. This presents a significant operation challenge to vitrification because of the problems described above. Therefore, a sample of the CNF sludge will be sent to ANL to determine the viability of magnetic separation pre-treatment. The CNF sludge has a wide variability in composition because of the different streams that the CNF treats. A composition range for the sludge is shown in Table 10 based on several analyses performed by Oak Ridge. Once the contents of the sample to be sent to ANL are well characterized,

a batch of surrogate can also be made by the SRTC and sent to ANL for pre-treatment studies. The surrogate can help determine the feasibility of the process without the concerns of working with radioactive wastes.

TABLE 10 - COMPOSITION RANGE FOR CNF SLUDGE (WT%)

Component	Range
Al	0.79 - 7.43
As	0.005 - 0.016
Ba	0.013 - 0.125
Ca	1.2 - 25.92
Cd	0.006 - 0.008
Cl	0.02 - 2.35
Cr	0.03 - 0.075
Cu	0.02 - 3.75
F	0.02 - 2.33
Fe	4.36 - 26.8
K	0.08 - 1.16
Mg	0.46 - 1.02
Mn	0.14 - 0.24
NO_3	0.02 - 1.011
Na	0.50 - 4.44
Ni	0.03 - 0.27
P	0.29 - 9.00
Pb	0.05 - 0.35
SO_4	0.20 - 11.04
Si	0.03 - 28.09
Sr	0.008 - 0.034
Ti	0.10 - 0.55
U	0.06 - 2.56
Zn	0.02 - 2.82
Inorganic Carbon	0.03 - 2.85
Organic Carbon	0.51 - 4.60

ASHES

Another vitrification program that the SRTC is involved with involves the stabilization of Rocky Flats ash. Rocky Flats ash was produced from the incineration of combustible materials highly contaminated with plutonium. Some of these materials included graphite scarfings and fines, MgO ceramic crucibles, firebrick, dirt, sand, slag, and sand. Extensive characterization of the ash materials has not been performed at the SRTC due to constraints on handling listed wastes. However, some information was available from a Rocky Flats paper[5] and from several other papers describing the ash. The composition from the Rocky Flats paper[5] is given in the RF column of Table 11, while the average composition based on all of the data available is shown in the Average column of Table 11.

TABLE 11 - TYPICAL ROCKY FLATS ASH COMPOSITION

Constituent	RF Wt%[5]	Average Wt%
Al_2O_3	3.3	3.5
AmO_2	N/A	0.1
BaO	0.9	0.9
B_2O_3	1.8	1.8
CaO	4.0	4.2
Cr_2O_3	0.7	0.7
CuO	1.0	1.0
Fe_2O_3	5.7	6.0
K_2O	0.7	0.8
MgO	4.6	4.8
MnO_2	0.1	0.1
Na_2O	1.2	1.3
NiO	0.5	0.5
PbO	0.8	0.8
PuO_2	2.8	2.9
SiO_2	48.5	46.1
SnO	N/A	0.1
Ta_2O_5	0.4	0.4
TiO_2	1.4	1.4
C	22.0	22.7

To date, only limited vitrification studies have been performed with this material. However, vitrification studies show that some problems exist with stabilizing the large amount of carbon based materials present in the ash. If the Superconducting OGMS process can remove some of these materials, then vitrification may prove to be a viable option.

Once a composition of the material is finalized, a surrogate will be made and shipped to the ANL for testing.

SOILS

Most of the soils that the SRTC has pursued vitrification treatment for were from the SRS. These soils contain very large amounts of silica, with very minor amounts of calcium, aluminum, and iron. Therefore, it was not felt that this material would be amenable to ANL's pre-treatment process. However, if a soil from another DOE site is identified as a potential candidate for vitrification treatment, then the pre-treatment option may be pursued.

University of South Carolina Activities

The purpose of this sub-program is to research and evaluate the application of HGMS for the pretreatment of radioactive and mixed waste vitrification feeds. In particular, the performance of HGMS is being compared with OGMS being evaluated at the ANL, with a focus on optimizing the engineering parameters in the complex separation of magnetic components from sludges present at the Savannah River Site and other DOE sites. The objectives also include gaining a deeper understanding of the underlying and controlling principles governing HGMS for treating these complex waste streams. Both experimental and theoretical studies are currently being carried out using non-radioactive sludges provided by the Savannah River and Hanford Sites.

An HGMS system from Advanced Environmental Systems, Inc. is being used in this study. This 0.3 T HGMS system has a magnetic bore 4.75 in. long and 2.06 in. in diameter, with a filter canister area of 0.01 ft2 (i.e., 4.75 in. long and 1.375 in. in diameter). The filter canister includes magnetic pole pieces which serve to evenly distribute the magnetic field over the matrix area. The matrix consists of graded expanded metal and steel wool discs stacked within the canister to a maximum height of 4.75 in. This HGMS system has been field tested by the manufacturer (Advanced Environmental Systems, Inc.), where they claim at least 99% of iron, cobalt, magnetite and other spinel ferrites, at least 50% of hematite, and at least 30% of hydrated irons (FeO*OH species), all of particle size 0.1 micron and larger, have been removed from aqueous streams.

The HGMS system has been set up for evaluating the separation of magnetic species from radioactive and mixed waste vitrification feeds. Simulant HLW sludge of Hanford Tank C103 HLW has also been received. A preliminary study has been initiated to see if there are any magnetic species that could be separated from the bulk of the HLW sludge.

Approximately one liter of the HLW sludge was processed through the HGMS system at 150 ml/min with the magnet field turned on. To, separate gross filtration from magnetic filtration, with the magnetic field still on, the filter canister was flushed with water at the same pH as the initial sludge until the water effluent was relatively clear. Then the magnetic field was turned off and the system was backed flushed again with water at the same pH as the initial sludge. A small amount of sludge was present in this step, indicating the presence of magnetic particles in the HLW sludge. Analyses of treated and untreated sludge samples are currently underway, including total filtered solids content, particle size distributions, and elemental analyses via flame atomic absorption spectroscopy.

University of Texas Activities

We will be collecting data on the ability of mineral phases to absorb a series of nuclides. The mineral phases that have been selected include a series of spinels that may include Fe_3O_4, $NiFe_2O_4$, Mg Fe_2O_4, $ZnFe_2O_4$, $MgAl_2O_4$ and Possible Hydrous Fe Oxide. In addition to the spinels, we may choose to also look at the absorption or partitioning of the same nuclides upon some particular hydrous oxides. Initially, it will be necessary to find the loading concentration for each of the various nuclide/mineral phase combinations. This will be done by varying the concentration of the nuclides over a range of values, while holding the amounts of the mineral phases constant. Other factors that will be held constant at this time will be the pH of the solution, the particle size, the temperature, and the duration of the absorption period. Once equilibrium has been obtained, the mixtures shall be filtered using a vacuum process. The solid samples will be neutron irradiated, and the activated species will be counted in order to determine the quantity of the nuclide absorbed onto the mineral phase. A simple calculation will allow the determination of the effectiveness of the miner&phase in absorbing particular types of nuclides.

Once the baseline saturation levels have been determined, we will begin a series of experiments in order to determine conditions to maximize the sorbancy of each combination. The factors that were initially held constant will now be varied one at a time. As each of the conditions are varied, data shall be recorded in an attempt to determine trends, and ultimately, to determine maximum sorbancy conditions. In addition, this data will be used to develop thermodynamic models to predict the partitioning of the radionuclides in the waste streams. It ‘is desirable to experiment first with the non-radioactive nuclides, both in order to minimize the radioactive waste problem, and to assist in the development of acceptable procedures. It is unknown at this time as to whether or not all of the selected nuclides will be available for study.

SUMMARY

The preliminary evaluation of the OGMS process has shown that it has potential to separate radionuclides and hazardous elements from solid particulate waste streams due to their magnetic nature. The results of the physical and chemical characterization measurements indicate that the OGMS process shows potential for use under actual waste conditions. Further work is necessary to determine the separation mechanism and to test the OGMS process on simulant and radioactive waste streams. In continuing development activities we are working to optimize the process using HGMS as prefilter for ferromagnetic particles and modeling the separation of the waste streams. Some of the issues yet to be resolved with this OGMS apparatus is the determination of the grade, separation performance, and production rates possible with radioactive and hazardous waste feed streams. Further studies will included OGMS separation with simulant and radioactive waste streams and computational studies to model the process.

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