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CHARACTERIZATION OF COMPOSITE CERAMIC HIGH LEVEL WASTE FORMS

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ABSTRACT

Argonne National Laboratory has developed a composite ceramic waste form for the disposition of high level radioactive waste produced during electrometallurgical conditioning of spent nuclear fuel. The electrorefiner LiCl/KCl eutectic salt, containing fission products and transuranics in the chloride form, is contacted with a zeolite material which removes the fission products from the salt. After salt contact, the zeolite is mixed with a glass binder. The zeolite/glass mixture is then hot isostatic pressed (HIPed) to produce the composite ceramic waste form. The ceramic waste form provides a durable medium that is well suited to incorporate fission products and transuranics in the chloride form. Presented are preliminary results of the process qualification and characterization studies, which include chemical and physical measurements and product durability testing, of the ceramic waste form.

INTRODUCTION

Argonne National Laboratory (ANL) is in the midst of a five-year demonstration project, supported by the U.S. Department of Energy, to develop an electrometallurgical conditioning process to treat specific types of DOE spent nuclear fuel that are not suitable for direct disposal in a geological repository. In support of this project, ANL in Illinois (ANL-E) has developed a composite glass/ceramic material for the disposition of high level radioactive waste produced during the electrometallurgical process [1]. The spent fuel conditioning and subsequent waste form production phase of the demonstration project is in progress at ANL in Idaho (ANL-W) [2]. The spent fuel currently being conditioned is a metallic, sodium-bonded fuel used in the Experimental Breeder Reactor II (EBR-II) at ANL-W.

Removal of fission products and transuranics, that accumulates in the electrorefiner LiCl/KCl eutectic salt during spent fuel conditioning, is accomplished by hot mixing the salt with a zeolite powder [3,4]. The zeolite is then mixed with a glass binder and processed by hot isostatic pressing (HIPing). HIPing the mixture results in compaction, solidification and glass encapsulation of the zeolite to produce the ceramic waste form [5-7]. EBR-II spent nuclear fuel conditioning began in the summer of 1996, and all "cold" mockup operations associated with the waste processing equipment have been completed. Initial production of the radioactive waste form at ANL-W is expected late in 1998. Waste form process qualification, for acceptance into the Civilian Radioactive Waste Management System [8], is underway at ANL-E and ANL-W.

Two baseline ceramic waste forms have been developed as candidates for the final waste form. These are salt occluded zeolite 4A mixed with a glass binder, which converts to a sodalite structure upon HIPing, and a salt occluded zeolite 5A/glass mixture which generally retains the zeolite structure after HIPing. Both candidate waste forms have advantages and disadvantages in regard to waste loading, materials preparation and product durability.

CERAMIC WASTE FORM PRODUCTION

Production of the ceramic waste form first involves drying the zeolite powder at approximately 900K, under vacuum, until a retained water content of less than 1 wt% is obtained. The eutectic salt, spiked with approximately 8 wt% surrogate fission products, and

dried zeolite are then hot mixed at approximately 775K at which time the surrogate fission products in the salt are occluded into the zeolite structure. For zeolite 5A, the salt loading is 21 wt% of the salt/zeolite mixture which is equivalent to 7.5 Cl/unit cell (uc) in the zeolite structure. For zeolite 4A an equivalent of 3.2 Cl/uc (10 wt% salt loading) is obtained. The salt occluded zeolite is then mixed with the glass binder. The mixture is then poured into an 11.4 cm diameter by 22.9 cm high stainless steel can through a pour tube and settled using a vibratory compactor. All preparations, prior to HIPing, are performed in a dry, argon atmosphere. The hot isostatic press operates at a pressure of approximately 170 Mpa and a temperature of 900K for formation of the zeolite waste form and 1173K for the in-situ converted sodalite ceramic waste form. The major elemental composition (wt%) and the surrogate fission product concentrations (ppm) of the two salt occluded zeolites and final ceramic waste forms (1:1 zeolite/glass mixture) are shown in Table I.

Table I. Major elemental composition for the surrogate, salt-loaded zeolite and the HIPed ceramic waste forms (1:1 zeolite/glass mixture) in weight percent (wt%).

Matrix Elements	Li	Na	K	Ca	B	Al	Si	O	Cl
Salt Occluded Zeolite 4A	0.8	14.8	1.9			17.1	17.8	40.5	6.5
Zeolite 4A Waste Form	0.4	10.1	1.2		3.0	10.4	24.4	47.1	3.2
Salt Occluded Zeolite 5A	0.8	4.6	1.9	7.6		15.4	16.0	36.6	13.1
Zeolite 5A Waste Form	0.4	5.0	1.2	3.8	3.0	9.5	23.5	45.2	6.6

Table I continued. Surrogate fission product elemental composition for the salt occluded zeolite and the HIPed ceramic waste form in parts-per-million (ppm).

F.P. Salt Elements	I	Br	Cs	Rb	Sr	Y	Ba	La	Ce	Pr	Nd	Sm	Eu
Salt Occluded Zeolite 4A	50	13	810	90	230	120	300	270	1930	260	860	150	11
Sodalite Waste Form	25	7	405	45	115	60	150	135	965	130	430	75	6
Salt Occluded Zeolite 5A	100	26	1620	180	460	240	600	540	386	520	1720	300	22
Zeolite Waste Form	50	13	810	90	230	120	300	270	193	260	860	150	11

CERAMIC WASTE FORM CHARACTERIZATION

Powder x-ray diffraction (XRD) was performed on the pre-HIPed materials after each processing step. After formation of the ceramic waste form by hot isostatic pressing, the compressed HIP can was cut into four radial sections using a high speed saw with a diamond blade and water lubricant. Core sections, 1 cm in diameter, were also obtained from numerous locations within each cut section. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were performed on polished ceramic monoliths or on powdered waste form samples. Density measurements of ceramic waste form monoliths were performed by gas displacement pycnometry and water immersion. Product durability testing of the ceramic waste form was determined both by leaching sample monoliths (3-day and 28-day MCC-1 leaching) and powdered samples (7-day PCT leaching) in deionized water (ASTM Type I) at 363K as per ASTM procedures [10,11]. Chloride and pH measurements were made of the leachate solution with ion specific electrodes and leachate elemental analyses were performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AA). Samples analyzed for species migration studies were prepared by half filling a stainless steel tube (1.2 cm in diameter by 20.3 cm long) with the salt occluded zeolite and filling the remaining tube with the glass binder. The tube ends were sealed and the tube HIPed under normal conditions. Cutting the tube axially allowed SEM and EDS analysis of the glass/zeolite interface.

RESULTS AND DISCUSSION

After densification of the zeolite/glass mixture by HIPing, the zeolite 5A ceramic waste form has a density of approximately 2.34 g/cm^3 and the density of the zeolite 4A ceramic waste form, which converts to sodalite upon HIPing, is approximately 2.40 g/cm^3 . The SEM micrographs in Figures 1 (a) and (b) show the microstructure of the ceramic waste forms. In Figure 1 (a), the zeolite phase is observed as the lighter contrast regions and glass phase as the dark contrast areas. Alkali and alkaline earth surrogate fission products are distributed throughout the zeolite or sodalite regions, as measured by EDS, indicating ion exchange of these species into the zeolite structure. Lanthanide surrogate fission products (including Ce acting as a Pu surrogate) behave much differently, however. The small bright clusters in Figure 1 (a), labeled Ln, are lanthanide oxy-chlorides of the structure LnOCl , where Ln is any of the surrogate species such as Nd, Ce, Sm, La, etc. These species are not occluded into the zeolite structure but form clusters and are encapsulated within the zeolite/glass matrix. The oxygen is believed to come from residual water occluded within the zeolite matrix after drying. A lower zeolite/salt contacting temperature may reduce the lanthanide oxy-chloride formation. The glass/zeolite phases in Figure 1 (b) are much less discrete and the material has much less open porosity than the zeolite waste form. The small white inclusions in Figure 1 (b) are either NaCl or lanthanide clusters.

Zeolite 4A has a unit cell formula of $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$, where-as with zeolite 5A, Ca ions are substituted with a charge equivalent number of Na ions for a unit cell formula of $\text{Na}_{32}\text{Ca}_{32}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$ [12]. HIPing of zeolite 4A at 1123K transforms the cuboctahedral structure of zeolite to sodalite which has a truncated octahedron structure. However, HIPing of zeolite 5A at 825K results in the retention of the zeolite structure. This is presumably due to stabilization of the zeolite 5A structure by Ca^{+2} ions occluded into the structure's β -cages [13]. Figure 2 shows an XRD overlay plot of the (a) dried zeolite pattern, (b) the salt occluded zeolite pattern which shows the contraction of the unit cell with salt occlusion, (c) the HIPed zeolite ceramic waste form pattern and (d) the sodalite waste form pattern. Minor phases of nepheline (NaAlSiO_4) and NaCl are observed in the sodalite waste form pattern. Also observed in the zeolite waste form pattern are minor phases of microsommitte ($(\text{NaKCa})_8(\text{AlSi})_{12}\text{O}_{24}\text{Cl}_{2.5}$), LiAlSiO_4 and NaCl.

Figure 1. (a) Backscatter electron micrograph of HIPed zeolite ceramic waste form and (b) the sodalite waste form. The porous zeolite regions are marked Z and the darker glass regions are labeled G. The small bright areas labeled Ln are the surrogate lanthanum oxy-chlorides. In Figure 1 (b), the glass and zeolite areas are much less discrete and very little open porosity is observed. The small white inclusions are primarily NaCl with some Ln clusters.

Figure 2. XRD overlay plot of (a) dried zeolite, (b) salt occluded zeolite, (c) the HIPed zeolite ceramic waste form and (d) the sodalite ceramic waste form. Minor phases observed in the zeolite waste form include microsommitte, LiAlSiO_4 , SiO_2 and NaCl . Minor phases in the sodalite waste form include nepheline (NaAlSiO_4) and NaCl .

To investigate the possibility of fission product migration between the zeolite and glass phases as a result of the HIPing process, the zeolite and glass interface regions were analyzed by SEM and EDS. Figure 3 shows a SEM image of the interface region with the glass phase on the left and the zeolite phase on the right-hand side of the micrograph. EDS line scans were acquired across the glass/zeolite interface for the zeolite matrix species (Al, K, Ca) or surrogate fission products (Cs, La, Nd and Cl) which were occluded into the zeolite as the chloride salt before HIPing. Also shown Figure 3 is the quantitative EDS analysis for Cs and Cl across the zeolite/glass interface. The EDS analysis indicates that, with the possible exception of Ca and K, the zeolite matrix species, surrogate fission products and Cl do not exchange or migrate to any significant extent across the zeolite/glass interface during the HIPing cycle. This is particularly important for Cs, which has been shown to be very mobile in other vitrified waste forms [14]. In the case of Ca and K, the EDS results indicate that Ca from the glass may be undergoing ion exchange with K from the zeolite.

Product durability testing is important both for determining the performance of the waste form in a geological repository and also for determining the effect of processing changes during waste form development. The durability of the ceramic waste form was monitored by leaching tests in deionized water at 90°C . Two types of test were conducted; a 3-day and 28-day monolith (MCC-1 type) test and a 7-day powder (PCT type) test. The concentrations of each element measured in the leachate are given as normalized release rates determined from the equation $\text{NRR} = C_i V / f_i A t$, where C_i is the concentration of element i in the leachate (g/mL), V is the volume of leachate (mL), f_i is the mass fraction of element i in the solid, A is the surface area of the sample (m^2) and t is the duration of the test in days. All tests were run in conjunction with standard glass reference materials and blanks. Results from the more aggressive, 7-day powder

test are shown in Tables II and III for both the zeolite and sodalite waste forms, respectively. The 7-day powder tests show good performance for all elements analyzed for, with many of the surrogate fission products concentrations below limits of quantification.

Table II. Average of triplicate analyses of the 7-day, static leach test of powdered samples from the HIPed zeolite waste form. The values are expressed as normalized elemental release rates (NRR) in $\text{g/m}^2\text{day}$. The uncertainties associated the triplicate measurements are 10% RSD or better. Less than values indicate normalized release rates below limit of quantification.

Li	Na	K	B	Al	Si	Cl	Cs	
0.70	0.57	0.30	0.16	1.1E-2	4.4E-3	1.1	6.3E-3	
Rb	Sr	Y	Ba	La	Ce	Pr	Nd	Sm
<2.1	<2.6E-3	<5.0E-3	<2.0E-3	<3.3E-3	6.3E-3	<4.8E-2	<4.9E-3	<2.0E-3

Table III. Average of triplicate analyses of the 7-day, static leach test of powdered samples from the HIPed sodalite waste form. The values are expressed as normalized elemental release rates (NRR) in $\text{g/m}^2\text{day}$. The uncertainties associated the triplicate measurements are 10% RSD or better. Less than values indicate normalized release rates below limit of quantification.

Li	Na	K	B	Al	Si	Cl	Cs	
5.2E-2	1.2E-2	5.8E-3	1.4E-2	1.2E-2	9.5E-3	1.6E-2	2.8E-3	
Rb	Sr	Y	Ba	La	Ce	Pr	Nd	Sm
<2.1	<2.6E-3	<5.0E-3	<2.0E-3	<3.3E-3	<5.0E-3	<4.8E-2	<4.9E-2	<2.0E-3

Figure 3. SEM image of glass/zeolite interface region and the concentrations of Cs and Cl (atom %) in the glass and zeolite phases measured by EDS (Ca, K, Al, Si and Nd were also measured). These results indicate that Cs, Cl, Al, Si and Nd do not migrate across the interface. However, EDS suggests that Ca, from the glass, and K from the zeolite are possibly undergoing ion exchange across the glass/zeolite boundary.

CONCLUSIONS

Ceramic waste forms have been developed in conjunction with Argonne National Laboratory's electrometallurgical techniques for the treatment of Department of Energy spent nuclear fuel. The surrogate ceramic waste form is currently undergoing process qualification and characterization before production of the radioactive waste form in the summer of 1998. Studies indicate that the alkali and alkaline earth fission products are incorporated into the zeolite structure of the waste form, but lanthanides form discrete oxy-chloride clusters. Very little interaction, either by ion exchange or species segregation occurs between the glass and zeolite phases. Product durability tests show superior leaching characteristics when compared to standard glass reference materials.

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