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by

B. G. Storey and T. R. Allen

Argonne National Laboratory-West
P.O. Box 2528
Idaho Falls, ID 83403-2528

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B. G. Storey, T. R. Allen
Argonne National Laboratory-West, Idaho Falls, ID 83403

ABSTRACT

Glass-bonded zeolite is being considered as a candidate ceramic waste form for storing radioactive isotopes separated from spent nuclear fuel in the electrorefining process. To determine the stability of glass-bonded zeolite under irradiation, transmission electron microscope samples were irradiated using high energy helium, lead, and krypton. The major crystalline phase of the waste form, which retains alkaline and alkaline earth fission products, loses its long range order under both helium and krypton irradiation. The dose at which the long range crystalline structure is lost is about 0.4 dpa for helium and 0.1 dpa for krypton. Because the damage from lead is localized in such a small region of the sample, damage could not be recognized even at a peak damage of 50 dpa. Because the crystalline phase loses its long range structure due to irradiation, the effect on retention capacity needs to be further evaluated.

INTRODUCTION

Glass-bonded zeolite is being considered as a candidate ceramic waste form for storing radioactive isotopes separated from spent nuclear fuel in the electrorefining process. During the lifetime of any nuclear waste form, mechanical and corrosion resistance properties may be degraded by gamma, beta, and alpha decay [1]. Some work has been performed on the effect of gamma and beta irradiation on the structural stability and leach rates of zeolites. No significant structural changes have been seen in zeolites irradiated with high energy gamma radiation [2-7] or low dose rate beta radiation from tritium decay [8]. Although the exchange capacity of A-type zeolites for Cs^+ decreases with gamma dose [5,7,9], the leach resistance of salt-occluded zeolite did not differ significantly for gamma doses up to 9.9×10^8 rad [2]. While work has been done on the effect of gamma irradiation on zeolites, the effect of alpha decay on zeolites is not as well understood.

To study the effect of alpha decay, transmission electron microscopy (TEM) samples of glass-bonded zeolite loaded with lanthanides (acting as surrogate actinides and fission products) were irradiated with high energy lead, krypton, and helium in the IVEM-Tandem User Facility at Argonne National Laboratory (ANL). Work by Weber et al. [10] found that the dose to amorphization was nearly identical in both Pu-doped (3×10^{-9} dpa/s) and ion irradiated (1×10^{-4} to 1×10^{-3} dpa/s) zircons (ZrSiO_4), suggesting that heavy ion beam irradiations, with a high dose rate compared to actual waste forms, can be used to simulate alpha-decay event damage in nuclear waste forms.

The energy of a typical waste form alpha particle is between 4-6 MeV. Lower energy (30 keV) helium irradiation was used to simulate the *knock-on displacement damage* from alpha particles. Helium ions with energies of 4-6 MeV will pass through a TEM sample and therefore are not a good simulation of the displacement damage in the waste form. The majority of the knock-on displacement damage from the helium comes at the end of range, after the helium loses most of its energy. Therefore, the displacement damage from helium is most closely simulated using low energy helium ions. Although helium ions at energies lower than 30 keV would have been a better simulation (10 keV would have been preferred), 30 keV was the lowest energy beam available. High energy (100 keV) lead produces similar damage to the recoil atoms from an alpha decay. Calculations using TRIM97 [11] indicate that 100 keV lead and 90 keV uranium (representing a typical actinide recoil particle and energy) produce damage at a similar rate. Using lead to simulate recoil damage has a potential drawback. The range of 100 keV lead is less than the thickness of a typical TEM disc (100-200 nm) and the damage from the lead is restricted to a narrow region within the TEM disk, making the damage difficult to discern. As an alternative to the lead irradiation, a sample was irradiated with 1 MeV krypton.

EXPERIMENT

Materials

The glass-bonded zeolite waste form was formed in a multistep process [12]. Zeolite 5A (composition in table 1) was combined with the surrogate salts listed in table 2. The salt-occluded zeolites were then mixed with P57 glass (composition in table 1) and the waste form produced in a hot isostatic press.

Table I: Zeolite and Glass Compositions (at %)

	Si	Al	B	Ca	Na	K	O	Cl
Zeolite 5A	13.1	13.8	----	5.0	3.9	----	64.2	----
P57 Glass	19.2	2.5	10.5	----	6.2	0.3	61.2	----

Table II: Surrogate Salt Composition (at%)

Cl	Li	K	Na	Br	Rb	Sr	Y	I	Cs	Ba	La	Ce	Pr	Nd	Sm
50.5	26.5	19	3.1	0.002	0.034	0.081	0.042	0.010	0.178	0.064	0.057	0.109	0.054	0.181	0.028

Sample Preparation

To prepare TEM samples, a bulk sample was taken from the waste form using a 1 cm diameter core drill. One-half mm slices were taken from the core drilled cylinder with a slow speed wafering saw; oil was used as the cutting lubricant. From the 0.5 mm thick wafers, 3 mm diameter disks were cored. An ultrasonic core drill was used with SiC and water as the cutting slurry. The 3 mm disks were mechanically polished on both sides to 0.08 mm thick; water was the grinding lubricant. A dimple was ground into the center of one side to a depth of ~0.07 mm using a 15 mm diameter grinding wheel. The final step was to ion mill (Gatan PIPS) at 5° with 3 keV Ar ions at room temperature.

Irradiations

Ion irradiations were performed using the IVEM-Tandem User Facility at Argonne National Laboratory. Samples were irradiated using 100 keV lead ions to a fluence of 10^{16} Pb⁺/cm² (peak displacement of 51 dpa, rate of 1.3×10^{12} Pb⁺/cm²s). A sample was irradiated with 1 MeV krypton ions to 10^{14} Kr⁺⁺/cm² (peak displacement of 0.11 dpa, rate of 8.2×10^{11} Kr⁺⁺/cm²s). Samples were irradiated with helium to a maximum fluence of 2×10^{16} He⁺/cm² (peak displacement of 0.80 dpa, rate of 1.1×10^{12} He⁺/cm²s). Irradiations were stopped at intermediate doses to determine the response to fluence. All irradiations were performed at room temperature. Doses were calculated using TRIM97 assuming a displacement energy of 25 eV. If the displacement energies were 35 eV, the calculated displacements are: 0.21 dpa (10^{16} He⁺/cm²), 37 dpa (10^{16} Pb⁺/cm²), and 0.07 dpa (10^{14} Kr⁺⁺/cm²). For TRIM calculations, the composition of zeolite 5A was used as the composition.

RESULTS

Unirradiated Characterization:

The unirradiated material has three distinct major phases: an amorphous glass phase, a crystalline phase resulting from salt-occluded zeolite, and a crystalline lanthanide bearing phase. To a lesser extent, alumina and potassium chloride phases have been found. Microsomite, sodium chloride, and lithium aluminum silicate were also identified using x-ray diffraction [12]. Figure 1 shows the glass, salt-occluded zeolite, and lanthanide phases distributed throughout the waste form.

The glass has an amorphous structure, shows no indication of any lanthanides and is low (< 0.2 at%) in Cl. The glass appears to not have interacted with the zeolite chemically, but is found in and around the zeolite phase. Lanthanide phases, dark black in appearance (in TEM bright field),

Fig. 1. TEM bright-field image of the phases in the glass-bonded zeolite waste form.

are the only place lanthanides are found at > 0.5 at%. The lanthanide particles are almost always in contact with the zeolite phase. Surrogate salts with a trivalent charge are found in the lanthanide phase.

The crystalline phase resulting from salt-occluded zeolite shows no indication of lanthanides at EDS detectability (~ 0.1 at%). Regions of this phase have been found that are low in Cl and most likely did not contact the salt mixture. Surrogate salts with a monovalent (Cs) or divalent (Sr) cation charge are found in the zeolite phase. The primary focus of this study is the radiation stability of this crystalline phase resulting from salt-occluded zeolite. Although electron diffraction does not show the phase to be zeolite, the phase derives from the salt-occluded zeolite and for simplicity in terminology will be identified as the zeolite phase.

Effect of the Electron Beam

The zeolite phase and the glass phase are both damaged by 100, 200, and 300 keV electrons. Under a focused electron beam, the glass phase vaporizes and cavities form in the zeolite phase. Figure 2 shows the cavities formed in the zeolite phase. Calcium, oxygen, and potassium concentrations are greatly reduced in the damaged region. A similar effect was seen in mesolite by Yokota et al. [13]. To minimize the contribution of electron beam damage to the samples, the electron beam was turned off during ion implantation and analysis time was minimized.

Helium Irradiation:

During helium irradiation, no major changes in composition of each phase were seen. A cursory examination noted no migration of lanthanides into either the glass or zeolite phases or chlorine into the glass phases. The zeolite phase remained crystalline with no loss of long range

Fig. 2. TEM bright-field image of bubbles generated by a 200keV focused electron beam in zeolite.

order (LRO) up to 10^{15} He^+/cm^2 . At 2×10^{16} He^+/cm^2 , the zeolite phase had little long range crystalline structure. Figure 3a shows selected area diffraction patterns of the sample irradiated with helium. Diffraction patterns from samples irradiated to doses of 3×10^{15} , 9×10^{15} , 1.2×10^{16} , and 2×10^{16} He/cm^2 are shown. Loss of LRO due to helium is present at 0.04 dpa and is nearly complete by 0.8 dpa.

Lead Irradiation:

During lead irradiation, the composition of each phase also remained consistent. The zeolite phase remained crystalline with no indication of loss of LRO, even at the largest dose (51 dpa). From the lead irradiation, the zeolite appears to be fairly resistant to irradiation damage. Because the majority of the lead damage is located in a 50 nm thick layer (only 25-50% of the TEM sample thickness), the damage from the lead irradiation is probably not detectable. A simulation study by Miller and Ewing [14] indicates that up to thirty percent of a sample can be amorphous before the damage is discernible in a high resolution TEM image. To determine if the zeolite was truly resistant to radiation damage from ballistic collisions, irradiations were performed with 1 MeV krypton.

Krypton Irradiation:

The zeolite phase remained crystalline with minimal loss of LRO up to 10^{13} $\text{Kr}^{++}/\text{cm}^2$. At 10^{14} $\text{Kr}^{++}/\text{cm}^2$, the zeolite phase had little LRO with a only a small amount of crystallinity apparent. Figure 3b shows selected area diffraction patterns of the sample irradiated with krypton. Diffraction patterns from samples irradiated to doses of 1×10^{13} , 3×10^{13} , 6×10^{13} , and 9×10^{13} $\text{Kr}^{++}/\text{cm}^2$ are shown. Loss of LRO due to krypton irradiation is present at 0.01 dpa and is nearly complete by 0.10 dpa.

DISCUSSION

Due to the longer half-lives of actinides in an actual waste form (e.g., Pu-239 has a half-life of 2.411×10^4 years), a waste form with approximately 3 wt% Pu-239 will reach about 1 dpa from alpha decay after approximately 10,000 years (about 0.90 dpa from recoil atoms and 0.1 dpa from alpha damage). For commercial high level waste, the cumulative damage after 1000 years is about 0.25 dpa [15]. The glass-bonded zeolite waste form is therefore expected to lose LRO during its lifetime; hence, the effect of the loss of LRO on the radioactive isotope retention ability of the glass-bonded zeolite needs to be investigated. The loss of LRO for room temperature irradiations at doses around 0.1-0.8 dpa was also seen in a detailed study of the Al_2O_3 - SiO_2 system [16]. A

Fig. 3. Electron diffraction patterns showing the loss of crystallinity resulting from ion irradiation.

comparison of the diffraction ring in the irradiated zeolite phase and the diffraction ring from the amorphous glass suggests that the zeolite is not amorphous, but may retain medium range order or undergo nanocrystallization. If the temperature is high enough during the waste form lifetime, the zeolite phase may experience grain growth.

The primary damage mechanism in the zeolite phase is probably ballistic collisions, with ionization damage less important. The dpa at which the samples lose LRO is 0.8 dpa for helium and 0.1 dpa for krypton. TRIM calculations indicate that the average energy transferred due to ionization is about 120 eV/atom for helium and 14 eV/atom for krypton. The krypton, which has the smaller energy transferred due to ionization, causes a complete loss of LRO, at a lower dose. The damaged state corresponds more closely to displacement damage than ionization damage.

Because the glass-bonded zeolite is easily damaged by the electron beam, the waste form may also be susceptible to ionization damage. As a rough rule, ionization damage is important if the energy of the bombarding particle, expressed in keV, is greater than its atomic weight [10]. Therefore, ionization could be significant in both the krypton and helium irradiations. Because the electron beam damage occurs most readily with a focused beam, sample heating or charging effects

may also contribute to the sample damage. To determine if the zeolite phase is susceptible to ionization damage, controlled irradiations using a low current electron beam are necessary.

As noted before, other work saw little change in zeolites irradiated with high energy gamma rays. Daniels and Puri [4] found that the Cs uptake in zeolite 4A increases with increasing neutron exposure. Weakening and broadening of x-ray diffraction peaks with increasing neutron dose indicated framework damage. In a parallel study, gamma irradiation decreased the Cs uptake [5]. Therefore, zeolites do have a different response to ballistic damage (neutrons) than ionization damage (gammas).

CONCLUSIONS

The zeolite phase of glass-bonded zeolite, responsible for radioactive isotope retention, loses LRO after irradiation with both 1 MeV krypton and 30 keV helium at comparable doses. The zeolite phase starts to lose LRO at around 0.01-0.04 dpa and is nearly amorphous by 0.1-0.8 dpa. Because the waste form is expected to reach displacements of greater than 0.1 dpa, the consequences of the loss of LRO on leach rates need to be investigated.

Lanthanides, acting as actinide and fission product surrogates, are not contained in the zeolite phase, but form a separate phase. Therefore, damage from the recoil atom in an alpha decay is only expected to damage the lanthanide phase and any zeolite within about 30-40 nm from the edge of the lanthanide phase. This localized damage in the zeolite phase around the lanthanide phase could lead to volume changes and possible phase separation and cracking. Since the range of the alpha particle is greater than the average spacing of the lanthanide phases, damage from the alpha particle will be distributed throughout the zeolite phase.

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