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Project Title: **Radiation Effects on Materials in the Near-Field of Nuclear Waste Repository**

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**Environmental Management Science Program**

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**Annual Progress Report on  
Radiation Effects on Materials in the Near-Field of  
a Nuclear Waste Repository**

Award Reference Number: DE-FG07-97ER45652  
Project ID Number 54691

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**1. INTRODUCTION AND RESEARCH OBJECTIVE**

Site restoration activities at DOE facilities and the permanent disposal of nuclear waste generated at DOE facilities involve working with and within various types and levels of radiation fields. Once the nuclear waste is incorporated into a final form, radioactive decay will decrease the radiation field over geologic time scales, but the alpha-decay dose for these solids will still reach values as high as  $10^{18}$  alpha-decay events/gm in periods as short as 1,000 years. This dose is well within the range for which important chemical (e.g., increased leach rate) and physical (e.g., volume expansion) changes may occur in crystalline ceramics. Release and sorption of long-lived actinides (e.g.,  $^{237}\text{Np}$ ) can provide a radiation exposure to backfill materials, and changes in important properties (e.g., cation exchange capacity) may occur. The objective of this research program is to evaluate the long term radiation effects in the materials in the near-field of a nuclear waste repository with accelerated experiments in the laboratory using energetic particles (electrons, ions and neutrons). The proposed target materials for study include zeolites, clays because they are important materials in the near-field expected to retard the migration of radionuclids by absorption or ion exchange processes.

Due to the moving of both PI and the co-PI of this program from the University of New Mexico to the University of Michigan in mid-1997, the program schedule has been delayed for several months and now with a DOE approved new ending date of November 14, 1999. Thus, this report is an annual report covering the period from June 1, 1998 to May 30, 1999, although the initial award was made in mid-1996. The final report will be submitted by the end of 1999.

**2. RESEARCH PROGRESS AND IMPLICATIONS**

During this reporting period, the study of radiation-induced changes in the structure and microstructure has been extended to cover more target materials, including several different natural and synthetic zeolite compositions, bentonite (montmorillonite) and crystalline silicotitanate. Since the major radiation-induced effect is amorphization in these materials, the effects of amorphization on the ion exchange and desorption capacity

for Cs and Sr have been conducted first on zeolite-Y. The major findings are: (1) amorphization greatly reduced the ion-exchange capacity of zeolite for Cs and Sr; (2) in samples preloaded with Cs, amorphization also reduced the desorption rate of Cs. Since the major radiation dose from the alpha-decay will be received after the incorporation of radionuclides into zeolites and sheet silicates, our results imply that radiation-induced amorphization may retard the further migration of radionuclides. Two major papers have been completed and submitted to the Journal of Nuclear Materials reporting these results during the last reporting period.

### 2.1 Radiation effects on the structure of zeolites, bentonite and crystalline silicotitanate

Three different zeolites (analcime, natrolite, and zeolite-Y) were irradiated with 200 keV and 400 keV electrons. All zeolites amorphized under a relatively low electron fluence. The transformation from the crystalline-to-amorphous state was continuous and homogeneous. The electron fluences for amorphization of the three zeolites at room temperature were:  $7.0 \times 10^{19}$  e<sup>-</sup>/cm<sup>2</sup> (analcime),  $1.8 \times 10^{20}$  e<sup>-</sup>/cm<sup>2</sup> (natrolite), and  $3.4 \times 10^{20}$  e<sup>-</sup>/cm<sup>2</sup> (zeolite-Y). The different susceptibilities to amorphization are attributed to the different channel sizes in the structures which are the pathways for the release of water molecules and Na<sup>+</sup>. Natrolite formed bubbles under electron irradiation, even before complete amorphization. Analcime formed bubbles after amorphization. Zeolite-Y did not form bubbles under irradiation. The differences in bubble formation are attributed to the different channel sizes of the three zeolites. The amorphization dose was also measured at different temperatures. An inverse temperature dependence of amorphization dose was observed for all three zeolites: electron dose for amorphization decreased with increasing temperature. This unique temperature effect is attributed to the fact that zeolites are thermally unstable. A semi-empirical model was derived to describe the temperature effect of amorphization in these zeolites [1].

Crystalline silicotitanate (CST) and montmorillonite (bentonite) powder samples were irradiated with 200 keV electrons with a dose rate in the range of  $8 \times 10^{16}$  ~  $8 \times 10^{17}$  electron/s·cm<sup>2</sup>. Both materials were also found susceptible to electron radiation damage and radiation-induced amorphization. At room temperature, the critical amorphization dose for montmorillonite is  $1.1 \times 10^{20}$  electron/cm<sup>2</sup>, which corresponds to an energy deposition of  $\sim 5.1 \times 10^{10}$  Gy.

### 2.2. Effects of amorphization on the ion-exchange capacity and desorption rate for Cs

Due to the small volumes affected by the ion or electron beam irradiations, ion exchange experiment cannot be performed on these radiation damaged samples. Our estimation based on the flux of the available  $\gamma$ -source indicated that about 50 year is needed to fully amorphize the zeolite-NaY samples with  $\gamma$  irradiation. We have decided to use neutron irradiations to obtain bulk powdered materials. We have 18 zeolite-Y powder samples (100 mg per sample) including some pre-loaded with  $\sim 15$  mol. % Cs and Sr in the Ford Reactor at the University of Michigan for up to 10,000 hours of neutron irradiations. The samples will be withdrawn intermittently for the study the changes in ion exchange and desorption capability with the increasing irradiation dose. The first group of the neutron irradiated samples will be ready for study in June, 1999.

In the meanwhile, we have studied the effects of amorphization on the ion exchange and desorption capacity using thermally amorphized zeolite samples. The zeolite-NaY

amorphized with thermal treatment at 900 °C lost approximately 95 percent of its ion exchange capacity for cesium due to the loss of exchangeable cation species and /or the blockage of access to exchangeable cation sites. A secondary phase was formed during the ion exchange reaction with cesium. The Cs-exchanged zeolite phase (with ~20 wt. % Cs loading) appears to have a slightly higher thermal stability than the original zeolite-NaY crystal. A desorption study have indicated that the amorphization of cesium-loaded zeolite may enhance the retention capacity of exchange Cs ions due to the closure of the channels [2].

### 3. PLANNED ACTIVITIES

(1) Systematic study on radiation effects on the microstructure of sheet silicates and zeolites with energetic particle irradiation (electrons, ions and neutrons) and transmission electron microscopy. The study will include more phases (e.g., bentonite and silicotitanite). The effects of irradiation temperature, various irradiation sources and the dose rate on amorphization and bubble formation will be compared with the chemical composition, crystal structure of the target material to further understand the mechanisms responsible for the microstructural change. This project shall be completed by the end of 1998.

(2) To complete a systematic study on radiation effects on the cation exchange capacity of zeolites and crystalline silicotitanate, the sorption capacity of bentonite, and the release rate of radionuclides (e.g., Cs and Sr). Neutron irradiated zeolite-Y samples will be available for this study during the next 6 months. For bentonite and crystalline silicotitanate, thermally amorphized samples will be used to simulate the radiation effects because neutron irradiations takes a long time to induce amorphization and the irradiated samples may be radioactive.

References (Journal papers submitted during this reporting period):

1. S.X. Wang, L.M. Wang and R.C. Ewing, Electron and ion irradiation of zeolites, *Journal of Nuclear Materials*, in press.
2. B.X. Gu, L.M. Wang and R.C. Ewing, The effect of amorphization on the Cs ion exchange and retention capacity of zeolite-NaY, *Journal of Nuclear Materials*, in review.