Progress Report on

“Radiation Effects on Materials in the Near-Field of a Nuclear waste Repository”

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1. Note

This grant was originally awarded to us through the University of New Mexico as award number DE-FG07-96ER45615 on 09/15/1996. However, because both of us (PI and co-PI) accepted positions at the University of Michigan by the end of 1996, we applied for transferring the entire award to University of Michigan on January 26, 1997. The transferred grant was not received at the University of Michigan until September 15, 1997 with a new award number DE-FGO7-97ER45652 for the period of 9/15/97 to 11/14/99. Due to this move and the grant transfer, progress on the project was slightly delayed. Nevertheless, we began the research program before receiving the funding at the University of Michigan and have made certain progress during the last four months which are covered in this brief report.

2. Temperature dependence of radiation induced amorphization of mica minerals

(work performed before the transferred grant was received on 09/15/97)

Sheet silicates (e.g. micas and clays) are important constituents of a wide variety of geological formations such as granite, basalt, and sandstone. Sheet silicates, particularly clays such as bentonite, are common materials in near-field engineered barriers in high-level nuclear waste (HLW) repositories. This is because migration of radionuclides from an underground HLW repository to the geosphere may be significantly reduced by sorption of

radionuclides (e.g., Pu, U and Np) onto sheet silicates (e.g., clays and micas) that line the fractures and pores of the rocks along groundwater flowpaths. In addition to surface sorption, it has been suggested that some sheet silicates may also be able to incorporate many radionuclides, such as Cs and Sr, in the inter-layer sites of the sheet structure. However, the ability of the sheet silicates to incorporate radionuclides and retard release and migration of radionuclides may be significantly affected by the near-field radiation due to the decay of fission products and actinides. For example, the unique properties of the sheet structures will be lost completely if the structure becomes amorphous due to irradiation effects. Thus, the study of irradiation effects on sheet-structures, such as structural damage and modification of chemical properties, are critical to the performance assessment of long-term repository behavior.

In this study, four different mica compositions, i.e., muscovite $[\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH},\text{F})_2]$, phlogopite $[\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH},\text{F})_2]$, biotite $[\text{K}(\text{Mg},\text{Fe})_3(\text{AlSi}_3\text{O}_{10})(\text{OH},\text{F})_2]$ and lepidolite $[\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH},\text{F})_2]$, were irradiated with 1.5 MeV Kr^+ ions in a temperature range between 20-1023 K using the HVEM-Tandem Facility at Argonne National Laboratory. The irradiation effects were characterized by *in situ* and high resolution transmission electron microscopy (TEM). All four micas were found to be susceptible to irradiation-induced amorphization with relatively low critical amorphization doses (D_c) ($1-2 \times 10^{14}$ ions/cm², fractions of a dpa) below or at the room temperature. D_c increased with irradiation temperature for all phases above 400 K. The critical temperatures (T_c), above which amorphization will not occur, for the four micas are all at or above 1000 K. Lepidolite is the most easily amorphized among the four micas at all irradiated temperatures with a T_c of 1300 K. Large gas bubbles (1-2 μm in diameter) were observed in a 800 keV Kr^{2+} irradiated biotite after 1×10^{15} ions/cm². The bubble volumes are too large to be explained by the implanted Kr content indicating chemical decomposition has occurred.

The results of this study were presented at the 9th International Conference on Radiation Effects in Insulators which was held in Knoxville, Tennessee during September 14 - 19, 1997, and a manuscript has been submitted to Nuclear Instrument and Method B for publication.

3. Radiation effects in zeolites and relevance to near-field containment

(work completed after 09/15/97)

Zeolites are among the group of minerals being currently considered to have the greatest potential for use as back-fill materials. Also, zeolite-group minerals, such as analcime ($\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$) are frequently found as precipitated phases on the surfaces of corroded nuclear waste glass. Zeolites which have precipitated on the reacted glass surface incorporate Cs and actinides through ion exchange reactions. Because zeolites have a high retention rate for radionuclides in the near-field, they will also be exposed to high radiation doses (α - and β - decay events). Irradiation of these phases may result in changes in the crystalline structure and properties, such as ion-exchange and sorption capacities and may finally lead to the redistribution or release of retained radionuclides. Electron beam irradiation in an transmission electron microscope has been used to simulate the effects of ionizing radiation caused by β -particles and γ -rays.

In this study, the temperature and electron energy dependence of electron irradiation-induced damage in analcime has been investigated with JEM 2000FX and JEM 4000EX transmission electron microscopes. The electron energy used with the two microscopes was 200 and 400 keV, respectively. The temperature range was between 300 to 673 K. The dose rate effect was studied in the range between 2×10^{17} to 1×10^{19} $\text{e}^-/\text{cm}^2\text{s}$. At room temperature, the average amorphization dose for analcime under a 200 keV electron beam is about 8×10^{19} e^-/cm^2 , or $\sim 2 \times 10^{10}$ Gy in ionizing dose. The electron dose required for amorphization under a 400 keV beam is significantly higher (3×10^{20} e^-/cm^2). This suggests

that the ionization mechanism is mainly responsible for the amorphization process because the ionization cross-section decreases with the increasing electron energy in the energy range. There was no significant dose rate effect on the amorphization dose within the dose rate range studied. However, under intensely focused electron beam, amorphization was almost instant although with the similar total doses, loss of Na was noted with energy dispersive x-ray analysis (EDS), and cavities were observed in bright field image. An anomalous temperature dependence of the amorphization dose was noted under the 200 kV electron irradiation, i.e., with increased temperature, the amorphization dose for analcime decreased, similar to that observed in electron-irradiated coesite, a high pressure polymorph of silica which undergoes spontaneous amorphization upon heating. Detailed study with *in situ* and high-resolution TEM on additional zeolite phases is under way.

In summary, analcime is very sensitive to ionizing irradiation and amorphizes by a radiolysis mechanism. The atomic-scale changes in structure may change the ion exchange capacity of the zeolite in the near-field. Ion exchange experiments of irradiated zeolite are being prepared to evaluate the impact of irradiation on the performance of zeolite for retaining radioactive elements.

An abstract based on the preliminary results has been submitted to the 1998 International High-Level Radioactive Waste Management Conference to be held in Las Vegas, Nevada during May 11-14, 1998.