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Radiation Effects on Materials in the Near-Field of Nuclear Waste Repository

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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}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). Experiments on the microstructural evolution during irradiation of two important groups of materials, sheet silicates (e.g., clays) and zeolites (analcime), have been conducted; and studies of radiation-induced changes in chemical properties (e.g. cation exchange capacity) are underway.

Research Progress and Implications

As of the mid-2nd year of the 3-year project, experiments on the microstructural evolution during irradiation of two important group of materials, sheet silicates (mica) and zeolites (analcime), have been conducted; and studies of radiation-induced changes in chemical properties (e.g., cation exchange capacity) are underway. The main results are as follows:

2.1 Radiation effects in sheet silicates

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, may be used as near-field engineered barriers in high-level nuclear waste (HLW) repositories. Migration of radionuclides to the geosphere may be significantly reduced by sorption of radionuclides (e.g., Pu, U and Np) onto sheet silicates that line the fractures and pores of the rocks along groundwater flowpaths. In addition to surface sorption, sheet silicates may also be able to incorporate radionuclides, such as Cs and Sr, into the inter-layer sites. However, the ability of the sheet silicates to incorporate radionuclides and retard the release and migration of radionuclides may be significantly affected by near-field radiation. For example, the unique properties of the sheet structures will be lost completely if the structure becomes amorphous due to irradiation. 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.

Four different sheet silicate compositions, i.e., muscovite [$KAl_2(AlSi_3O_{10})(OH,F)_2$], phlogopite [$KMg_3(AlSi_3O_{10})(OH,F)_2$], biotite [$K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$] and lepidolite [$K(Li,Al)_3(Al,Si)_4O_{10}(OH,F)_2$], have been irradiated with 1.5 MeV Kr^+ ions 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 at relatively low critical amorphization doses (D_c) (1-2×10^{14} ions/cm^2, 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 was 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/cm^2. The bubble volumes are too large to be explained by the implanted Kr-content indicating chemical decomposition has occurred.

2.2. Radiation effects in zeolites

Zeolites are often considered to have the potential for use as back-fill materials because of their ability to sorb radionuclides. Zeolite-group minerals, such as analcime ($NaAlSi_2O_6$•H_2O), 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 a transmission electron microscope has been used to simulate the effects of ionizing radiation caused by β-particles and γ-rays.

Temperature and electron energy dependence of electron irradiation- induced damage in analcime has been investigated with 200 and 400 keV electron beams in the transmission electron microscope. The temperature range was between 300 to 673 K. The dose rate effect was studied in the range between 2x10^{17} to 1x10^{19} e^-/cm^2s. 1.5 MeV Kr^+ ion irradiation with *in situ* TEM was conducted at Argonne National Laboratory using the HVEM-Tandem Facility in a temperature range between 300 to 973 K with an ion flux of 5x10^{11} ions/cm^2s. At room temperature, the average amorphization dose for analcime under a 200 keV electron beam is 8x10^{19} e^-/cm^2, or ~2x10^{10} Gy. The electron dose required for amorphization under a 400 keV beam is significantly higher (3x10^{20} e^-/cm^2). This suggests that the ionization mechanism is mainly responsible for amorphization under electron irradiation because the ionization cross-section decreases with the increasing electron energy in this 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 bubbles were quickly observed in the bright-field image regardless of the electron energy. The bubbles grow rapidly with the increasing electron dose, and they were confirmed to contain molecular water by TEM conducted below 200 K, which gave the diffraction pattern of ice and a unique diffraction contrast from the bubbles which only appeared at the cryo-temperatures. An anomalous temperature dependence of the amorphization dose was noted under electron irradiations, i.e., with increased temperature, the amorphization dose for analcime decreased, which is related to the thermal instability of the material. Amorphization of analcime was also easily achieved under Kr^+ irradiation at doses <0.1 dpa between 300 to 973 K. Collisional displacements are the main mechanism for amorphization under Kr^+ irradiation during which the energy deposition through ionization is less than 10^8 Gy.

In summary, sheet silicates and zeolites are susceptible to radiation-induced amorphization. Amorphization of these materials can be induced by either radiolysis or collisional displacement mechanisms. For analcime (zeolite), the radiation dose required for amorphization drops with increased temperature. Accompanying amorphization, bubbles are induced in both sheet silicates and zeolites under intense irradiation. Amorphization and formation of bubbles may change the sorption and ion exchange capacity of sheet silicates and zeolites as well as the release rate of radionuclides. This change has to be considered in the accessment of the long term reliability of a radioactive waste repository.

Planned Activities

Future research includes the following two general topics:

(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 silico-titanite). 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) Systematic study on radiation effects on the cation exchange capacity of zeolites and release rate of radionuclides (e.g., Cs and Sr). For these experiments, powdered samples of specified sizes will be irradiated with neutrons in the Ford Reactor of the Phoenix Memorial Laboratory at the University of Michigan because the available gamma source can not provide enough dose for amorphization in a reasonable time frame. Experiments on unirradiated control samples are underway, and the results from these experiments will be compared with those from the neutron irradiated samples which are expected in the Summer of 1999.

Other Access To Information

1. L.M. Wang, S.X. Wang and R.C. Ewing, Radiation effects in zeolite: Relevanve to near-field containment, Proceedings of the 9th International Conference on High-Level Radioactive Waste Management (American Nuclear Society, Las Vegas, NV, May 11-14, 1998), pp. 772-774.
2. L.M. Wang, S.X. Wang, W.L. Gong and R.C. Ewing, Temperature dependence of Kr ion-induced amorphization of mica minerals, Nuclear Instruments and Methods in Physics Research B, in press.
3. L.M. Wang, Application of advanced transmission electron microscopy techniques in the study of radiation effects in insulators, Nuclear Instruments and Methods in Physics Research B, in press.