

Environmental Management Science Program

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(continued from project 54691)**

**Radiation Effects on Sorption and Mobilization of Radionuclides
during Transport through Geosphere**

Annual Progress Report

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1. Background 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. Radionuclide decay and the associated radiation fields lead to physical and chemical changes that can degrade or enhance material properties. The principal sources of radiation at the DOE sites are the actinides and fission-products contained in high-level wastes currently in storage. Alpha-decay of the actinide elements and beta-decay of the fission products lead to atomic scale changes in the material (radiation damage and transmutation). During site restoration, materials will be exposed to radiation fields that exceed 10^4 rad/hr. The radiation exposure due to the release and sorption of long-lived actinides (e.g., ^{237}Np) and fission products (e.g., ^{137}Cs and ^{90}Sr) may cause changes in important properties (e.g., cation exchange capacity) in geological materials (e.g., clays and zeolites) along transport pathways. Among these materials, clays and zeolites, which are expected to sorb and immobilize radionuclides, are known to be extremely susceptible to radiation-induced structure changes (e.g., bubble formation and solid state amorphization) through both collisional displacement and ionization processes. These changes will inevitably affect (either negatively or positively) the further sorption and the migration of radionuclides at waste sites (e.g., vadose zone at Hanford). Current models used for the longterm prediction of radionuclide transport have proven to be inadequate and unrealistic; however, these previous models did not take radiation effects into consideration.

This research program has been aimed at the understanding radiation effects on the sorption/desorption and ion exchange capacity of radionuclides in two major groups of geologic materials, clays and zeolites. The experiments are designed for investigating the effects of ionizing and particle irradiation on the zeolites and clays. We are focusing on changes in the ion exchange capacity of radionuclides (Cs, Sr, U, and Se), and changes in the retention capacity of already incorporated radionuclides after the sample is damaged by radiation. Through a comprehensive study of the microstructure and ion exchange capacity under varying types of irradiation (collision versus ionization), dose rate, temperature and ion exchange conditions, we will develop a first principles understanding of radiation effects on the ion exchange and retention capacity of clays and zeolites. The database will provide a basic understanding the longterm effectiveness of clays and zeolite in radionuclide retention, as well as the mobility of the radionuclides in contaminated sites. These results will form the scientific basis for the development of both better models for the prediction of the longterm migration of radionuclides and better techniques for the effective confinement of radionuclides at the DOE sites.

2. Research Progress

During the past year, experiments of proton and neutron irradiation, XPS, MAS NMR and XAS analyses have been conducted on zeolite samples with or without preloading of radionuclides (Sr or Cs). A brief summary of the results of these experiments is in the following sections. Also during the period, a Ph.D. Thesis has been completed and successfully defended by the former graduate student, Binxi Gu supported by this EMSP program (Project 54691 and then continued as 73762). Four research papers including one in Journal of Nuclear Materials and one in Journal of Material Chemistry have been published during the last funding year (see section 3, Information Access). Our results have so far implied that radiation effects on the zeolite and clays in the near-field of a radioactive waste repository may help to retard the migration of radionuclides through

geosphere due to decreased desorption rate of trapped radionuclides in the damaged zeolite and clay structures. The results need to be further confirmed and the mechanisms need to be further understood.

2.1 Proton and Neutron Irradiation

During the first phase of this research program (Project No. 54691), we have demonstrated that the porous and layer structured materials (i.e., zeolites and clays) that are expected to absorb radionuclides in the near field of a radioactive waste repository are all sensitive to radiation induced amorphization. Amorphization (i.e., the loss of crystallinity) will greatly reduce the ion exchange capacity and the desorption rate of these materials for radionuclides, such as Sr and Cs. However, the ion exchange and desorption experiments performed during the previous phase of the study were mostly on thermally induced amorphous materials since the electron and ion irradiation could not produce enough materials for the traditional ion exchange and desorption experiments. During the first year of the second phase of this research program, we have conducted ion exchange and desorption experiments on zeolite samples amorphized by proton irradiation followed by cross-sectional transmission electron microscopy (TEM) and electron microprobe analysis (EMPA). The results have confirmed that of the previous experiments on thermally amorphized samples, i.e., both ion exchange and desorption capacity of zeolite for Cs and Sr are greatly reduced as the result of amorphization (either radiation-induced or thermally-induced) (See Gu, Wang and Ewing, *J. Mater. Chem.* 2001).

In order to generate more irradiated materials for detailed traditional ion exchange and desorption experiments, neutron irradiation on 24 zeolite samples has been conducted in the Ford Nuclear Reactor (FNR) at the Memorial Phoenix Laboratory (PML) of the University of Michigan. Eight batches of zeolite samples, each containing 300 mg zeolite-NaY, 100 mg zeolite-Cs NaY (zeolite-NaY with 20 wt. % loading of Cs) and 100 mg zeolite-SrNaY (zeolite-NaY with 10 wt. % loading of Sr), have been loaded in the core area of the FNR for irradiation with neutrons for a period of time ranging from 2,000 to 20,000 hours. Samples prepared for irradiation were wrapped in high purity aluminum foil and then put in a water-proof rifle. The estimated fast neutron flux at this particular location is 1.25×10^{12} /cm²-s. The total neutron dose after 10,000 hours of irradiation will be 4.5×10^{19} /cm². More accurate cumulative doses for each batch of samples will be determined by measuring the activity of the high purity Ni and Fe wires loaded within the sample pocket at the end of irradiation. The activity of irradiated sample was estimated 1 mCi/100 mg for Cs-exchanged zeolite, after one year in the reactor. For Sr-exchanged zeolite, the activity was estimated to be 7 μ Ci/100 mg after one-year irradiation. To date, irradiation of 5 batches (totally fifteen samples) out of the 24 samples in 8 batches has been completed. The radiation safety staff at PML of the University of Michigan has conducted careful measurement on the radioactivity of the samples. Due to the radioactivity (especially in those preloaded with Cs and Sr), only five out of the 15 unloaded samples have been released from the PML to the PIs so far. The safe procedure for handling these samples has been developed and approved by Occupational Safety and Environmental Health (OSEH) staff. Analyses on these samples have begun. More samples will be released to the PIs from OSEH during the next few months. There have been a few months of delay in this part of the research due to the very strict safety requirement on handling these radioactive sample.

2.2 XPS and MAS NMR Analyses

In order to understand the mechanisms for the reduction of ion exchange capacity and desorption for radionuclides in amorphized zeolites, x-ray photoelectron spectroscopy (XPS) and magnetic angle spinning nuclear magnetic resonance (MAS NMR) analyses have been conducted on thermally treated and some neutron irradiated samples with or without preloading of radionuclides.

The XPS results have indicated that the binding energy value of Si 2p, Na 1s does not change for the zeolites after ion exchange and being treated at different temperatures. This suggests that $[\text{SiO}_4]$ structural units are still kept in the zeolites even after amorphization. This is consistent with the results from other previous research. For hydrated SrNaY-zeolite, there is no strontium occupation at site I. This is because that the radius of hydrated strontium ion is larger than that of hexagonal prisms. Strontium ions usually occupy site I' and II at this stage. For dehydrated SrNaY-zeolite, besides occupying site I' and II site, strontium can also occupy site I due to the low energy of this site. This is consistent with the changes of the full width at half maximum (FWHM) from 1.80 to 2.21 when SrNaY-zeolite was treated at 500°C. When the temperature further increase to 900°C, FWHM increase from 2.21 to 2.43. At the same time, the binding energy value of $\text{Sr}3d_{3/2}$ increases from 134.2 eV to 134.6 eV. From the available literature it can be conclude that the Sr-O distance varies between 0.2405 nm for the strongest bond and 0.2973 nm for the weakest bond. The difference in binding energy of $\text{Sr}3d_{3/2}$ is the consequence of the difference of the effective negative charge on strontium. The lower the binding energy value, the higher the average electron density on strontium. The increase of binding energy of $\text{Sr}3d_{3/2}$ indicates a lower average electron density on the strontium ion. This suggests that the Sr-O bond becomes longer after SrNaY-zeolite has been treated at 900°C for 30 min and strontium ions can occupy site I when its host zeolite is heat-treated. In other words, strontium can migrate to site I in hexagonal prisms after thermal treatment. Compared with that of the supercage, the space of hexagonal prisms is much smaller, thus the radionuclide can be easily trapped in thermally treated zeolite. The XPS results have also indicated that the binding energy of aluminium changed when SrNaY-zeolite was heat-treated.

^{29}Si and ^{27}Al magic angle spinning (MAS) NMR has been widely applied to determine the structure of Y-zeolites. ^{29}Si MAS NMR provides information about the Si/Al ratio of the framework, assuming Loewenstein's Rule is obeyed. The isotropic chemical shift of aluminium in ^{27}Al MAS NMR provides information about the coordination of the aluminum species. The MAS NMR spectra of NaY-zeolite, SrNa-zeolite and SrNaY-zeolite treated at 900°C for 30 min have been collected and analyzed. The spectrum of NaY-zeolite consists of lines at chemical shifts of -89.42, -94.64, -100.99 and -109.59 ppm originating from Si(nAl) atoms with n=4, 3, 2, and 0, respectively. When strontium was loaded to NaY-zeolite, the chemical shifts become -90.10, -94.90, -101.10 and -109.60 ppm. The peak assigned to Si (0Al) does not change, this also means that the structure of $[\text{SiO}_4]$ units have not changed after the ion exchanges.

The ^{27}Al MAS NMR spectra for NaY-zeolite, SrNa-zeolite and SrNaY-zeolite treated at 900°C for 30 min have been collected and analyzed. In these spectra, only the line of tetrahedral coordinated framework aluminium at about 58 ppm appears. No octahedral coordinated extra framework aluminium is observed.

Compared with those of NaY-zeolite and SrNaY-zeolite, the chemical shift value decrease from 58.41ppm to 49.95 ppm in the MAS NMR spectrum from SrNaY-zeolite treated at 900°C. The deduction is consistence with the result of the XPS work, in which

we found the binding energy value of Al 2p decrease after heat-treatment and the results of our previous XRD study.

Due to the strict regulation on radioactive materials handling, the MAS NMR work on neutron irradiated and strontium-loaded zeolites has just began. During the next year, we are expecting to obtain the information on the following:

- 1) The framework structural units changes of $[\text{SiO}_4]$ and $[\text{AlO}_4]$ before and after neutron irradiation;
- 2) The location site changes of strontium ions before and after neutron irradiation;
- 3) The relationship between radiation dose and the structure change.

At the same time, the effects of radiation on the retention of strontium in neutron-irradiated SrNaY-zeolite and on the ion-exchange capacity of neutron-irradiated NaY-zeolite will also be studied.

2.3. X-ray Absorption Spectroscopy (XAS) experiments

XAS experiments were conducted during year 1 as part of the proposed effort to characterize the near coordination environment of radionuclides exchanged with zeolite materials before and after exposure to damaging irradiation. The goal of these initial experiments was to determine the utility of XAS for probing changes in the exchange site coordination environment caused by amorphizing radiation. Another goal of these experiments was to determine the feasibility of demonstrate that thermal treatments may also effectively mimic the effects of radiation damage.

XAS can be used to characterize the near coordination environment (within 6\AA) surrounding an element by providing bond distances and coordination numbers of neighboring atoms within this distance. The structural information results from analysis of the photoelectronic production from the interaction of x-rays and the element under excitation. Both XANES (x-ray absorption near edge structure) and EXAFS (extended x-ray absorption fine structure) analyses have been conducted in the year 1 feasibility study.

The initial results show promise for using XAS to characterize the impact of radiation damage on the near coordination environment for important radionuclides such as Sr and Cs. Based on the two sample loadings and heat treatment conditions investigated, it is clear that collapse of the zeolite structure causes discernable changes that can be quantified in terms of CNs and bonding distances through XAS data analysis. However, these initial studies have not been setup for the most optimal XAS conditions nor have Sr exchange samples been prepared over a wide range of loadings or for other proposed types of radiation treatments. We have also not attempted to look at samples after desorption of Sr has been accomplished.

For the upcoming year, we propose to look at a wider range of Sr loadings, at samples from which Sr has been desorbed, and using other irradiation sources. The desorption samples should help to minimize static disorder due to multiple bonding structures that could be present for partially damaged material. To minimize thermal disorder and to enhance the signal-to-noise, XAS data will also be collected at low temperature (approximately 20 K) using a liquid helium cryostat. A recent study of Sr by Sahai et al. (2000) has confirmed that freezing Sr structure does not affect the structural analysis of sorbed or aqueous samples, but significantly improves the signal to noise. We will also expand these XAS investigations to include more Cs exchanged samples. Due to the monochromator glitch for the Si(220) crystals in the EXAFS region for the Cs samples, future work will need to be performed with a different orientation of those crystals (e.g., using Si (220) to eliminate the crystal glitch in the Cs L(III)-edge EXAFS region).

During the past year, work was performed at SSRL as part of an on-going program for which this work was related. Based on these promising results, a proposal to SSRL to

establish an experimental XAS program will be prepared. In order to study the effects of irradiation damage for other energy sources, in which non-uniform damage with depth results, it may be necessary to utilize microprobe analysis tools that can be focused on a specific surface region of a sample. Such facilities are available at the Advanced Photon Source (APS) Synchrotron facilities at Argonne National Laboratory. In the next year, we will investigate the feasibility of performing XAS studies at APS. As mentioned above, it may also be desirable to investigate zeolite samples that become radioactive by various irradiation sources. Both SSRL and APS facilities are capable of handling radioactive samples, but this will require special permission and implementing the proper safety precautions. During the next year, a request to perform experiments with activated samples will be made.

3. Information Access

3.1 Web Site: <http://www-ners.engin.umich.edu/relw/>

3.2 Publications Generated during the Year:

1. B.X. Gu, L.M. Wang, L.D. Minc and R.C. Ewing, Temperature effects on the radiation stability and ion exchange capacity of smectites, J. Nuclear Materials 297 (3) (2001) 345-354.
2. Binxi Gu, Lumin Wang, Shixin Wang, Donggao Zhao, Victor H. Rotberg, R.C. Ewing, Effects of proton irradiation in zeolite-Y, Materials Research Society Symposia Proceedings 650 (2001) R3.16.1-6.
3. B.X. Gu, L.M. Wang and R.C. Ewing, Radiation effects on the microstructure and chemical properties of zeolite-Y, Transactions of the American Nuclear Society 84 (American Nuclear Society, Chicago, IL, 2001), pp. 358-359.
4. B.X. Gu, L.M. Wang, S.X. Wang and R.C. Ewing, Radiation effects on materials in the near-field of a nuclear waste repository, Materials Research Society Symposia Proceedings 663 (2001) 883-891.
5. B. Gu, L. Wang and R.C. Ewing, The effects of radiation on the retention of strontium in zeolite-NaSrY, J. Materials Chemistry 12 (2002) 233-238.

3.3 Ph.D. Thesis Completed:

Binxi Gu, "Radiation and Thermal Effects on Zeolites, Smectites and Crystalline Silicotitanates", University of Michigan, Ann Arbor, Michigan (2001).

3.4 Presentations:

1. L.M. Wang and R.C. Ewing, "Nuclear waste forms for the future": at the 221st National Meeting of the American Chemical Society, San Diego, CA (April 1-5, 2001).

2. B.X. Gu, L.M. Wang and R.C. Ewing, "Radiation effects on the microstructure and chemical properties of zeolite-Y": at the 2001 Annual Meeting of American Nuclear Society, June 17-21, 2001, Milwaukee, Wisconsin.
3. L.M. Wang, "Effects of ionizing irradiation on the structure and ion exchange capacity of zeolite and clays": at the Laboratory of Mineralogy and Crystallography, Paris University VI & VII, Paris, France (September 18, 2001).