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

Final Progress Report
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L.M. Wang\textsuperscript{a}, R.C. Ewing\textsuperscript{a,b} and K.F. Hayes\textsuperscript{c}

\textsuperscript{a}Department of Nuclear Engineering and Radiological Sciences
\textsuperscript{b}Department of Geological Sciences
\textsuperscript{c}Department of Materials Science and Engineering

Department of Civil and Environmental Engineering

The University of Michigan, Ann Arbor, MI 48109

PI contact information:
Dr. Lu-Min Wang
Department of Nuclear Engineering and Radiological Sciences
University of Michigan
Cooley Building
2355 Bonisteel Blvd.
Ann Arbor, MI 48109
Phone: 734-647-8530
Fax: 734-647-8531
E-mail: lmwang@umich.edu
ABSTRACT

Site restoration activities at DOE facilities and the permanent disposal of nuclear waste inevitably involve understanding the behavior of materials in a radiation field. Radionuclide decay and the associated radiation fields lead to physical and chemical changes that can degrade or enhance important material properties. Alpha-decay of the actinide elements and beta-decay of the fission products lead to atomic-scale changes in materials (radiation damage and transmutation). The radiation exposure due to the release and sorption of long-lived actinides and fission products (e.g., $^{137}$Cs and $^{90}$Sr) may cause changes in important transport properties (e.g., sorption and cation exchange capacity) in geological materials, such as colloidal clays and zeolites, along transport pathways. Thus, the effect of radioactive decay on soils and geologic materials during transport (e.g., through the vadose zone) are an important aspect of understanding the migration and retention of radionuclides in the geosphere.

During the previous funding period of this project, we have evaluated radiation effects in selected near-field materials with accelerated laboratory experiments utilizing energetic electrons and ions and in situ transmission electron microscopy (TEM) during irradiation at the HVEM/IVEM-Tandem National Facility at Argonne National Laboratory. The materials irradiated included zeolites and layered silicates (mica and clays). We have found that all of these materials are susceptible to irradiation-induced solid-state amorphization. Amorphization can either be induced by ionization processes ($\beta^-$ or $\gamma^-$ irradiation) or by direct displacement damage processes ($\alpha^-$-decay events). The critical doses for complete amorphization of these phases are as low as <0.1 displacement per atoms (dpa) or $10^8$ Gy in ionization energy deposition (a dose expected in a zeolite with 10 wt.% loading of $^{137}$Cs in 400 years). Experiments on thermally-induced amorphization have shown that even partial amorphization will cause a dramatic reduction (up to 95%) in ion-exchange and sorption/desorption capacities for radionuclides, such as Cs and Sr. Because the near-field or chemical processing materials, e.g., zeolites or crystalline silicotitanate (CST), will receive a substantial radiation dose after they have incorporated radionuclides, our results suggest that radiation effects may, in some cases, retard the release rate of sorbed or ion-exchanged radionuclides. These results have a direct bearing on repository performance assessments (e.g., the extent to which zeolites can retard the release of radionuclides) and on the technologies used to process high-level liquid wastes (e.g., separation of $^{137}$Cs from HLW using CST at the Savannah River Site). Because the dose rate of available gamma sources is too low to achieve significant effects in a reasonable period (e.g., requires 50 years to reach the critical amorphization dose for zeolite-NaY), heavy ions or energetic electrons in an electron microscope were used in our previous studies. Although these experiments are adequate for studying the radiation effects on the microstructure of the target material, the radiation affected volume is too small for studying changes in bulk properties, such as sorptive or ion-exchange capacities of clays and zeolites which is of critical importance because these phases play an important role in the retardation of radionuclides in the geosphere.

During the last two years, we have continued our study of radiation effects on the sorption and ion-exchange capacities of two important groups of materials: clays and zeolites with newly designed experimental methods (proton and neutron irradiation).
These newly designed experiments generated much larger quantity of damaged materials for the ion exchange and leaching tests as well as for detailed structural and microstructural studies. Cross-sectional analytical electron microscopy on proton irradiated zeolite samples with or without Cs or Sr loading has shown similar results as previously observed in thermally amorphized samples. Twenty four zeolite samples have been irradiated in the Ford Nuclear Reactor with thermal neutrons in eight batches. One third of the samples were preloaded with Sr and another one third was preloaded with Cs. These nuclides are important because: 1.) they represent a range of sorptive behavior that should bracket the behavior of most other radionuclides and 2.) they are considered to make important contributions to total radiation exposures, as illustrated in the Total Systems Performance Assessment-Viability Assessment of the proposed repository at Yucca Mountain. Ion exchange/sorption experiments are being conducted for samples irradiated to various doses to determine the impact of the radiation effects on the sorption capacity and retention of radionuclides. The irradiated material are also being characterized by a wide variety of analytical techniques (e.g., x-ray diffraction, X-ray absorption spectroscopy, and X-ray absorption spectroscopy) to precisely describe the nature of the radiation damage at the near atomic-scale. These analysis combined with the sorption and cation-exchange results are providing important information for determining the relationships among key parameters: radiation damage dose, microstructure at the surface, materials properties (e.g., aperture size of the zeolites), and radionuclide sorption and/or ion exchange.

However, our research is still incomplete at this stage. Extended duration and increased funds are needed to complete the tasks specified in our original proposal mainly because of the following facts: (1) The lower than expected neutron flux in the reactor has caused a longer time needed for achieving the radiation dose required for amorphizing the zeolite samples. (2) The unexpected levels of radioactivity of the neutron irradiated samples (especially with Sr and Cs loadings) due to trace amount impurities have caused extensive extra work for handling and analyzing these samples safely. So far, neutron irradiation of twenty one of the twenty four zeolite samples (eight loaded with Sr and another eight loaded with Cs) have been completed, the remaining three will be out of the reactor by the end of March, 2003. Several the Sr loaded samples and all of the Cs loaded samples became highly radioactive after neutron irradiation. It took almost a year for us to get permission for handling the Sr loaded samples with several revisions of processing methods for ion exchange/leaching and analytical work since every step was checked very strictly by the health physicist from OSEH. All of the Cs loaded samples showed >1.5 R/hr radioactivity and they have to be processed in the hot cell in the Phoenix Memorial Laboratory in our university by specially trained staff. In addition, we have finally obtained a special permission from the Stanford Synchrotron Radiation Laboratory for conducting X-ray absorption spectroscopy studies on some of the radioactive samples during the next two years. Based on the above justification, we have applied for a two year renew to complete this project.
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PROGRESS REPORT

Previous results (1997-2000)

During our previous studies (1997-2000), radiation effects on the microstructures of layered silicates (micas) and zeolites have been investigated by electron microscopy after electron and ion beam irradiations. The results have shown that these materials are extremely susceptible to irradiation-induced solid-state amorphization (i.e., the materials’ unique sheet or porous crystalline structure is completely destroyed by irradiation). Amorphization can either be induced by ionization processes (as occurs with β− or γ− irradiation) or by direct displacement damage processes (as by α-recoils). The critical doses for complete amorphization of these phases can be as low as <0.1 displacement per atom (dpa) or \(10^6\) Gy in ionization energy deposition (a dose equivalent to that expected in a zeolite with 10 wt.% loading of \(^{137}\)Cs in 400 years) (Wang, Wang, Gong and Ewing, 1998; Wang, Wang and Ewing, 1998; Wang and Weber, 1999). The progressive process of amorphization of these materials under electron irradiation is clearly demonstrated by electron diffraction (Figure 1) and by high resolution transmission electron microscopy (HRTEM) (Figure 2).

![Fig. 1](image)

Fig. 1  Electron diffraction patterns showing the progressive changes of zeolite-Y structure from crystalline-to-amorphous under 200 keV electron irradiation at the room temperature. (A) beginning of the irradiation, (B) \(2 \times 10^{20}\) e/\(\text{cm}^2\), (C) \(3.5 \times 10^{20}\) e/\(\text{cm}^2\), and (D) \(3.4 \times 10^{20}\) e/\(\text{cm}^2\) (1.6x10\(^{11}\) Gy).

The critical amorphization dose for several sheet silicates (e.g., mica) increased with the increasing temperature due to the increased efficiency of structural recovery at elevated temperatures (Figure 3). However, in the case of zeolites and some layer silicates, radiation-induced amorphization is significantly enhanced at higher temperatures (Figure 4). Amorphization of zeolites or layered silicates may be preceded or accompanied by dehydration, layer spacing reduction and gas bubble formation (Figure 5) which may cause significant volume swelling. The critical radiation dose for amorphization or bubble formation in zeolites strongly depends on the size of channels available in the structure for gas release (Wang, Wang and Ewing, 2000). The amorphization of the crystal structure and the formation of bubbles will inevitably change the ion exchange and retention capacity of these materials for radionuclides due to the disruption of the structure or by blocking access to exchangeable cation sites. However, due to the small volumes affected by the ion or electron beam irradiations, it is difficult to conduct the ion exchange experiments with these radiation-damaged materials. Although
γ-irradiation can affect larger volumes of the samples, available sources of γ-irradiation cannot generate the extent of damage predicted for the long term effects in a reasonable experimental time frame, partly because γ-irradiation only causes ionizing damage and cannot reproduce the displacement damage caused by direct collision, as in α-decay of actinides. Estimates based on the flux of the currently available $^{60}\text{Co}$ γ-source and the results of the electron irradiation experiment have indicated that more than 50 years would be needed in order to totally amorphize zeolites by γ-irradiation.

![HRTEM images of zeolite-Y showing the uniform and progressive change from the crystalline-to-amorphous state under a 400 keV electron irradiation at the room temperature. (A) beginning of the irradiation, (B) $2 \times 10^{20} \text{e}^{-}/\text{cm}^{2}$, (C) $4 \times 10^{20} \text{e}^{-}/\text{cm}^{2}$, and (D) $6 \times 10^{20} \text{e}^{-}/\text{cm}^{2}$.](image)

Because zeolites are thermally unstable and can be amorphized by thermal annealing, we have compared the ion exchange and retention capacity for Cs in zeolites before and after thermally-induced amorphization (Gu, Wang and Ewing, 2000). In this study, zeolite-NaY samples with or without Cs loading were first amorphized by thermal annealing at 900-1000°C, and then subjected to ion exchange and desorption experiments. The amorphized zeolite-NaY lost nearly 95% of its ion exchange capacity for Cs due to the loss of exchangeable cation species and/or the blockage of access to exchangeable cation sites (Figure 6). Also, the desorption study indicated that amorphization of Cs-loaded zeolite may enhance the retention capacity of exchanged Cs due to the closure of the channels (Figure 7). Because the near-field or chemical processing materials (e.g., zeolites or CST) will receive a substantial radiation dose after they have incorporated radionuclides, our results suggest that radiation-induced amorphization may, in some cases, retard the release rate of sorbed or ion-exchanged
radionuclides due to the closure of internal channels. The results of these studies have a direct bearing on repository performance assessment (e.g., the extent to which zeolites can retard the release of radionuclides) and on the technologies used to process high-level liquid wastes (e.g., separation of $^{137}$Cs from HLW using CST at the Savannah River Site).

Fig. 3  Temperature dependence of critical amorphization dose of four sheet silicates under 1.5 MeV Kr$^+$ irradiation.

Fig. 4  Temperature dependence of amorphization dose of zeolite under 200 and 400 KeV electron irradiation.
Fig. 5 TEM micrographs showing radiation-induced bubbles in sheet silicate and zeolites. (A) biotite (mica) after 800 keV Kr$^{2+}$ irradiation to $1 \times 10^{15}$ ions/cm$^2$ at room temperature; (B) analcime (zeolite) and (C) natrolite (zeolite) after 200 keV electron irradiation at room temperature.

Fig. 6 Variation of ion exchange capacity for Cs in crystalline and amorphous zeolite-NaY.

However, thermally-induced and radiation-induced amorphous phases may have different structures and compositions, as well as physical and chemical properties (e.g., during the thermal process, the water vapor may be much more efficiently released from the structure than during the irradiation processes). As such, quantitative relationship between the radiation dose and the ion exchange capacity for radionuclides in concerned phases has not yet been established. More efficient irradiation sources and better designed experiments are needed to simulate the long-term radiation effects (on relatively larger volumes of sample) over relatively short periods.

1. Neutron irradiation of zeolites

Twenty four zeolite samples have been irradiated to eight various doses in the Ford Nuclear Reactor (FNR) with thermal neutrons up to $4.5 \times 10^{19}$ n/cm$^2$. One third of the samples were preloaded with Sr and another one third was preloaded with Cs. These nuclides are important because: 1.) they represent a range of sorptive behavior that should bracket the behavior of most other radionuclides and 2.) they are considered to make important contributions to total radiation exposures, as illustrated in the Total Systems Performance Assessment-Viability Assessment of the proposed repository at Yucca Mountain. Ion exchange/sorption experiments are being conducted for samples irradiated to various doses to determine the impact of the radiation effects on the sorption capacity and retention of radionuclides. The irradiated material are also being characterized by a wide variety of analytical techniques (e.g., magic angle spinning nuclear magnetic resonance spectroscopy, x-ray diffraction, X-ray absorption spectroscopy, and X-ray absorption spectroscopy) to precisely describe the nature of the radiation damage at the near atomic-scale. These analysis combined with the sorption and cation-exchange results are providing important information for determining the relationships among key parameters: radiation damage dose, microstructure at the surface, materials properties (e.g., aperture size of the zeolites), and radionuclide sorption and/or ion exchange.

1.1 MAS NMR work

In the present work, high-resolution solid-state MAS NMR (magic angle spinning nuclear magnetic resonance) spectroscopy was performed on original and strontium loaded zeolites since MAS NMR is a powerful tool in providing the coordination number change or distortion of the zeolite framework tetrahedron under neutron irradiation.
Figure 8 and 9 show the MAS NMR spectra of the two series zeolites before and after neutron irradiation (at different dose levels). As we know, zeolite three-dimensional framework is consisted by [SiO$_4$] or [AlO$_4$] structural unit. The replacement of one or more Si by Al in the second coordination sphere would result in significant low-field shifts (i.e., less negative $\delta$ values). In general, each substitution of Al-O-Si to Si-O-Si (Loewenstein rule forbids the two tetrahedrally coordinated aluminum atoms on neighboring T positions (Loewenstein, 1954), so there is no bond of Al-O-Al in synthesized zeolites) brings about a deshielding of ca 5 ppm for central silicon atom. Thus the different chemical shifts in the $^{29}$Si MAS NMR spectra are resulted from the contribution of different secondary coordination number of Al atoms. The deconvolution
of one of the present $^{29}$Si MAS NMR spectra is shown in Figure 10. From the spectrum and other deconvoluted spectra

![Deconvolution of $^{29}$Si MAS NMR spectrum of Zeolite-NaY](image)

(not shown), it suggests that the second coordination number of Si in the present two series zeolites are 4, 3, 2 and 1 aluminum ions, respectively. The intensities of the peaks can be used to calculate the overall Si/Al ratio of the framework according to the following formula:

$$\frac{Si}{Al} = \frac{\sum_{n=0}^{4} I_n}{\sum_{n=0}^{4} n I_n}$$

where $I_n$ is the intensity of the peak associated with Si(nAl). The Si/Al ratio changes of original zeolites (Z series) and strontium loaded zeolites (Sr series) with neutron irradiation dose are shown in Figure 11. Noting that the original Si/Al ratio of the zeolite provided by the purchased company (Zeolyst International) is 2.55, the result of 2.57 by NMR is rather accurate. The increase of Si/Al ratio implies that the neutron irradiation lead to the mild dealumination of the two zeolites. The chemical shift of the two series zeolites are tabulated in Table 1. We find the most apparent chemical shift value changes occurred in Si(4Al) for both series. The chemical shift values for those silicon polyhedra with different secondary aluminum do not change so much comparing with those in Si(4Al). However, it can be seen that all the chemical shifts become less negative with the increase of neutron dose level. To our knowledge, the present MAS NMR research on neutron-irradiated zeolites is the first conducted work. Up to now, most MAS NMR work on neutron irradiation effect are focused on SiO$_2$. Chan et al. found that the chemical shift of $^{29}$Si MAS NMR changed from -107.1 ppm to -106.0 ppm when the neutron dose increased from $1.99 \times 10^{17}$ to $8.7 \times 10^{19}$ n/cm$^2$ in quartz (Chan et al., 1988). Wright et al. indicated that the chemical shift of $^{29}$Si MAS NMR became less negative when vitreous silica was subjected to a dose of $2.8 \times 10^{20}$ fast neutrons/cm$^2$ (Wright et al., 1992). By calculation, they found the decrease of the average Si-O-Si bond angle is around 9.5°.
The correlations between chemical shift and mean Si-O-Si bond angle was first suggested by Thomas et al. (Thomas et al., 1982). One year later, Smith and Blackwell reported empirical correlations for aluminum silicate (Smith and Blackwell, 1983). Thomas et al and Engelhardt et al. (Thomas et al., 1983; Engelhardt et al., 1984) shown different semi-empirical chemical shifts–$T$-$O$-$T$ correlations in different zeolites, respectively. However, the relationships are limited to silicon rich zeolites. In 1984, Ramdas and Klinowski (Ramdas and Klinowski, 1984) firstly reported a relationship which are valid for chemical shifts in all five Si(4Al), Si(3Al), Si(2Al), Si(1Al) and Si(0Al) tetrahedral environments, and also holds for the Si(0Al) shifts in silica polymorphs listed by Smith and Blackwell (Smith et al., 1983). Radeglia and Engelhardt gave another relationship (Radeglia and Engelhardt, 1985). Both of their relationships are in agreement with experimental findings. Equation (2) is derived from Ramdas and Klinowski:

$$\delta = 126.6 + 5.6n - 247.5\sin\theta$$  \hspace{1cm} (2)
where $\delta$ is the chemical shift, $n=0, 1, 2, 3, 4$ in Si(nAl) tetrahedral environment, $\theta$ is the Si-O-T (T=Si, Al) bond angle. According to this equation, the Si-O-T angle of neutron irradiated zeolites and strontium-loaded zeolites are calculated and listed in Table 2. It displays that the bond angle of Si-O-Al in Si(4Al) decrease from 144.1° to 140.4° for Z series and from 145.1° to 139.3° for Sr series. The changes of Si (3Al) is not apparent for Z-series (as shown in Figure 12), but for Sr-series, there is still 1.27° difference between Sr-0 and Sr-5. Although the changes for other Si (nAl) (n=0, 1, 2) are not so large compared with that of Si(4Al), the trend that Si-O-T bond angle decrease with increase of neutron exposure can be concluded. Obviously, in the present dose range, Si-O-Al is more sensitive to neutron irradiation, Si-O-Si seems more rigid than Si-O-Al. This may be the reason that a larger dose level ($10^{20}$ order) was applied in neutron irradiation of SiO$_2$ in order to lessen the bond angle of Si-O-Si. The decrease of Si-O-Al bond angle will lead to the increase of Al-O bond length or increase of coordination number of aluminum polyhedron. Also, the decrease of Si-O-T bond angle is found in the high pressure induced amorphization in zeolites (Huang, 2001; Huang, 1998). This suggests that there are some similarities between irradiation- and high pressure-induced amphization in zeolites in short or intermediate range.

Figure 13 and 14 are the $^{27}$Al NMR spectra of Z-series and Sr-series zeolites. When the dose level reaches $2.25 \times 10^{19}$ n/cm$^2$, six-folded aluminum polyhedron emerges in both spectra (small peaks indicated by arrows in both Figures 13 and 14). This is consistent with the dealumination conclusion drawn from the Si/Al ratio obtained from the $^{29}$Si MAS NMR spectra above. The chemical shift values of $^{27}$Al MAS NMR are listed in Table 3. A complication of $^{27}$Al MAS NMR spectrum is the second order quadrupolar interaction of the central transition. Resonances move from their isotropic chemical shift due to the quadrupolar induced shift and broaden into specific powder line shapes, even under MAS conditions. Hence, the $^{27}$Al MAS NMR spectra may consist of resonances shifted with respect to their isotropic chemical shifts, which are not well-resolved, and even some aluminum may escape detection due to extreme broadening.

### Table 2. T-O-T angles of zeolite-NaY/zeolite-SrNaY under different neutron dose

<table>
<thead>
<tr>
<th>Samples</th>
<th>Si (4Al)</th>
<th>Si (3Al)</th>
<th>Si (2Al)</th>
<th>Si (1Al)</th>
<th>Si (1Al)</th>
<th>Si (0Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-0</td>
<td>144.07</td>
<td>140.28</td>
<td>139.43</td>
<td>137.65</td>
<td>140.95</td>
<td>138.79</td>
</tr>
<tr>
<td>Z-1</td>
<td>141.94</td>
<td>140.23</td>
<td>139.63</td>
<td>138.10</td>
<td>141.41</td>
<td>139.22</td>
</tr>
<tr>
<td>Z-3</td>
<td>141.13</td>
<td>140.38</td>
<td>139.51</td>
<td>137.93</td>
<td>141.20</td>
<td>139.14</td>
</tr>
<tr>
<td>Z-5</td>
<td>140.35</td>
<td>139.89</td>
<td>139.19</td>
<td>137.45</td>
<td>140.64</td>
<td>138.91</td>
</tr>
<tr>
<td>Sr-0</td>
<td>145.05</td>
<td>141.37</td>
<td>139.87</td>
<td>137.79</td>
<td>141.09</td>
<td>139.27</td>
</tr>
<tr>
<td>Sr-1</td>
<td>144.40</td>
<td>141.42</td>
<td>139.97</td>
<td>137.97</td>
<td>141.41</td>
<td>139.36</td>
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<tr>
<td>Sr-3</td>
<td>144.49</td>
<td>141.35</td>
<td>140.02</td>
<td>138.02</td>
<td>141.40</td>
<td>139.59</td>
</tr>
<tr>
<td>Sr-5</td>
<td>139.32</td>
<td>140.10</td>
<td>139.43</td>
<td>137.47</td>
<td>140.80</td>
<td>138.98</td>
</tr>
</tbody>
</table>
Fig. 12 Variation of T-O-T bond angles of different secondary coordinated polyhedral with neutron influence.

Fig. 13 $^{27}$Al MAS NMR spectra of Z-series zeolites at different neutron irradiation dose levels.
Fig. 14 $^{27}$Al MAS NMR spectra of Sr-series zeolites at different neutron irradiation dose levels.

Table 3. Chemical shift in $^{27}$Al MAS NMR Spectra-δ (ppm)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Al$_{tet}$</th>
<th>Al$_{oct}$</th>
<th>Corrected Al$_{tet}$</th>
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<tbody>
<tr>
<td>Z-0</td>
<td>59.4</td>
<td>-</td>
<td>60.32</td>
</tr>
<tr>
<td>Z-1</td>
<td>58.9</td>
<td>-</td>
<td>62.09</td>
</tr>
<tr>
<td>Z-3</td>
<td>58.9</td>
<td>-</td>
<td>62.17</td>
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<tr>
<td>Z-5</td>
<td>55.2</td>
<td>-10.7</td>
<td>62.34</td>
</tr>
<tr>
<td>Sr-0</td>
<td>58.0</td>
<td>-</td>
<td>61.96</td>
</tr>
<tr>
<td>Sr-1</td>
<td>58.5</td>
<td>-</td>
<td>61.88</td>
</tr>
<tr>
<td>Sr-3</td>
<td>58.0</td>
<td>-</td>
<td>61.87</td>
</tr>
<tr>
<td>Sr-5</td>
<td>59.8</td>
<td>2.2</td>
<td>62.25</td>
</tr>
</tbody>
</table>

Therefore, care must be taken when interpreting $^{27}$Al MAS NMR spectra. Lippmaa et al. found semi-empirical chemical shifts Al-O-Si correlation considering the correction of the second order quadrupolar interaction effect (Lippmaa and Magi, 1986):

$$\delta_{CS}(Al) = -0.50\theta + 132$$  \hspace{1cm} (3)

where $\theta$ is the bond angle of Al-O-Si. According to this relationship, the corrected chemical shifts of aluminum are listed in last column in Table 3. Obviously, the chemical shifts changing trends for both series after second order quadrupolar interaction corrections are the same as those of silicon (i.e., the bond angle of Al-O-Si decrease upon neutron irradiation).

When comparing the $^{27}$Al MAS NMR spectra of Sr-series with that of strontium loaded zeolite treated at 900°C for 30 minutes (not shown), the $^{27}$Al NMR spectrum shows the peak maximum shifted upfield, ca -10 ppm, and the peak width (approximated FWHM) increased by more than 3 times. Both the substantial shift and increase in peak width and asymmetry are indicative of second order quadrupolar broadening. The additional shift of ca –10 ppm observed for the Sr-loaded, thermally treated sample
indicates an increase in the quadrupolar coupling of approximately 2.8-3.2 MHz. This analysis of the change in the quadrupolar peak shape as well as the lack of any additional peak near 0 ppm suggests that the aluminum species in the thermally treated zeolite are in a highly distorted tetrahedral environment. Thus, the microstructure changes of the framework under neutron irradiation and thermal treatment are different.

It is believed that the origin of the octahedral aluminum is resulted from the γ-irradiation of the (n, γ) process. Ali and Selim even found tricoordinated aluminum in γ-irradiated zeolites (Ali et al., 1994; Selim et al., 1992). Carvalho et al. attributed the dealumination of offretite under γ-irradiation to the presence of water in the sample since they did not observe the dealumination as the samples irradiated in vacuum. Instead, they found only crystallinity loss under vacuum condition. However, Durrani et al. indicated that the effect of γ-radiolysis is only significant at low doses up to 0.5 MGy, with little change occurring as the dose was further increased (Durrani et al., 1993). According to Primak et al., when vitreous silica was irradiated by neutron irradiation, the estimated temperature (thermal spike) and pressure around the site of the primary knocked-on atom would be 5000~10000°C and 3000~7000 atm (Primak et al., 1964). Thus, ballistic collision and ionizing are both possible reasons for the decrease of Al-O-Si bond angle and the formation of aluminum octahedron and thus result in the amorphization of the zeolites.

1.2 Ion exchange ability

The ion exchange capacity changes also indicate the neutron effect on the microstructure of zeolite. The equilibrium study for ion exchange capacity was carried out by placing zeolite-NaY samples in contact with SrCl₂ solution with initial concentration in the range of 0.2 mN to 2 mN. At equilibrium, the mass of solute adsorbed per unit mass of sorbent can be calculated from:

\[ Q_e = \frac{(C_0 - C_e) \times L}{M_z} \]  

(4)

where \( C_0 \) is the original solution concentration, \( C_e \) is the equilibrium solution concentration, \( L \) is the volume of the solution in contact with zeolite-NaY, \( M_z \) is the mass of zeolite-NaY used in each experiment. Figure 15 shows the ion exchange isotherms of SrCl₂ with original (untreated), neutron-irradiated (Z-5) and thermally treated (900°C, 30 minutes, x-ray amorphization) zeolite-NaY. It can be seen that the amorphous zeolite-NaY has lost almost all of the exchangeable sites while the original zeolite keep strong ion exchange ability with strontium ions. The ion exchange ability of neutron-irradiated sample is between them. This indicates that some exchange sites in neutron-irradiated zeolite have already lost due to the possible breakage of the framework or contraction (collapse) of the cages in zeolite, but the changes is not so large as that of the thermally treated zeolite-NaY. This is consistent with the indication of MAS NMR results demonstrated above.
1.3 XAS (X-ray absorption spectroscopy) study

Sr K-edge edge x-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) using wiggler beam line 4-3 with Si(220) monochromators, beam energy 3.0 GeV, and beam current ranging from 50 to 100 mA. The EXAFS and XANES experiments were conducted and analyzed in a manner described in this report for the heat treatment samples. Synchrotron XRD experiments were performed at SSRL beam line 2-1.

The Sr-preloaded neutron-irradiated zeolite sample (Sr-5) has a very distinct and unique EXAFS spectrum and corresponding radial structure function (RSF) compared to that of aqueous Sr\(^{2+}\) (SrCl\(_2\)) or Sr sorbed (N-5) on heated zeolites (Table 4 and Figure 16). For Sr-5, the EXAFS shows a distinct "beat" pattern (shoulders on the main oscillations) with the Sr EXAFS fitting indicating the presence of first shell coordination of oxygen atoms and a second shell of Si/Al neighbors (Table 4). XANES analysis of Sr-5 also indicates that the neutron-irradiation affects the local environment of Sr compared to that of heat treated samples (Figure 17). A first derivative plot of the XANES spectrum shows different locations for peak features, strong evidence of the different first shell coordination environment among the neutron-irradiated and heated treated zeolites at different temperatures. This noticeable difference in the XANES is consistent with the EXAFS data which together indicate that neutron-irradiation of Sr loaded zeolite (Sr-5) leads to a different Sr coordination environment compared to heat treatment (Sr-2-900) and Sr sorbed to the neutron irradiated sample (N-5). Interestingly, Sr sorbed to a neutron damaged sample (N-5), has a coordination environment similar to heat treated sample with similar CN and R for nearest neighbor oxygens and second nearest neighbor oxygens.
Al/Si. This suggests that on neutron damaged material (N-5) Sr has limited access to the
type of site that leads to the Al/Si neighbors found for Sr-5. The comparison of Sr-5 with
N-5 and Sr-2-900 also indicates that the neutron irradiation may caused to some
amorphization of the surface but not throughout the sample with this surface
amorphization resulting in similar coordination of Sr in N-5 and Sr-2-900. Further
investigations on samples that have had longer exposure to neutron irradiation are needed
to determine if complete amorphization may result from increased exposure to neutron
irradiation.
Table 4. EXAFS fit results for Sr sorbed on zeolite before and after neutron-irradiation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr-Z a</th>
<th>CN b</th>
<th>R c</th>
<th>σ^2 d</th>
<th>∆E_0 e</th>
<th>0.01M SrCl_2 solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl_2(aq)</td>
<td>Sr-O</td>
<td>8.699</td>
<td>2.58</td>
<td>0.01331</td>
<td>-5.927</td>
<td></td>
</tr>
<tr>
<td>Sr-5</td>
<td>Sr-O</td>
<td>9.551</td>
<td>2.60</td>
<td>0.01877</td>
<td></td>
<td>Sr-zeolite neutron-irradiated</td>
</tr>
<tr>
<td>Sr-5</td>
<td>Sr-Si/Al</td>
<td>5.470</td>
<td>4.34</td>
<td>0.01399</td>
<td>-8.303</td>
<td></td>
</tr>
<tr>
<td>Sr-5</td>
<td>Sr-Si/Al</td>
<td>2.854</td>
<td>4.74</td>
<td>0.01399</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr-5</td>
<td>Sr-Si/Al</td>
<td>1.771</td>
<td>3.42</td>
<td>0.01399</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr-5</td>
<td>Sr-Si/Al</td>
<td>1.587</td>
<td>3.71</td>
<td>0.01399</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-5</td>
<td>Sr-O</td>
<td>8.911</td>
<td>2.57</td>
<td>0.01331</td>
<td>-6.409</td>
<td>Neutron-irradiated 4mM Sr</td>
</tr>
<tr>
<td>N-5</td>
<td>Sr-Si/Al</td>
<td>1.364</td>
<td>3.44</td>
<td>0.16000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-5</td>
<td>Sr-Si/Al</td>
<td>1.947</td>
<td>3.79</td>
<td>0.16000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr-zeolite</td>
<td>Sr-O</td>
<td>7.581</td>
<td>2.54</td>
<td>0.01331</td>
<td>+10.384</td>
<td>Sr-zeolite 0.2M Sr 900°C</td>
</tr>
<tr>
<td>Sr-zeolite</td>
<td>Sr-Si/Al</td>
<td>1.466</td>
<td>3.37</td>
<td>0.01239</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sr-zeolite</td>
<td>Sr-Si/Al</td>
<td>1.566</td>
<td>3.78</td>
<td>0.01239</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a Z = backscattering; CN = coordination number; R = interatomic distance; σ^2 = Debye-Waller factor; E_0 = Energy at k = 0

In summary, the bond angle of Al-O-Si decrease with the increase of neutron-irradiation dose level. At the same dose level, the Al-O-Si bond angles change in zeolite-SrNaY are larger than those of zeolite-NaY. This may due to the effect of strontium on the framework bond property in zeolites. From the bond angle changing trend, it is expected that at higher dose levels, Si-O-Si bond angle will decrease. It is also found that [AlO_6] formed at higher dose level, which means that mild dealumination occurred under neutron irradiation. This may be induced by the (n, y) reaction. The ion exchange results show that the ion-exchange ability of neutron irradiation zeolite is between the original and heat-treated zeolite. This implies that the ion-exchange sites begin to lose due to the microstructure changes in the framework under neutron irradiation. The XAS study on neutron-irradiated zeolite samples show different impact on the microstructure and sorption properties compared to heat treatment. The neutron irradiated sample suggests only partial amorphization occurred. Synchrotron XRD shows that the neutron damaged zeolite maintains some of its original structure but has additional features compared to untreated samples, indicating that some of the zeolite has been converted to other phases. The XAS study shows that Sr has some coordination features consistent with heat treated samples, but also additional other features unique to neutron irradiation. Given that the coordination environment of Sr on neutron damaged zeolite is similar to that on heat treated zeolite (which is known to be completely amorphized), suggests that partial amorphization may occur during neutron irradiation.

2. Proton irradiation effect on zeolites

2.1 DRIFT and XPS works

In this section, zeolite-NaY powders were pressed to form tablets which are 2 cm in diameter and 1.5 mm in thickness. The zeolite tablets were irradiated with a 500 keV H^+ beam at the dose rate of 5×10^{12} ions/cm^2·s for 10, 20 and 30 hours, respectively. The
cumulative doses were measured with a Faraday cap, which yielded total doses of $2 \times 10^{17}$, $4 \times 10^{17}$, and $6 \times 10^{17}$ ions/cm$^2$ for the three samples, respectively. The microstructural changes of zeolite-NaY before and after proton irradiation was characterized by using diffuse reflectance Infrared Fourier transformation (DRIFT). Also, the x-ray photoelectron spectroscopy (XPS) works on the evolution of the microstructure as a functional of displacive radiation dose have been conducted.

Figure 18 is the DRIFT spectra of proton-irradiated zeolite-NaY at different dose levels. It can be seen that there are three apparent bands at 468, 1040 and 1153 cm$^{-1}$ in unirradiated sample. According to the classification of Flanigen (Flaningen, 1971), these three bands assign to T-O bending mode, asymmetric stretching mode (internal tetrahedra) and asymmetric stretching mode (external tetrahedra), respectively. Among them, the 468 cm$^{-1}$ T-O bending vibration and 1040 cm$^{-1}$ T-O asymmetric stretching vibration are structural insensitive, whereas 1153 cm$^{-1}$ T-O asymmetric stretching vibration is structural sensitive. When zeolite-NaY was subjected to proton irradiation, this structural sensitive band turned into a broadening shoulder with increase of irradiation dose level. This suggests that the connection between TO$_4$ tetrahedra become less order.

The striking observation regarding the structural evolution is that the structural insensitive bands at 468 and 1040 cm$^{-1}$ rapidly lose intensity and become broaden with the increase of irradiation dose. After irradiated for 30 hours, the band belonging to T-O bending vibration even disappeared. Since the bend mode appearing at 468 cm$^{-1}$ and the stretching mode at 1040 cm$^{-1}$ belong to the structural insensitive, the changes of structural insensitive bands suggest the changes of basic structural units of the framework in the zeolites. This is quite different from those of thermal-treated, high pressure and high-energy ball milling induced amorphization of zeolites, in which only the structural sensitive bands changed (Flaningen, 1971; Huang, 1998; Auroux et al., 1996). Therefore, besides altering the connectivity of the tetrahedra, the broadening and loss of DRIFT intensity suggest a breakdown in the TO$_4$ building units of the zeolitic framework and turns it into a disordering (amorphous) state. This suggests that the amorphization induced by proton irradiation is actually “more disorder” than that resulted from thermal treatment, high pressure and high-energy milling. After zeolite-NaY was irradiated for 30 hours, a broadening band reappeared at 1133 cm$^{-1}$. This may be due to the rebonding of the broken T-O at higher density of broken T-O linkages.

Although it is difficult to distinguish AlO$_4$ from SiO$_4$ in TiO$_4$ intratetrahedral modes from the spectrum (Stubican. and Roy, 1961; Szostak and Thomas, 1986), through the shift of bands in infrared spectrum, we can know the changes of Al/Si in the framework. Indeed, there are some reports on a nearly linear decrease for the position of the main asymmetric stretching vibration with increasing atomic fraction of aluminum in the tetrahedral sites in faujasite-type framework (Flaningen, 1971). Since the mass of aluminum and silicon are nearly the same, the decrease in frequency (wave number) with increasing aluminum concentration appears to be related to variation in bond length and bond order. The longer bond length of Al-O and less electronegativity of aluminum result in a decrease in force constant. In the IR study of thermally treated zeolite-NaY, Flanigen et al. found that the asymmetric stretching brand increased from 1000 cm$^{-1}$ at 85% x-ray crystallinity to 1020 cm$^{-1}$ at x-ray amorphization (Flaningen, 1971). As we know, thermal treatment process, especially for hydrated zeolite, is a dealumination process.
for zeolitic framework. Thus, the decrease in Al/Si would lead to the increase for the position of the main asymmetric stretching vibration. However, from Figure 18, we see that after proton irradiation for only 10 hours, the asymmetric stretching vibration shifts from 1040 cm\(^{-1}\) to 1022 cm\(^{-1}\). This changing trend suggests the decrease of silicon content in the zeolitic framework, which suggests that more Si-O bonds were broken compared with Al-O bonds. This is reversible to that occurs in thermal treatment process. Up till now, most of the mechanisms proposed for ionizing radiation-induced damage are associated with the breakage of Al-O bonds in the zeolitic framework under electron irradiation (Bursill et al., 1980, Treacy and Newsam, 1987). To the best of our knowledge, our DRIFT result is the first experiment evidence of the breakage of Si-O bonds in zeolitic framework under proton irradiation. In fact, in the bond-type criterion for the bombardment-induced structural changes in non-metallic solids, Naguib and Kelly have already pointed out that Si-O bonds are easier to be broken than Al-O bonds (Naguib and Kelly, 1975). In the study of fast neutron-metamict quartz, Qin et al. found a possibility of reduction in the average coordination number of silicon from the radial distribution functions obtained from energy-filtered electron diffraction data (Qin and Hobbs, 1995).

Recently, Camblor et al. found that the isomorphic substitution of Si by Al in the zeolitic framework resulted in the contraction of the framework (Camblor et al. 1996; Hong et al., 1997). Since the bond length of Al-O (0.17-0.178 nm) is longer than that of Si-O (0.157-0.167 nm), they contributed the contraction of the framework to the decrease of bond angle of Si-O-T. From other related researches (Hosono, 1991; Devine and Marchand, 1993), it was found that the band shifts to lower frequency in IR spectra after ion irradiation. This suggests the decrease in Si-O-T bridging bond angle. We could approximately calculate the changes of the bridging bond angle according to a central-force idealized continuous-random-network theory (Sen, 1977; Galeener, 1979):
where $f$ is the angular frequency, $m_o$ and $m_T$ are the masses of the oxygen and network former atoms, respectively. $K$ is the T-O bond stretching force constant. For small changes in $\theta$, $\Delta \theta$ can be related to $\Delta f$ by differentiation Equation (5):

$$\Delta f = \left(\frac{k}{m_o}\right) \times \sin \theta \times \left(\Delta \theta / 2f\right)$$

Putting $K=665$ N/m and $\bar{\theta}=142$ for zeolite-NaY, according to this equation, the changes of Si-O-T bond angle after being subjected to proton irradiation can be calculated (shown in Table 5). It can be seen that proton irradiation result in the decrease of Si-O-T bond angles. This is consistence with the observation of the above neutron irradiation in zeolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta f_1$ (cm$^{-1}$)</th>
<th>$\Delta \theta$ (deg)</th>
<th>$\Delta f_2$ **(cm$^{-1}$)</th>
<th>$\Delta \theta$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>-3.9</td>
<td>21</td>
<td>-6.1</td>
</tr>
<tr>
<td>2</td>
<td>18</td>
<td>-4.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>-2.7</td>
<td>20</td>
<td>-6.1</td>
</tr>
</tbody>
</table>

* reference to the peak position at 1040 cm$^{-1}$

** reference to the shoulder position at 1153 cm$^{-1}$

The XPS results of proton irradiated zeolite-NaY support the findings in the above DRIFT spectra. As shown in Figure 19. After proton irradiation, a peak emerges at the lower binding energy side of the Si 2p XPS spectra. The decrease in binding energy of an element is the consequence of the increase in the effective negative charge on it (Chen et al., 2001). In the present case, the decrease in binding energy of Si 2p electrons indicates an increase in the average electron density on the silicon ions, which implies that the shortening of the Si-O bond length. This can be achieved by the distortion or the decrease of coordination number of silicon tetrahedra. Figure 19 also displays the Si 2p electron XPS spectrum of thermally treated zeolite-NaY (X-ray amorphization). Unlike those of proton-irradiated samples, the Si 2p electron XPS spectrum is characterized by only one peak and its binding energy value is nearly the same to that of untreated zeolite-NaY. This strongly suggests that the silicon tetrahedra be kept after thermal treatment.

It should be note that after irradiated by proton for 30 hours, the intensity of the XPS peak located at lower binding energy side is reduced. This consists with the results of DRIFT spectrum of the same sample. As already stated above, the stochastic rebonding of the damaged structure will occur when there is an enough density of broken Si-O linkages. However, the less intense and more broaden peak in the spectrum suggest the disordering exists in the small range. This means proton induced amorphization is more disorder than that of thermal treatment induced amorphization.
The similar results can be obtained from the Al 2p electron XPS spectra of proton-irradiated samples (not shown). Like Si 2p XPS spectrum, the emergence of the peak at lower binding energy side of Al 2p spectrum indicates the distortion or the changes of the coordination number of aluminum polyhedra. After irradiated for 20 hours, the peak at lower binding energy even grows higher. This suggests more Al-O bonds breakages occurred at this stage. Further increase of irradiation time results in a closer distance of the two peaks. This suggests the rebonding of broken Al-O bonds.

2.2 Ion exchange ability

To quantify the radiation effects on the ion exchange capacity of zeolite-NaY, we performed detailed measurement of the concentrations of Cs and other elements along the cross-section of the irradiated samples. The irradiated zeolite samples were placed in a 10 mM CsCl solution at room temperature for 25 hours without agitation. The solid:solution ratio was 50 mg zeolite:50 mL solution. Because the density of the pressed sample was only ~50% of the theoretical density, the samples contained a large amount of void space. The large inter-particle pore size allowed the CsCl solution to quickly diffuse into the interior of the samples and ensured that all the particles were in effective contact with the solution throughout the ion exchange experiment. Based on a previous study, a complete Cs-zeolite-NaY ion exchange reaction occurred almost instantly under stirred conditions. Figure 20 shows the variation of Cs-concentration as a function of depth from the

![Graph showing Si 2p XPS spectra for different irradiation times and conditions.](image-url)
irradiated sample surface. For the sample irradiated for 20 hours, the Cs-concentration decreased gradually with increasing target depth and reached the lowest concentration (~1 wt.%) at 12 μm, indicating that the ion exchange capacity decreased with increasing radiation damage. When the zeolite was irradiated for 30 hours, the region with the lowest Cs-concentration widened. However, the Cs-concentration did not decrease further with an increase of ionizing energy deposition; this suggests that once complete amorphization is reached, further radiation does not have an effect on the ion exchange capacity.

The concentration profiles in Figure 20 and the energy deposition profiles suggest that the radiation damage to the zeolite by energetic protons is dominated by an ionization mechanism in the low displacement rate region. According to Monte Carlo simulation with the SRIM 2000 code, the damage produced by nuclear collision processes should be restricted to a narrow band with an abrupt structural and Cs-concentration change in the region at the end of the ion range. However, the wide range of low Cs-concentration in the sample irradiated for 30 hours and the gradual decrease in Cs-concentration with increasing target depth in the 20 hour irradiated sample indicates that the extent of structural damage and the change in ion exchange capacity are a function of the ionizing radiation dose. For the sample irradiated for 10 hours, even at the peak damage region, the Cs-concentration did not reach a Cs-concentration as low as in the cases of higher dose irradiations. This result supports the suggestion that ionizing radiation is the dominant process leading to structural damage. The average Cs-concentration measured in the undamaged region was ~20 wt.%. A measurement of Cs-concentration in the point mode by EMPA showed that the average Cs-concentration in the bright spots is 30-50% higher than in the undamaged zeolite matrix. Figure 21 shows the change of concentration for all cations in the zeolite-NaCsY sample irradiated for 30 hours. Although the measured Na-concentration is lower than the actual concentration due to the migration of Na under the electron beam during the electron microprobe
analysis, Figure 21 shows that the Na-concentration profile moves in the opposite direction as compared with the Cs-concentration. No significant concentration changes were observed for Al and Si.

In summary, the diffuse reflectance infrared Fourier transformation (DRIFT) spectrum analysis on proton-irradiated zeolite-NaY indicate that the structural insensitive bands at 468 and 1040 cm\(^{-1}\) rapidly lose intensity and broaden with the increase of irradiation dose level. Comparing with the IR of thermally treated and pressure induced amorphous zeolite-NaY by other researchers, it can be concluded that proton irradiation result in the breakage of the framework unit (silicon and aluminum tetrahedron). XPS results support the findings of DRIFT. The peak of DIFT shift to low frequency suggests the a little more silicon have been remove from the framework comparing with aluminum. This is reversal to those of electron irradiation and thermal treatment process. The ion exchange capacity of the irradiated zeolite-NaY with 10 mM CsCl solution varies with the extent of damage to the crystalline structure. After 25 hours of exchange, the Cs-concentration in the amorphous region is ~0.8 wt.%, which is much lower than in the undamaged region (~20 wt.%). This result confirms that radiation-induced amorphization can cause a significant loss of ion exchange capacity.

3. Thermal effect on zeolites

3.1 XPS works

In the previous study, we found that the amorphized zeolite-NaY lost nearly 95% of its ion exchange capacity for Sr due to the loss of exchangeable cation species and/or the blockage of access to exchangeable cation sites. Also, the desorption study indicated that amorphization of Sr-loaded zeolite may enhance the retention capacity of exchanged Sr due to the closure of the channels. However, the microstructure considering the bonding environment is still missing. In this section, we have conducted the XPS work on the thermally treated zeolite-NaY and strontium-loaded zeolite (zeolite-SrNaY) in order to get more information about the structure changes of the zeolites under thermal treatment.
In the experiment, we found that the binding energy value of Sr3d\textsubscript{3/2} increases from 134.2 eV to 134.6 eV (Figure 22). From the available literature it is found that the Sr-O distance varies between 0.2405 nm for the strongest bond and 0.2973 nm for the weakest bond. In a six-fold coordination (Sr(I)), the bonds are longer than in a threefold coordination of Sr(I') and Sr(II), which are similar. The difference in binding energy of Sr3d\textsubscript{3/2} is the consequence of the difference of the effective negative charge on strontium ions. The lower the binding energy value, the higher the average electron density on strontium ions. Thus the increase in binding energy of Sr3d\textsubscript{3/2} indicates that the lower average electron density on strontium ion. This suggests strontium ions have diffused to sites I after SrNaY-zeolite has been treated at 900°C for 30 min. The rapid change of strontium coordination number brings the possibility in the breakage of some T-O-T bonds. The

![Binding Energy (eV)](image)

Fig. 22 The XPS Spectra of Sr 3d Photoelectron of Zeolite-SrNaY treated under Different Temperature (Mg K\textsubscript{α}, x-ray source, electrical charging effect did not subtract in binding energy values).

migration of strontium ions to sites I at higher temperature is benefit for the “capture” of strontium ions because the cations at sites I are stabilized by a large (0.5 Å) inward relaxation of the surrounding oxygen atoms (Georger et al., 1991). For the amorphized zeolites-SrNaY, the collapse of the aperture would further prevent strontium ions from migrating out of the hexagonal prisms. Both of the above reasons would be benefit for the immobilization of radionuclide \(^{90}\)Sr. At room temperature and 500°C, the spectra of Al2p can be fitted by one Gaussian function. This reveals that a symmetrical [AlO\textsubscript{4}] polyhedra are still kept in the temperature range. However, when treating temperature is up to 900°C, a peak at lower binding energy side emerges. This suggests distortion of aluminum tetrahedron or aluminum polyhedron with other coordination number has occurred in the structure. The corresponding Auger parameter values of aluminum in zeolite-NaY, zeolite-SrNaY and zeolite-SrNaY (900°C) are listed in Table 6. In the study of aluminum coordination of dealuminated mordenites by x-ray photoelectron spectroscopy, Remy et al. deconvoluted the Al KLL auger spectra into three components (Remy et al., 1993). The corresponding Auger parameters \(\alpha'\), by adding these kinetic
values of deconvoluted Al KLL peak with the binding energy of Al 2p, were in three different kinds of range: 1458.7–1459.3eV, 1459.8–1460.2eV and 1460.9–1461.5eV,

Security

Table 6. Comparison of Auger parameter of present work with other works

<table>
<thead>
<tr>
<th>Samples</th>
<th>Al\textsuperscript{III}/\alpha’(eV)</th>
<th>Al\textsuperscript{IV}/\alpha’(eV)</th>
<th>Al\textsuperscript{VI}/\alpha’(eV)</th>
<th>Reference:</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1460.1</td>
<td>1460.2</td>
<td>1460.6</td>
<td>This work</td>
</tr>
<tr>
<td>β-zeolite</td>
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<td>1461.1</td>
<td>Remy et al.</td>
</tr>
<tr>
<td>β-zeolite</td>
<td>1458.3</td>
<td>1460.8</td>
<td>1460.9</td>
<td>Collignon et al.</td>
</tr>
<tr>
<td>ZM760</td>
<td>1458.7</td>
<td>1459.8</td>
<td>1460.9</td>
<td>This work</td>
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<tr>
<td>NaY-zeolite</td>
<td>1460.6</td>
<td>1460.3</td>
<td>1460.3</td>
<td>This work</td>
</tr>
<tr>
<td>SrNaY-zeolite (ambient)</td>
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<td>1460.2</td>
<td>1460.2</td>
<td>This work</td>
</tr>
<tr>
<td>SrNaY-zeolite (900°C, 30min.)</td>
<td>1458.1</td>
<td>1459.2</td>
<td>1460.9</td>
<td>This work</td>
</tr>
</tbody>
</table>

respectively. They ascribed these three ranges to three kinds of III, IV and VI fold coordination of aluminum in zeolite. Collignon et al. probed the coordinated state of aluminum in β-zeolite by using similar method (Collignon et al., 2001). Compared with the results of Remy and Collignon et al., we found that our Auger parameter values of aluminum listed in table 6 have very good correlation with theirs. From these results, we find that there are only 4-fold coordinated polyhedra in zeolite-NaY and zeolite-SrNaY at room temperature. This suggests the loading of strontium ions has no apparent effect on the structure of zeolite-NaY at this stage. For the heat-treated zeolite-SrNaY, tricoordinated aluminum polyhedra exist besides tetrahedral aluminum.

3.2 XAS works

XAS experiments were performed to determine the impact of heat treatment at three different temperatures: room temperature (RT), 500 °C and 900 °C on the near coordination environment of Sr and Cs exchanged zeolite. Previous X-ray diffraction (XRD) work has indicated that at temperatures above 900 °C, the zeolite structure is completely destroyed through a dehydroxylation amorhization process (Gu et al., 2000, 2002). However, below this temperature, the zeolite structure is retained although XRD peaks are lower in intensity. Hence, the three temperatures provided an opportunity to determine the impacts of thermal treatment on the near coordination environment above and below amorhization.

XAS can be used to characterize the near coordination environment (within 6Å) 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) analysis are reported in this feasibility study.

Sr K-edge and Cs L-III edge x-ray absorption spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) using wiggler beam line 4-3 with Si(220) monochromators, beam energy 3.0 GeV, and beam current ranging from 50 to 100 mA. Spectra were collected in fluorescence mode for all samples using a 13-element Ge array detector interfaced to a multichannel analyzer. The monochromator was detuned 70% at the highest energy of the scan in order to minimize contributions from higher-order harmonics. Beam energy was calibrated by assigning the first inflection point on the
absorption edge of Bi foil to energy of 16388 eV for Sr samples and the absorption edge of Ti foil to 4966 eV for Cs samples. Multiple scans (4 to 12) were collected to obtain a signal-to-noise ratio sufficiently high for extended x-ray absorption fine structure (EXAFS) analysis.

EXAFS analysis was performed for Sr using the EXAFSPAK software (George and Pickering, 1995) and the following procedure. Acceptable spectra were averaged and the background absorption was subtracted by a straight line through the pre-edge region and a three-segment spline fit in the region above the edge. The background-subtracted spectra were normalized using a Victoreen polynomial and tabulated McMaster atomic absorption fall-off coefficients. The spectra were then converted from energy to frequency space using the photoelectron wave factor, $k$ (Brown et al., 1988; Teo, 1986). The normalized, background-subtracted, $k^3$-weighted XAFS spectra for reference compounds and the sorption samples were filtered over similar $k$ ranges and Fourier–transformed with an unsmoothed window to obtain the radial structure functions (RSFs). Individual major peaks in the Fourier transform were back transformed to produce filtered XAFS in order to isolate individual shell contributions to the XAFS (Brown et al., 1988; Sayers and Bunker, 1988). Least–squares fitting of each shell was performed to determine the coordination number (CN) and bonding distance ($R$). The Debye-Waller factor, $\sigma^2$, and $E_0$ (defined as the energy at which $k=0$), were allowed to vary during this optimization. The phase and amplitude parameters needed for the fitting were obtained from theoretical calculation results using FEFF 8.0 (Ankudinov et al., 1998). Based on this fitting procedure, the resulting CN and $R$, were expected to be accurate to ±20% and ±0.02 Å, respectively, for the first shell (Brown, 1990). In the case of Cs, a crystal glitch for the Si(220) monochromator crystals in the EXAFS region precluded performing a detailed EXAFS analysis.

X-ray absorption near edge structure (XANES) analysis was conducted for both Sr and Cs. For this purpose, the XANES spectra were normalized to the average absorption at higher k range ($k=3-12$) to allow different samples to be compared over the same scale. First derivative plots of the XANES of model compounds and samples were taken from the normalized XANES spectra; the Golay-Savitzky method was used to smooth the derivative data (Chapra and Canale, 1988). Comparison of the first derivative features provides a basis for distinguishing similarity and discrepancy in the first-shell coordination environment (Brown, 1990).

Results of the EXAFS analysis of the Sr exchanged zeolite samples and a model aqueous Sr solution are presented in Table 7. The EXAFS spectra and the corresponding radial structure functions (RSFs) are shown in Figure 23. These data show that for the RT samples, at both the 0.2 and 0.05 M loading conditions, exchanged Sr is very similar in structure to aqueous Sr (e.g., compare the Sr-O distances and coordination numbers (CN) in Table 7). As indicated, the Sr-O CN is near 9 and bonding distances at 2.57 Å for both the RT samples and the aqueous Sr samples. This is expected at RT in that an outer- sphere association is expected for Sr with waters of hydration retained by Sr in supercage structure where Sr is expected to reside. A Sr-Si/Al feature is found for the heat treated samples where collapse of the supercage structure of zeolite NaY is suspected and the possible the proximity of Si/Al in the near coordination environment is consistent with such a collapse. Based on leaching studies, a recent report by Gu et al.
(2002) on radiation damaged zeolite NaSrY indicated that Al is leached from the zeolite structure while leaving structural Si in place in the collapsed structure.

Table 7. EXAFS fit results for Sr sorbed on zeolite before and after heat-treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr-Z a</th>
<th>CN b</th>
<th>R c</th>
<th>σ² d</th>
<th>∆E₀ e</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrCl₂(aq)</td>
<td>Sr-O</td>
<td>8.699</td>
<td>2.58</td>
<td>0.01331</td>
<td>-5.927</td>
</tr>
<tr>
<td></td>
<td>Sr-O</td>
<td>8.923</td>
<td>2.57</td>
<td>0.01331</td>
<td>-8.639</td>
</tr>
<tr>
<td>Sr_2 rt</td>
<td>Sr-Sr</td>
<td>3.063</td>
<td>3.86</td>
<td>0.01678</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>0.974</td>
<td>3.38</td>
<td>0.00550</td>
<td></td>
</tr>
<tr>
<td>Sr_2_500</td>
<td>Sr-O</td>
<td>8.654</td>
<td>2.57</td>
<td>0.01331</td>
<td>-7.272</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.566</td>
<td>3.78</td>
<td>0.01239</td>
<td></td>
</tr>
<tr>
<td>Sr_2_900</td>
<td>Sr-O</td>
<td>7.581</td>
<td>2.54</td>
<td>0.01331</td>
<td>-10.384</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.466</td>
<td>3.37</td>
<td>0.01239</td>
<td></td>
</tr>
<tr>
<td>Sr_05 rt</td>
<td>Sr-O</td>
<td>9.582</td>
<td>2.56</td>
<td>0.01331</td>
<td>-8.592</td>
</tr>
<tr>
<td>Sr_05_500</td>
<td>Sr-O</td>
<td>8.515</td>
<td>2.55</td>
<td>0.01331</td>
<td>-9.399</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>2.118</td>
<td>3.38</td>
<td>0.01297</td>
<td></td>
</tr>
<tr>
<td>Sr_05_900</td>
<td>Sr-O</td>
<td>6.245</td>
<td>2.54</td>
<td>0.01331</td>
<td>-7.434</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>2.106</td>
<td>3.35</td>
<td>0.01171</td>
<td></td>
</tr>
</tbody>
</table>

a Z = backscatterer; b CN = coordination number; c R = interatomic distance; d σ² = Debye-Waller factor; e E₀ = Energy at k = 0

Fig. 23 Normalized EXAFS spectra and RSFs of Sr-zeolite after heat-treatment. Solid lines, experimental data; dotted lines, nonlinear least squares fit (Table 7).
For the heat treated samples two trends seem apparent from this initial study: (1) a consistent Sr-O distance but lower CN from heat treatment, and (2) a shorter and more obvious Sr-Si/Al neighbor for the heat treated samples compared to the RT samples. Both of these results support the idea that the near coordination environment of exchanged Sr is changing upon heat treatment and amorphizing the sample, and that the environment is more restrictive (shorter Sr-Si/Al distances with fewer waters of hydration), consistent with a collapsed of the supercage structure in which the Sr ion is exchanged. X-ray absorption near edge structure of (XANES) analysis of the Sr XAS

Fig. 24  (a) Normalized XANES spectra and (b) first derivative of XANES spectra of strontium in zeolites. Vertical bars represent the different features shown on the spectra between samples.

also indicates that heat treatment affects the near coordination environment of Sr (Figure 24a). A first derivative plot (Figure 24b) of the XANES shows different locations for peak features, strong evidence of different near coordination environment among the different loading conditions and heat treatment. More loading conditions and heat treatment XAS data need to be collected to further substantiate the cause and effect to the XANES attributes. Nonetheless, the fact that differences are noticeable is strong evidence of a clear heat treatment effect. XANES and first derivative plots of heat treated and untreated Cs exchanged zeolite are shown in Figure 25a and 25b, respectively. Although the exact basis for the features is not known at this time, the clear difference between the treated and untreated samples indicates a very different near coordination environment for the two samples. Further EXAFS and XANES analyses will be needed to further clarify the basis for these differences for Sr and Cs.
In summary, the XPS work on the thermally treated zeolite-SrNaY indicates strontium ions have diffused to sites I after the sample has been treated at 900°C for 30 min. The migration of strontium ions to sites I at higher temperature is benefit for the “capture” of strontium ions because the cations at sites I are stabilized by a large (0.5 Å) inward relaxation of the surrounding oxygen atoms. On the other hand, the Auger parameters of thermally treated zeolite-SrNaY suggests the existence of tricoodinated aluminum polyhedra. The XAS can be used to characterize the near coordination environment of irradiation damaged samples for important radionuclides such as Sr and Cs. Based on the two sample loadings and heat treatment conditions investigated in this heat treatment study, it is clear that collapse of the zeolite structure causes discernable changes in the near coordination environment of both Sr and Cs and that these changes can be quantified in terms of CNs and bonding distances through XAS data analysis.

4. Thermal effects on the Sr sorption on clay

Sr sorption experiments were performed on heated clay minerals as part of an effort to investigate the impact of heating on the sorption properties of these common geosorbents used in barrier and binder applications. The local coordination environment of Sr sorbed on montmorillonite before and after thermal-treatment was characterized using XAS. Heat-treatment was performed either before or after the Sr-loading. Heating was originally proposed as a convenient and efficient alternative for the irradiation of minerals. It was expected that heat treatment simulates the impact of ionizing radiation on the mineralogical and sorptive properties of clay minerals at least to the extent that amorphization is the primary damage result. Heating also has relevance to the nuclear waste disposal in that many of the potential nuclear waste repositories have undergone or may experience various thermal events.
Cheto montmorillonite (SAz-1) from Arizona and kaolinite (KGa-1) from Georgia were supplied from the Source Clays Repository of the Mineralogical Society of America. The clay samples were pretreated to remove organic and inorganic impurities following the procedure described in detail in Morton et al. (2001).

Heating was performed at various temperatures using an automated programmable electrical furnace (Lindberg Blue). Heating at 900°C for 30 minutes was selected to simulate the amorphization caused by ionizing radiation based on our previous research (Gu, 2001). The temperature was increased at the rate of 20°C/min. The montmorillonite and kaolinite heated at 900°C for 30 minutes were fully amorphized and no new high temperature phase formed as is confirmed by XRD. The heat-treatment of Sr-preloaded clay minerals was performed at the same conditions following the same procedure.

10⁻⁴M Sr was adsorbed on montmorillonite and kaolinite before and after heat-treatment. 100mg or 10mg clay was reacted with 10mL of background electrolyte solution containing Sr. The ionic strength of the suspension was adjusted using an ACS grade NaCl (Fisher Chemical) to 0.1 or 0.01 M. The pH of the suspension was adjusted using a 1N NaOH or HCl volumetric standard solution (Fisher Chemical). All solutions were prepared using ultrapure water (18MΩ-cm, MilliQ-water system). The suspension was continuously shaken using an end-over-end shaker at room temperature and allowed to reach equilibrium in a tightly capped 15mL polypropylene centrifuge tube. After 5 days of equilibration period, the final pH of the suspension was measured (Orion 520 pH-meter and Ross Combination Electrode) and the solid phase was separated from the solution by centrifugation at 6000 rpm for 30 minutes. The final Sr concentration in solution was measured using an atomic absorption spectrometer (GBC 903). The solid was used for Sr XAS study. Sr sorption on montmorillonite showed no distinct dependency on the solution pH (Figure 26a). As an alkaline earth element, the driving force for the adsorption of Sr to montmorillonite is expected to be the electrostatic attraction due to the net negative charge at the surface originating from the isomorphous substitution in the structure. This structural charge is independent of the pH of the bathing solution. Therefore, the Sr sorption is pH-independent. However, this weak electrostatic nature of sorption makes the amount of sorbed Sr strongly dependent on the Na⁺ concentration that can effectively compete with Sr²⁺ for cation exchange sites. Montmorillonite heated at 400°C shows similar Sr sorption behavior to that of unheated montmorillonite(Figure 26b). The maintenance of the sorption property suggests that the montmorillonite structure is retained after 400°C heating. The XRD also confirms the maintenance of the montmorillonite structure (Gu et al., 2001b) at this temperature. 900°C-heated montmorillonite, however, shows different sorption properties (Figure 26c). At this temperature amorphization results and the layer structure of montmorillonite collapses through complete dehydroxylation.

We also performed Sr sorption montmorillonite samples that had been amorphized 900°C. Sr sorption to this surface as a function of pH has a U-shaped sorption curve. The minimum amount sorbed at near neutral pH and increase in sorption with decreasing pH at acidic pH conditions are quite different than that expected for ordinary sorption behavior of metal cations on aluminosilicates in which uptake is either independent of pH (Figure 26a) or increasing with pH like that shown in the high pH region when sorption is predominantly at edge sites. One possible reason for the unusual behavior at low pH is that referential leaching of aluminum from the montmorillonite occurs at these low pH
conditions for samples that have been amorphized. This might have left the remaining structure with positive charge deficiency and very reactive to the positively charged Sr$^{2+}$. More study is needed for a more precise characterization of the sorption mechanism at low pH.

Sorption capacity of kaolinite for Sr is much lower than that of montmorillonite as expected from the surface area and surface charge consideration. The sorption data are quite scattered and the sorption is almost pH-independent but is strongly dependent on the Na$^+$ concentration under the experimental condition (Figure not shown). The Sr sorption on 900°C-heated kaolinite is very similar to that on 900°C-heated montmorillonite. This similarity suggests the possibility of the formation of similar amorphized material from both minerals upon heating at 900°C.

XAS studies were performed on the untreated and heat treated Sr loaded clay samples. The Sr sorbed on unheated montmorillonite has an EXAFS spectrum similar to that of fully hydrated aqueous Sr$^{2+}$ ions (Table 8 and Figure 27). Regardless of sorption pH (4.1 or 6.7), outer-sphere complex is formed at the interlayer or edge surface, retaining its first hydration sphere upon adsorption (CN=9.2–9.4, R=2.57–2.58 Å). The Sr-montmorillonite heated at 400°C has almost the same EXAFS parameters as untreated to this temperature does not cause a full structural change, so that the mineral retains its specific sorption property. Sr sorbed to montmorillonite at 900°C, however, has a different local coordination environment characterized by a low coordination number for the first shell of oxygens (4.5–4.7) and shorter bond length (2.53–2.54 Å) between Sr and nearest neighbor O atoms. Sr in these samples also shows the appearance of Si/Al neighbors. Sr on preheated montmorillonites, either at 400°C or 900°C, apparently forms an outer-sphere complex similar to that on unheated montmorillonite as indicated by the similarities of the CN and R distances of sorbed Sr and aqueous Sr (Table 8, Figure not shown).
Table 8. EXAFS fit results for Sr sorbed on montmorillonite before and after heat-treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr-Z</th>
<th>CN</th>
<th>R</th>
<th>σ²</th>
<th>ΔE₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mtun_4_rt</td>
<td>Sr-O</td>
<td>9.222</td>
<td>2.58</td>
<td>0.01331</td>
<td>-5.608</td>
</tr>
<tr>
<td>Mtun_4_400</td>
<td>Sr-O</td>
<td>7.859</td>
<td>2.57</td>
<td>0.01331</td>
<td>-7.459</td>
</tr>
<tr>
<td>Mtun_4_900</td>
<td>Sr-O</td>
<td>4.458</td>
<td>2.54</td>
<td>0.01331</td>
<td>-7.734</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>2.034</td>
<td>3.28</td>
<td>0.01425</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.499</td>
<td>3.76</td>
<td>0.01425</td>
<td></td>
</tr>
<tr>
<td>Mtun_7_rt</td>
<td>Sr-O</td>
<td>9.401</td>
<td>2.57</td>
<td>0.01331</td>
<td>-6.164</td>
</tr>
<tr>
<td>Mtun_7_900</td>
<td>Sr-O</td>
<td>4.676</td>
<td>2.53</td>
<td>0.01331</td>
<td>-7.411</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.591</td>
<td>3.27</td>
<td>0.01275</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.432</td>
<td>3.76</td>
<td>0.01275</td>
<td></td>
</tr>
<tr>
<td>Mt400_4_rt</td>
<td>Sr-O</td>
<td>9.004</td>
<td>2.58</td>
<td>0.01331</td>
<td>-5.807</td>
</tr>
<tr>
<td>Mt900_10_rt</td>
<td>Sr-Sr</td>
<td>1.872</td>
<td>3.49</td>
<td>0.02017</td>
<td>-7.789</td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.591</td>
<td>3.27</td>
<td>0.01275</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sr-Si/Al</td>
<td>1.432</td>
<td>3.76</td>
<td>0.01275</td>
<td></td>
</tr>
</tbody>
</table>

except a slight decrease in coordination number of 7.9 is noted. This means that heating

Fig. 27 Normalized EXAFS spectra and RSFs of Sr-montmorillonite after heat-treatment.

These results show that the outer-sphere coordinated Sr, either in the interlayer or at surfaces edges at room temperature, migrates into the lattice structure upon heating at 900°C and becomes incorporated into a newly formed amorphous structure. However, no Sr neighbors were observed in the local environment of Sr. This means that the adsorbed
Sr ions do not form a Sr-mineral upon heating. Instead, they are scattered more uniformly over the newly formed amorphous phase.

It should be noted that in Figure 27, an unusual feature showed up in the EXAFS at a $k$ value near $6 \text{ Å}^{-1}$. This is not a real feature but was a glitch in the beam energy and was not fit. The similarities of the fitting results shown in Table 3 to previous XAS work for Sr sorbed to montmorillonite at RT (Chen et al., 1998; Chen and Hayes, 1999), indicates that this did not affect the fits significantly or our conclusions for the RT and 400° C sample. These samples will be rerun for future publication of these results.

In summary, these sorption and XAS studies on heated clay samples show that heat-treatment has positive impact on the retardation of Sr migration when applied after Sr sorption. However, the impact of heat-treatment on the Sr sorption capacity of clay minerals is complicated, showing a strong dependence on solution pH that is absence in the untreated clay samples. Amorphous material formed by the heat-treatment of clays shows unique Sr sorption behavior that indicates a potential sensitivity of amorphized materials to enhanced leaching of Al and the formation of new aluminum phases. Future work needs to include irradiation damage studies using these clays and irradiation sources that more closely approach that found for neutron irradiation damage. As was shown for the zeolite samples studies above, neutron irradiation may cause surface amorphization but not complete amorphization. Along these lines, studies utilizing electron beam sources may simulate better the neutron irradiation damage. Electron beam irradiation causes damage through ionization mechanisms (Wang et al., 2000), which is a component of neutron irradiation damage that is not captured by heat treatment.
Publications generated from this research program:

(A) Refereed articles in journals or conference proceedings:


(B) Ph.D. Thesis completed:

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