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THERMAL STABILITY OF ZEOLITIC TUFF FROM YUCCA MOUNTAIN, NEVADA

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ABSTRACT

Thermal models of the proposed repository at Yucca Mountain, Nevada, suggest that rocks near the proposed host rock will experience elevated temperatures for at least 1000 yrs. In order to assess the effects of elevated temperatures on zeolitic tuffs, the thermal stabilities of the zeolites clinoptilolite and mordenite, common in the rocks at Yucca Mountain, were investigated using a combination of high-temperature X-ray powder diffraction, thermogravimetric and differential scanning calorimetric analysis, and long-term heating experiments. Clinoptilolite undergoes an anisotropic decrease in volume upon heating or dehydration, accompanied by evolution of water. Mordenite experiences a relatively minor decrease in volume, accompanied by evolution of water. The details of the thermal behavior of both zeolites are dependent on exchangeable cation composition and the water fugacity of the environment. Long-term (years) heating to 200°C causes irreversible collapse of the clinoptilolite structure that is also composition dependent; sorptive proparties are only slightly affected. Because of the different behavior of zeolitic and non-zeolitic tuffs when heated and the large volume effects associated with zeolite dehydration/hydration, significant differential stresses may develop as a result of repository-induced heating. The zeolites will probably act as both a source of and later a sink for water in the repository environment.

INTRODUCTION

The tuffs at Yucca Mountain, Nevada, are being considered by the U.S. Department of Energy as a potential high-level radioactive waste repository. The proposed repository host rock is a densely welded, devitrified, and non-lithophysal portion of the Topopah Spring Member of the Paintbrush Tuff at approximately 360 meters depth at drill hole [illegible] dant alkali feldspar with lesser amounts of quartz and cristobalite.[1] The partially saturated nature of the host rock, the repository-induced drying of the rock, and the relative stability of these minerals should limit significant alteration to possible calcite precipitation or dissolution of cristobalite.[2,3] Directly underlying the host rock is a series of partially to non-welded tuffs containing abundant clinoptilolite, mordenite, smectite, and volcanic glass. These zeolitic zones were designated as I through IV.[4] The thin zeolite zone I, containing up to 30% Ca-heulandite (isostructural with clinoptilolite) and up to 50% smectite, closely underlies the proposed host rock and overlies the basal vitrophyre of the Topopah Spring Member. Large amounts of zeolitic tuff in zeolite zone II, containing 50 to 70% clinoptilolite and 0 to 20% mordenite, are less than 100 m below the host rock in the northern portion of the exploration block. At the southwest portion of the exploration block, distances from the base of the potential repository to zeolitic rocks are significantly greater, exceeding 150 m. Broxton et al.[5] showed that the clinoptilolites in Yucca Mountain tuffs vary considerably in exchangeable-cation composition, ranging from alkalic (Na-K) in the western portion of the exploration block to calcic in the eastern portion of the exploration block. These compositional variations give rise to significant changes in the thermal behavior of clinoptilolite.

Current repository design considerations and thermal models[6] demonstrate that emplacement of radioactive waste in the Topopah Spring Member host rock would give rise to significant temperature increases in some of the underlying zeolitic rocks, yielding peak temperatures (at approximately 1000 yrs.) exceeding 90°C in rock 100 m below the repository floor and temperatures exceeding 100°C in rock 60 m below the repository [illegible] power·density (APD) of 57 kW/acre which is equivalent to a local power density (LPD) of 70 kW/acre. An APD of 57 kW/acre is based on a near-field constraint limiting the temperature to 100°C in the floor of the waste-disposal rooms. The thermal profiles obtained[6] for an APD of 57 kW/acre are shown in Fig. 1 superimposed on the generalized stratigraphy near the center of the exploration block (USW G-4). The location of the static water level and the proposed depth of the repository horizon are also shown. An areal power density of 80 kW/acre results in significantly higher temperatures in the near-field environment (Fig. 1).[6]

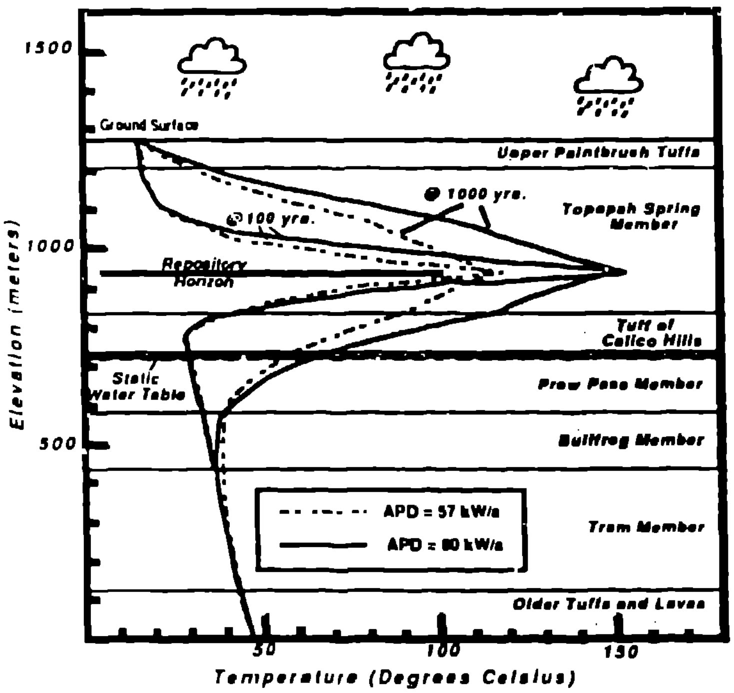

Fig. 1. Schematic cross section of Yucca Mountain showing the approximate stratigraphy, the position of the proposed repository horizon, and the depth of the static water level. Superimposed on the stratigraphy are predicted temperatures for two waste loadings (57 kW/acre and 80 kW/acre) at 100 and 1000 years.[6]

Repository-induced heating of underlying zeolitic rocks can have several important effects, some of which appear to be reversible and others that appear to be irreversible on a several year time scale. These effects include release (or incorporation) of water,[7,8] volume decrease (or increase),[9] development of differential stresses,[10] reduction in rock strength,[11] and modification of the sorptive properties of zeolitic rock. The potential effects of heating the zeolitic rocks underlying the proposed repository horizon have been investigated using a reaction times ranging from hours to years. Experiments were carried out under atmospheres varying from a 20-mtorr vacuum to water-saturated (at 22°C) air and at temperatures from 0° to 300°C. Such experiments may provide limits on the types of reactions expected in rock dried by the repository, but they may not accurately reflect the reactions expected in partially saturated rock in which steam is present. In addition, the relatively low temperatures expected in a repository environment make understanding kinetic effects very important.

EXPERIMENTAL METHODS

The potential effects of heating the zeolitic rocks underlying the proposed repository horizon have been investigated using a combination of elevated-temperature X-ray powder diffraction and thermogravimetric analyses (TGA). These methods have been integrated with experimental mechanical test results obtained by Kranz et al.[10] All X-ray diffraction measurements used a Siemens D-500 powder diffractometer with Cu-Kα radiation and either a scintillation detector and graphite monochromator or a Kevex Psi solid-state Si detector. Elevated-temperature diffraction experiments used the Siemens diffractometer with a scintillation detector and an Anton-Paar TTK heating stage. A typical heating experiment consisted of examining a given sample under room conditions, under a ~20 mtorr vacuum at 22°C, and then under vacuum at 50°C-temperature intervals up to 300°C. At the conclusion of the heating cycle, samples were examined again at 22°C in a vacuum and then under room conditions after re-admitting air. Equilibration times between runs was at least 30 min. A series of experiments was also conducted using air that had been saturated with water at 22°C instead of vacuum conditions; because of equipment limitations, these experiments had a maximum temperature of 250°C. Temperature was measured with a Pt-resistance thermometer at a point immediately beneath the sample cavity, within the sample holder. Volumetric changes were determined from X-ray diffraction data using lattice parameters calculated with the least-squares program of Appleman et al.[12] and the Rietveld refinement program DBW.[13] Diffraction maxima were indexed with the aid of computer-calculated powder patterns; the automatic indexing feature of the Appleman program was not used. X-ray powder diffraction was also used to assess the changes resulting from long term (several year) heating of samples of clinoptilolite and mordenite. Samples were heated in convection ovens at 50°, 100°, and 200°C and were examined periodically using X-ray diffraction. These

Thermogravimetric analyses were made using a DuPont 951 thermogravimetric analyzer and a DuPont Model 1090 system with and without a dry-N_2 purge. Heating rates ranged from 1° to 20°C/min, although most analyses were conducted with a 10°C/min heating rate. Sample sizes were ~10mg. Derivative thermogravimetric analysis (TGA) curves were calculated from the raw TGA data and were reproducible for different samples of the same zeolite. Differential scanning calorimetry (DSC) analyses used a DuPont Model 910 differential scanning calorimeter. DSC experiments used sealed Al capsules with a ~10-μm hole in the lid. All DSC experiments were run from -100° to 600°C, and TGA experiments were run between 0° and 800°C. The TGA experiments represent dehydration in a dry atmosphere and the DSC runs apparently approached saturated conditions. Samples were initially equilibrated at between 10 and 30% relative humidity.

The zeolites examined included reference samples of clinoptilolite and mordenite obtained from Minerals Research (Clarkson, NY) and subsequently purified in our laboratory. The clinoptilolite samples included #25524, Buckhorn, New Mexico; #25525, Castle Creek, Idaho; #25526, Sheaville, Oregon; #27054, Fish Creek Mountains, Nevada. Mordenite from Custer City, Idaho, #107119, also was examined. Some of these purified materials were cation exchanged to assess the effects of exchangeable-cation composition on thermal stability. Cation exchange was performed using 1.0-M solutions of the appropriate chloride (e.g., Na, Ca, K). Samples of zeolitic tuff from drill hole USW G-4 at Yucca Mountain also were examined (400.5, 420.9, 424.3, 443.9, and 450.5 m depth). The purity of all samples was assessed using X-ray powder diffraction before experiments were begun; minor amounts of anhydrous impurities caused no difficulties in analysis.

RESULTS AND DISCUSSION

The unit-cell volumes of all clinoptilolite samples examined by X-ray powder diffraction in a vacuum at elevated temperatures are significantly smaller than their 22°-C values, and the amount of volume decrease is a function of the exchangeable-cation composition. Na-saturated clinoptilolite underwent an 8.4% volume decrease between 22°C and 300°C, the volume of Ca-saturated clinoptilolite decreased by 3.6%, and that of K-clinoptilolite decreased by 1.6%. In general, for all clinoptilolites examined, the decrease in volume is very anisotropic, with the highest percentage decrease along the b crystallographic axis and the smallest decrease usually along the a axis.[9] Unit cell volumes as a function of temperature are shown for several samples in Fig. 2 together with data for those samples examined in a humid atmosphere. Note that the bulk of the volume decrease for K-clinoptilolite occurs upon evacuation at 22°C. In contrast, Ca-clinoptilolite steadily decreases in volume up to 300°C, whereas Na-clinoptilolite suffers the greatest volume decrease between 50° and 100°C. Samples of intermediate composition exhibited behavior intermediate between the three cation-exchanged end members. For example, samples of clinoptilolite from drill hole USW G-4 experienced 3.7% (100.5 m depth), 2.2% (420.9 m depth), 2.5% (424.3 m depth), and 2.2% (450.5 m depth) decreases in volume up to 300°C. Most samples of clinoptilolite re-expanded after cooling to 22°C in air but did not return completely to their original volumes. Samples containing predominantly

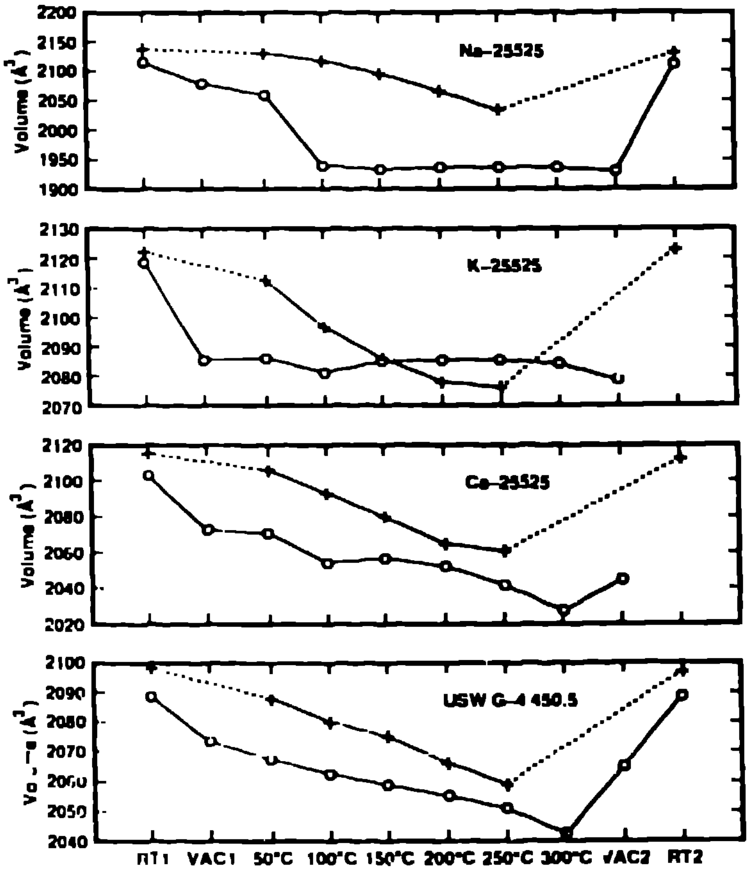

Fig. 2. Unit-cell parameters of Na-, K-, Ca-exchanged 25525 clinoptilolite and clinoptilolite from 450.5 m depth in USW G-4 (K > Na > Ca) as a function of temperature. Open circles are data collected under vacuum, and pluses are data collected in water saturated air. RT1 and RT2 signify experiments done under room conditions, before and after heating, respectively. VAC1 and VAC2 signify experiments conducted under vacuum at 22°C, before and after heating, respectively.

univalent exchangeable cations (K or Na) did not immediately re-expand.

Heating clinoptilolite samples in air that was saturated with water at 22°C usually resulted in volume changes that were smaller than those measured in a vacuum (Fig. 2). In addition, the cell volumes at 22°C in water-saturated air (before heating) were invariably greater than when the samples were examined in ambient room air (~20% relative humidity). For example, the sample from 400.5 m depth in USW G-4 experienced a 2.91% volume decrease upon heating to 250°C in a vacuum and a 2.12% volume decrease upon heating in humid air. However, clinoptilolite from 450.5 m depth in USW G-4 (Fig. 2) had a 1.80% volume decrease in a vacuum and a 1.87% decrease upon heating to 250°C in humid air, although the magnitude of the volume was still greater at 250°C for the sample in humid air. Without exception, all samples heated in humid air had a smaller volume loss to 100°C than those heated in a vacuum. It is notable that all samples heated in humid air virtually completely re-expanded upon cooling in humid air.

The sample of mordenite heated in a vacuum up to 300°C suffered a small, relatively isotropic volume decrease of less than 2% (Fig. 3). Upon cooling in air, the sample readily re-expanded to near its original volume.

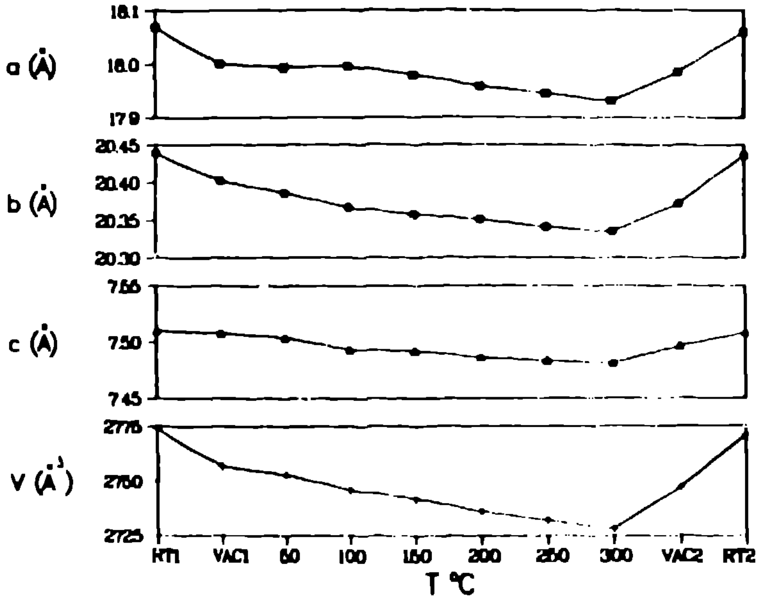

Fig. 3. Unit-cell parameters of mordenite (#107119) as a function of temperature in vacuum. Conventions as in Fig. 2.

Samples heated for long periods in room atmosphere included both natural and cation-exchanged clinoptilolites. Unexchanged clinoptilolites were heated at 100°C for more than one year, and both exchanged and unexchanged samples were heated for over four years at 200°C and were examined periodically by X-ray powder diffraction. Clinoptilolites heated at 100°C exhibited only a minor decrease in the b crystallographic dimension, similar to the decreases occurring on short-term heating in the heating stage. However, clinoptilolite samples heated to 200°C exhibited variable behavior depending on exchangeable-cation composition, with some samples remaining virtually unchanged, some exhibiting collapse of only a portion of the sample, and some exhibiting collapse of the entire sample. Natural K-rich clinoptilolite (#25526) showed only a minor decrease in volume, mainly along the b axis, but natural Na-rich samples (#25523, #25524, #25525) collapsed significantly along b. Clinoptilolite #25523 showed an intermediate amount of collapse, whereas #25525 underwent inhomogeneous collapse. For this latter sample, a portion of the material did not collapse significantly and a part of the sample underwent collapse along the b axis comparable to that observed for the Na-exchanged samples (Fig. 4). Na-exchanged clinoptilolites experienced the largest amount of collapse, with a decrease in the d-spacing of the 020 reflection from 9.08Å (9.74°2θ) to 8.78Å (10.07°2θ) (Fig. 4). It is significant that collapsed samples examined after equilibration at ambient temperature and humidity for several months had not re-expanded.

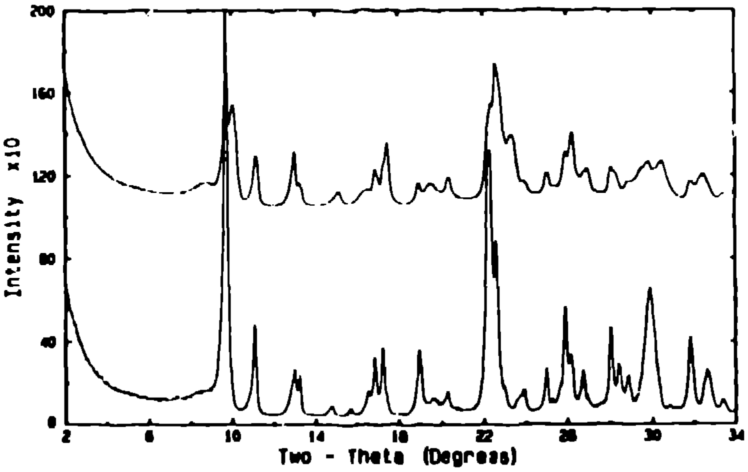

Fig. 4. X-ray powder diffraction patterns for 25525 clinoptilolite (exchangeable cations: $Na_{4.0}K_{1.53}Ca_{0.91}$) unheated (lower) and after heating at 200°C for 385 days (upper). Note the splitting of peaks for the heated sample near 10° and 23°2θ resulting from partial collapse of the zeolite structure

In order to assess the effect of partial structural collapse on the sorptive properties of clinoptilolite, sorption ratios for several of the heated samples were measured for Sr, Cs, Ba, and Eu. The sorption ratio, R_d, is defined as the ratio of activity on the solid phase per unit mass of solid to the activity in solution per unit volume of solution. Surprisingly, there were no consistent and systematic distinctions in sorption ratios between heated and unheated samples, and the behavior of the sample showing significant structural collapse (#25525) did not differ significantly for Sr, Ba, and Eu from those showing no structural collapse. However, the sorption ratio for Ba decreased by about 40% for two of the three samples studied. The sample exhibiting structural collapse showed about a 170% increase in the sorption ratio for Cs. It is noteworthy that the changes in sorption behavior accompanying the structural transformations resulting from long-term heating are either minor or act to increase the sorption ratios. The sorption ratios for all elements examined are very high (between 10^3 and 10^5), and the effects of structural collapse will probably be insignificant.

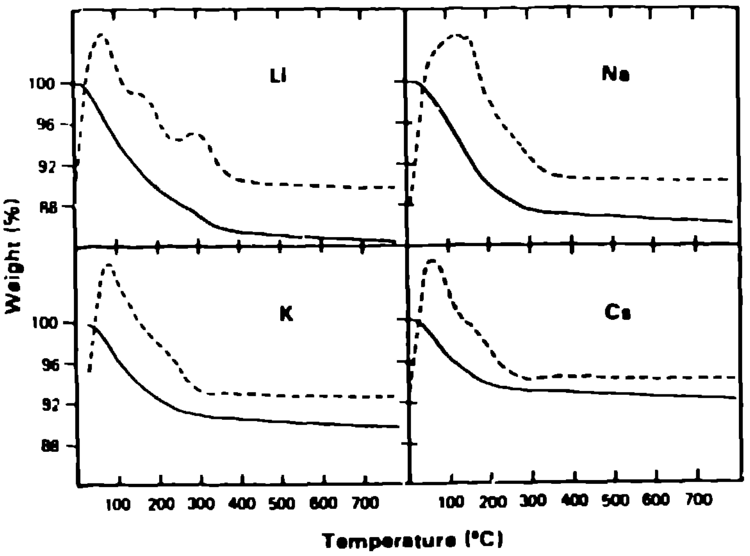

Fig. 5. TGA curves for univalent-cation clinoptilolites. Solid lines are weight-loss curves and dashed lines are derivative curves (%/min).[8]

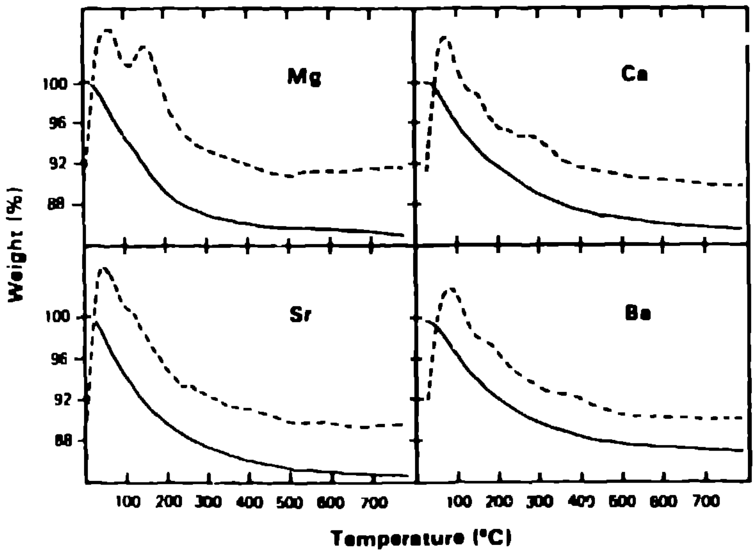

Fig. 6. TGA curves for divalent-cation clinoptilolites. Solid lines are weight-loss curves and dashed lines are derivative curves (%/min).[8]

Results of thermogravimetric analyses on a variety of clinoptilolite samples are summarized in Figs. 5 and 6.[8] As noted above, the data in these figures were collected using a dry N_2 purge gas and therefore probably more closely represent dehydration in an unsaturated (dry) rock rather than the partially saturated conditions expected in Yucca Mountain rocks. DSC data, which apparently more closely represent dehydration in a saturated environment, demonstrate that dehydration temperatures are significantly elevated in comparison with TGA data. For example, Ca-saturated #25525 clinoptilolite exhibited a peak in dehydration rate in TGA experiments at about 75°C (Fig. 6), whereas the analogous dehydration event occurred at about 120°C in the DSC experiments. Na-saturated #25525 clinoptilolite exhibited peak dehydration at about 130°C in the TGA, whereas DSC data for this sample gave a maximum dehydration at about 180°C. The direct applicability of these data notwithstanding, the data demonstrate that the details of dehydration are dependent upon the water fugacity surrounding the sample and the exchangeable-cation composition of the zeolite, with the common natural clinoptilolites (Na, K, and Ca) losing about 4% water (as a percentage of total sample weight) by 100°C. Differences in dehydration behavior between these different cation-exchanged clinoptilolites can most easily be seen from the derivative thermogravimetric curves (dotted in Figs. 5 and 6). It appears that dehydration is an equilibrium process within a small sample but is kinetically controlled in a larger solid sample such as a rock. The dehydration reactions invariably proceeded more slowly and peaked at higher temperatures when using larger samples or powders with large crystallite sizes. Thus, although dehydration and rehydration are rapid processes in a small powder sample, these processes in a rock will be significantly affected by the permeability of the rock. In addition, because the zeolitic rocks at Yucca Mountain are partially saturated, it is probable that the absolute amounts of water evolved upon heating will be different than in the laboratory experiments conducted in a dry N_2 atmosphere, although the zeolites in the partially saturated rocks will undoubtedly contain more water than samples in equilibrium with the room atmosphere. Nevertheless, it is likely that the zeolites will act as a source significant volume effects associated with dehydration of these zeolites, fractures may form as a result of repository-induced heating of the tuffs. Such fractures could provide better access to the sorptive zeolites for fluids potentially migrating through these relatively impermeable rocks. Depending on the reversibility of the dehydration reactions and associated volume decrease, such fractures may close upon cooling and rehydration of the rock. Based on these data, it is likely that any newly available water will be strongly re-adsorbed by the zeolites.

The effects of these temperature-dependent mineral properties on the bulk behavior of rock are illustrated by the results of several mechanical tests conducted by Kranz et al.[10] These experiments were performed at 22°C under pressures ranging from room conditions up to 6.9 MPa, the pressure corresponding to the depth of burial of the tuff of Calico Hills at Yucca Mountain. These tests, performed on vacuum-dried tuff of Calico Hills, were designed to measure the strain changes produced by hydration of the tuff, both with and without confining pressure. Figure 7[10] illustrates the stress generated due to unconfined hydration of dehydrated clinoptilolite. For comparison, data for a welded, devitrified tuff from the unzeolitized Topopah Spring Member of the Paintbrush Tuff are included in the figure. Note that the tuff of Calico Hills produces stresses approximately an order of magnitude larger than those produced by welded, non-zeolitic tuff. The small amount of expansion induced in the welded tuff may be due to the presence of small amounts of smectite, an expandable clay mineral. The swelling observed on hydration of the zeolitic tuff is due to interaction of water in the exchange sites of clinoptilolite; experiments conducted with a silicon fluid of high molecular weight and viscosity similar to that of water resulted in axial stresses equal to the injection pressure of the liquid.[10]

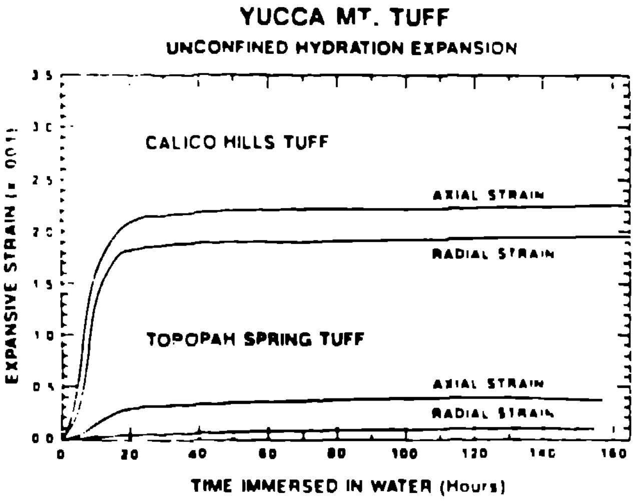

Fig. 7. Swelling strains after vacuum drying and immersion in water.[10]

CONCLUSIONS

The data presented in this paper illustrate that zeolitic tuffs containing clinoptilolite are susceptible to significant changes when exposed to small increases in temperature. These changes include significant decreases in volume and evolution of water for clinoptilolite and mordenite. The behavior of both zeolites on heating is strongly composition dependent and is also a function of the water fugacity. These observed volume and water-content changes appear to be reversible over the short term, but long-term heating of clinoptilolite results in structural collapse that appears to be irreversible, at least over periods of months. Although the zeolites can be significantly modified by long-term, low-temperature reactions, preliminary data suggest that the beneficial sorptive properties of these minerals are not significantly impacted. Thus it is possible that repository-induced heating of the zeolitic rocks below the potential repository horizon will result in opening of fractures with concomitant evolution of water vapor. Such fractures could provide increased access to the sorptive zeolitic rocks for migrating fluids. Depending on the long-term reversibility of the dehydration and volume-reduction reactions, such fractures may close during cooling and re-admission of water. Under these conditions, the zeolites will probably act as an important sink for water.

These data support and amplify the results of Kranz et al.[10] that illustrate the large stresses that are generated when hydrating or dehydrating zeolitic tuff. In addition, they help to explain the results of Riecker and Rooney[11] showing a significant decrease in strength of zeolitized tuffs when they are heated. The volume (structural) and water-content changes that are fundamental properties of these materials must be considered when predicting the response of zeolitic tuff underlying the proposed repository to long-term elevated temperatures.

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