CALORIMETRIC MEASUREMENT OF THE ENTHALPY OF HYDRATION OF CLINOPTILOLITE

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Abstract—The enthalpy of hydration of natural clinoptilolite was determined by isothermal immersion calorimetry on Ca-, Na- and K-exchanged clinoptilolite (Fish Creek Mountains, Nevada). Heats of immersion of clinoptilolite were determined at initial H_2O contents ranging from $\theta = 0.02$ to 0.85 (where θ is the ratio $[H_2O$ content$]/[$maximum H_2O content$]$). The heat of immersion (liquid H_2O reference state) of Ca-clinoptilolite ranged from -7.5 ($\theta = 0.87$) to -25.7 kJ/mol-H_2O ($\theta = 0.19$); values for Na-clinoptilolite ranged from -6.3 ($\theta = 0.85$) to -21.8 kJ/mol-H_2O ($\theta = 0.11$); and values for K-clinoptilolite ranged from -7.7 ($\theta = 0.80$) to -24.6 kJ/mol-H_2O ($\theta = 0.02$). Linear regression of the calorimetric data provided the following values for the complete heat of immersion (from $\theta = 0$): Ca-clinoptilolite, -30.3 ± 2.0; Na-clinoptilolite, -23.4 ± 0.6; and K-clinoptilolite, -22.4 ± 0.8 kJ/mol-H_2O.

    The heat of immersion measurements were compared with the enthalpy of hydration results of Carey and Bish (1996) determined in a thermogravimetric study of the same samples. The heat of immersion data are similar but of smaller magnitude than the values of enthalpy of hydration and are believed to be more accurate because they represent direct measurements of this thermodynamic property.

    The effect of dehydration of clinoptilolite on the thermal evolution of the potential high-level radioactive waste repository at Yucca Mountain was considered by comparing the amount of energy consumed by clinoptilolite dehydration with the amount of energy necessary to heat rocks lacking hydrous minerals. The extra energy consumed on heating clinoptilolite from 25 to 200 °C ranges between 70 and 80% in excess of that required for nondehydrating materials (that is, clinoptilolite acts as a heat sink). These results indicate that accurate thermohydrologic modeling of rock units at Yucca Mountain should consider the thermal effect of dehydration/hydration processes in clinoptilolite and other hydrous minerals, in addition to the water produced/adsorbed during heating/cooling.

    Key Words—Calorimetry, Clinoptilolite, Energetics, Enthalpy, Hydration, Zeolite.

INTRODUCTION

Clinoptilolite, ideally (Na, K, ½Ca)$_6$Al$_6$Si$_{30}$O$_{72}$·20 H_2O, is a common zeolite found in altered volcanic tuffs and tuffaceous sediments, saline lakes and deep sea sediments (Gottardi and Galli 1985). It is the most abundant hydrous mineral in volcanic tuffs at the site of the potential repository for high-level radioactive waste at Yucca Mountain, Nevada, approaching 80% in zeolitized tuffs below the repository horizon (Bish and Chipera 1989). Understanding the response of clinoptilolite to the elevated temperatures that will follow emplacement of radioactive waste is an important aspect of the evaluation of the suitability of Yucca Mountain for disposal of radioactive waste. In particular, it is important to quantify the effects of hydration and dehydration of clinoptilolite on the thermal evolution and pore saturation of Yucca Mountain rocks.

There have been several previous studies of the thermodynamics of hydration of clinoptilolite, including those of Barrer and Cram (1971), Johnson et al. (1991) and Carey and Bish (1996). The first two of these studies provided integral heats of hydration for a synthetic Na end-member and a natural crystal of intermediate composition, respectively. Carey and Bish derived integral and partial molar heats of hydration for Na, K and Ca end-members from equilibrium H_2O data as a function of temperature and pressure.

In this study, calorimetric measurements were made to determine the integral and partial molar enthalpy of hydration. These measurements represent an improved basis for quantitative calculations of the heat of hydration and dehydration because partial molar data were obtained on cation-exchanged, natural crystals and because the measurements are more accurate than those obtained by Carey and Bish (1996). The calorimetric experiments were done by immersion calorimetry on a series of cation-exchanged (Ca, Na and K), natural clinoptilolite samples. The calorimetric measurements allow quantitative calculation of the amount of thermal energy consumed by clinoptilolite as a function of H_2O content.

This study also integrates the calorimetric measurements with the thermogravimetric study of Carey and Bish (1996), which gives the equilibrium water content of clinoptilolite as a function of temperature and water vapor pressure. The combination of the calorimetric and thermogravimetric studies allows a quantitative prediction of the energy consumed by clinoptilolite-bearing rocks during a thermal event such as would occur at Yucca Mountain following the emplacement of high-level radioactive waste. The thermogravimetric studies provide the equilibrium water content as a function of temperature and pressure, whereas the calorimetric results allow calculation of

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Table 1. Summary of the heat of immersion measurements on Ca-, Na- and K-clinoptilolites.

Temp. (°C)	PH_2O (mbar)	Clino-ptilolite	Initial mass (mg)	Measured dry mass (mg)	Measured θ	Calculated θ	Calculated dry mass (mg)	Q (J)	Q/Z (J/g)	Q/H_2O (J/g)
22	26.45	Na	48.20	38.74	1.31	0.95	40.97	0.1	2.44	243.6
		K	56.40	46.63	1.34	0.95	49.12	−0.025	−0.51	−64.63
22	5.289	Ca	72.72	62.32	0.86	0.87	62.25	−0.67	−10.76	−415.1
		Na	70.65	59.47	1.01	0.85	60.98	−0.58	−9.56	−348.1
		K	65.25	57.52	0.86	0.80	58.03	−0.78	−13.44	−627.9
		K	66.54	58.66	0.86	0.80	59.18	−0.77	−13.01	−413.4
22	0.4	Ca	71.84	63.48	0.68	0.69	63.35	−1.92	−30.23	−503.7
		Na	59.94	52.81	0.73	0.69	53.16	−1.55	−29.16	−498.5
		Na	69.52	61.25	0.73	0.69	61.67	−1.87	−30.33	−518.5
		K	65.01	58.13	0.76	0.58	59.59	−2.07	−34.74	−534.9
		K	74.99	67.06	0.76	0.58	68.74	−2.05	−29.82	−459.2
50	0.4	Ca	48.24	42.32	0.72	0.58	43.34	−3.65	−84.20	−1038
		Na	56.60	46.48	1.17	0.55	51.38	−2.58	−50.12	−593.5
		K	79.99	75.19	0.41	0.45	74.79	−4.33	−57.89	−670.3
100	0.4	Ca	63.89	58.46	0.48	0.44	58.83	−5.70	−96.89	−897.8
		Na	65.45	61.98	0.30	0.36	61.38	−6.83	−11.3	−929.6
		K	63.89			0.27	61.28	−5.91	−96.45	−851.64
150	0.4	Ca	48.53	45.76	0.31	0.34	45.52	−7.06	−155.1	−1212
		Na	57.19	55.23	0.19	0.21	54.99	−8.01	−145.7	−997.4
		K	62.38	59.72	0.29	0.15	60.94	−7.55	−123.9	−936.7
200	0.4	Ca	40.26	37.93	0.32	0.26	38.35	−7.84	−204.3	−1416
		Na	37.60	35.75	0.28	0.11	36.85	−7.14	−193.8	−1170
		Na	34.75	32.86	0.31	0.11	34.06	−6.835	−200.7	−1211
		K	36.74	36.66	0.01	0.07	36.36	−5.9	−162.3	−1116
245	0.4	Ca	47.78	45.97	0.20	0.19	46.05	−9.1	−197.6	−1263
		Ca	31.91	30.30	0.27	0.19	30.76	−6.88	−223.7	−1429
		K	40.26	39.74	0.08	0.02	40.11	−7.85	−195.6	−1285
		K	38.33	38.22	0.02	0.02	38.19	−6.7	−175.3	−1153

Notes: For the purposes of calculating θ the following saturated water contents of clinoptilolite were used: Ca-clinoptilolite, 16.25 wt%; Na-clinoptilolite, 15.68 wt%; K-clinoptilolite, 13.49 wt% (Carey and Bish 1996). The temperature and pressure refer to the equilibration conditions of the samples prior to the measurements. Measured θ was determined from the measured dry mass. Calculated θ was determined using the P and T of equilibration and the results of Carey and Bish (1996).

the heat evolution associated with changes in hydration state. Idealized calculations indicate that clinoptilolite-bearing tuffs will consume significantly more energy for a given rise in temperature than anhydrous rocks. In addition, for rock units in the unsaturated zone, the dehydration of clinoptilolite will release a significant amount of water leading to pore saturation and water migration.

EXPERIMENTAL METHODS

Natural clinoptilolite was obtained from Minerals Research in the form of a clinoptilolite-rich tuff from Fish Creek Mountains, Nevada (Minerals Research reference # 27054). This material was purified by gravitational settling in water (Chipera et al. 1993) and contained minor amounts of feldspar and quartz after purification, but no other hydrous minerals, including smectite, were detected. The natural material was cation exchanged with 1–2 Molar Na-, K- and Ca-chloride solutions at room temperature to provide nearly homoionic exchanged clinoptilolite. The chemical compositions of these samples were determined by X-ray fluorescence and inductively coupled plasma atomic absorption spectrometry and are as follows:

Natural: $(Na_{0.86}K_{1.91}Ca_{1.49}Mg_{0.69})(Al_{6.70}Fe_{0.17}Si_{29.04})O_{72} \cdot 21.9H_2O$

Na-exchanged: $(Na_{5.01}K_{0.75}Ca_{0.12}Mg_{0.29})(Al_{6.78}Fe_{0.06}Si_{29.20})O_{72} \cdot 21.3H_2O$

K-exchanged: $(Na_{0.27}K_{5.84}Ca_{0.13}Mg_{0.25})(Al_{6.85}Fe_{0.10}Si_{29.04})O_{72} \cdot 18.5H_2O$

Ca-exchanged: $(Na_{0.18}K_{0.90}Ca_{2.34}Mg_{0.57})(Al_{6.70}Fe_{0.17}Si_{29.04})O_{72}(H_2O \text{ n.d.})$

On a charge basis, the cation exchanges were approximately 76% complete for Na, 85% for K and 68% for Ca. (See Carey and Bish 1996 for further details.)

The clinoptilolite samples were prepared for immersion calorimetry by loading 2 samples in paired glass ampoules. The samples were equilibrated at conditions ranging from 22 °C and 100% relative humidity (maximum water content) to 250 °C and a 0.4-mbar vacuum (minimum water content; Table 1). The samples were assumed to be at equilibrium with respect to the internal distribution of H_2O molecules and exchangeable cations. This assumption is consistent with the observations of Carey and Bish (1996) in which reversible exchange of H_2O was readily achieved in thermogravimetric experiments. The samples were

Table 2. Parameters for the calculation of the enthalpy of hydration from thermogravimetric data (Carey and Bish 1996). Also shown are the integral molar enthalpy of hydration and the mass ratio of H_2O to anhydrous zeolite at saturation, F.

Clinoptilolite	H°_{Hy} kJ/mol	W_1 kJ/mol	W_2 kJ/mol	$\Delta \bar{H}_{Hy}$ kJ/mol	F g/g
Ca-exchanged	−120.5	137.1	−74.9	−76.9	0.1940
Na-exchanged	−99.6	72.2	−32.1	−74.2	0.1860
K-exchanged	−91.2	74.6	−41.7	−67.8	0.1559

sealed under the equilibration conditions by melting the filling tube of the ampoule. One of the ampoules was used in the calorimetric measurements, and the other was used to determine the water content of the clinoptilolite.

The water contents of the clinoptilolite samples were determined by loss on ignition (LOI) to 1000 °C for 1 h (Table 1). These values were used to determine the initial value of θ, the ratio of observed water content to the maximum observed water contents at saturation determined on the same samples by Carey and Bish (1996; compare Table 2 for water contents at saturation). The measurements of θ are of low precision with several samples having unrealistic values. For example, the Na-clinoptilolite prepared at 50 °C and 0.4 mbar has a measured θ of 1.17. The low-precision results from the measurement of a small loss in mass of H_2O relative to the sum of the sample, ampoule and measuring crucible. The process of breaking the ampoules prior to the LOI measurement may have also resulted in a systematic error due to the potential loss of sample. This error would produce unreasonably high values of θ, as is observed in Table 1.

An alternative method of evaluating the initial water content of the samples is to calculate the water content from the temperature and H_2O vapor pressure of equilibration using the results of the equilibrium study of Carey and Bish (1996; Table 1). The difference between the calculated and measured values of θ is within ±0.06 when samples with obvious errors are excluded. The differences appear adequately random (when systematic errors are considered) to conclude that the calculated values provide a reasonable measure of the water content of the clinoptilolite samples. Consequently, the calculated values of θ and anhydrous mass are regarded as being more accurate than the measured values. In the analysis that follows, the water contents will be assumed to be given by the calculated water contents. The likely error associated with the calculated value of θ is estimated to be ±0.05.

Calorimetric measurements were conducted with a Tronac isothermal calorimeter. The calorimeter is isolated in an isothermal bath maintained at 25.8 ± 0.1 °C. The calorimeter is vacuum insulated and equipped with a cooling Peltier coil and a heating thermistor that maintain the temperature of the water within the cal-
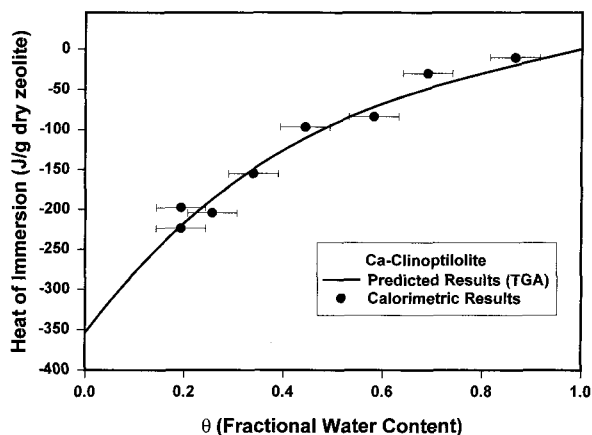

Figure 1. Calorimetric measurements (Q/Z) of the integral heat of immersion of Ca-clinoptilolite (this study) and calculated heats of immersion (TGA) from the study of Carey and Bish (1996).

orimeter to ± 2 × 10^{-5} °C/h. During sample equilibration and prior to reaction, the constant cooling rate supplied by the Peltier coil is balanced by a constant heating rate from the thermistor. The sample in the sealed ampoule is suspended from a constant-speed stirring rod. Following thermal equilibration, the ampoule is broken against the calorimeter floor, exposing the sample to the water in the calorimeter. The heat evolved is measured by the change in the thermal energy supplied by the heating thermistor integrated over time. The calorimeter is calibrated electrically by applying a known voltage to a constant-resistance heater within the calorimeter. The precision of the calorimetric measurements was examined by measuring the heat of immersion of empty ampoules and is judged to be ±0.1 J. However, almost all of the uncertainty associated with the measurements is due to uncertainty in sample mass.

RESULTS

The calorimetric results for the cation-exchanged clinoptilolite samples are expressed in terms of the heat evolved (Q) normalized to the anhydrous mass (Q/Z) or to the moles of H_2O adsorbed (Q/H_2O) as a function of water content (Table 1; Figures 1–4). The normalizations were made in terms of the amount of anhydrous zeolite or H_2O as calculated from the equilibrium study of Carey and Bish (1996). In the analysis of the data, it was necessary to determine the amount of H_2O adsorbed during the immersion experiment. It was assumed that the clinoptilolite adsorbs sufficient H_2O to yield a value of $\theta = 1$, for which the saturated water content is the same as that determined by Carey and Bish (1996). (Carey and Bish determined the maximum water content by thermogravimetric measurements of the same samples equilibrated in water-saturated N_2 at temperatures near 25 °C.) This assumption
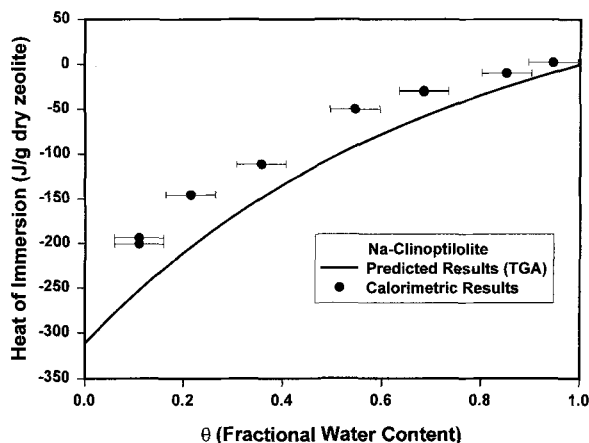
Figure 2. Calorimetric measurements (Q/Z) of the integral heat of immersion of Na-clinoptilolite (this study) and calculated heats of immersion (TGA) from the study of Carey and Bish (1996).
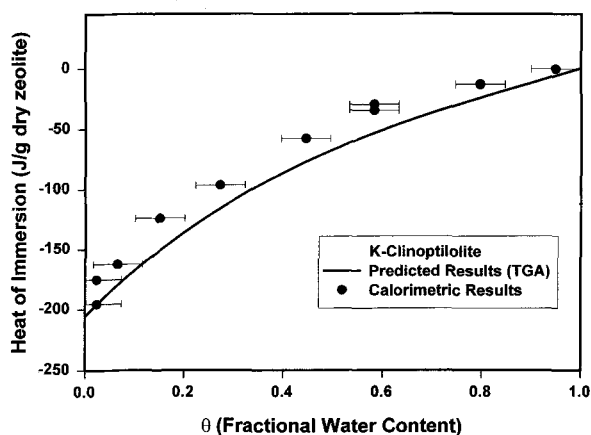

Figure 3. Calorimetric measurements (Q/Z) of the integral heat of immersion of K-clinoptilolite (this study) and calculated heats of immersion (TGA) from the study of Carey and Bish (1996).

was examined by measuring the heat of hydration of Na- and K-clinoptilolite equilibrated in a closed container in air above pure water (a 100% relative-humidity environment). According to the assumption, these samples should yield a heat of hydration near zero. The results for the fully hydrated samples are indistinguishable from zero within the precision of the measurements (Table 1). However, it is also possible that clinoptilolite adsorbs H_2O in excess of $\theta = 1$ with negligible heat of immersion.

The calorimetric data (Q/Z) show that samples with a smaller initial H_2O content have a greater heat of immersion as expected from the greater adsorption of H_2O by these samples (Figures 1–3). The upward curvature in the plots indicates that the partial molar heat of hydration in clinoptilolite increases with decreasing θ. Error bars for the initial water content represent ± 0.05 units of θ, and the error in the heat of immersion is about the size of the symbol.

The measured integral heat of immersion in J/mol of gaseous H_2O adsorbed (Q/H_2O) indicates a significant uncertainty in the heat of immersion at high values of θ (Figure 4). The error bars were calculated assuming an absolute error in the measurements of 0.1 J. The measured values for K- and Na-clinoptilolite have an apparent precision of better than 2 kJ/mol-H_2O for 3 sets of repeated measurements. The values for Na-clinoptilolite are slightly more energetic than those for K-clinoptilolite, in the range of 1 to 2 kJ/mol-H_2O. Ca-clinoptilolite is considerably more energetic (1 to 5 kJ/mol-H_2O as the initial value of θ decreases), but the precision is worse and the range of coverage of θ is not as great. For Ca-clinoptilolite the precision is in the range of 3 to 5 kJ/mol-H_2O and reflects, in part, smaller sample sizes with a smaller calorimetric signal. The convergence of all measurements to similar values at high initial θ is expected from the de-

creasing importance of the exchangeable cation as saturation is approached (compare Barrer and Cram 1971; Carey and Navrotsky 1992).

DISCUSSION

The measured heat of immersion is equivalent to the integral enthalpy of hydration for clinoptilolite hydrating in water from an initial state of θ (Table 1) to a final state of $\theta = 1$. (For a discussion of the relationship between isothermal measurements of the heat of immersion and the enthalpy of hydration, see Ross and Olivier 1964.) The partial and integral molar enthalpies of hydration of the same clinoptilolite samples were also determined by Carey and Bish (1996) through analysis of thermogravimetric data. A comparison of the 2 studies can be made by calculating the integral enthalpy of hydration predicted by Carey
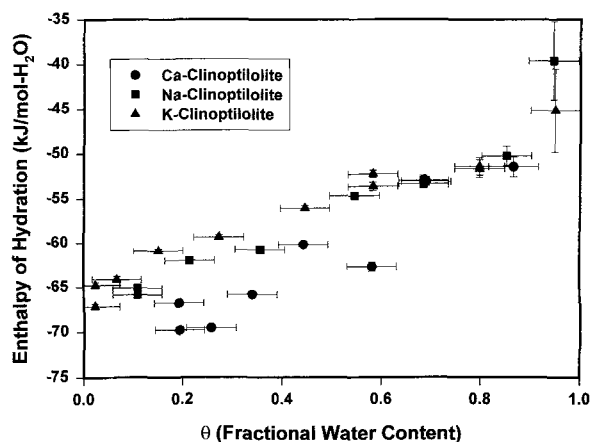

Figure 4. Calorimetric measurements (Q/H_2O) of the enthalpy of hydration for Ca-, Na- and K-clinoptilolite. The values were derived from the heat of immersion experiments by subtraction of the enthalpy of vaporization of liquid water.

Table 3. Results of the weighted nonlinear regression of the integral heat of immersion data (Q/H_2O) as a polynomial in $\theta(\bar{H} + k_1\theta + k_2\theta^2)$. The integral molar enthalpy of hydration and its uncertainty are given by $\bar{H}$.

Clinoptilolite	$\bar{H}$ kJ/mol	Error† kJ/mol	k_1 kJ/mol	Error† kJ/mol	k_2 kJ/mol	Error† kJ/mol
Ca-exchanged	−74.3	2.0	26.6	4.2	n.r.‡	
Na-exchanged	−67.4	0.6	20.9	1.2	n.r.‡	
K-exchanged	−66.4	0.8	31.6	4.2	−15.7	4.8

† Error derived from regression statistics.
‡ n.r. Parameter not statistically justified in regression.
Note: The values in this table may be compared with those of Carey and Bish (1996) by observing that $H_{Hy}^0 = \bar{H} - k_1$, $W_1 = 2(k_1 - k_2)$ and $W_2 = 3k_2$.

and Bish (1996). This can be done with the following equation:

$$(Q/Z) = ((H_{Hy}^0 + H_{vap})(1 - \theta) + W_1/2(1 - \theta^2) + W_2/3(1 - \theta^3))F/18.015 \quad [1]$$

The parameters H_{Hy}^0, W_1, and W_2 are derived from Carey and Bish (1996) and are standard-state and excess enthalpy of hydration parameters on a per mol of H_2O vapor basis (Table 2). The parameters H_{vap} (enthalpy of vaporization, 44.016 kJ/mol-H_2O); F (mass ratio of H_2O to anhydrous zeolite at saturation, Table 2); and 18.015 (molecular weight of H_2O) convert the units (enthalpy of hydration per mole of gaseous H_2O) used by Carey and Bish to Q/Z (enthalpy of hydration per gram of anhydrous zeolite). The general features of the calorimetric data are modeled well by the thermogravimetric results (Figures 1–3). The predicted values for Ca-clinoptilolite are close, but the predicted values for Na- and K-clinoptilolite are too high.

A useful quantity in many thermodynamic calculations is the partial molar enthalpy of hydration. This may be obtained directly from the calorimetric data illustrated in Figures 1–3 by linear regression with respect to $(1 - \theta)$, $(1 - \theta^2)$, and $(1 - \theta^3)$ as suggested by Equation 1. More directly, it can be obtained by multiple linear regression of the data expressed as Q/H_2O in powers of θ (Table 1). In the regression, the data at the highest value of θ for Na- and K-clinoptilolite were not used because of the large uncertainties. Because of the large uncertainties in the measured values of θ, a nonlinear regression model was used in which both dependent and independent variables were weighted (Deming 1943). The enthalpy values in the regression were weighted by an error of 0.1 J normalized to the amount of H_2O adsorbed, and the values of θ were assigned a constant uncertainty of 0.05. The results of the weighted, nonlinear regression indicate that the partial molar enthalpy of hydration is linearly dependent on θ for Ca- and Na-clinoptilolite and is quadratically dependent for K-clinoptilolite (Figures 5–7; Table 3). The partial molar enthalpy of hydration in these figures was plotted with the equation:
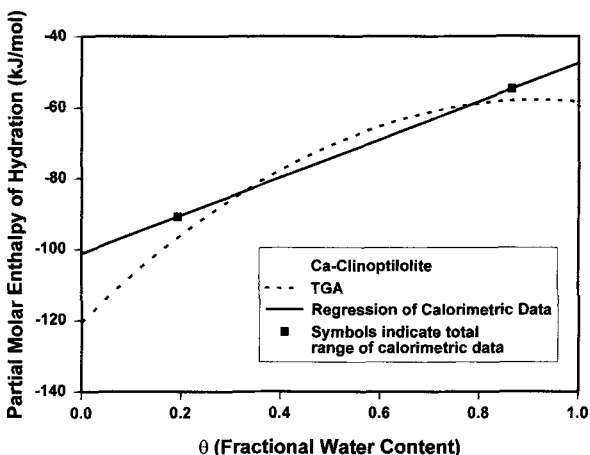

Figure 5. Partial molar enthalpy of hydration of Ca-clinoptilolite derived from weighted nonlinear regression of the immersion calorimetry data compared with the thermogravimetric results (TGA) of Carey and Bish (1996).
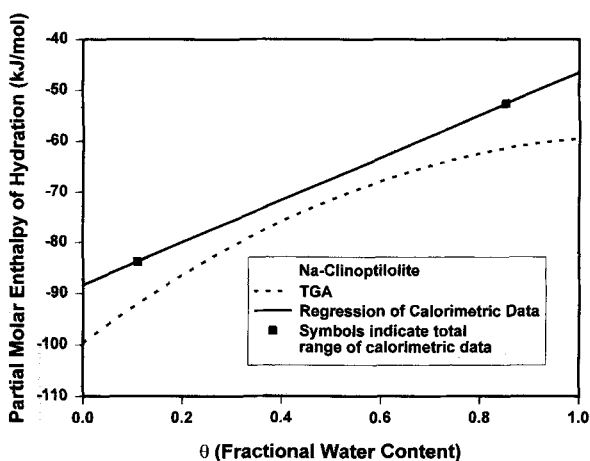
$$\bar{H}_{Hy} = H_{Hy}^0 + W_1\theta + W_2\theta^2 \quad [2]$$

The partial molar enthalpy values determined calorimetrically for Ca- and Na-clinoptilolite are almost linear, but this is probably a reflection of the limited range of data. The calorimetric data for K-clinoptilolite mimic the curvature observed in the thermogravimetric results. The calorimetric values for Na- and K-clinoptilolite are systematically low relative to the thermogravimetric results, whereas the data for Ca-clinoptilolite agree well with the thermogravimetric data over the range of data collected. The calorimetrically determined integral ($\theta = 0$ to 1) molar enthalpies of hydration are systematically lower than the thermogravimetric values, differing by 3.5% for Ca-, 9.8% for Na- and 2.1% for K-clinoptilolite (Tables 2 and 3).

Figure 6. Partial molar enthalpy of hydration of Na-clinoptilolite derived from weighted nonlinear regression of the immersion calorimetry data compared with the thermogravimetric results (TGA) of Carey and Bish (1996).
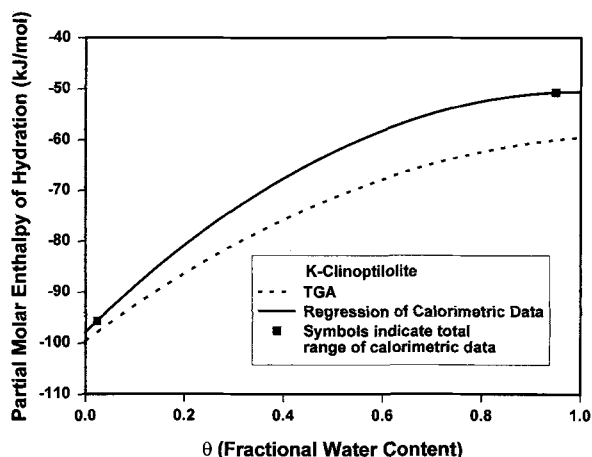
Figure 7. Partial molar enthalpy of hydration of K-clinoptilolite derived from weighted nonlinear regression of the immersion calorimetry data compared with the thermogravimetric results (TGA) of Carey and Bish (1996).

Table 4. Relative amount of energy necessary to heat equivalent rock units to 200 °C, with all conditions identical except case #1 allows clinoptilolite to dehydrate whereas case #2 ignores the effect of dehydration. Calculations are shown using the enthalpy of dehydration from both Carey and Bish (1996) (TGA) and from this study (Cal).

Clinoptilolite	E (dehydration)/ E (no dehydration) TGA	E (dehydration)/ E (no dehydration) Cal
Ca	1.84	1.84
Na	1.93	1.81
K	1.79	1.71

There is no clear explanation as to why the calorimetric and thermogravimetric results for Ca-clinoptilolite are in closer agreement than are the results for Na- and K-clinoptilolite. It is possible that the higher enthalpy of hydration of Ca-clinoptilolite, which produced more significant changes in the thermogravimetric isotherms, led to a more accurate analysis of the thermogravimetric data.

The molar values may also be compared with the heat of immersion measurement of Barrer and Cram (1971) on synthetic Na-clinoptilolite: −66.1 versus −67.4 ± 0.6 kJ/mol-H_2O measured in this study. Johnson et al. (1991) determined the molar enthalpy of hydration of a sodic, natural clinoptilolite by solution calorimetry and obtained a value of −67.4 kJ/mol-H_2O. Thus the calorimetric values measured in this study differ by less than 2% from previous calorimetric studies.

The relatively high enthalpies of hydration determined thermogravimetrically may be due to limitations in the thermogravimetric method. All of the thermodynamic parameters describing hydration were extracted from the equilibrium thermogravimetric analysis (TGA) data, including the standard-state Gibbs free energy and enthalpy of hydration, and 2 excess mixing parameters. Although the predicted equilibrium values are in good agreement with the TGA data, it is possible that the enthalpy of hydration is not as accurate as the calorimetric values due to the number of unknown parameters. One possible explanation for the relatively larger discrepancy between the thermogravimetric and calorimetric results for Na-clinoptilolite is that experiments at the highest degree of dehydration (low values of θ) were not possible because of irreversible changes in the sorption capacity (compare Carey and Bish 1996). For this reason, the ther-

mogravimetric experiments were limited to a maximum of 220 °C and the calorimetric experiments to a maximum of 200 °C. Thus, the partial molar enthalpies of hydration for Na-clinoptilolite were not as well constrained and the molar values were subject to potentially larger uncertainties.

APPLICATION TO YUCCA MOUNTAIN

The calorimetric data (Figure 4) and the equilibrium study of Carey and Bish (1996) can be combined to provide insight into the effects of clinoptilolite (and by analogy other hydrous minerals) on the thermal and hydrologic evolution of Yucca Mountain following emplacement of a potential waste repository. A simple comparison can be made of the total energy necessary to heat a unit of rock to a given temperature with and without the effect of dehydration. For this calculation, 2 rock units were compared, both containing clinoptilolite, but in one case the clinoptilolite was allowed to dehydrate and in the other it was not. For the dehydration case, the equilibrium evolution of the rock unit with temperature is considered for a maximum H_2O vapor pressure of 1 bar (higher vapor pressures are assumed to be less probable at Yucca Mountain; see Carey and Bish 1996 for more information and other examples of calculations on the effect of clinoptilolite on the thermal history of Yucca Mountain).

The results of the calculation are given in Table 4 as the ratio of the energy necessary to reach 200 °C for the dehydration case versus the no-dehydration case. Results using the partial molar enthalpy expressions from both the thermogravimetric and calorimetric studies are shown. In all cases, substantially more energy is required to reach a given temperature in rocks that contain dehydrating clinoptilolite. (Note that if higher H_2O vapor pressures are used in the calculations, the difference in required energy is reduced due to a reduction in the amount of dehydration.) The smallest difference is the calorimetric case of K-clinoptilolite, which still requires 71% more energy to reach 200 °C than rocks which lack clinoptilolite. Na-clinoptilolite requires from 81 to 93% more energy than if dehydration is ignored. The ratio of energy requirements remains approximately constant over the

temperature range from 150 to 250 °C. These results indicate that rocks with a substantial amount of clinoptilolite at Yucca Mountain may act as a thermal buffer, delaying or preventing the achievement of the temperatures that would occur in the absence of dehydration phenomena.

Dehydration of clinoptilolite will release a significant amount of H_2O as discussed by Carey and Bish (1996). Vaniman and Bish (1995) showed that the total amount of water in clinoptilolite is roughly equivalent to that which would be present in saturated pores of typical clinoptilolite-rich rocks having 29% porosity. Dehydration to 200 °C will release an amount of water equivalent to approximately 27% of the available porosity in such a rock containing 80% clinoptilolite (compare Carey and Bish 1996). This may result in significant production of H_2O from clinoptilolite-rich rock units.

A full evaluation of the effect of dehydration/hydration processes in clinoptilolite in the performance of the potential repository at Yucca Mountain would require a coupled thermohydrologic model of heat and mass transfer. The simplified calculations cited here indicate that thermal buffering and H_2O release from clinoptilolite could reduce the degree of dry-out achieved in zeolitic rocks, thus enhancing transport processes during repository-induced heating. On the other hand, the thermal buffering capacity of clinoptilolite has the potential to reduce the ultimate temperature achieved by zeolitic rocks, and may therefore act to stabilize clinoptilolite, preserving its sorptive capacity for radionuclides. Following repository-induced heating, (partially) dehydrated clinoptilolite would have the capacity to delay the onset of resaturation of zeolitic rocks, which during this period may diminish transport processes.

A second application of the calorimetric data concerns the calculation of the percent saturation of rocks in the unsaturated zone at Yucca Mountain. Saturation is usually defined as the ratio of the total amount of water to the porosity. The amount of pore water is determined by drying the rock samples in a 110 °C oven, cooling the samples over a desiccant, and then weighing the samples after minimal exposure to the atmosphere. The presence of hydrous minerals in the samples complicates the interpretation of the saturation values because some of the water lost in the 110 °C oven is not pore water but intracrystalline H_2O. Consequently, erroneously high saturation values may be obtained. For example, clinoptilolite in rock units at Yucca Mountain will have a water content corresponding to approximately $\theta = 0.95$ in the unsaturated zone because of the high relative humidity in the rock matrix. Drying such clinoptilolite samples at 110 °C will reduce the water content of clinoptilolite to approximately $\theta = 0.5$. For a rock sample with 30% porosity that is 50% saturated and contains 50% cli-

noptilolite, the drying process will remove sufficient H_2O from the clinoptilolite to give an apparent rock saturation of about 85%. Loeven's (1993) summary of the hydrologic properties of the Calico Hills unit from the unsaturated zone at Yucca Mountain included several samples with saturation values well in excess of 1. These values may be explained by the presence of hydrous minerals, and care should be taken in interpreting saturation values from rocks with hydrous minerals.

A more detailed examination of the effect of dehydration processes on the thermal and water budget of Yucca Mountain is underway and involves numerical models of rock units with varying amounts and distributions of clinoptilolite.

CONCLUSIONS

1) The enthalpy of hydration of Ca-, Na- and K-exchanged clinoptilolite has been determined by immersion calorimetry. For all 3 clinoptilolite samples, the enthalpy of hydration per mole of H_2O becomes increasingly negative with decreasing fractional water content (θ). These data and the results of Carey and Bish (1996) demonstrate that the partial molar enthalpy of hydration increases smoothly from low to high θ. This indicates that the H_2O in clinoptilolite occupies a continuum of energetic states as concluded by Bish (1988). Weighted nonlinear regression of the measurements indicates integral molar enthalpies of hydration for Ca-, Na- and K-clinoptilolite of -74.3 ± 2.0, -67.4 ± 0.6 and -66.4 ± 0.8 kJ/mol-H_2O from the gas phase.

2) The calorimetrically determined enthalpies of hydration are systematically lower than those determined thermogravimetrically by Carey and Bish (1996). The differences probably reflect the difficulty in solving for multiple thermodynamic properties using the thermogravimetric data. The calorimetrically determined values of enthalpy are believed to be more accurate.

3) The calorimetric and thermogravimetric studies were combined to give an estimate of the likely significance of dehydration of clinoptilolite on the thermo-hydrologic evolution of Yucca Mountain following emplacement of a potential high-level nuclear waste repository. The energy to heat and dehydrate clinoptilolite is 71 to 81% greater than the energy to simply heat (and not dehydrate) the clinoptilolite to an equivalent temperature of 200 °C. This indicates that rocks with abundant clinoptilolite will have a significant effect on the thermal evolution of Yucca Mountain. Clinoptilolite-rich rocks will also produce significant amounts of H_2O, corresponding to 27% of the saturated capacity of representative rocks at 200 °C.

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REFERENCES

Barrer RM, Cram PJ. 1971. Heats of immersion of outgassed and ion-exchanged zeolites. In: Flanigen EM, Sand LB, editors. Molecular sieve zeolites—II. Washington, DC: Am Chem Soc. p 105–131.

Bish DL. 1988. Effects of composition on the dehydration behavior of clinoptilolite and heulandite. In: Kalló D, Sherry, HS, editors. Occurrence, properties and utilization of natural zeolites. Budapest: Akadémiai Kiadó. p 565–576.

Bish DL, Chipera SJ. 1989. Revised mineralogic summary of Yucca Mountain, Nevada. Los Alamos Nat Lab Rept LA-1149-MS. 68 p.

Carey JW, Bish DL. 1996. Equilibrium in the clinoptilolite-H_2O system. Am Mineral 81:952–962.

Carey JW, Navrotsky A. 1992. The molar enthalpy of dehydration of cordierite. Am Mineral 77:930–936.

Chipera SJ, Guthrie GD, Jr, Bish DL. 1993. Preparation and purification of mineral dusts. In: Guthrie GD, Mossman, BT, editors. Health effects of mineral dusts. Washington, DC: Mineral Soc Am. p 235–249.

Deming WE. 1943. Statistical adjustment of data. New York: J Wiley. 261 p.

Gottardi G, Galli E. 1985. Natural zeolites. Berlin: Springer-Verlag. 409 p.

Johnson GK, Tasker IR, Jurgens R, O'Hare PAG. 1991. Thermodynamic studies of zeolites: Clinoptilolite. J Chem Thermo 23:475–484.

Loeven C. 1993. A summary and discussion of hydrologic data from the Calico Hills nonwelded hydrogeologic unit at Yucca Mountain, Nevada. Los Alamos Nat Lab Rept LA-12376-MS. 102 p.

Ross S, Olivier JP. 1964. On physical adsorption. New York: Interscience Publ 401 p.

Vaniman DT, Bish DL. 1995. The importance of zeolites in the potential high-level radioactive waste repository at Yucca Mountain, Nevada. In: Ming DW, Mumpton FA, editors. Zeolites '93. Brockport, NY: Int Committee on Natural Zeolites. p. 533–546.