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

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