Thermodynamics of ion-exchanged and natural clinoptilolite

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ABSTRACT

Natural clinoptilolite (Cpt: Na0.085K0.037Ca0.010Mg0.020Al0.182Si0.818O2·0.528H2O) from Castle Creek, Idaho, and its cation-exchanged variants (Na-Cpt, NaK-Cpt, K-Cpt, and Ca-Cpt) were studied by high-temperature calorimetry. The hydration enthalpy for all the clinoptilolites is about –30 kJ/mol H2O (liquid water reference state) at 25 °C. The energetic stabilization effect of hydration on each clinoptilolite can be largely correlated to its hydration capacity. The higher the average ionic potential of the extra-framework cations, the larger the hydration capacity of the clinoptilolite. This trend may be attributed to the small size as well as the efficient water-cation packing of high field strength cations in the zeolite structure. The hydration properties of these clinoptilolites are compared with those previously reported in the literature. The dehydration conditions as well as the measurement direction (dehydration of the initially hydrated sample or rehydration of the dehydrated zeolites) are important factors to control to obtain consistent thermodynamic properties for hydration.

The standard enthalpy for formation of the clinoptilolites from the constituent elements at 25 °C based on two framework O atoms was obtained from the calorimetric data: –1117.57 ± 0.95 kJ/mol Cpt, –1130.05 ± 1.00 kJ/mol Na-Cpt, –1109.49 ± 1.04 kJ/mol NaK-Cpt, –1094.21 ± 1.12 kJ/mol K-Cpt, and –1153.78 ± 1.07 kJ/mol Ca-Cpt. Their molar entropy was determined by a summation method based on the thermodynamic properties of the component oxides. Thus the standard free energy based on two framework O atoms was derived: –1034.01 ± 1.05 kJ/mol Cpt, –1044.19 ± 1.10 kJ/mol Na-Cpt, –1027.26 ± 1.13 kJ/mol NaK-Cpt, –1014.89 ± 1.21 kJ/mol K-Cpt, and –1064.95 ± 1.16 kJ/mol Ca-Cpt.

INTRODUCTION

Heulandite group zeolites, including mineral clinoptilolite and heulandite and their synthetic analogues, have the same framework topology (structure code HEU). According to Coombs et al. (1997), clinoptilolite is distinguished from heulandite based on Si/Al ratio, i.e., clinoptilolite if Si/Al > 4 and heulandite if Si/Al < 4. It is well known that the thermal stability of heulandite group zeolites is strongly influenced by extra-framework cations (Mason and Sand 1960; Mumpton 1960; Boles 1972; Zhao et al. 1998). This property warrants the heulandite group zeolites to be a preferred system for investigation of the cationic effects on thermodynamic (in contrast to thermal) stability.

The framework structure of various HEU type species and the site distributions of the exchangeable cations and water molecules have been extensively studied by X-ray and neutron diffraction techniques (e.g., Mason and Sand 1960; Mumpton 1960; Alietti 1972; Alberti 1975; Koyama and Takéuchi 1977; Hambley and Taylor 1984; Armbruster 1993; Yang and Armbruster 1996; Yang et al. 1997). There are three types of channels: one 8-membered channel and one 10-membered channel are parallel with the c-axis, the other 8-membered channel is parallel with the a-axis. Although HEU-type zeolites have been difficult to synthesize (Chi and Sand 1983; Satokawa and Itabashi 1997; Zhao et al. 1998), they are the most abundant zeolites in nature (Gottardi and Galli 1985).

The Yucca Mountain site in southeast Nevada is being developed as a geological repository for high-level radioactive waste (Kerr 2000). Primary volcanic glass at Yucca Mountain is partially altered to clinoptilolite, mordenite, analcime, and a variety of other zeolites. Clinoptilolite is the most abundant species among these zeolites. Over the past decade, numerous studies concern evaluation of the thermodynamic properties of clinoptilolites and their implications for the suitability of the Yucca Mountain site as a nuclear waste repository (e.g., Johnson et al. 1991; Glassley et al. 1994; Murphy et al. 1996; Carey and Bish 1996, 1997; Chipera and Bish 1997; Wilkin and Barnes 1998, 1999; Pabalan and Bertetti 1999; Benning et al. 2000). The role of clinoptilolite as a barrier to radionuclide migration is an important factor on these considerations.

HEU type zeolites have also been used in many other applications such as catalysis, soil amendment, formulation of nonphosphate detergents, contaminant remediation, and nuclear