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A predictive model for the enthalpies of hydration of zeolites

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ABSTRACT

A compilation of the average hydration enthalpies per mole of water of 145 diversely originating zeolites measured using different technical methods [76 data from transposed-temperature drop calorimetry (TTDC), 57 data from immersion calorimetry (IC), 6 data from phase equilibria (PE), 5 data from gas-adsorption calorimetry (GAC), and 3 data from hydrofluoric acid solution calorimetry (HF)] was generated. Statistical regressions between three parameters involving the average hydration enthalpy per mole of water $\{\Delta H_{hyd\text{-}W}, \Delta H_{hyd\text{-}W}/(Al/Si), \ln[-\Delta H_{hyd\text{-}W}/(Al/Si)]\}$ and six parameters namely: (1) the charge defined by the Al/Si ratio; (2) the ratio of the framework charge to the number of H_2O molecules (Al/H_2O); (3) the framework density (FD) calculated from the molecular volume of the anhydrous zeolite, FD_{anh}, and hydrated zeolite, FD_{hyd}; (4) the average cation electronegativity in the exchange site characterized by parameter $\Delta_H O^=(\text{site A})_{aq}$; and (5) the intracrystalline water porosity (WP) determined from the volume of liquid water that can be recovered upon thorough outgassing of the hydrated zeolite. The regressions were performed by taking into account either the nature of the measurement technique, or the nature of the zeolite family. Within the zeolites from the TTDC and IC populations (133 data), the best results were obtained with $\ln[-\Delta H_{hyd\text{-}W}/(Al/Si)]$ and $Al/(Al + Si)$. Whatever the measurement technique, considering the nature of the zeolite family having a constant framework density of the anhydrous form (129 data), the $Al/(Al + Si)$ ratio remains the best parameter and the enthalpy of hydration can be expressed as follows:

$$\Delta H_{hyd\text{-}w} = -(Al/Si)*e^{\{5.491 - 4.674*[Al/(Al + Si)]\}}$$

This general relationship can be improved by considering the following parameters: FD_{anh}, $\Delta_H O^=(\text{site A})_{aq}$, WP and a new parameter that is the product of three parameters Al/Si, $\Delta_H O^=(\text{site A})_{aq}$, and WP weighing the variation of the water porosity related to the nature of the cation and to the total charge of the exchange site. Therefore, an understanding of the chemical formulae and unit-cell volumes of anhydrous and hydrated zeolites is required to evaluate the enthalpy of hydration with an accuracy of ±3.25 kJ/mol H_2O.

Keywords: Hydration enthalpy, integral hydration enthalpy, zeolites, framework density, anhydrous zeolites, hydrated zeolites, thermal stability, water porosity, zeolite X, zeolite Y