Molecular H_2O in microporous silicates: Thermodynamic and H-bonding behavior of confined H_2O

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H_2O-bearing minerals provide an excellent starting point to investigate how the H_2O molecule interacts with natural crystalline materials. Many types of minerals contain H_2O and they interact with it in various ways. One general group of minerals, namely microporous silicates, offer the possibility to investigate the nature of hydrogen bonding and thermodynamic behavior, especially heat capacity, C_p, of confined H_2O at a relatively simple, yet fundamental level.

The microporous silicates armenite, $BaCa_2Al_6Si_9O_{30}\cdot 2H_2O$, and epididymite, $Na_2Be_2Si_6O_{15}\cdot H_2O$, and their dehydrated analogs were studied by relaxation calorimetry between 5 and 300 K to determine the C_p behavior of their confined H_2O. DTA/TG measurements, FTIR spectroscopy, electron microprobe analysis and powder Rietveld refinements were undertaken to characterize the phases and the local environment around the H_2O molecule. The X-ray diffraction data show that armenite and its dehydrated analog have similar structures, whereas in the case of epididymite there are structural differences between the natural and dehydrated phases. The standard entropy for armenite is S^o = 795.7 ± 6.2 J/(mol·K) and its dehydrated analog is S^o = 737.0 ± 6.2 J/(mol·K). For epididymite S^o = 425.7 ± 4.1 J/(mol·K) was obtained and its dehydrated analog has S^o = 372.5 ± 5.0 J/mol·K. The entropy of dehydration at 298 K is 319.1 J/mol·K and 135.7 J/mol·K for armenite and epididymite, respectively. Of the three different H_2O phases ice, liquid water and steam, the C_p behavior of confined H_2O in both armenite and epididymite is most similar to that of ice.

Hydrogen-bonding behavior and its relation to the entropy of confined H_2O at 298 K was analyzed for various microporous silicates. The entropy of confined H_2O increases approximately linearly with increasing average wavenumber of the OH stretching vibrations. The interpretation is that decreased hydrogen-bonding strength between a H_2O molecule and the silicate framework, as well weak ion-dipole interactions and extra framework cations, results in increased entropy of H_2O. This results in larger amplitude external H_2O vibrations, especially the translations of the molecule, and they contribute most strongly to the entropy of confined H_2O at 298 K.

Stability analysis of a horizontal coalbed methane borehole in the San Juan Basin, USA

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Borehole stability analysis was conducted using STABView and FLAC geomechanical modeling for a horizontal coalbed methane well planned to be drilled in the San Juan Basin. The objective was to determine whether the coal seam at 3000 ft depth would yield under certain drilling and production conditions. Triaxial cell tests using 1-inch diameter core plugs were performed to construct the Mohr-Coulomb and Hoek-Brown failure envelopes. A reduction of the peak coal strength by approximately 30% was needed to correct the scale-dependent strength to a value believed to be representative of the a 4.75-ich diameter horizontal borehole. No yielding was predicted at underbalanced and overbalanced drilling conditions when the uncorrected M-C and H-B lab strength data were used in the models. A 30% reduction in peak strength predicted no yielding during overbalanced drilling, and only minor yeilding during underbalanced drilling and during production. The maximum extend of the yielded zone at bottom-hole pressure of 100 psi predicted by STABView was 37% over gauge. FLAC simulations gave directionally similar but slightly more conservative results compared tom SATView. A reasonable amount of yielding and subsequent detachment of the coal is expected along the horizontal well at the highest drawdown pressures. Stability analysis showed that drilling a horizontal well in Coal A in the location under study in an overbalanced mode would be possible. Drilling the same coal seam underbalanced will produce a rim of yielded coal but no catastrophic failure, provided that the coal seam is not highly fractured naturally.