COMPUTER SIMULATION BY ENERGY MINIMISATION ON FIBROUS ZEOLITE STRUCTURES

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There is an extensive set of papers dealing with fibrous zeolites in past and recent literature, focussing largely on order–disorder issues. The hottest debate concerns the question of tetragonal species sharing natrolite topology, *i.e.* the validity of and distinction between gonnardite and tetranatrolite (*e.g.* ALBERTI *et al.*, 1995; ARTIOLI & GALLI, 1999; EVANS *et al.*, 2000). The aim of this presentation is to report the first results of computer simulation on structures with natrolite topology.

Two input structures were analysed in depth, a reportedly completely ordered natrolite (ARTIOLI *et al.*, 1984) and a completely disordered gonnardite structure (ARTIOLI & TORRES SALVADOR, 1991). The method chosen was to calculate the lattice energy of the structures with the GULP code (GALE, 1997). This method has previously been used to locate extraframework species in zeolite A by HIGGINS *et al.* (2002), and the interatomic potentials used in that work were applied. The structure and unit cell of each phase were optimised by energy minimisation whenever possible. Initial atomic coordinates were directly taken from the neutron diffraction data of ARTIOLI *et al.* (1984) in the case of natrolite and occupancies were all set to 1. In the case of gonnardite (sample no. 3 in ARTIOLI & TORRES SALVADOR, 1991, Rietveld refinement from X-ray powder data), H positions were added to the data set and T1 and T2 positions were given shared occupancies by Si and Al.

In all successful calculations on all cell contents, cell parameters a and b are slightly smaller than experimental ones. In unsuccessful calculations the reason for failure was mostly the unreasonable displacement of channel contents, especially H_2O. Water molecules are well known to be difficult to model empirically and further development of the potentials may be advantageous.

Simulation runs on the natrolite structure were unsuccessful. With symmetry constraints on, the structure could not be optimised. With symmetry off, the non-primitive cell first distorted (β the most, *i.e.* through monoclinic) and then the calculations failed completely, the distortion did not stabilise the structure. The reasons are yet unknown, could be that the potentials used were derived for a different system.

The first few tentative simulation runs on the tetragonal structure were simplified to the level of using only Na as secondary cation and omitting W2's (additional H_2O not present in natrolite) completely. These configurations were successfully optimised with symmetry constraints. The introduction of Ca + H_2O for Na substitution was more problematic. Static lattice calculations represent shared or partial occupancies by calculating appropriate weighted potentials. This approach is invalid in the case of fibrous zeolites because in the shared/partial occupancy model each hybrid secondary cation is paired with a "partial" H_2O molecule whereas the water molecule W2 should only be present in conjunction with Ca. If in the (Na, Ca) positions there are "hybrid" atoms (*e.g.* 0.75 Na and 0.25 Ca), W2 in the resulting configuration behaves differently from what is expected.

To correct the problem, the structure was rebuilt with $P1$ symmetry, *i.e.* all positions symmetrically inequivalent (160 atoms per unit cell altogether). This allows looking at hypothetical substitution configurations, in such a way that the complete but long range disorder is not taken into account and "pure" channel contents are present with an occupancy of 1. (However, the shared occupancy of the T positions was retained for simplicity.) The calculations have shown that the split W2 positions in ARTIOLI & TORRES SALVADOR (1991) cannot be optimised in static simulation runs. After "probing" several W2 positions, a structure with one Ca and one adjacent H_2O in the average of the two W2 positions, however, was found to achieve optimisation. Another simulation run on a structure with 2 Ca + 2 H_2O(W2) in the unit cell was also optimised when all the channel contents were allowed to move (the framework was held fixed in position).

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