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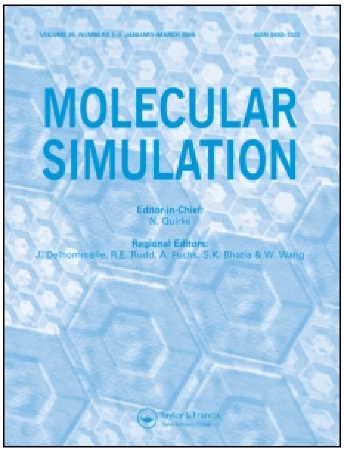

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Computer-Simulation of De-Hydration in Zeolites: First Steps in a Complex Problem

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COMPUTER-SIMULATION OF DE-HYDRATION IN ZEOLITES: FIRST STEPS IN A COMPLEX PROBLEM

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The choice of suitable interatomic potentials, simulation cell and procedure are discussed in relation to the first attempts at a Monte-Carlo study of the final stages of dehydration of Ca-zeolite A. The method leans heavily on the known crystallographic structure of the anhydrous zeolite and comparisons are also made with temperature-resolved X-ray and neutron diffraction data obtained during dehydration. The results reveal four types of hydration site, the populations of which reflect their relative stabilities. It is anticipated that these methods will now be extended to cover a wider range of applications.

KEY WORDS: Dehydration, zeolite A, Ca-zeolite A, time-resolved powder diffraction, X-ray diffraction, neutron diffraction; Monte Carlo.

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INTRODUCTION

Great effort has, understandably, been expended in the study of zeolite action using both experimental and modelling/simulation techniques. Much less time has been directed at the *synthesis* of zeolites, partly because of expediency and partly because of inherent difficulties in studying this stage by either experimental or simulation means. In this paper we consider conditions that are appropriate to the later stages of a hydrothermal synthesis, that is the final dehydration (drying out) of a synthesised zeolite, or conversely the first steps of re-hydration in a subsequent stage.

Clearly the full study is a demanding exercise; During de-hydration it is known [1, 2] that there can be substantial cation movement and, in addition to this, there is the question of whether the water-framework interactions might modify the overall structure. Even more problematically, under aggressive drying conditions, synthesised zeolites can transform to related zeolites: this has now been unambiguously demonstrated by means of dynamic diffraction techniques used by Barnes *et al.* [3, 4, 5]. The first step, of an ongoing programme to consider all these effects, is described here. Ca-Zeolite A was chosen as a model zeolite and simulated with varying water content and temperature, and the results compared with data from dynamic (time-resolved) diffraction experiments.

METHODOLOGY

1. Potentials

With Ca-zeolite A, there are 4 water interactions with framework atoms to consider viz. with Al, Si, O and Ca. In this first study, framework re-arrangements are suppressed; consequently there is no need for inter-atomic potentials between framework species.

The potentials used are derived using a hybrid approach: this combines the formal cation/anion models used by Catlow *et al.* [6, 7] in energy minimisation studies on minerals and zeolites, with QM-calculations on clusters containing a water molecule and cation/anion surrounded by representative charges. It has been previously shown [8] that such calculations on the following clusters;

$H_2O + Si^{4+}$ + 4 tetrahedral point charges;

$H_2O + Al^{3+}$ + 4 tetrahedral point charges;

$H_2O + Ca^{2+}$ + 12-fold point charge cluster;

$H_2O + O^{2-}$ + 6 octahedral point charges;

can yield short range repulsion parameters, while taking into account the counterion and lattice effects that occur in practice within structures of interest such as quartz, zeolite A and tricalcium silicate. These short range repulsions are then combined with the desired water-water potential in the following form:

$$V_i = A_i \,.\, \exp(-R/b_i) + \sum_j (n_i e) \,.\, (q_j e)/R_{ij} \qquad (1)$$

where R represents the separation of the water and the ith. cation/anion which carries a formal charge of $n_i e$; $q_j e$ are the point charges employed with the chosen water-water potential; and R_{ij} is the distance between the cation/anion and the jth. point charge of the water model. For the present study the values for A_j and b_j (Table 1) were obtained by the method of Aloisi *et al.* [8] referred to above, while the TIP4P point charge model [9] was used for the water parameters.

2. *Simulation Cell*

Of the two recent structures given in the literature [10, 11] for dehydrated Ca-zeolite A (Al/Si = 1), the latter was chosen since it gives a clearer picture of Ca-cation and Al, Si positions. The unit cell is cubic (space group $Fm\bar{3}c$) with a lattice parameter a = 24.44Å and contains 624 atoms (96 Al; 96 Si; 384 O; 48 Ca). The structure is seen (Figure 1a) to be composed essentially of eight β-cages connected by their 4-membered rings, and which in turn enclose the larger α-cage. Altogether there are 128 possible sites for the Ca-cations these being either just to

Table 1 Ion-water potential parameters, n_i, A_i, b_i in equation (1), calculated using a formal ion-couterion cluster method [8].

i (ion pair)	n_i	$A_i (eV)$	$b_i (Å)$
$H_2O - Si^{4+}$	4	14780	0.287
$H_2O - Al^{3+}$	3	18650	0.205
$H_2O - Ca^{2+}$	2	6190	0.261
$H_2O - O^{2-}$	−2	2121	0.348

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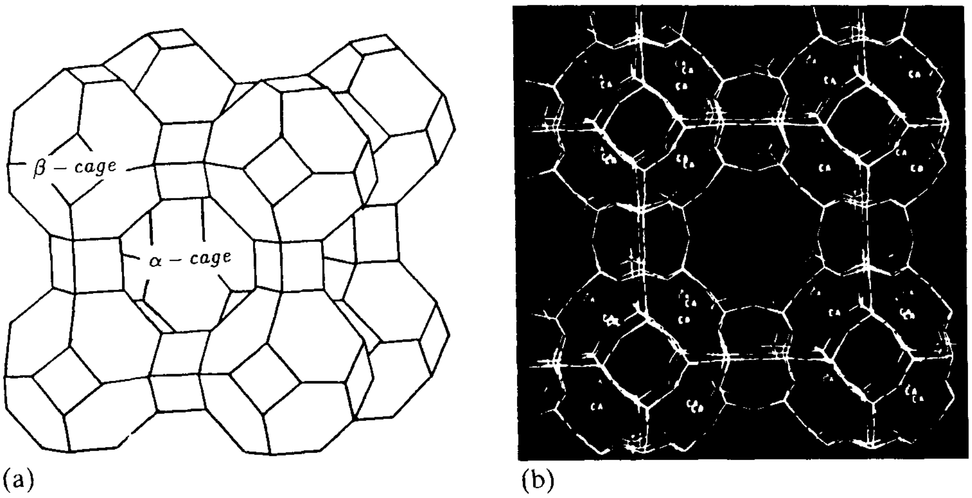

Figure 1 (a) Schematic representation of zeolite A, illustrating the α- and β-cages. (b) Actual cell used in the simulations showing statistical occupation of calcium cations (CA).

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the α-cage-side or to the β-cage-side of the centres of the connecting 6-membered rings. A simulation cell was constructed from this crystallographic cell by devising a suitable scheme to assign "whole" calcium-cations amongst these sites rather than using the partial occupancy device of the crystallographer. The scheme involves random assignment of the 48 Ca-cations amongst the 128 sites but with the provision that the overall statistical occupancy indicated by Pluth and Smith [11] is maintained, i.e. no 6-membered ring is allowed to have more than one Ca-cation in its proximity. Figure 1b illustrates the final simulation cell. By utilising a standard minimum image periodic boundary condition, that is a potential interaction cut-off distance of a/2 and consideration also of all repetitions residing within (±a/2, ±a/2, ±a/2) of the edge of the basic cell, a fully connected simulation cell is achieved. Thus water molecules may percolate between cages with full simulation consistency and conserving the required number of water molecules.

3. Simulation Procedures

To consider various possible hydration states of Ca-zeolite A and make comparisons with X-ray and neutron diffraction data, simulations were conducted using 20, 14, 10, 6 and 2 water molecules introduced into the central α-cage at temperatures of 300, 400, 500, 600 and 700 K respectively. Standard Metropolis [12] Monte-Carlo (MC) configurations were generated, starting from initial configurations in which the required number of water molecules were placed on a lattice within the central α-cage. Successive configurations were made by random pertubations of water positions and orientations but treating the zeolite framework and cations as rigid entities. The program codes were written specifically to exploit the CRAY/CONVEX architecture at ULCC thus allowing vectorisation of the most time-consuming calculations. Typically 7000 configurations would take 1 hour of CONVEX-C220 (Pluto) c.p.u. time; for example, with the 20 water molecule simulation, 70 000 configurations were used to "equilibrate" the system and a further 7000 "production" configurations used to obtain ensemble averages. In

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addition to the monitoring of standard Monte-Carlo parameters, averaged neutron/X-ray structure factor contributions from the water component (equation (2)) were calculated for the first 31 prominent (hkl) reflections.

$$\langle F_{hkl}^{water} \rangle = 1/N_{config} \sum_{N_c=1}^{N_{config}} \sum_{N=1}^{N_{waters}} \sum_{j=1}^{3} f_j \, . \, \exp 2\Pi i[h \, . \, x_N(j) + k \, . \, y_N(j) + l \, . \, z_N(j)] \quad (2)$$

(f_j = atomic O,H,H–X-ray or O,D,D-neutron atomic scattering factors; N_{waters} = number of water molecules; N_{config} = number of MC-configurations; $x_N(j)$, $y_N(j)$, $z_N(j)$ are the fractional coordinates of the oxygen ($j = 1$) and hydrogen/deuterium ($j = 2, 3$) atoms of the Nth. water molecule).

Even though the centro-symmetry of the Ca-zeolite A structure requires that the imaginary part of the overall structure factor remains zero, this condition was not imposed on the permitted water configurations. The original reason for introducing this $\langle F_{hkl} \rangle$ averaging procedure was to gain some idea of the sensitivity of the powder pattern predictions to the length of the simulation runs, and also to assess the contribution of the water component to the overall temperature (diffraction) factor. The standard crystallographic method for incorporating the effect of temperature into the structure factor equation is to modify the atomic scattering factors f_j using the Debye-Waller temperature factor corrections, to take into account the increasing atomic vibrations with temperature. Since the water excursions, in between visiting hydration sites, would in principle be substantial (i.e. more than just "vibrational") it was felt that an alternative and more fundamental method for calculating the water contribution would be desirable. F^{water} averages were therefore performed dynamically during simulation (see Figure 2) and combined with the corresponding cage contribution F^{cage}, taking into account the differing phases of F^{cage} and F^{water}. In the event, the hydration sites were fairly well defined in these studies but the situation could be different at higher temperatures or with greater water contents.

RESULTS

Convergence of a typical set of Monte-Carlo parameters is illustrated in Figure 2 for the case of the 20-water molecule simulation. It is clear that convergence of the internal energy E, is far faster than that of the F^{water} component. This is particularly notable since the water structures were relatively static in these simulations in so far

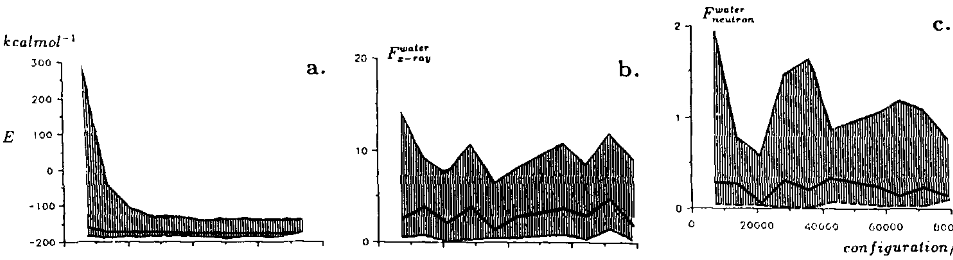

Figure 2 Behaviour of typical Monte-Carlo parameters during the simulation with 20 water molecules: (a) potential energy (E); (b) water contribution to the X-ray (200) strucure factor; (c) water contribution to the neutron (200) structure factor. The shaded regions indicate the bounds of variation, and the central lines the mean value. The horizontal scale is identical for all 3 plots.

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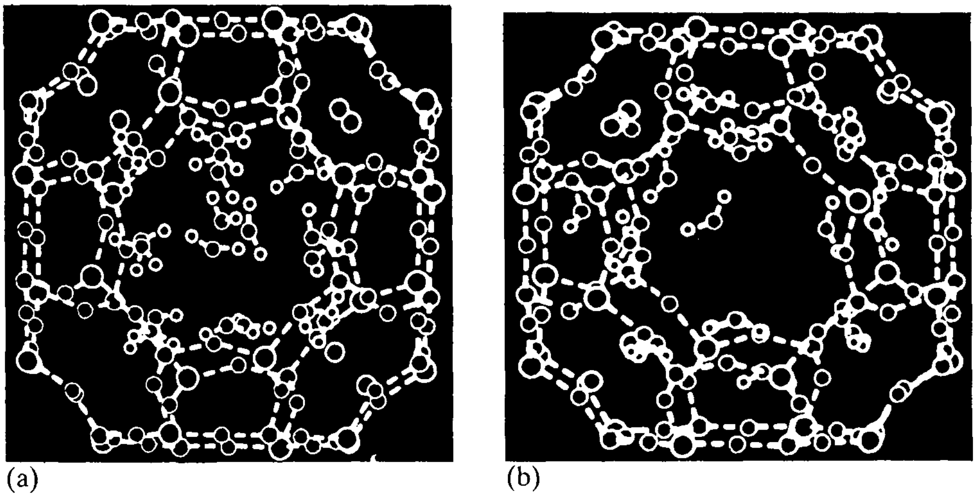
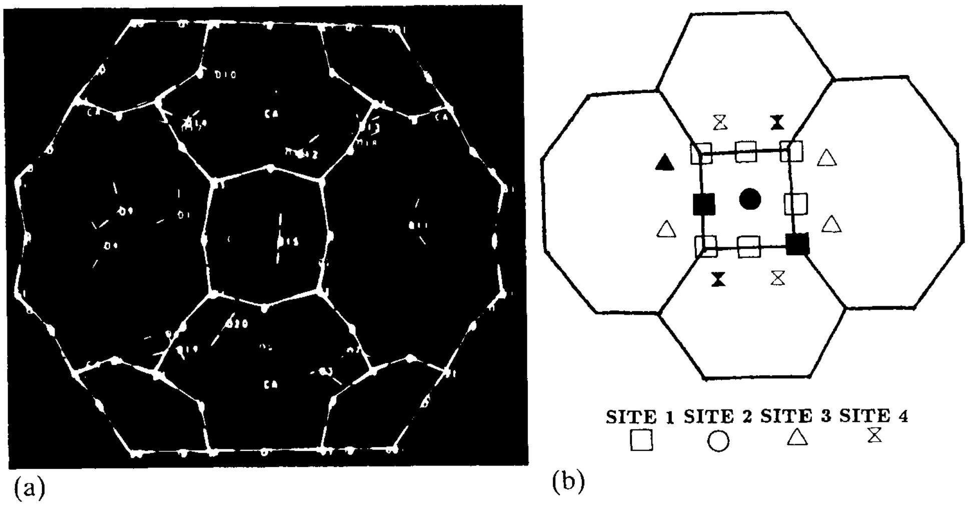

(a) (b)

Figure 3 Computer-graphic snapshots of the α-cage region near (a) the start, and (b) the termination of the 20-water molecule simulation at 300 K. Water molecules are seen to move away from the centre (a) to their eventual hydration sites (b).

as the waters remained associated with their hydration sites yet, clearly from the F^{water} fluctuations (Figure 2), suffered movements about an order of magnitude greater than the cage vibrational amplitudes which are typically in the tenths of an Ångstrom range at these temperatures. Two graphic snapshots of the 20-water molecule simulation are given in Figure 3 to illustrate initial and final water molecule positions at identifiable hydration sites as discussed below.

For these hydration levels investigated it transpires that four fairly well defined hydration sites are available to most of the 20 water molecules, as illustrated in Figure 4. This analysis shows that sites 1 and 2, both associated with the 4-rings,



(a) (b)

Figure 4 (a) Computer-graphic view through the 4-ring, showing typical hydration sites for the 20-water molecule simulation at 300 K. (b) Schematic to illustrate the types of hydration sites as given in Table 2. The filled-in symbols relate to those sites actually occupied in Figure 4a.

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Table 2 Hydration site populations for decreasing number of water molecules and increasing temperature. R_{bond} refers to the average distance to the closest bridging oxygen; N_{max} refers to the maximum number of waters that can be simultaneously accommodated at each site: also a separate column is given conjoining sites 1 and 2, these representing the total population within the 4-ring; in the cases of "<24" and "<36" the values are highly water-model dependent.

SITE		*1 border 4 – ring*	*2 centre 4 – ring*	*1 + 2 above 4 – ring*	*3 above 8 – ring*	*4 above 8 – ring*	*α – cage*
R_{BOND}	*Å*	*2.79*	*2.81*	*2.80*	*2.70*	*2.90*	
N_{MAX}		*<24*	*12*	*<36*	*12*	*12*	
N_{WATER}	T (K)						
20	300	5	8	13	4	1	2
14	400	6	5	11	2	0	1
10	500	4	5	9	0	0	1
6	600	6	0	6	0	0	0
2	700	1	1	2	0	0	0

remain the most-populated; conversely the 6- and 8-ring positions (sites 3 and 4) and the α-cage are only populated with higher hydration levels at the lower temperatures. Additionally, from the bond distance analysis (see Table 2) and the stereo-chemistry perceived from the graphic output (e.g. Figures 3 and 4), it is clear that the hydration sites are formed by hydrogen-bonding framework oxygens. Sometimes the water molecule orientations are closer to producing a bifurcated, rather than linear, hydrogen-bond though this is believed to be due to an inherent limitation of the TIP4P potential rather than to any subtle combination of interactions. The hydration sites appear to be well defined once simulation equilibration is complete, the water molecules remaining located around their sites throughout the remainder of each simulation.

This study has also made steps towards comparing simulation results with dynamic diffraction data. There already exist many powerful powder diffraction pattern simulation and Rietveld [13] refinement programs. One of these, "Lazy-Pulverix" [14], was used to generate powder patterns from the structures simulated in this study. However the well-defined nature of the hydration sites identified meant that averaged water positions could indeed be reasonably used, rather than using slowly converging F-factor components. Since the object of this exercise was to model dehydration behaviour, it was more important to be able to predict *changes* in the powder patterns than to achieve close agreement to any one particular pattern of a changing set: these requirements are quite different from those of conventional structure refinement. A simple method for comparing *changes* in pattern intensities is presented in Table 3 for the most significant reflections and compared with the dynamic diffraction data for the dehydration process collected using both X-ray [4] and neutron [3] sources; the agreement obtained is very satisfying given the exploratory nature of the study.

CONCLUSIONS

An examination of the ways to simulate the behaviour of water in Ca-zeolite A during dehydration has been made. Amongst the complexities encountered was the

Table 3 A method for comparing the changes in peak intensities, obtained from dynamic diffraction measurement and from simulation-prediction, during deydration of calcium zeolite A. The direction and number of arrows indicate the change in peak intensity (up = increase; down = decrease; sideways = negligble change; double arrows = >10% change in intensity for significant peaks; stars = immeasurable peak intensity).

h,k,l	X-ray		Neutron		h,k,l	X-ray		Neutron	
	Expt.	Sim.	Expt.	Sim.		Expt.	Sim.	Expt.	Sim.
2,0,0	⇑	↓	↓	↓	8,4,2	↑	↔	*	*
2,2,0	*	*	↑	↑	6,6,4	↔	↔	↔	↔
2,2,2	⇑	↑	↔	↔	8,6,0	↔	↔	↔	↓
4,0,0	↔	↔	*	*	8,6,2	↔	↔	↑	↔
4,2,0	⇑	⇑	↓	↔	9,5,1	*	*	↓	↓
4,2,2	⇑	↑	↑	↑	6,6,6	⇑	↑	*	*
4,4,0	⇑	↔	↔	↔	8,8,0	↔	↔	↔	↔
4,4,2	↔	↔	↑	↑	9,7,1	*	*	↔	↔
6,2,2	↔	↔	↑	↔	9,7,3	*	*	↔	↔
4,4,4	↔	↔	*	*	8,8,4	↔	↔	*	*
6,4,0	↓	↓	↔	↔	10,6,4	↔	↔	*	*
6,4,2	↔	↔	↑	↔	9,7,3	*	*	↔	↔
8,2,0	↔	↔	↓	↑	8,6,6	*	*	↔	↔
8,2,2	↔	↔	↔	↔	8,8,6	↔	↔	↔	↔
6,6,2	↑	↔	↔	↔	10,10,0	↔	↔	*	*
8,4,0	↓	↓	↔	↔					

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large unit cell (624 atoms plus waters) and that the filling of Ca-sites is statistical in nature. Nevertheless an effective simulation cell was devised, based on the experimental structure and necessarily therefore close to the final stages of dehydration when the cation sites become (statistically) defined. The results demonstrate a progressive de-population of four types of hydration sites as the water content is reduced. Subtle changes in scattering intensity can be predicted and reasonably matched to those of X-ray/neutron diffraction experiments. Current success suggests it is now time to attempt to address the limitations of the present study: A more general simulation program, permitting unrestricted cation movement and restrained cage-flexing for a wide range of zeolites and interatomic potentials, is now planned. Also further experimental data on dehydration is desirable since clearly such a complex study-area requires a mix of experiment and judicious simulation. Such efforts are justifiable in view of the importance of zeolite dehydration, as part of the useful function of some zeolites (e.g. gas-drying) and also as a necessary stage in the synthesis of others.

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