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Comparison of proton field-cycling relaxometry and molecular dynamics simulations for proton–water surface dynamics in cement-based materials

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Abstract

Diffusion coefficients of water in hydrated cement pastes and mortars obtained from proton field cycling NMR spin lattice relaxation over three orders of magnitude in magnetic field strength are in good agreement with values from molecular dynamics simulations of water on the surface of tobermorite. The level of agreement from these two independent approaches provides mutual support for their validity.

Keywords: Cement; Hydrated cement; Water; Water at surfaces; Water dynamics; NMR relaxation; Molecular dynamics simulations

1. Introduction

In two companion papers, we show new results concerning the dynamics of water in cement obtained experimentally using NMR field cycling methods by some of us [1] and computationally using molecular dynamics (MD) simulations obtained by others of us [2]. This short report highlights the agreement between these completely independent results that – by mutual support – adds considerably to the value of both.

2. Methods and results

The NMR field cycling experiments reported in the first companion paper [1] probe the frequency dependence of the spin-lattice (T_1) relaxation rate of ^1H in pore water over more than three orders of magnitude from 10 kHz to 20 MHz. Samples were cement pastes prepared using OPC and white cement and mortar prepared using OPC, sand, silica fume, water and superplasticizer. The relaxation rate at a given frequency is the abundance-weighted average of that for ^1H in water molecules transiently adsorbed onto the pore surface and in the pore bulk. This average is dominated by the surface term, which is itself described by a model in which the transiently adsorbed ^1H undergoes two-dimensional translational diffusion across the pore surface. Repeated encounters with paramagnetic impurities (Fe^{3+}) embedded in the surface modulate the magnetic dipolar interaction, thus causing relaxation. The data obtained for samples hydrated for times from approximately 7 min to 100 h show a high degree of self-similarity. After appropriate renormalisation, the results can be fit to a single master curve from which two critical parameters can be evaluated: the pore surface residence time, τ_s, for hydrogens of transiently adsorbed water molecules and the mean pore surface diffusional jump time, τ_m. The former is of the order of a few μs and the latter of the order of 1 ns. It is this latter time, $\tau_m = 1$ ns, which can be compared to the MD results and that is central to the conclusions of this note.

The computer simulations in the second companion paper [2] use classical MD algorithms to calculate the structure, dynamics, and energetics of water molecules on the surface of tobermorite, which has long been considered a model for the C–S–H structure based on X-ray diffraction and spectroscopic data. The tobermorite model used was the 9 Å phase described by Merlino et al. [3]. The interatomic potentials were those of the CLAYFF [4] force field, which includes the SPC model [5]

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for the water molecules. This model is known to reproduce the bulk crystal structure of tobermorite and other cement-related phases quite well [6], and the calculations, the results of which are discussed here, focus on the dynamics of water molecules associated with silicate tetrahedra on the tobermorite surface (Fig. 1). They assume a fully polymerized drierkette chain structure, recognizing that the C–S–H of OPC and even cements with pozzolanic components, such as the mortars examined by NMR field cycling, is less polymerized. The X-ray crystal structure [3] does not specify the positions of the H atoms of Si–OH groups. To have the stoichiometric composition of $Ca_5Si_6O_{16}(OH)_2$, 50% of the non-bridging oxygens (NBOs) need to be $Si–O^-$ and 50% Si–OH. In the simulations, those NBOs pointing outward were assumed to be Si–OH, and those pointing parallel to layers $Si–O^-$ (Fig. 1). Diffusion coefficients were calculated from the root-mean-square displacement of the water molecules using standard methods.

Detailed analysis of the MD-computed trajectory shows that it is possible to distinguish effectively water molecules that spend most of their time within channels between the tetrahedral chains from those that reside above the surface defined by the exterior non-bridging oxygens of the bridging tetrahedra (Fig. 1). The former have diffusion coefficients of the order of $5\times10^{-11}\,m^2\,s^{-1}$, and the latter coefficients of about $6\times10^{-10}\,m^2\,s^{-1}$. Both of these values are significantly less than the value for bulk water in simulations using the same force field, $2.3\times10^{-9}\,m^2\,s^{-1}$. The average diffusion coefficient for all surface-associated H_2O molecules is of the order of $1\times10^{-10}\,m^2\,s^{-1}$.

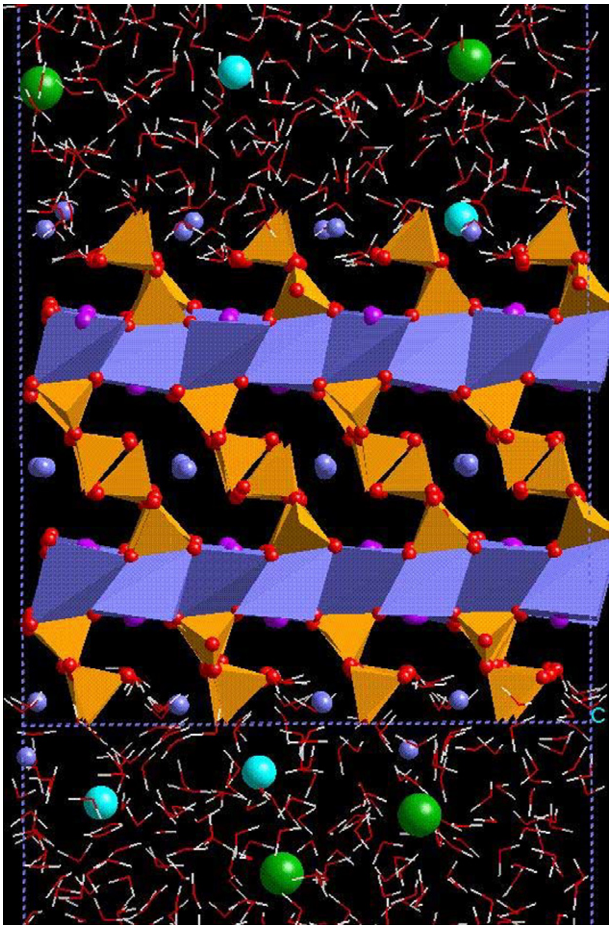

Fig. 1. MD simulation snapshot of the tobermorite, $Ca_5Si_6O_{16}(OH)_2$, interface with 0.25 M KCl aqueous solution. Dark small balls and octahedra – Ca atoms in two different structural positions within the "tobermorite 9 Å" structure [3]; one clearly sees the Si tetrahedra and O atoms of tobermorite; "v" – O of water; gray cylinders – H atoms of water; large balls – Cl^- ions; light intermediate-size balls – K^+ ions. Only parts of the solution layers close to the interfaces are shown above and below the crystal.

3. Discussion

A direct link between these two sets of results can be made as follows. The Einstein equation for diffusion in two dimensions is:

$$D=\frac{\langle r^2\rangle}{4t} \tag{1}$$

where D is the two-dimensional translational self-diffusion coefficient, $\langle r^2\rangle$ is the mean square displacement and t is the observation time. At a microscopic level, it is possible to replace $\langle r^2\rangle$ by $\langle r_m^2\rangle$ where r_m is the mean size of a molecular jump across the surface, and t by τ_m, the mean jump time is expected to be of the order of the size of a water molecule: ~3.2 Å. τ_m is calculated from the results of the fitting to the data of the NMR experiments: ~1 ns. Eq. (1) therefore predicts a value of D of $2.6\times10^{-11}\,m^2\,s^{-1}$. This value is circa 100 times smaller than the value for bulk water and but is in reasonably good agreement with the values found from the MD simulations of water on tobermorite. Given the assumptions that the molecular jump distance, which influences the diffusion coefficient as r_m^2, is the size of a water molecule, that ideal tobermorite is an appropriate model for C–S–H, and that the surface Si–O sites are protonated in a particular way, the agreement within a factor of 4 is remarkably good.

We suggest that this level of agreement between the experimental and MD-computed surface diffusion coefficients is more than coincidental and provides, in fact, strong circumstantial evidence for the underlying correctness of both the analysis of the experimental results and the MD simulations. It remains to be seen whether the universality of τ_m discovered across a broad range of cement materials and degrees of hydration is reflected in a range of model structures representative of those present in hydrated cement paste. Both the experiments and calculations are now readily undertaken, and the comparison can be readily made. Several cements can be measured at a range of hydration times and for various temperatures in a modest experimental period. Advanced computational algorithms with improved parallelization as well as large, multi-processor supercomputers are now readily available, allowing calculations of the type described here but for much larger systems and longer time. MD simulation runs at least several times longer than the pore surface residence time of $\tau_m\sim1$ ns are feasible, allowing a more detailed and more quantitative comparison between experiment and simulation in the near future.

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