SLOW DIFFUSIONAL DYNAMICS OF WATER IN CEMENT NANOPORES: MULTISCALE CHALLENGES FOR ATOMISTIC MODELING

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ABSTRACT

Molecular modeling of the properties of aqueous solutions confined in the nanopores and at the interfaces of cementitious materials is complicated by the significant structural and compositional heterogeneity of these phases and also by the fact that many of the important processes span several orders of magnitude both in time and in length. Here we present an attempt to quantify the diffusional dynamics of 0.25 M KCl aqueous solution in contact with a model C-S-H binding phase (tobermorite) on the basis of molecular dynamics computer simulations. At the (001) surface of tobermorite, two types of H_2O molecules can be effectively distinguished: the ones that spend most of their time within channels between the drierketten chains of silica on the tobermorite surface, and the more mobile adsorbed molecules that reside right above the interface. Within the channels, H_2O molecules donate H-bonds to both the bridging and non-bridging oxygens of the Si-tetrahedra as well as to other H_2O. Some of these molecules form particularly strong H-bonds persisting well over 100 ps, but many others undergo frequent librational motions and occasional diffusional jumps from one surface site to another. The average diffusion coefficients of the surface-associated H_2O molecules that spend most of their time in the channels and those that lie above the nominal interface differ by about one order of magnitude (D_{H2O}[internal]$=5.0\times10^{-11}$ m^2/s and D_{H2O}[external]$=6.0\times10^{-10}$ m_2/s, respectively). The average diffusion coefficient for all surface-associated H_2O molecules is about 1.0×10^{-10} m^2/s. All of these values are significantly less than the value of 2.3×10^{-9} m^2/s, characteristic of H_2O self-diffusion in bulk liquid water. The MD simulations provided an opportunity to further quantify these relatively slow diffusional motions of H_2O at the tobermorite interface on the longer time- and length-scale in terms of the Van Hove self-correlation function (VHSCF). The emerging picture is in surprisingly good agreement with available experimental data on the dynamics of surface-associated water in similar cement materials obtained by ^{1}H NMR [1,2].

1. Korb J.P., Monteilhet L., McDonald P.J., Mitchell J., Microstructure and texture of hydrated cement-based materials: A proton field cycling relaxometry approach. Cement and Concrete Research, 37, 2007, 295-302.
2. Korb J.P., NMR and nuclear spin relaxation of cement and concrete materialsCurrent Opinion in Colloid & Interface Science, 14, 2009, 192-202.