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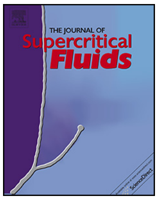

Effect of confinement on the hydration and diffusion of chloride at high temperatures

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ABSTRACT

Molecular dynamics simulations were conducted of a chloride ion in high temperature water confined between parallel iron hydroxide surfaces. Simulated temperatures were 567, 715, 814 and 913 K with densities ranging from 0.620 to 0.044 g cm^{-3}, and surfaces spaced at 10, 20 and 80 Å apart. Radial distribution functions, coordination numbers, diffusion coefficients, and density profiles across the gap are provided. Hydration numbers increased as the spacing of the surfaces increased and diffusion coefficients were seen to be lower than their values for chloride in bulk water. The chloride was observed to have a diffusion coefficient an order of magnitude less than that of water and showed less dependence on the spacing of the surfaces. The effect of confinement on the water structure was seen to disappear at 80 Å.

1. Introduction

Over the past two decades, scientific and engineering interest in high temperature and supercritical water has been growing quickly as new technologies are developed to harness the unique properties of water at extreme temperatures and pressures. It holds great promise in an ever broadening scope of applications ranging from materials processing, geological applications such as carbon dioxide sequestration and in the destruction of hazardous wastes [1–9]. Supercritical water is the heat exchange medium in the proposed GEN-IV Supercritical Water Cooled Reactor (SCWR) [10–17]. Before such technologies can be utilized, an understanding of the complex properties of water and aqueous solutions involving the nucleation and transport properties of corrosive species, such as oxygen, hydroxyl radicals and chloride ions at high temperatures, is required in order to develop a suitable chemistry control strategy for the SCWR [18–26]. However there is a lack of experimental data in the literature, particularly in the supercritical regime, resulting from the inherent difficulties of obtaining data at these extreme temperatures and pressures.

Much experimental work has been done to measure the corrosion rates of alloys and ceramic materials in an environment representative of that expected in a SCWR core [27]. Identifying a fuel cladding material is the most challenging materials issue as the fuel cladding is exposed to a combination of very high temperature and pressure plus the effects of irradiation on both the alloy and the coolant [28]. In spite of these challenges, significant progress has been made over the last decade in identifying and testing candidate fuel cladding alloys [19,29–39]. Most of the candidate alloys are stainless steels and therefore it is prudent to understand the behaviour of the $Fe(OH)_2$ layer likely to form on the outermost surfaces of the alloys under these conditions. The formation of low solubility oxide and hydroxide layers provides a barrier to diffusion of reactants from the coolant to and from the alloy surface that protects the stainless steel from further oxidation.

While corrosion in a SCWR is recognized as being a serious problem, the molecular level picture of local corrosion events and stress corrosion cracking (SCC) at high temperatures and low water coolant densities is missing. SCC has been a significant ageing degradation mechanism for major components of both pressurized water reactors (PWRs) and boiling water reactors (BWRs) and remains an important technical issue due to the constant increase in average age of existing nuclear power plants (NPPs). Staehle et al. [40] carried out a detailed assessment of current and past research and operating experience on SCC from early 1950s until the present and predicted that aging will result in significant changes in grain boundary chemistry and structure in SCWR in-core materials, leading to changes in SCC susceptibility. Testing during the US nuclear reheat development program in the 1960s found that chloride deposition eventually led to failure of austenitic stainless steel fuel cladding alloys by SCC, even with the best available efforts to remove chloride. While Unit 2 at the Beloyarsk NPP

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(a pressure-tube boiling water reactor with nuclear steam reheat channels) operated for many years with a typical chloride concentration of 25 μg kg^{-1} with no reported negative effects [17], laboratory tests showed that the stainless steel used for the channel elements (1Kh18N10T) cracked due to SCC after 144–1100 h of temperature and pressure cycling in an environment containing chloride. It was suggested that in situations where cracking was observed, deposition of moisture on the outer surface and subsequent evaporation may have led to chloride concentration on the surface. The effect of chloride on the surface films formed on candidate alloys under SCWR conditions is therefore of great importance, specifically whether chloride ions could disrupt the oxide (hydroxide) surface layer. As the mass transport characteristics of these ions play an important role in diffusion limited reaction rates, the diffusion coefficients of chloride along with their hydrated coordination numbers are also of relevance.

Viewed from the atomistic perspective, molecular dynamics (MD) simulations have now become a viable and time effective method for providing detailed information of the reaction dynamics of water and solvated species at high temperature and supercritical conditions. The simple point charge-extended (SPC/E) water model has been found to accurately reproduce physical and thermodynamic properties, including self-diffusion coefficients, over a wide range of temperatures and pressures [41,42].

The SPC/E model provides through the principle of corresponding states, accurate thermodynamic behaviour of water, particularly at high temperatures and in the supercritical region [43,44]. The more recently developed clay force field (CLAYFF) has been used successfully to model the interaction energies of amorphous solids, oxides, layered hydroxides and interfacial systems [3,45].

In a previous study we have examined the characteristics of supercritical water inside $Fe(OH)_2$ surfaces spaced 40 nm from one another [46]. This represented a large crack in the hydroxide corrosion surfaces produced by the oxidation of stainless steel by supercritical water. Surface layer densities were compared to the region in the gap as well as water adsorbed per surface OH group. Density profiles were provided along with the spatial configurations of the water molecules.

In this study MD simulations have been used to acquire diffusion coefficients, hydration numbers and density profiles of an infinitely dilute chloride ion in nanometer spaced $Fe(OH)_2$ surfaces at both high temperature, sub-critical water as well as at supercritical conditions. These smaller spacings, of 10, 20 and 80 Å, were simulated to mimic the environment expected at crack tips; as noted by Staehle [40], such an environment requires a molecular, not a continuum, analysis.

2. Simulation details

Two electrostatically neutral $Fe(OH)_2$ surfaces were created by cleaving the equilibrated brucite crystal structure, at 298 K and 1 bar pressure, along the interlayer (0 0 1) plane and the OH groups were left intact. The simulation cell thus contained two crystalline slabs comprised of two $Fe(OH)_2$ sheets each, consisting of a total of 72 Fe atoms and 144 OH groups per slab, with 36 OH groups, or equivalently, 36 unit cells of the brucite structure on each side of the gap exposed to the water. The slabs had the dimensions of 19.5917 × 16.9669 × 9.2082 Å, with an additional 10, 20 and 80 Å added in the z-direction to account for the gaps for each state point. Simulations were conducted at 567, 715, 814 and 913 K with the $Fe(OH)_2$ surfaces spaced at 10, 20 and 80 Å for each state point (see Table 1). The number of water molecules between the slabs was varied to yield the density of confined water ranging from 0.044 g cm^{-3} to 0.620 g cm^{-3}. The density estimates are based on formal geometric volume of confinement [47]. These state points mimic coolant conditions in the heat transport system of the SCWR.

The water molecules were initially placed in a random configuration between the surfaces, and the system was allowed to equilibrate for the first 50 ps. The equations of motion were integrated using the Verlet Leap-Frog algorithm with a 1 fs time step [48]. An NVT ensemble was used and the temperature was maintained using the Nose–Hoover thermostat [49]. Periodic boundary conditions were employed and the atomic pair interactions were calculated using the Lorentz–Berthelot mixing rules, with a spherical cut off radius set at half the smallest side cell length. Long-range Coulombic interactions were handled via the Ewald Summation method [48]. Intermediate averaging was performed every 1 ps and the simulations were allowed to proceed for a total time of 5 ns. For the infinitely dilute, bulk water simulations, 1 chloride and 500 waters were simulated, also with a 5 ns trajectory.

The SPC/E water potential used was taken from Berendsen et al. [50], the OH potential was taken from Wiener et al. [51], the CLAYFF force field for Fe was taken from Cygan et al. [45] and the chloride potential was taken from Smith and Dang [52].

The simulations were performed on the Shared Hierarchy Academic Resource Computing Network (SHARCNET), a consortium of Ontario universities and colleges operating a network of high performance computer clusters.

3. Results and discussion

3.1. Radial distribution functions

The radial distribution functions (RDFs) for chloride–water and water–water pairs are presented in Fig. 1(a)–(d), for both the 567 and 913 K bulk water–chloride system simulations as well as the 567 K, 10 Å and 913 K, 80 Å surface spacing configurations. They provide insights into the solvent molecules organization and hydrogen bonding within the gap. For example, the oxygen–hydrogen RDF in Fig. 1(d) reveals hydrogen (H—) bonding between H_2O molecules (i.e. the average number of hydrogen bonds O—H. . .O), while the chloride–hydrogen RDF shown in Fig. 1(b) reveals H— bonding between solvent and the solute.

In Fig. 1(a), the radial distribution functions for the Cl^-—O_W pairs for 567 and 913 K bulk water–chloride systems show the first coordinated shell of water molecules around the chloride ion to lie within a distance of 3 to 3.75 and 3 to 4.3 Å, respectively. The first peak corresponding to the highest probability to find the oxygen of the neighbouring water is observed at around 3.25 Å which remained relatively constant for all systems. It can be seen from the Cl^-—O_W RDF for the 567 K systems that the peak height increases when the water is confined between the $Fe(OH)_2$ surfaces spaced at 10 Å apart. Both RDFs for the bulk and 80 Å surface spacing are identical, suggesting there is little effect when the gap size reaches this distance. There is no appreciable ordering of waters beyond this distance as the curves are flat beyond this range. For the Cl^-—H_W pair distributions shown in Fig. 1(b), a distinct maximum corresponding to hydrogen bonded waters, is observed at around 2.3 Å that was observed in all of the systems, both bulk and confined. A second, less pronounced peak in probability is observed outwards to around 3.75 Å, which corresponds to hydrogen atoms of coordinated water molecules not directly bonded to Cl^- (i.e. reflecting H—O—H. . .Cl^- pairs). Beyond this second peak, the RDF falls off steadily with no indication of any ordering at distances greater than 4.75 Å. There is essentially no change seen in the Cl^-—H_W RDF's when moving from the bulk systems to those confined between the $Fe(OH)_2$.

From the O_W–O_W RDF's in Fig. 1(c), the coordination shell around water lies at a distance 2.5 to 3.5 Å. The peak maximum is located at 2.75 Å with no significant ordering beyond this first coordination