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Corrosion in the SCWR: Insights from Molecular Dynamics Simulations of the Supercritical Water - Iron Hydroxide Interface

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Summary

The adsorption properties of supercritical water confined between parallel iron (II) hydroxide surfaces were determined through molecular dynamics simulations. Simulations were conducted at temperatures and water densities typically found in the heat transport system of the supercritical water cooled nuclear reactor (SCWR). Surface water layer densities were compared to those of the bulk water. Adsorption coverage was calculated as a function of the number of waters per surface OH group. Images of the water molecules configurations are provided along with the density profile of the adsorption layer. The observed localized adsorption and surface clustering of supercritical water, would likely produce more localized corrosion phenomena in the water bearing components of the SCWR.

INTRODUCTION

Supercritical water holds promise as the thermodynamically favorable medium of both neutron moderator and heat transfer fluid in the prospective GEN-IV supercritical water cooled nuclear reactor (SCWR). The lack of cavitation and high thermodynamic efficiency of the homogeneous supercritical phase provide the advantages of increased thermal efficiency and simpler design. The extreme corrosive properties of water in the supercritical state, is of particular concern in the physical design and choice of material for the heat exchange infrastructure. Much experimental work has been done in measuring the corrosion rates of different alloys and ceramic materials in an oxidative supercritical water environment. Thus far there is no one novel material capable of withstanding the corrosive properties of such an environment [1-7]. Stainless steel is one potential candidate for the supercritical water bearing components of the GEN-IV SCWR and it is prudent to understand the behavior of the $Fe(OH)_2$ hydroxide layer formed under these conditions. In order to minimize the corrosion in the heat transport systems of the currently deployed pressurized water reactors (PWRs), oxygen scavenging species such as hydrogen gas and hydrazine are added to the coolant, as well as lithium hydroxide for alkalinity control. The formation and accumulation of the hydroxide (and oxide) layer serves as a corrosion inhibiting surface that will protect the stainless steel from further oxidation, inhibiting more catastrophic corrosion such as stress corrosion cracking. To understand how such a layer forms, the adsorption characteristics of water must first be determined. Whether the water exhibits full or partial wetting will indicate if the corrosion is a general, surface wide phenomenon, or if rust will form in a more localized scenario, typical of pitting corrosion.

In this study, molecular dynamics simulations have been used as a means of overcoming the experimental challenges of the harsh supercritical water environment. Adsorption characteristics of supercritical water on the $Fe(OH)_2$ surface are presented for 715, 814 and 913 K at different water densities. Surface water layer densities were obtained and compared to those of the bulk water.

SIMULATION DETAILS

Classical molecular dynamics techniques were used to obtain the equations of motion via Lagrangian based methods. The simple point charge extended (SPC/E) model of water was used as it provides accurate thermodynamic properties over a wide range of temperatures and pressures, particularly at high temperatures. The equation of state (EOS) obtained from the SPC/E model is in good agreement with experimental results and so affords an accurate method, through the corresponding states principle, of investigating water systems at elevated temperatures and pressures [8, 9]. The recently developed CLAYFF force field was used to obtain interaction parameters of the $Fe(OH)_2$ surfaces. 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 (001) plane, and the OH groups were left intact. The simulation cell thus contained two crystalline slabs (comprised of two $Fe(OH)_2$ sheets each), placed 400 Å apart, consisting of a total of 324 Fe atoms and 648 OH groups, with 81 OH groups on each side of the gap exposed to the water.

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.

RESULTS

The atomic density profile of the iron (II) hydroxide – supercritical water system is shown in Figure 1. In this figure it is evident that the majority of the adsorbed water molecules are positioned within a few Angstroms, to about 15 Å, from the edge of the iron hydroxide surface. Their dipoles are generally oriented away from the surface at approximately 45 degrees relative to the normal of the plane of the surface. Integration of the density profile yielded the actual surface and bulk water densities as well as the actual number of water molecules found at the surface, and the results are shown in Table 1.

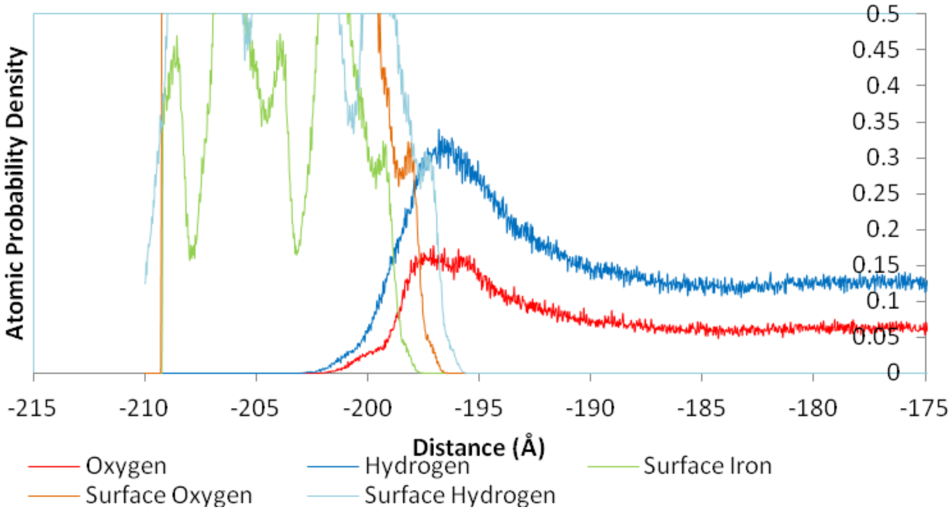

Figure 1: Atomic densities distribution at the supercritical water – iron (II) hydroxide interface at 715 K and total water density of 0.093 g cm^{-3}. Atomic density of the oxygen of the water molecule is shown in red, and hydrogen in blue. The region shown is a magnified view of the region at the left $Fe(OH)_2$ surface.

Temperature (K)	Bulk Water Density (g cm^{-3})	Surface Water Density (g cm^{-3})	Number of H_2O on Surface	Θ
715	0.075	0.262	107	1.31
814	0.055	0.153	63	0.77
913	0.045	0.094	38	0.47
913	0.036	0.079	33	0.40

Table 1: Simulation results showing the bulk and surface water densities, number of adsorbed waters and Θ, the number of adsorbed waters per exposed OH group.

Figure 2 shows the density of the surface layer relative to that of the bulk water. The relative density decreases from around 3.5 for the 715 K and 0.093 g/cc system down to 2.1 for the system at 913 K and 0.055 g/cc.

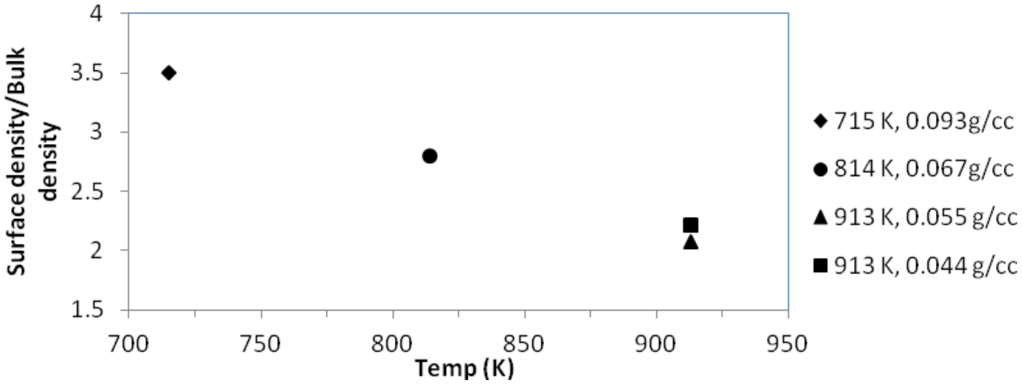

Figure 2: Density of the surface layer relative to bulk density for 715 K, 814 K, 913K at 25 MPa and varying desities.

Figure 3 shows typical configurations of water molecules near the surface at supercritical water conditions of 715 K and water density of 0.093 g cm^{-3}. From the images of water configurations, localized clustering is seen on the ionic surface at supercritical conditions, forming a higher (than bulk) density adsorption layer with a distinctly non uniform coverage. The presence of the surface regions with low and non uniform water coverage suggests that the gas phase chemical oxidation mechanism may dominate in low density supercritical water [10].

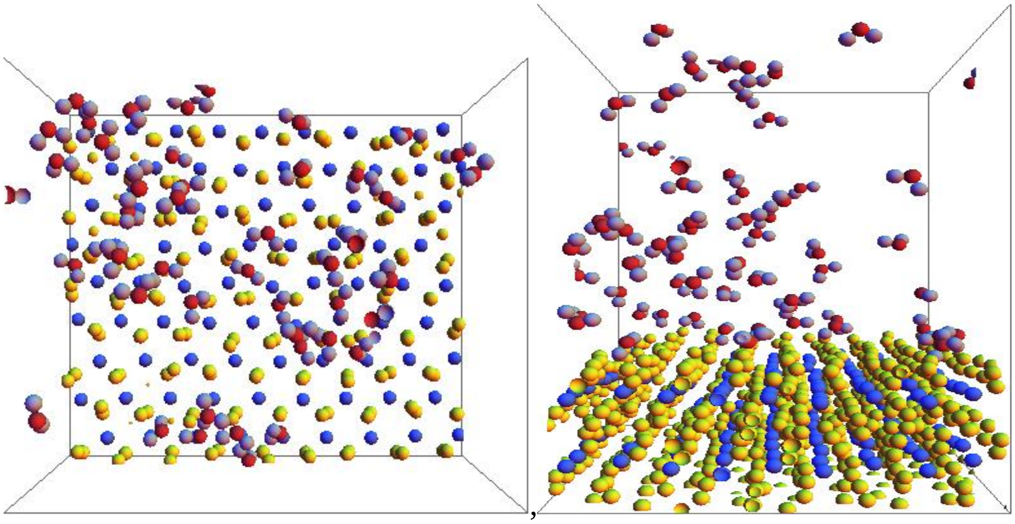

Figure 3: Typical configurations of water molecules near the surface region at supercritical water conditions, at 715 K and total water density of 0.093 g cm^{-3}. Surface oxygens are shown in yellow and surface irons are shown in dark blue. The oxygens of the water are shown in red and the hydrogens in violet. Left: top view. Right: side view.

The tendency of supercritical water to favor ion association implies that the hydroxide/oxide layer would be relatively stable, and any further metal oxidation would occur by reaction with oxygen, in localized areas resulting in pitting corrosion.

CONCLUSIONS

Molecular dynamics simulations show that the supercritical water will form a surface layer on the iron (II) hydroxide surface, with a density higher than that of the bulk water in the gap. It can be seen that most of the surface layer will accumulate within 15 Å from the surface and the adsorption occurs in small localized clusters. The gas phase chemical oxidation mechanism will likely dominate in the low density supercritical water environment, leading to pitting corrosion of the metal. Water may also accumulate in narrow fissures in the structure leading to more catastrophic stress corrosion cracking.

References:

[1] J. Bischoff, A.T Motta, Oxidation behaviour of ferritic-martensitic and ODS steels in supercritical water, Journal of Nuclear Materials 424 (2012) 261-276.

[2] X. Luo, R. Tang, C. Long, Z. Maio, Q. Peng, C. Li, Corrosion behaviour of austenitic and ferritic steels in supercritical water, Nuclear Engineering and Technology 40 (2007) 147-154.

[3] G.S. Was, P. Ampornrat, G. Gupta S. Teysseyre, E.A. West, Corrosion and stress corrosion cracking in supercritical water, Journal of Nuclear Materials 371 (2007) 176-201.

[4] P. Kritzer, Corrosion in high temperature and supercritical water an aqueous solutions: a review, Journal of Supercritical Fluids 29 (2004) 1-29.

[5] P. Kritzer, N. Boukis, E. Dinjus, The corrosion of alloy 625 (NiCr22Mo9Nb; 2.4856) in high temperature, high pressure aqueous solutions of phosphoric acid and oxygen, corrosion at sub and supercritical temperatures, Materials and Corrosion 49 (1998) 831-839.

[6] P. Kritzer, N. Boukis, E. Dinjus, Factors controlling corrosion in high temperature aqueous solutions: contributions to the dissociation and solubility data influencing corrosion processes, Journal of Supercritical Fluids 15 (1999) 205-227.

[7] C. Sun, R. Hui, W. Qu, S. Yick, Progress in corrosion resistant materials for supercritical water, Corrosion Science 51 (2009) 2508-523.

[8] M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids,* (Clarendon Press, NY, USA, 1989).

[9] A. Plugatyr, I.M. Svishchev, Accurate thermodynamic and dielectric equations of state for high temperature simulated water, Fluid Phase Equilibria 227 (2009) 145-151.

[10] D.A. Guzonas, W.G. Cook, Cycle chemistry and its effect on materials in a supercritical water-cooled reactor: A synthesis of current understanding, Corrosion Science 65 (2012) 48-66.