Interaction of nitrite ions with hydrated portlandite surfaces: Atomistic computer simulation study

Tararushkin E V[@] and Pisarev V V

National Research University Higher School of Economics, Myasnitskaya 20, Moscow 101000, Russia

[@] etararushkin@hse.ru

The nitrite admixtures in cement and concrete are used as corrosion inhibitors for steel reinforcement [1]. The characterization of the protective properties should account for the decrease of the concentration of free NO_2^- in the pores of cement concretes due to their adsorption. We study adsorption of sodium and nitrite ions of $NaNO_2$ aqueous solution on a portlandite surface using classical molecular dynamics simulation approach. The new parameterization [2] to model the hydrated NO_2^- ions in combination with the recently upgraded ClayFF force field (ClayFF–MOH) [3] for the structure of portlandite were used.

The simulations show that despite the formation of a well structured layer of water on the portlandite (001) crystal surface, NO_2^- ions can be strongly adsorbed. The nitrite adsorption is primarily due to the formation of hydrogen bonds between the structural hydroxyls on the portlandite surface and both the nitrogen and oxygen atoms of the NO_2^- ions. Due to that, the ions do not form surface adsorption complexes with a single well defined structure, but can assume various coordinations. However, in all cases the adsorbed ions do not show significant surface diffusion. Moreover, we demonstrate that the nitrite ions can be adsorbed both near the previously-adsorbed hydrated Na^+ ions as surface ion pairs, but also separately from the cations.

[1] Rosemberg J and Gaidis J 1979 *Mater. Perform* **18(11)** 45–48
[2] Tararushkin E 2022 *Russ. J. Phys. Chem. A* **96(7)** 1439–1444
[3] Cygan R, Greathouse J and Kalinichev A G 2021 *J. Phys. Chem. C.* **121** 17573–17589