



Organic Inhibitors to Prevent Chloride-Induced Corrosion in Concrete: Atomistic Simulations of Triethylenetetramine-Based Inhibitor Film

Giuseppina Raffaini,* Michelina Catauro, Fabio Ganazzoli, Fabio Bolzoni, and Marco Ormellese

Inhibitors are largely used to prevent chloride-induced corrosion in reinforced concrete structures thanks to both a barrier effect on chloride penetration and a competition with the adsorption of the inhibitor. The interaction mechanisms between passive film on carbon steel, the inhibitor molecule, and chlorides still require deeper understanding. Theoretical studies based on molecular mechanics (MM) and molecular dynamics (MD) methods can be useful to better understand the passive film formation and its interaction with chlorides. In this work, the interaction between a triethylenetetramine (TETA) inhibitor film on γ -FeOOH surface and chlorides is studied using MD methods. After MM optimization in the initial adsorption stage, some chlorides are close to protective TETA film. After MD run at room temperature effectively, chlorides remain close to the protective film. In order to have an effective barrier on chloride attack, the metal oxide must remain wholly covered by the protective film. The TETA film well covers the lepidocrocite surface but cannot kinetically efficiently prevent the chloride-induced corrosion compared to other organic films exposing COO^- groups because it does not exert any repulsion to chlorides.

substituents, and moreover, they are also able to develop a repulsive action towards chloride ions. Thanks to the repulsive interactions this kind of inhibitors can avoid chlorides to be in contact with the carbon steel passive layer.^[13] Interestingly, also alkyl chains or voluminous substituent groups, which form a physical barrier, can keep away chloride ions from concrete surface.^[14]

Molecular mechanics (MM) and molecular dynamics (MD) methods are useful theoretical methods for understanding possible protective film formation and the noncovalent interactions with chloride ions.^[5–9] In a previous work, organic inhibitors adsorbed on lepidocrocite γ -FeOOH surface were studied, comparing theoretical results with experimental data.^[1] In our research group, the film formation of inhibitors based on sodium tartrate, sodium benzoate, sodium glutamate, dimethylethanolamine, and triethylenetetramine was recently

theoretically studied and experimentally investigated.^[5] Then, the theoretical noncovalent interactions between these films and chloride ions using MM theoretical methods were studied only in the initial adsorption stage.^[6] In this paper only, the interaction after MD simulation with chlorides and the film based on triethylenetetramine (TETA, molecular structure $\text{NH}_2\text{-CH}_2\text{CH}_2\text{-(NHCH}_2\text{CH}_2)_2\text{-NH}_2$) is reported, in order to better understand the efficiency of the physical barrier to chlorides on lepidocrocite (γ -FeOOH) passive surface at room temperature during time. In fact, it is always more and more important not only to study the stability of the film well adsorbed on lepidocrocite surface and its possible repulsion against chlorides, but also the capability to repel the chloride ions, responsible of the corrosion process initiation, for a long time, thus achieving a permanent effect. The TETA film covering lepidocrocite (γ -FeOOH) surface weakly attracts the chlorides, hence it is not an effective corrosion inhibitor, as observed in practice.^[5]

1. Introduction

Corrosion of steel embedded in concrete is one of the major causes of the degradation of reinforced concrete structures. The study of chloride-induced corrosion inhibitors is important in order to prevent this corrosion process.^[1–9] The development of new organic corrosion inhibitors is based on compounds containing nitrogen, oxygen, and sulfur atoms.^[10–12] The adsorption is favorable thanks to specific functional groups that can act on two fronts: at first they can promote the adsorption process on concrete surface through the negative charge localization on the oxygen atoms and on carboxylic groups or negatively charged

G. Raffaini, F. Ganazzoli, F. Bolzoni, M. Ormellese
Dipartimento di Chimica
Materiali e Ingegneria Chimica “G. Natta” Politecnico di Milano
piazza Leonardo da Vinci 32, Milano 20131, Italy
E-mail: giuseppina.raffaini@polimi.it

M. Catauro
Department of Engineering
University of Campania “Luigi Vanvitelli,”
Via Roma 29, Aversa I-813031, Italy

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2. Molecular Mechanics and Molecular Dynamics Simulations

The simulation protocol adopted here to model the surface physisorption is reported in previous works.^[15–17] The study of

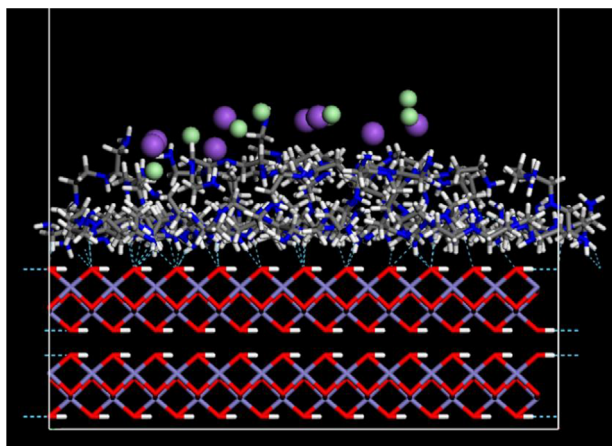


Figure 1. Optimized geometry obtained after initial MM calculations considering eight Na⁺ ions, in violet, and eight Cl⁻ ions, in green, near the triethylenetetramine film. The carbon atoms are in grey, the nitrogen's in blue, the oxygens in red, the iron atoms light purple, and the hydrogens in white.

the interactions between a lepidocrocite (γ -FeOOH) passive surface and some Na⁺ cations and Cl⁻ anions was carried out through atomistic simulations based on MM and MD theoretical methods with the Materials Studio package (Accelrys Inc.) and the COMPASS force field^[18,19] in vacuo using periodic boundary conditions. The lepidocrocite γ -FeOOH surface, in particular the (0 1 0) crystallographic face, which exposes hydroxyl groups, has the size of 39.96 Å × 38.70 Å with the b axis perpendicular to the surface.^[5] After energy minimizations with respect to all variables (atomic coordinates) performed with the conjugate gradient algorithm up to an energy gradient lower

than 4×10^{-3} kJ mol⁻¹ Å⁻¹, eight Na⁺ ions, shown in violet in **Figure 1**, and eight Cl⁻ ions, shown in green in **Figure 1**, are near the TETA film. The protective TETA film just studied in previous work^[5] is formed by 36 inhibitor molecules, and it is well adsorbed on the solid surface forming also hydrogen bonds with the surface as indicated by dotted lines light blue in **Figure 1**.

The simulation protocol proposed in previous work^[5] was adopted to model the organic film on the lepidocrocite solid surface. Using MD methods, it will be important to better understand the distribution of chloride ions and their possible interactions, not only near the organic film but also close to the lepidocrocite substrate if the latter becomes eventually exposed. After initial energy minimization performed with the conjugate gradient algorithm up to an energy gradient lower than 4×10^{-3} kJ mol⁻¹ Å⁻¹, in this work, the MD run lasting 500 ps were performed at constant temperature ($T = 300\text{K}$) in order to study the mobility of the chloride ions interacting with the protective film. **Figure 2** reports the final optimized conformation assumed by the system at equilibrium after the MD run.

Interestingly, if the surface cannot be covered by protective film, the chlorides attack the solid surface as reported at left in **Figure 2** by two anions near the bar surface of lepidocrocite γ -FeOOH. Furthermore, it will be important to note at the end of the MD simulations that four chloride anions and only one Na⁺ cation is dispersed on the organic inhibitor film, near the lepidocrocite surface but not in real contact with it (see especially the top right view in **Figure 2**). The TETA film dynamically well covers the surface of the γ -FeOOH surface forming hydrogen bonds and can form a protective film to prevent the adhesion of chlorides. Importantly, this kind of inhibitor is not, however, an efficient inhibitor because the chloride ions are anyway close to the film and are not electrostatically repelled from the solid surface of the lepidocrocite. It will always be important to have

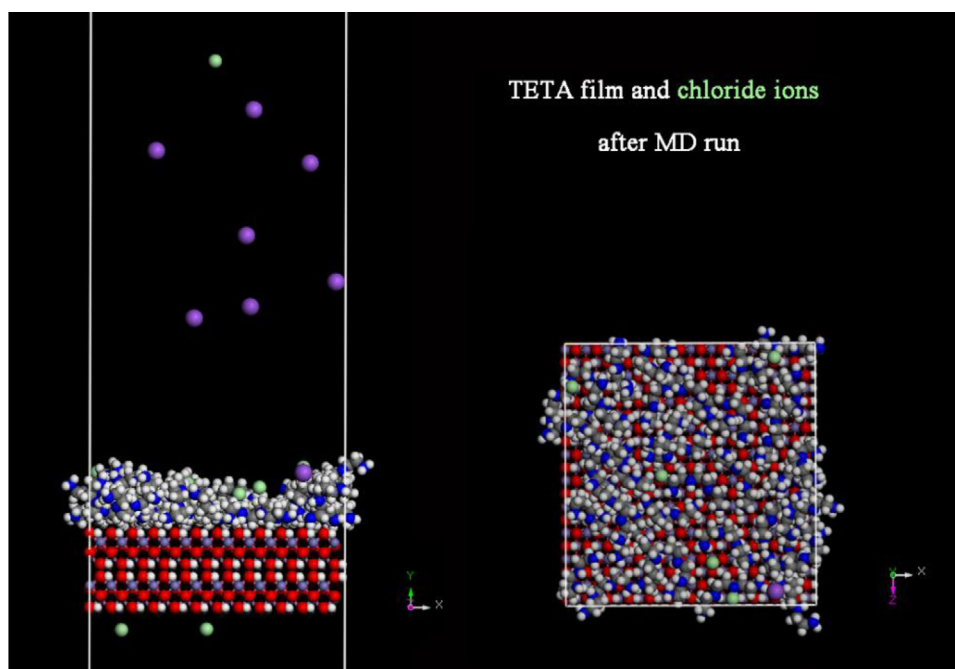


Figure 2. Optimized geometry obtained after MD run calculations considering eight Na⁺ ions, and eight Cl⁻ ions (see color code in **Figure 1**) near the TETA film, adsorbed on the γ -FeOOH surface, side view at left, and top view at right.

the protective film both that fully covers the whole lepidocrocite surface exposed to chlorides, and that can prevent the contact of chloride ions with the lepidocrocite surface.

3. Conclusion

The interaction between the TETA organic inhibitor film adsorbed on a fully covered model lepidocrocite surface in the presence of chloride ions near the protective film was studied using MD methods in order to investigate the noncovalent interactions and the mobility of chlorides near the film at room temperature. During the MD run, the chloride ions interact with the exposed atoms of the inhibitor film, while the Na⁺ cations are always distant due to electrostatic repulsion by the groups exposed by film. Hence, the TETA film covers the surface forming a stable protective substrate thanks to many hydrogen bonds with the lepidocrocite γ -FeOOH surface. However, this film cannot efficiently keep the chloride ions away from the exposed surface. Therefore, they cannot prevent the chloride-induced corrosion in reinforced concrete structures, unlike what is experimentally found by inhibitor films that expose charged carboxylated groups. The study of the same noncovalent interactions in presence of explicit water molecules that can influence the mobility of chloride ions near the concrete surface is work in progress and it will be published in a future paper.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chloride-induced corrosion, concrete, corrosion inhibitors, corrosion protection, molecular dynamics, organic film

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