Modeling the chloride-induced corrosion initiation of steel rebar in concrete

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Abstract: Corrosion of rebar in concrete is one of the most prominent durability problems in reinforced concrete, especially where de-icing or seawater salts come into contact with the structures. Previous electrochemical and microscopic investigations have shown that local crevices between the mill scale and the underlying steel surface accelerate the corrosion initiation of rebar in concrete. Steel depassivation in concrete depends highly on the chloride-to-hydroxide ratio of the pore solution. The differential equations for the transport of hydroxide, chloride and seven other ionic species in the concrete pore solution, coupled with the electrochemical reactions on the steel surface, were numerically modeled in simulated crevices that exist between the mill scale and the steel surface using the COMSOL finite element software. The numerical results verify that the mill-scale on the surface of rebar enhances the initiation of corrosion which is also in agreement with experimental findings

Keywords: Corrosion, Modeling, Steel rebar, Concrete, COMSOL

1. Introduction

Corrosion of rebar is one of the most prominent durability problems in reinforced concrete, especially where de-icing or seawater salts come into contact with structures. When steel is placed in concrete, a protective passive oxide film forms on its surface due to the alkaline environment provided by the concrete pore solution. This oxide film is thermodynamically stable and protects the steel against corrosion. It is established that chloride concentrations beyond a threshold can cause the passive film to lose its protective properties and lead to depassivation [2]. This threshold is typically defined in terms of the chloride-to-hydroxyl concentration ratio (Cl^-/OH^-) since the alkalinity (i.e. OH^- concentration) is also known to be a key factor in the depassivation process [3]. Unfortunately, the reported values of threshold Cl^-/OH^- show significant variability. This paper hypothesizes that one of the reasons for this variability is the presence of mill scale on the rebar surface.

The cooling process during the production of steel results in the formation of an insoluble oxide layer that is approximately 50μm thick, crystalline in nature but poorly and non-uniformly attached to the rebar surface [1]. This layer is referred to as mill scale, and it exists on rebar that is used in the construction of reinforced concrete structures. Electrochemical and microscopic studies have shown that the presence of mill scale causes the passive film on the rebar surface to form non-uniformly with imperfections [4]. These imperfections include cracks that link the free surface of the oxide layer and the underlying steel, and crevices along the interface between the mill scale and the steel [4]. These cracks and crevices are implicated in the depassivation of rebar in concrete.

In this paper, the role of mill scale cracks and crevices on Cl^-/OH^- near the rebar surface is studied numerically using the COMSOL finite element software. The differential equations for the transport of hydroxide, chloride and seven other species in the concrete pore solution, coupled with the electrochemical reactions on the steel surface, were solved using the finite element technique. The implications of the depassivation of steel in concrete are discussed.

2. Numerical Modeling Using COMSOL Multiphysics

In this study, it was assumed that the simulated concrete pore solution (pH = 12.5) was saturated with $Ca(OH)_2$. Figure 1 shows the two-dimensional domain representing a crack that links the free surface of the oxide layer and the underlying steel, and a crevice along the interface between the mill scale and the steel. In this figure, boundary 1 is the opening of the mill
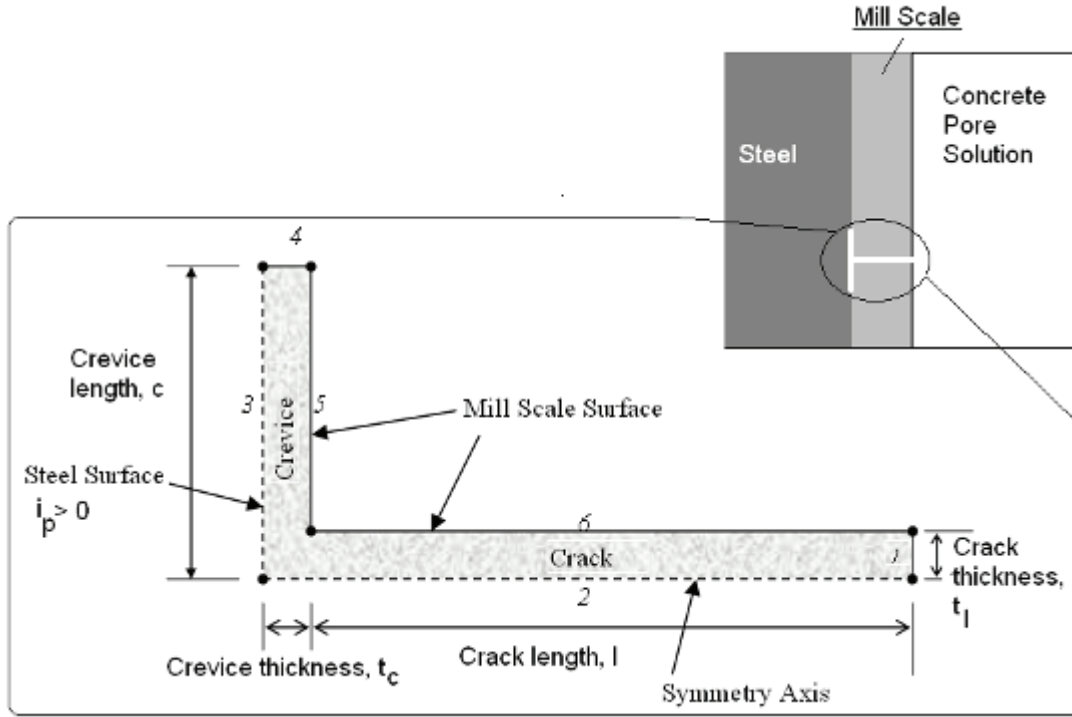
Figure 1: The domain and boundaries of the crevice area between the surface of steel and mill scale. The analysis presented in this paper was carried out using the following dimensions: $c = 5 \times 10^{-4}$ m, $t_c = 1 \times 10^{-6}$ m, $l = 5 \times 10^{-5}$ m, $t_l = 5 \times 10^{-8}$ m.

scale crack to the concrete pore solution; boundary 2 is the axis of symmetry; boundary 3 is the steel surface; and boundaries 4, 5 and 6 represent the mill scale surfaces. Initially, the pore solution inside the crack and crevice were not contaminated with chloride, but the bulk concrete pore solution contained chloride. A passive current density (i_p) of 0.01 A/m^2 was assumed on the steel surface to simulate iron dissolution and hydroxyl production in the passive state.

The transport of nine species within the domain was modeled using the extended Nernst-Planck equation [5] that incorporates ionic diffusion, electrical migration and chemical activity processes:

$$\frac{\partial c_{i_s}}{\partial t} + \frac{\partial c_i}{\partial t} + \nabla \left(\underbrace{- D_i \nabla c_i}_{Diffusion} - \underbrace{\frac{D_i z_i F}{RT} c_i \nabla \phi}_{Electrical\,Migration} - \underbrace{D_i c_i \nabla (\ln \gamma_i)}_{Chemical\,Activity} \right) = 0 \tag{1}$$

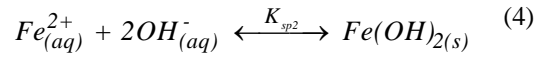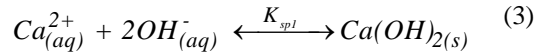where c_i is the concentration of species in the ionic state (i.e. OH$^-$, Fe^{2+}, Ca^{2+}, Cl$^-$, Na$^+$), c_{is} is the concentration of species in the solid (i.e. the components Fe$_{(s)}$, Ca$_{(s)}$ and OH$_{(s)}$ as they exist in Ca(OH)$_{2(s)}$ and Fe(OH)$_{2(s)}$) or the gaseous state (i.e. O$_{2(g)}$), $\nabla \phi$ is the potential gradient, γ_i is the chemical activity for the various ionic species in water, D_i is the diffusion coefficient for the ionic species, R is the ideal gas constant (8.3143 J/mol/K), T is temperature (298 K) and t is time.

The electrical neutrality of the system was guaranteed with Poisson's equation such that

$$\nabla^2\phi + \frac{F}{\varepsilon}\sum_{i=1}^{N} z_i c_i = 0 \qquad (2)$$

where N refers to the total number of ionic species, F is Faraday's constant (96488 C/mol), ε is the dielectric constant of the medium, z_i is the charge of species i [5].

The following reversible chemical reactions were assumed to occur in the pore solution [6]:

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \xleftrightarrow{K_{sp1}} Ca(OH)_{2(s)} \qquad (3)$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \xleftrightarrow{K_{sp2}} Fe(OH)_{2(s)} \qquad (4)$$

These require that the following two solubility relations should be also satisfied simultaneously in the domain:

$$\gamma_{Ca}[Ca^{2+}]\,\gamma_{OH}^2\,[OH^-]^2 = Ksp_1 \qquad (5)$$

$$\gamma_{Fe}\,[Fe^{2+}]\,\gamma_{OH}^2[OH^-]^2 = Ksp_2 \qquad (6)$$

where Ksp_1 (5500 mol^3/m^9) and Ksp_2 (4.87x10^{-8} mol^3/m^9). Finally, the following additional relation ensures stoichiometric balance between calcium hydroxide and iron hydroxide compounds:

$$2\{[Fe]_{(s)} + [Ca]_{(s)}\} = [OH]_{(s)} \qquad (7)$$

Using the finite element technique, Equations (1), (2), (5), (6) and (7) were solved for the concentrations of nine species over time. The initial conditions of these equations were defined by the initial concentrations of species in the concrete pore solution before chloride contamination.

3. Results and Discussions

In Fig.2, Cl$^-$/OH$^-$ is shown along the boundary 2 and 3 for different levels of chloride contamination in the bulk concrete pore solution after the steady-state conditions are reached. The dimensions of the domain for which the analysis was carried out are provided in Fig.1.

The results indicate that Cl$^-$/OH$^-$ increases in the mill scale crack (boundary 2) and along the crevice between the mill scale and underlying steel (boundary 3). For example, in the case of 0.5 M chloride contamination, the ratio increases from 13 in the bulk solution to 26 in the crevice near the steel surface. The change of Cl$^-$/OH$^-$ within the crevice becomes larger as the chloride contamination of the bulk pore solution increases.

Although, the details are not presented here, the main reason for such a change in Cl$^-$/OH$^-$ can be briefly explained as follows: Due to the cathodic reaction on the steel surface, oxygen in the crevice decreases over time, and this leads to reduced levels of hydroxyl production. In parallel, iron ions that are dissolved in the pore solution react with hydroxyl to form the iron hydroxide (Eq.4). This further decreases the hydroxyl concentration inside the crack and crevice. The reduced levels of hydroxyl disturb the electrical neutrality balance and chloride ions flow from the bulk solution into the crevice to compensate. As a result, the Cl$^-$/OH$^-$ becomes larger inside the crevice compared to the levels in the bulk concrete pore solution, and thus these crevices associated with the mill scale are more susceptible to depassivation.

It is suggested that the variability of Cl$^-$/OH$^-$ threshold values reported in the literature can be partly explained by the variability in the mill scale found on rebar resulting from the variability in manufacturing.

4. Conclusions

Numerical results of this study showed that Cl$^-$/OH$^-$ in the mill scale crack and along the crevice between the mill scale and underlying steel is larger than in the bulk concrete pore solution. Therefore, the crevices associated with the mill scale are more susceptible to depassivation.

5. References

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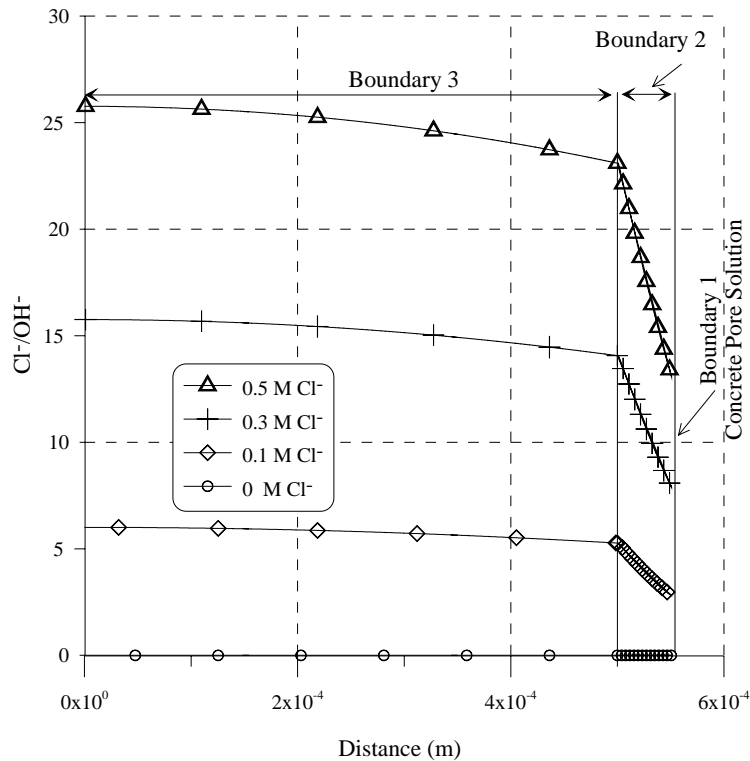
Figure 2: Chloride-to-hydroxyl ratio along boundaries 2 and 3 at different levels of chloride of bulk solution.

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