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

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Outline:

- Introduction
- Modeling: Chemistry of Concrete Pore Solution
- Modeling: Transport of Ionic Species
- Modeling: Domain and Boundary Conditions
- Results
- Conclusion

Introduction:

- Generally-stable passive film formed on the steel surface under high alkaline conditions protects the steel against corrosion.

- Once passive film is destroyed (depassivation), corrosion will start.

- Mill-scale is an insoluble oxide layer that forms during steel production.

- It is approximately 50 μm thick, crystalline in nature but poorly and non-uniformly attached to the rebar surface.

Mill-scale   Concrete

Steel

e^- O_2, H_2O

OH^-

Fe ⟶ Fe^{2+}

Passive oxide layer

Passive oxide layer
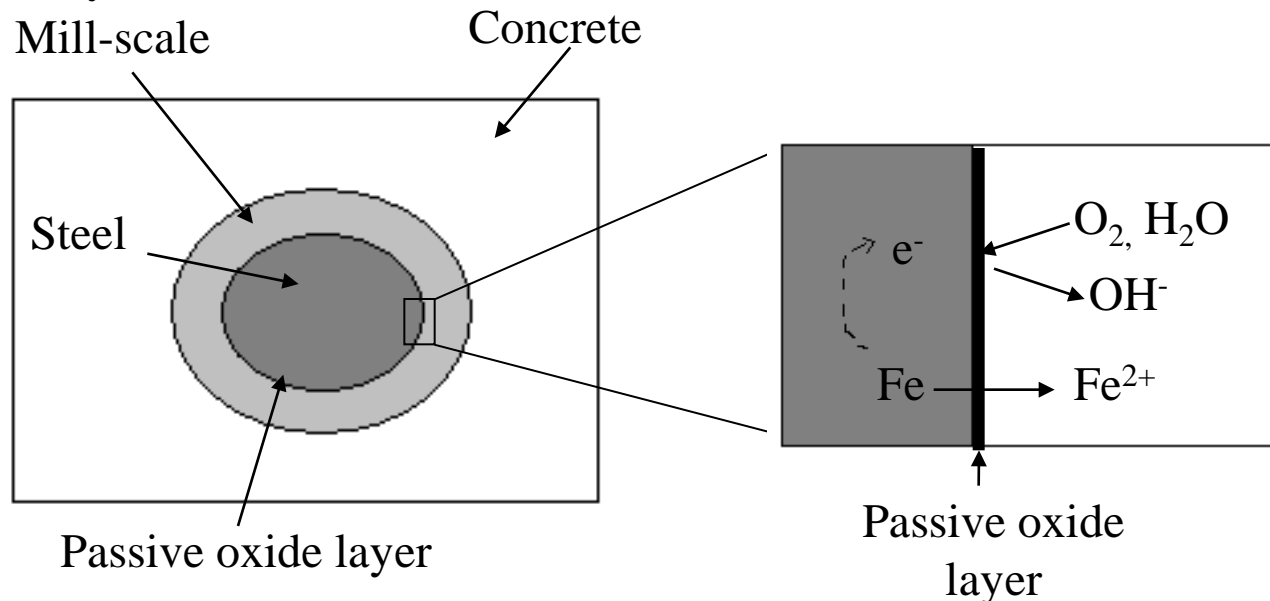
Introduction:

- ☐ Corrosion preferentially initiates in the mill-scale crevices.

- ☐ Objective of this research is to explain the changes in chemistry of pore solution inside mill-scale crevices.

- ☐ Specifically to investigate the changes in the Cl^-/OH^-, which is an indicator of depassivation process.

Passive oxide layer   mill scale
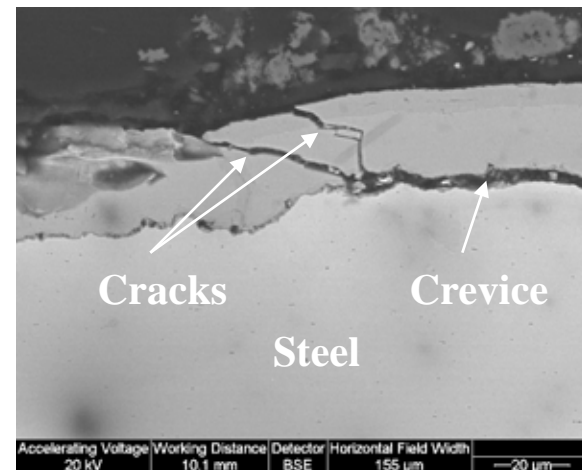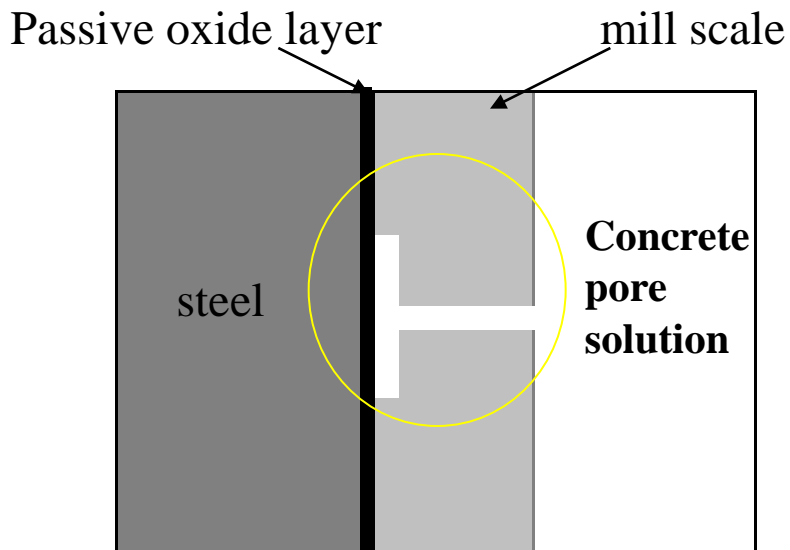
Modeling: Chemistry of Concrete Pore Solution
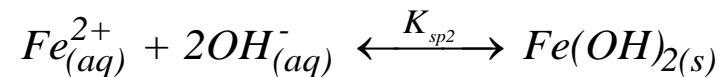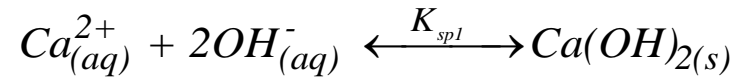
- pH of concrete varies between 12.5 and 13.5.
- Solution 1(pH=12.5): 9 species were considered in concrete pore solution:
  - OH^-, $OH_{(s)}$, Fe^{2+}, $Fe_{(s)}$, Ca^{2+}, $Ca_{(s)}$, Cl^-, Na^+, O_2

- Solution 2 (pH=13.5): 10 species were considered in concrete pore solution:
  - OH^-, $OH_{(s)}$, Fe^{2+}, $Fe_{(s)}$, Ca^{2+}, $Ca_{(s)}$, Cl^-, Na^+, K^+, O_2

Modeling: Chemistry of Concrete Pore Solution

☐ Reversible chemical reactions:

$$Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \xleftarrow{\quad K_{sp1} \quad} Ca(OH)_{2(s)}$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \xleftarrow{\quad K_{sp2} \quad} Fe(OH)_{2(s)}$$

■ Solubility relations:

$$\gamma_{Ca}[Ca^{2+}] \, \gamma_{OH}^2 \, [OH^-]^2 = Ksp1$$

$$\gamma_{Fe} \, [Fe^{2+}] \, \gamma_{OH}^2[OH^-]^2 = Ksp2$$

■ $Ca(OH)_{2(s)}$ and $Fe(OH)_{2(s)}$ relation:

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

Modeling: Transport of Ionic Species

□ Nernst-Planck differential equation

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

□ Poisson's equation (electroneutrality)

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

c_i = concentration of species in the ionic state (mol/m^3)
c_{is} = concentration of species in the solid state (mol/m^3)
ϕ = potential gradient (V)
γ_i = chemical activity coefficient
D_i = diffusion coefficient (m^2/s)
z_i = valence of the species
R = ideal gas constant (8.3143 J/mol/K)
T = constant temperature (298K)
F = Faraday's constant (96488 C/mol)
ε = dielectric constant (7.092 x $^{-10}$ C^2/N/m^2)

Modeling: Transport of Ionic Species

□ Modified Davies equation (Activity calculation)

$$\ln \gamma_i = -\frac{Az_i^2 \sqrt{I}}{1 + a_i B \sqrt{I}} + \frac{(0.2 - 4.17 \times 10^{-5} I) A z_i^2 I}{\sqrt{1000}}$$

where a_i is the radii of the ions, A and B are temperature dependent parameters, and I is the ionic strength of the solution
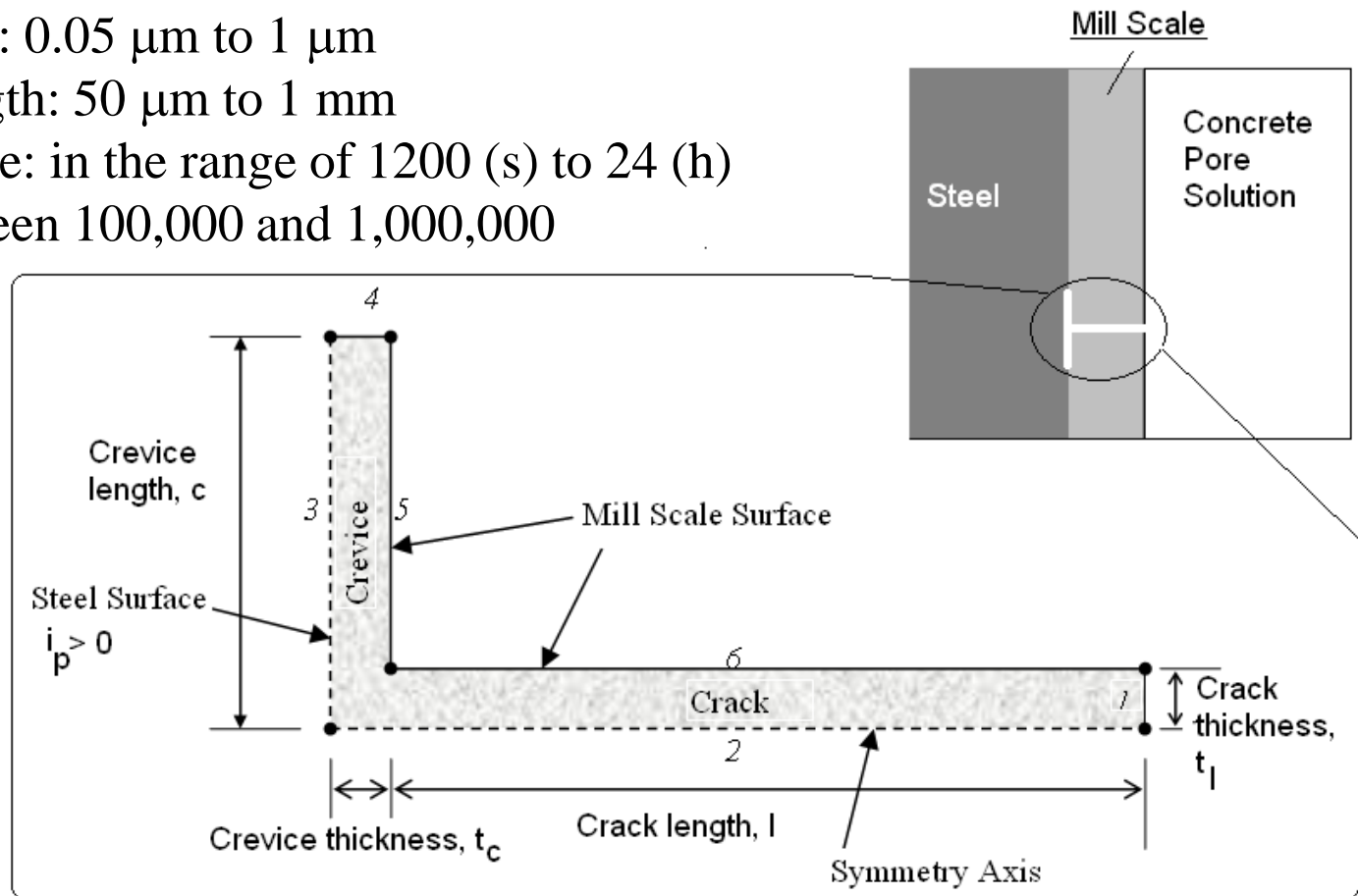
$$A = \frac{\sqrt{2} F^2 e_0}{8\pi (\varepsilon RT)^{3/2}} \qquad B = \sqrt{\frac{2F^2}{\varepsilon RT}} \qquad I = 0.5 \sum_{i=1}^{N} z_i^2 c_i$$

□ Transient nonlinear finite element model was solved using COMSOL software

Modeling: Domain and Boundary Conditions

- Crack width: 0.05 μm to 1 μm
- Crevice length: 50 μm to 1 mm
- Solution time: in the range of 1200 (s) to 24 (h)
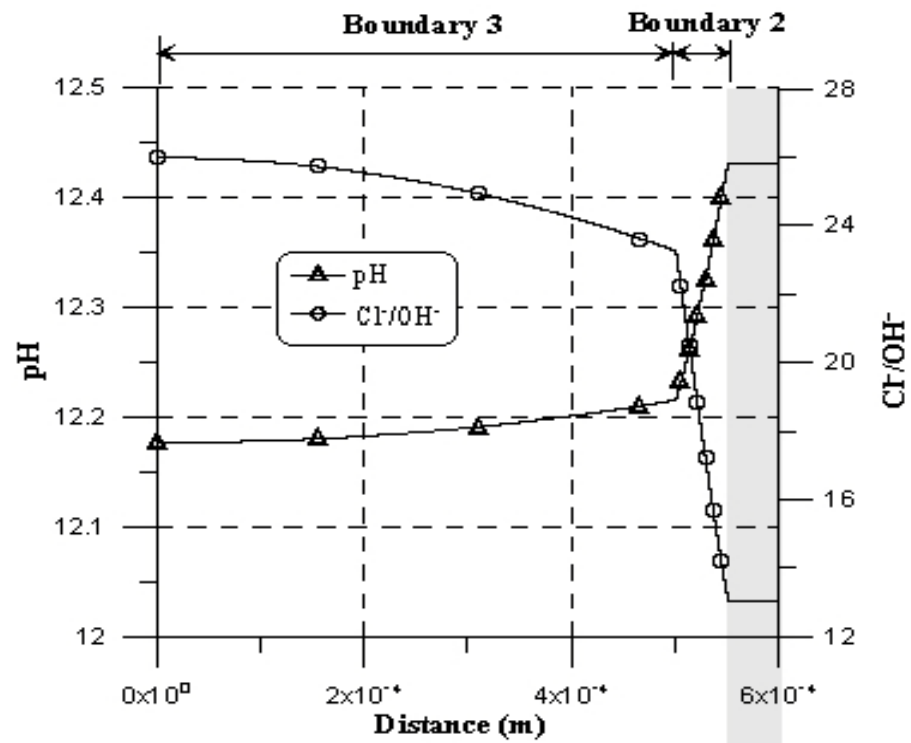- DOF: between 100,000 and 1,000,000

Results – Oxygen, Chloride

- pH = 12.5, passive current density of 0.01 A/m^2, 0.5 M chloride in bulk solution
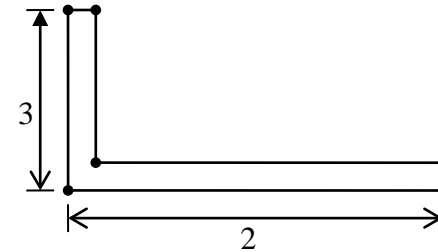
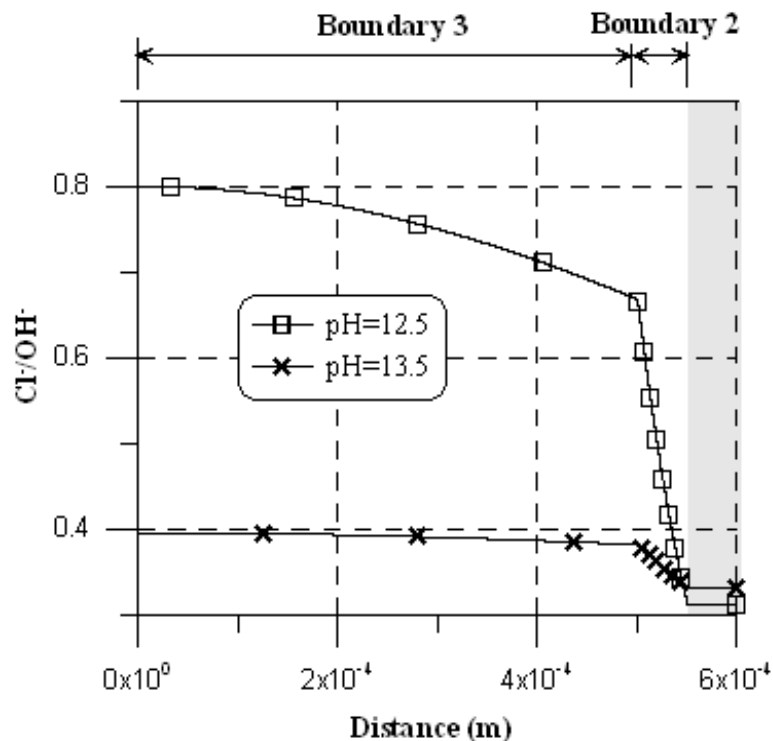- crack width = 0.1 µm, crevice length = 1 mm
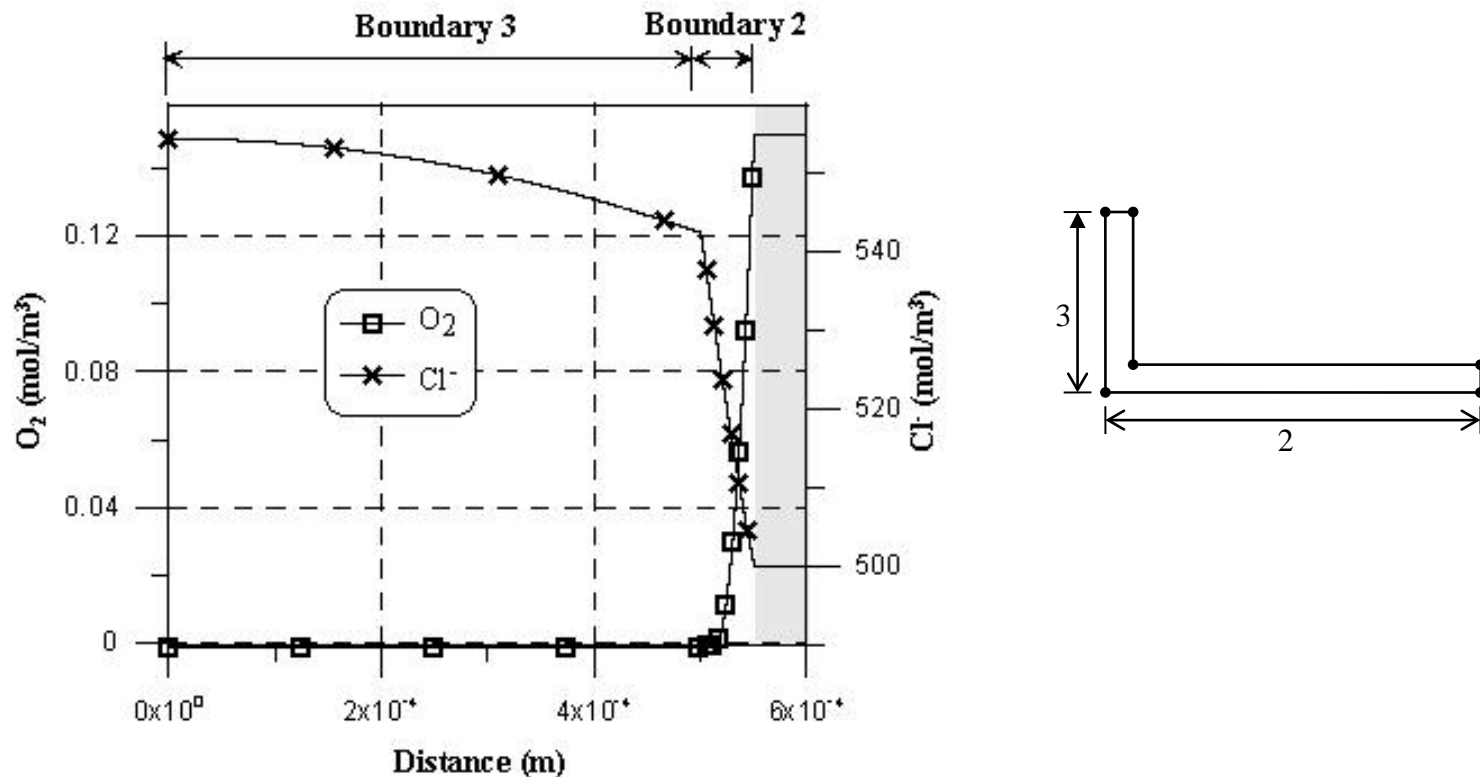
Results - pH, Chloride-to-Hydroxide ratio

- pH = 12.5, passive current density of 0.01 A/m^2, 0.5 M chloride in bulk solution

- crack width = 0.1 μm, crevice length = 1 mm

Results – Chloride-to-Hydroxide ratio

- Cl^-/OH^- at different concrete pore solutions (pH = 12.5, pH=13.5)
- Passive current density of 0.01 A/m^2, $Cl^-/OH^- = 0.32$, crack width = 0.1μm, crevice length = 1mm

Conclusions

- The corrosion of rebar in concrete, a combination of electrochemical reaction and coupled ionic transport equation of several species, was successfully modeled using COMSOL(Ver. 3.5)

- The probability of corrosion initiation in the mill-scale crevices are higher:

  - Local acidification in crevice (reduction of OH^-)

  - Accumulation of chloride ions

  - Increasing chloride-to-hydroxide ratio (Cl^-/OH^-), which is considered to be a key factor in corrosion initiation.

Thank You