Numerical Method for Analyzing Time-dependent Localized Corrosion under Accumulated Rust

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Classification of Corrosion

- **General corrosion**
  Corrosion dissolving metal **uniformly and slowly** in electrolyte.

- **Localized corrosion**
  Corrosion dissolving metal **locally and quickly**.
  **More important issue for safety!**
Localized Corrosion in Plants

- Localized corrosion occurs in corrosion-resistant alloy such as stainless steel, and shorten a life of structures.
- For example, Crevice corrosion of several millimeters occurred at a flange of a seawater pump after 5 years operation.

Fig. Crevice corrosion occurred at a flange of a seawater pump[1]

Localized Corrosion in the Nuclear Plant

In Hamaoka nuclear power station on May 14, 2011, damage to the main condenser tubes resulted in an inflow of seawater into the condensate storage tank.

Localized Corrosion in the Nuclear Plant

Crud had built up in the condensate storage tank. (Crud is formed mainly by iron rust from the inner walls of the pipes, etc.) Crevice environment created by the inflow of seawater and rust caused pitting corrosion in less than 5 months.

Fig. Pitting corrosion occurred under accumulated rust.[2]

Methods for Localized Corrosion Evaluation

It is difficult to estimate the corrosion rate by experiments because localized corrosion is a multiphysics problem.

Numerical evaluation of localized corrosion is expected to be an effective approach to this issue.
Objective

Developing a numerical method for analyzing time-dependent localized corrosion under accumulated rust

Contents

- Mechanism of localized corrosion under accumulated rust
- Analysis method
- Example of analysis
- Summary
Mechanism of localized corrosion under accumulated rust
Mechanism of corrosion under rust

1. Passive film is locally destroyed at a micropit on stainless steel surface.

- **No rust**
  - Micropit
  - Passive film
  - Stainless steel

- **Under accumulated rust**
  - Micropit
  - Passive film
  - Stainless steel
  - Seawater
  - Iron rust

Micropit is a spot at which anodic regions of microcells are concentrated incidentally.
Mechanism of corrosion under rust

2. $\text{H}^+$ ions diffuse quickly in seawater.

No rust

2'. $\text{H}^+$ ions cannot diffuse much in rust layer.

Under accumulated rust

$\text{H}^+$ ions are generated by the hydrolysis of chromium ions

$$\text{Cr}^{3+} + \text{H}_2\text{O} \rightarrow \text{CrOH}^{2+} + \text{H}^+$$

Iron rust

Seawater

Loss of passive film
Passive film
Stainless steel
Mechanism of corrosion under rust

3. H⁺ ions diffuse entirely, and passive film is restored.

No rust

3’. Passive film is destroyed more.

Under accumulated rust

Seawater

Cr³⁺

Iron rust

Loss of passive film

Passive film

Stainless steel

Stainless steel
Mechanism of corrosion under rust

4. Stable passive film is maintained.

No rust

4’. Pitting corrosion is initiated under rust.

Under accumulated rust

Seawater

Iron rust

Passive film

Stainless steel

Seawater

Passive film

Stainless steel

$H^+$
Analysis method
Governing equations

Poisson equation of the electric field

\[ \nabla^2 \phi = \frac{F}{\varepsilon} \sum_{i \in \Pi} z_i C_i \]

Mass transport equation

\[ \frac{\partial C_i}{\partial t} = -\nabla \cdot \left( -z_i u_i C_i F \nabla \phi - D_i \nabla C_i \right) + E_i(C_i) \]

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Phi )</td>
<td>Electrostatic potential [V]</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday’s constant [F m(^{-1})]</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>Permittivity [(Ωm(^{-1})]</td>
</tr>
<tr>
<td>( z_i )</td>
<td>Charge number of ion i</td>
</tr>
<tr>
<td>( C_i )</td>
<td>Molar concentration of ion i [mol m(^{-3})]</td>
</tr>
<tr>
<td>( D_i )</td>
<td>Diffusion coefficient of ion i [m(^2) s(^{-1})]</td>
</tr>
<tr>
<td>( u_i )</td>
<td>Mobility of ion i [m(^2) mol J(^{-1}) s(^{-1})]</td>
</tr>
</tbody>
</table>

Solve these 2 equations with the weak-coupling method
Boundary conditions

Cathodic boundary

<table>
<thead>
<tr>
<th>Target</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
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</tbody>
</table>

- **Electrostatic analysis**

\[ J = P_{\text{anode}}(\Phi, \text{pH}) \]

\[ J = P_{\text{cathode}}(\Phi, \text{pH}) \]

Polarization curves represent relationship between potential and current density for each pH.

- **Mass transport analysis**

\[ N_i = \frac{\lambda_i}{F \sum_{k \in I} \lambda_k z_k} P_{\text{anode}}(\Phi, \text{pH}) \]

\[ N_i = \frac{r_i}{F \sum_{k \in I} r_k z_k} P_{\text{cathode}}(\Phi, \text{pH}) \]

Ionic molar flux density as a function of a polarization curve

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J )</td>
<td>Current density ([\text{A m}^{-2}])</td>
</tr>
<tr>
<td>( \Phi )</td>
<td>Electrostatic potential ([\text{V}])</td>
</tr>
<tr>
<td>( N_i )</td>
<td>Ionic molar flux density vector of ion ( i ) ([\text{mol m}^{-2} \text{s}^{-1}])</td>
</tr>
<tr>
<td>( \lambda_i )</td>
<td>Composition ratio of metal of ion ( i )</td>
</tr>
<tr>
<td>( F )</td>
<td>Faraday’s constant ([\text{F m}^{-1}])</td>
</tr>
<tr>
<td>( C_i )</td>
<td>Molar concentration of ion ( i ) ([\text{mol m}^{-3}])</td>
</tr>
<tr>
<td>( z_i )</td>
<td>Charge number of ion ( i )</td>
</tr>
<tr>
<td>( r_i )</td>
<td>Cathodic reaction ratio</td>
</tr>
</tbody>
</table>
Localized corrosion is calculated with voxel-based finite volume method (Voxel FVM).

Metal shape and surface area are updated.

Corrosion rates are calculated with considering multiphysics problem.

**Voxel method**

1. Form metal surface and calculate surface area in cells
2. Solve electrostatic problem
3. Calculate mass transports
4. Consider chemical reactions
5. Update VOF of cells
Representation of metal surface

Corrosion rate \( \propto \) Surface area \( \times \) Current density

\[ \therefore \] Surface area must be estimated accurately.

Surface area is estimated with level set method using volume of fluid (VOF) of cells.
The spatial distribution of iron rust is defined as the distribution of concentration of iron rust in each cell.

Diffusion coefficients ($D_i$) and electrical conductivity ($\kappa$) are defined as a function of the concentration of rust ([FeOOH]).
Example of analysis
Example of analysis

The progress of corrosion simulating the actual through hole caused by localized corrosion under accumulated rust

The target is the initiation of the through hole detected in Hamaoka nuclear power station.

Fig. Overview of localized corrosion under accumulated rust

Through hole detected in Hamaoka nuclear power station[2]

Analysis conditions on metal

Boundary condition: Polarization curves (SUS304)
Composition ratio: Fe 80%, Cr 20%
Density: 20 [kg m\(^{-3}\)] (0.25% of the actual density to emphasize the change in shape)
Analysis conditions

Configuration

Cathodic boundary

Plane symmetry

Rust

100 μm

Micropit

Metal

100 μm

1mm

1mm

Anodic polarization curve of stainless steel

Cathodic polarization curves of stainless steel
Analysis conditions on cathodic boundary

Boundary condition: Polarization curves

\[ \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

Constant concentration

\( \text{pH}7, \ C_{\text{NaCl}} = 550 \text{ [mol m}^{-3}] \)
\( C_{\text{O}_2} = 0.0025 \text{ [mol m}^{-3}] \)

Polarization curve including the effect of all cathode in the tank was draw and used.
Analysis conditions

As the initial condition, we set the micropit of pH 3 in the cell of the lower left corner in the solution.

<table>
<thead>
<tr>
<th>Initial concentration [mol m(^{-3})] and pH</th>
<th>Micropit</th>
<th>Rust</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>550</td>
<td>550</td>
</tr>
<tr>
<td>(O_2)</td>
<td>(2.5 \times 10^{-3})</td>
<td>(2.5 \times 10^{-3})</td>
</tr>
<tr>
<td>FeOOH</td>
<td>(1.0 \times 10^{-3})</td>
<td>(1.0 \times 10^{-3})</td>
</tr>
<tr>
<td>pH</td>
<td>3</td>
<td>7</td>
</tr>
</tbody>
</table>
Analysis conditions

Time step
1 × 10^{-2} s

Mesh size
100 μm × 100 μm

Chemical reactions
Cr^{3+} + H_2O ⇌ CrOH^{2+} + H^+
H_2O ⇌ H^+ + OH^−
Cr^{3+} + Cl^- ⇌ CrCl^{2+}

Chemical species
Cr^{3+}  Fe^{2+}  H^+  OH^-  FeOOH  O_2  Cl^-  Na^+  CrOH^{2+}  CrCl^{2+}

Configuration

Cathodic boundary
Plane symmetry
Micropit
Rust
Metal

1mm
100 μm
Analysis results

Our method qualitatively reproduced
• the high concentration of H⁺ ions (lower pH)
• the initiation of pitting corrosion at the initial micropit under the accumulated rust.
Summary

• A numerical method for analyzing time-dependent localized corrosion under accumulated rust was developed.
• It considers the multiphysics problem including electrostatics, electrophoresis, mass diffusion, chemical reactions, and moving boundaries.
• The effect of accumulated rust was modeled as diffusion inhibition of chemical species.
• An example of analysis showed that our method qualitatively reproduced the initiation of pitting corrosion under the accumulated rust.