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

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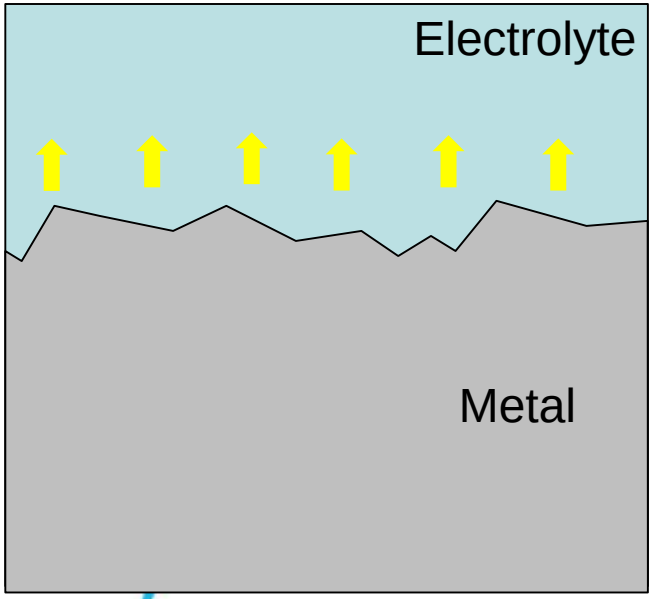
Classification of Corrosion

- **General corrosion**

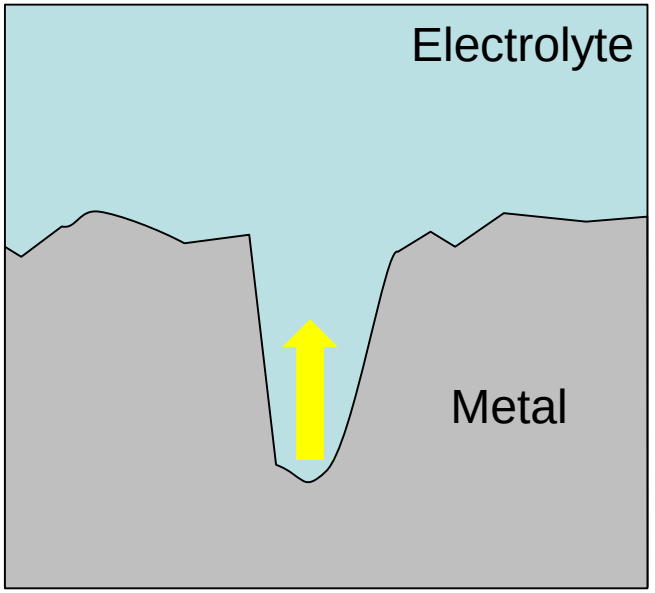
  Corrosion dissolving metal uniformly and slowly in electrolyte.



- **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.**

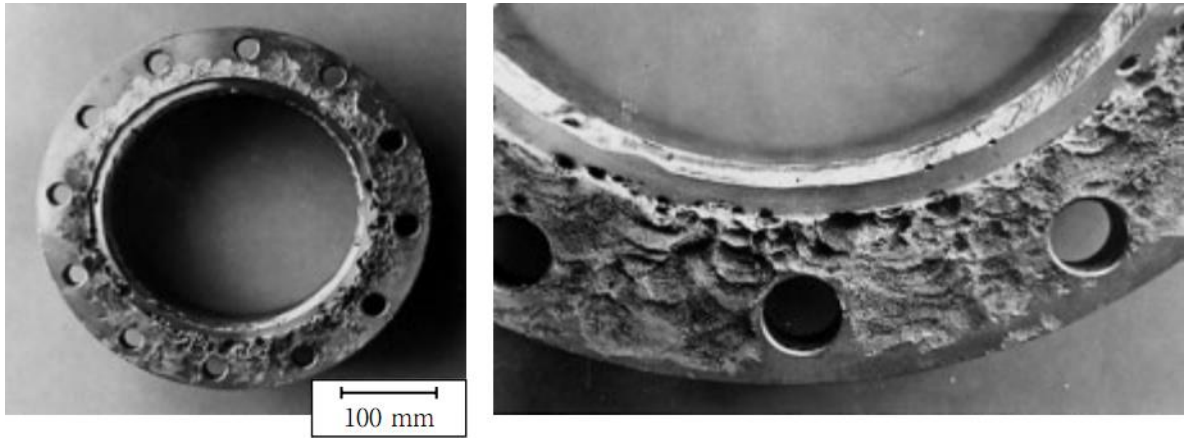


Fig. Crevice corrosion occurred at a flange of a seawater pump[1]

[1]Matsuho MIYASAKA, Lecture on Corrosion and Corrosion Protection of Seawater Pumps-, Ebara Engineering Review No.224 pp.28-37 (2009)

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.

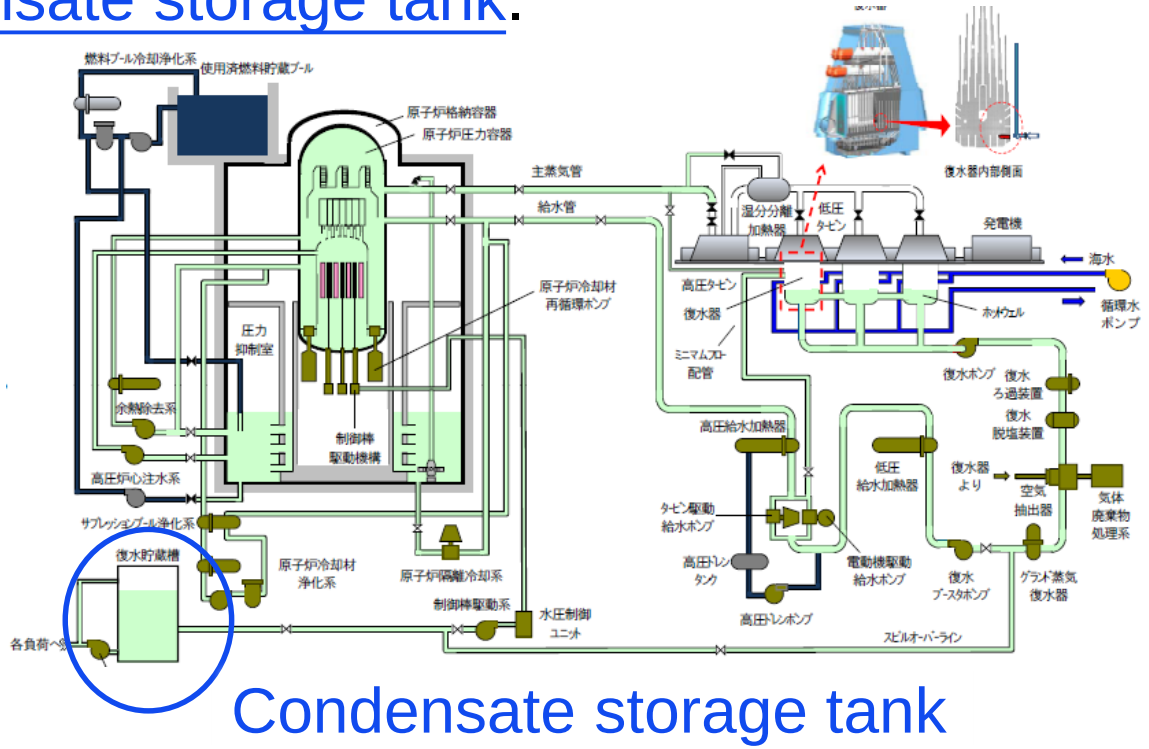
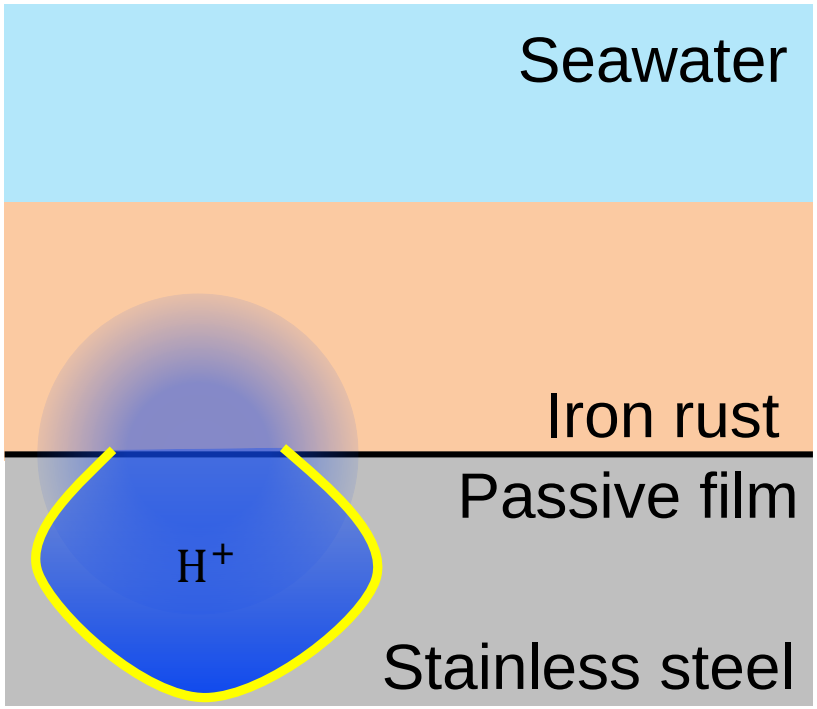


Fig. Outline of Hamaoka Nuclear Power Station Reactor No. 5 [2]

[2]Ministry of Economy, Trade and Industry: Reporting causes of corrosion holes in condensate storage tank lining and Measures to prevent recurrence in Unit 5 Chubu Electric Power Co., Inc. Hamaoka Nuclear Power Station, 2012.

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.



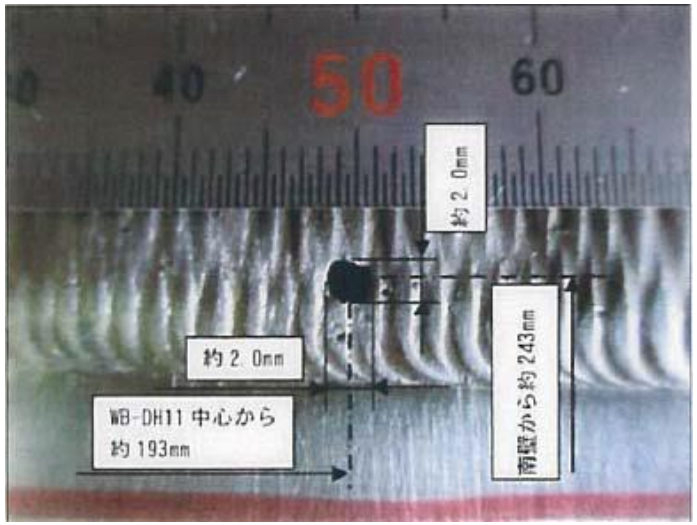


Fig. Pitting corrosion occurred under accumulated rust.[2]

[2]Chubu Electric Power Co., Inc., 2012.

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

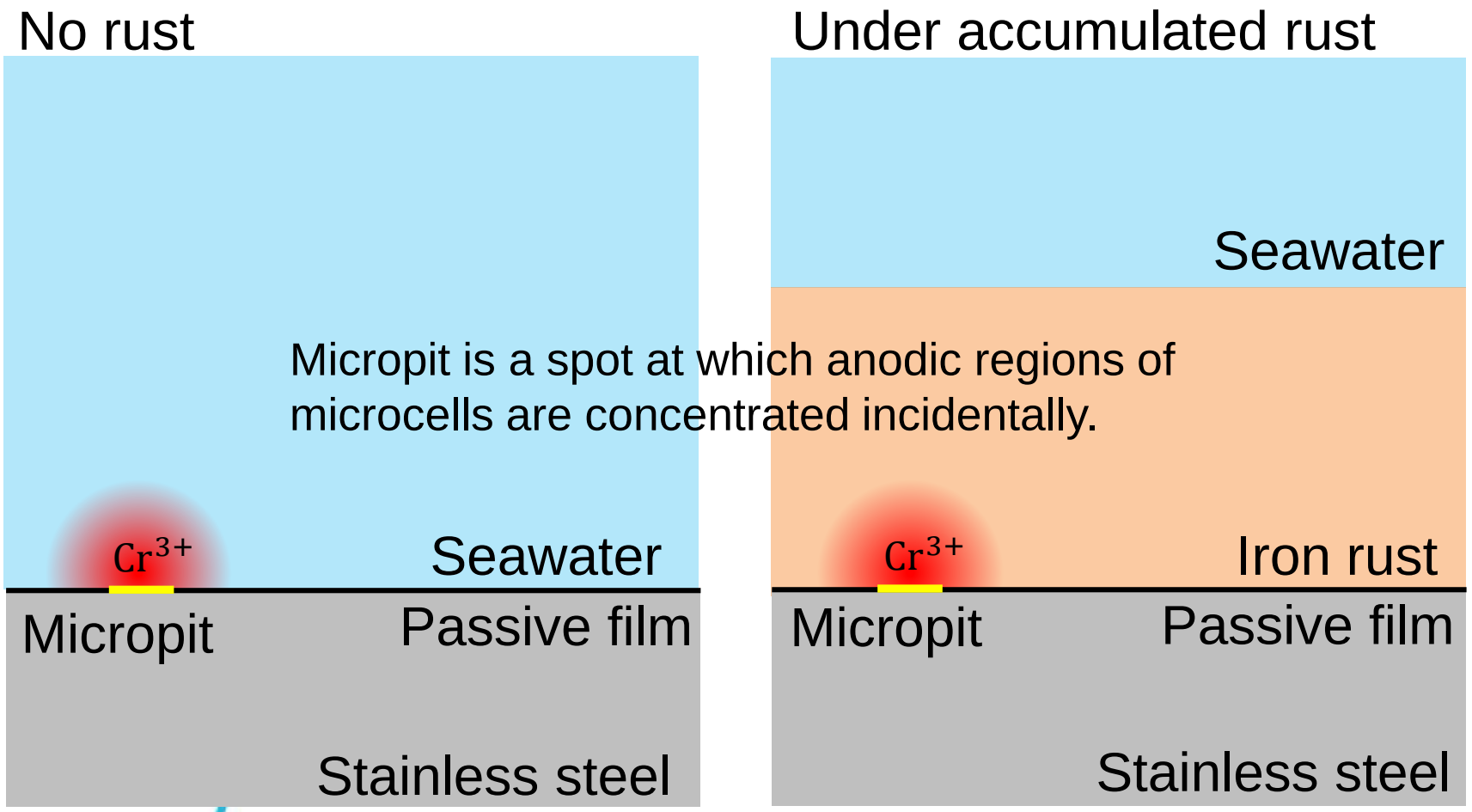
Contents

- **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

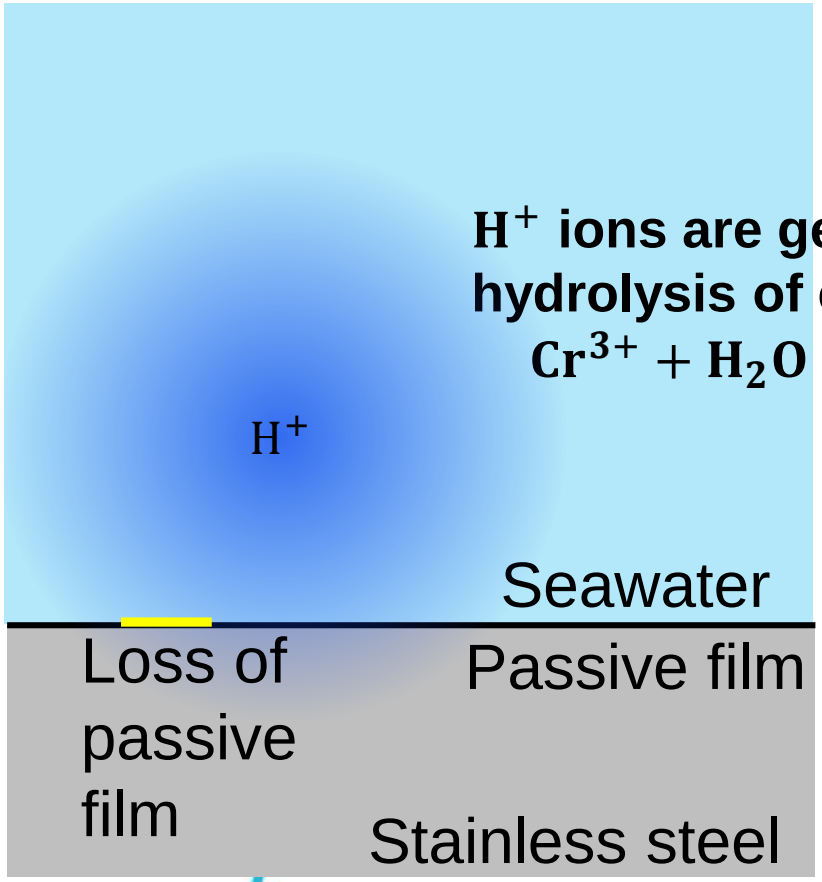
1. Passive film is locally destroyed at a micropit on stainless steel surface.



Mechanism of corrosion under rust

2. H^+ ions diffuse quickly in seawater.

No rust

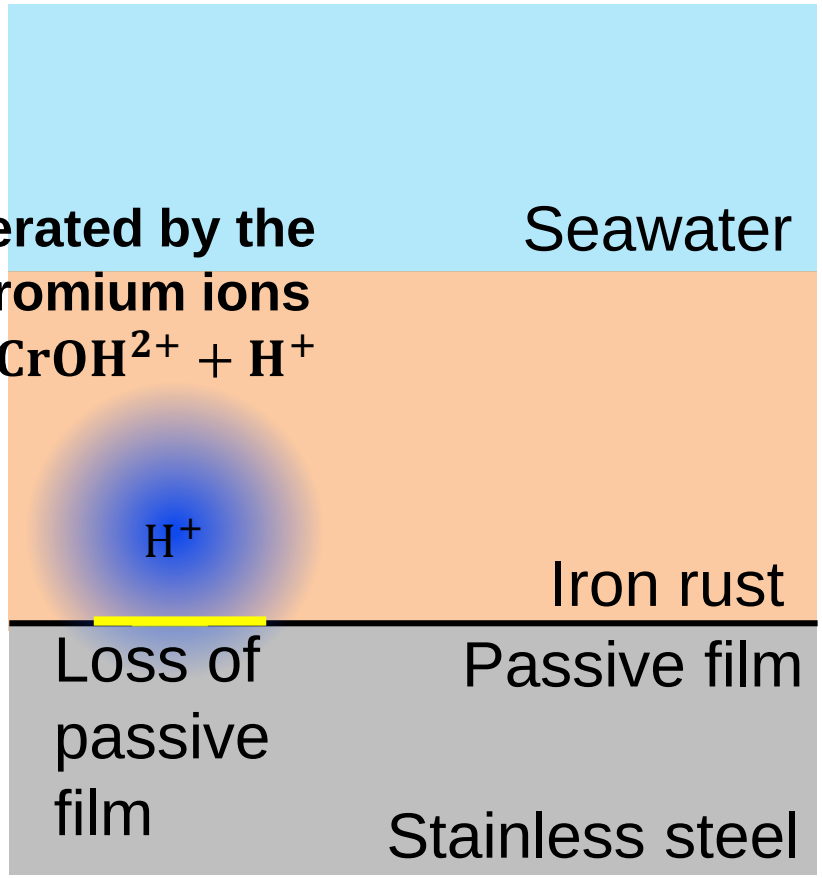


H^+ ions are generated by the hydrolysis of chromium ions

$$Cr^{3+} + H_2O \rightarrow CrOH^{2+} + H^+$$

2′. H^+ ions cannot diffuse much in rust layer.

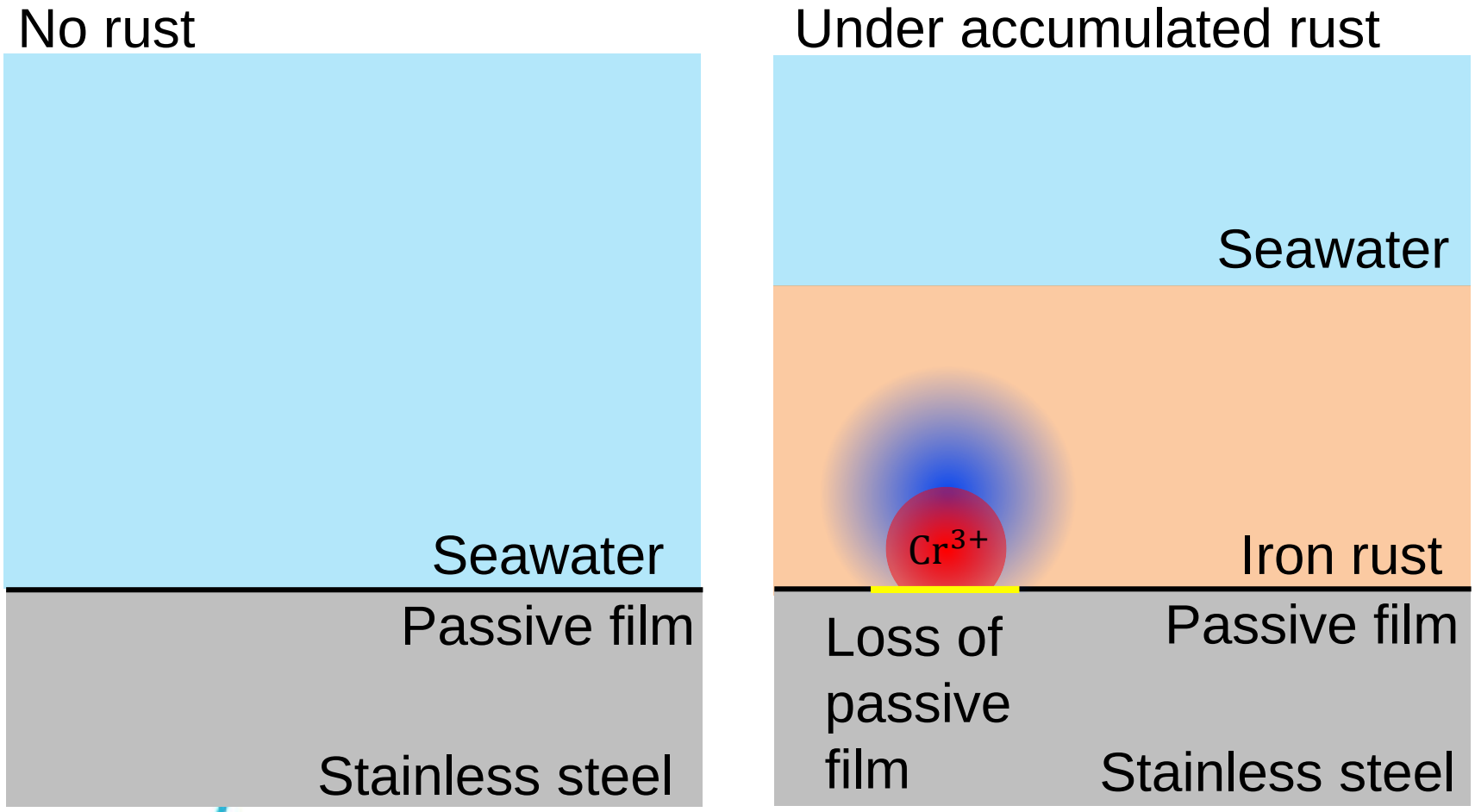
Under accumulated rust



Mechanism of corrosion under rust

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

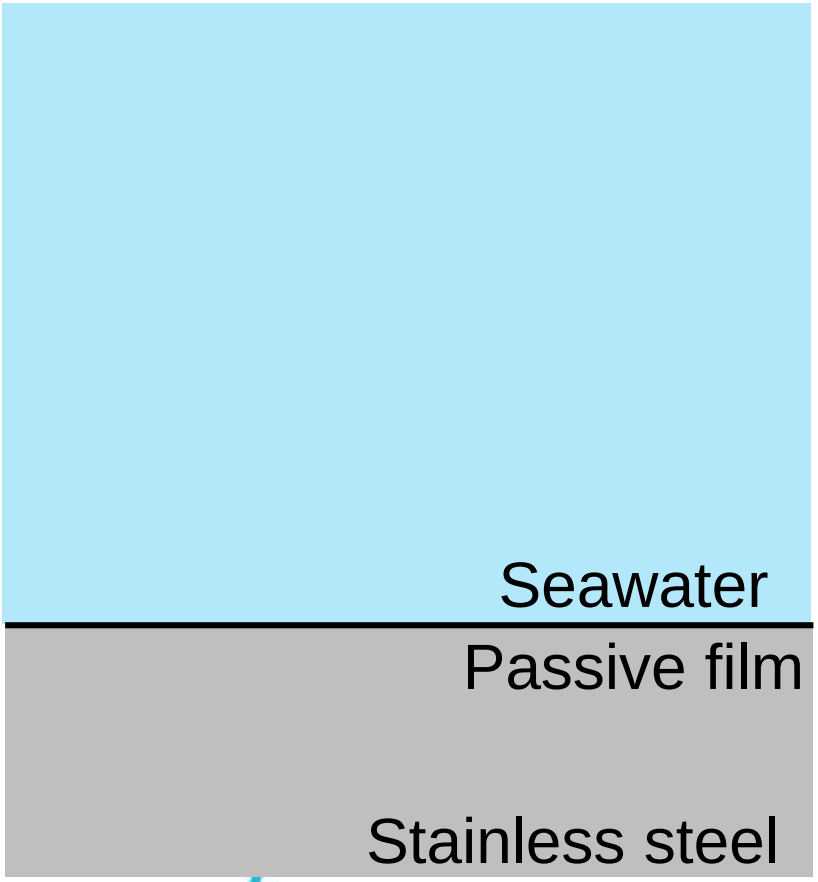
3′. Passive film is destroyed more.



Mechanism of corrosion under rust

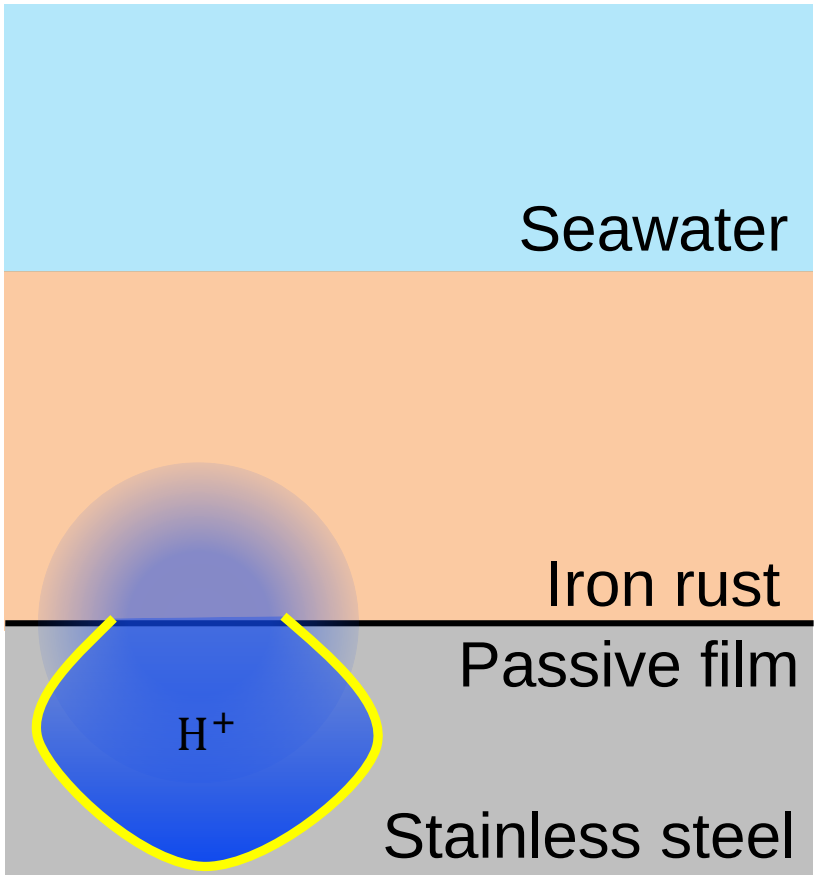
4. Stable passive film is maintained.

No rust



4′. Pitting corrosion is initiated under rust.

Under accumulated rust



Analysis method

Governing equations

Poisson equation of the electric field

$$\nabla^2\phi = \frac{F}{\varepsilon}\sum_{i\in\mathbb{I}} z_i C_i$$

Φ	Electrostatic potential [V]
F	Faraday's constant [F m^{-1}]
ε	Permittivity [$(\Omega m)^{-1}$]
z_i	Charge number of ion i
C_i	Molar concentration of ion i [mol m^{-3}]
D_i	Diffusion coefficient of ion i [m^2 s^{-1}]
u_i	Mobility of ion i [m^2 mol J^{-1} s^{-1}]

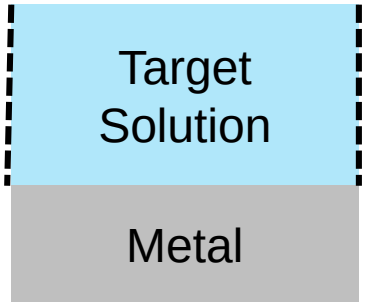
Mass transport equation

$$\frac{\partial C_i}{\partial t} = -\nabla\cdot\underbrace{(-z_i u_i C_i F\nabla\phi}_{\text{electrophoresis}} \underbrace{- D_i\nabla C_i)}_{\text{Mass diffusion}} + \underbrace{E_i(C_i)}_{\text{Chemical reaction}}$$

Solve these 2 equations with the weak-coupling method

Boundary conditions

Cathodic boundary



J	Current density [A m^{-2}]
Φ	Electrostatic potential [V]
N_i	Ionic molar flux density vector of ion i [mol m^{-2} s^{-1}]
λ_i	Composition ratio of metal of ion i
F	Faraday's constant [F m^{-1}]
C_i	Molar concentration of ion i [mol m^{-3}]
z_i	Charge number of ion i
r_i	Cathodic reaction ratio

- Electrostatic analysis

$$J = P_{\mathrm{anode}}(\Phi, \mathrm{pH})$$

$$J = P_{\mathrm{cathode}}(\Phi, \mathrm{pH})$$

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

- Mass transport analysis

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

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

Ionic molar flux density as a function of a polarization curve

Numerical Analysis Method

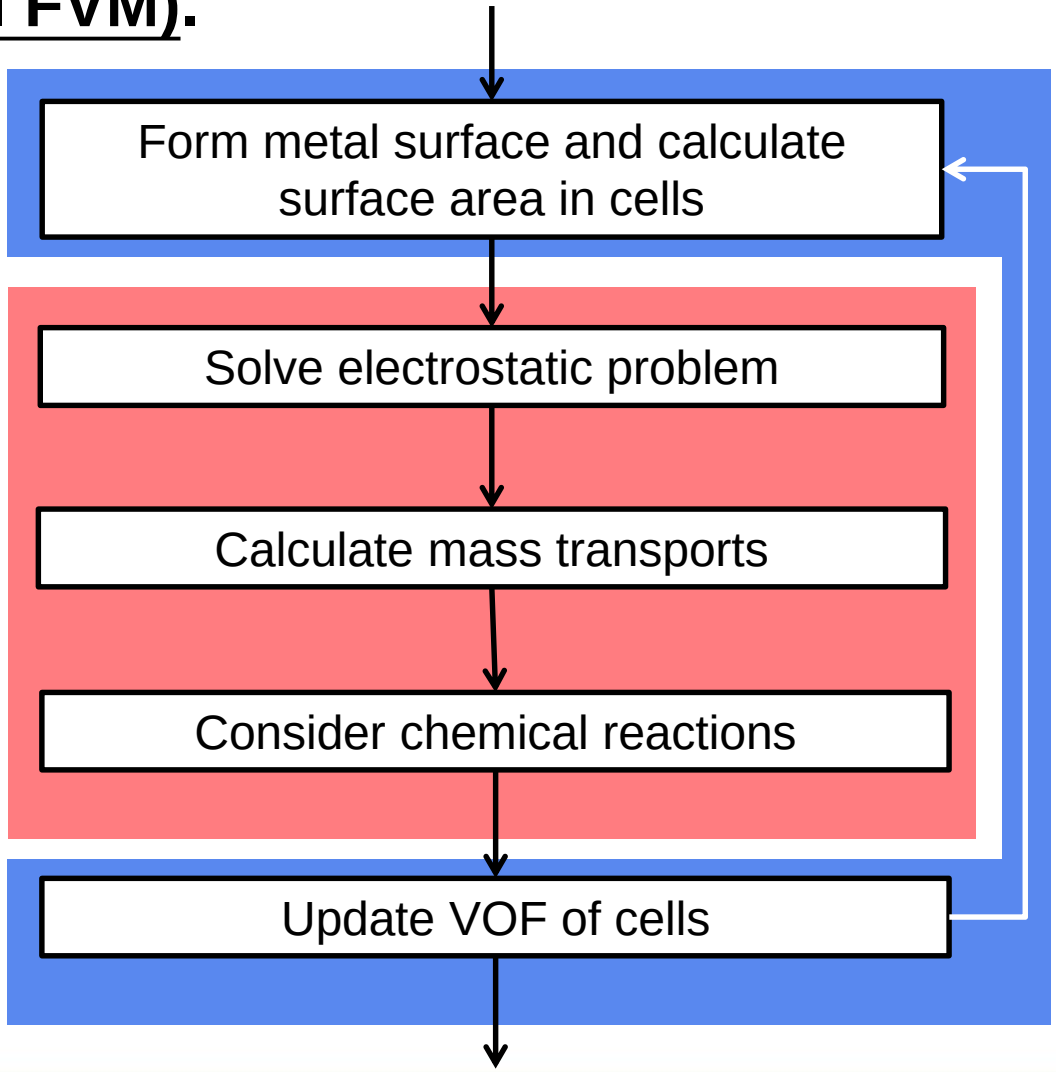
Localized corrosion is calculated with voxel-based finite volume method (Voxel FVM).

FVM

Corrosion rates are calculated with considering multiphysics problem.

Voxel method

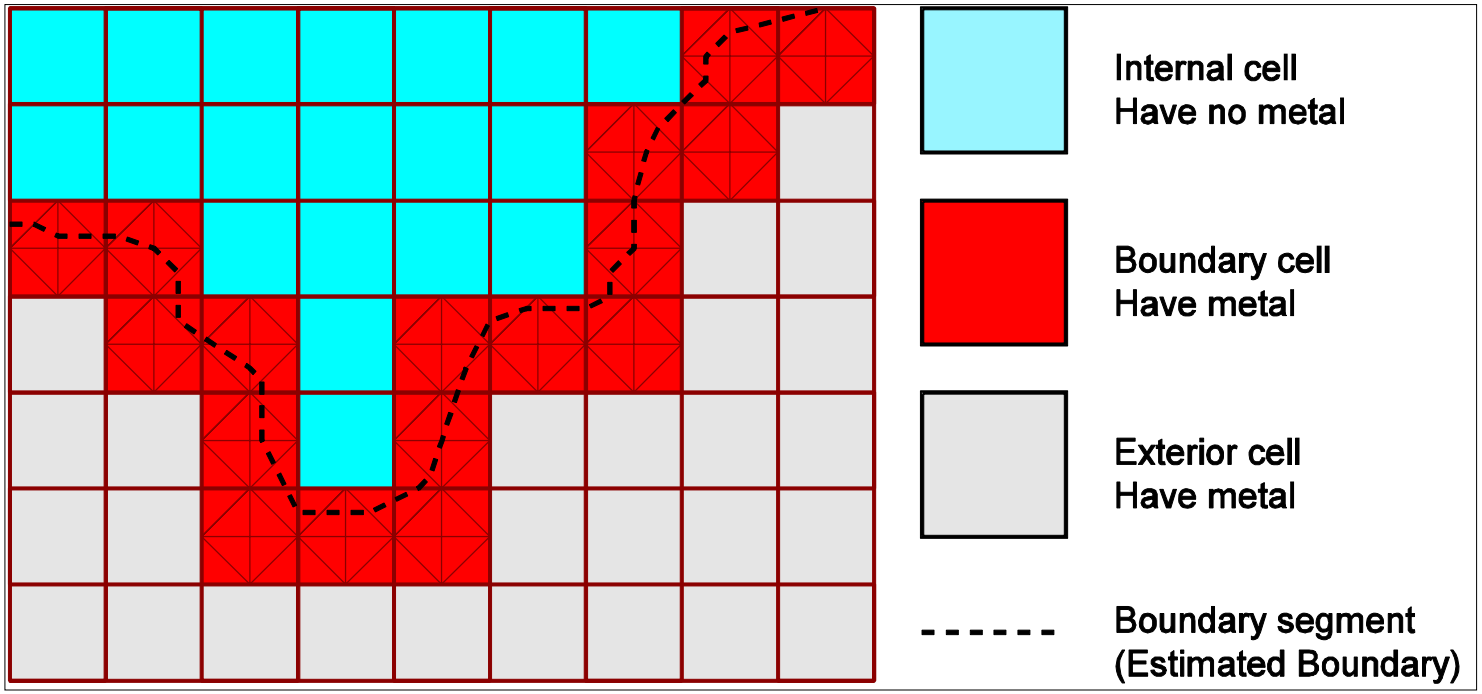
Metal shape and surface area are updated.



Representation of metal surface

$$\text{Corrosion rate} \propto \text{Surface area} \times \text{Current density}$$

∴ Surface area must be estimated accurately.



Surface area is estimated with level set method using volume of fluid (VOF) of cells.

Modeling of accumulated rust

The spatial distribution of iron rust is defined as the distribution of concentration of iron rust in each cell.

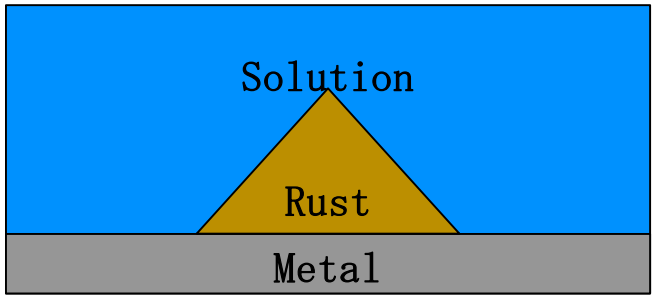


Fig. The actual triangular distribution of rust

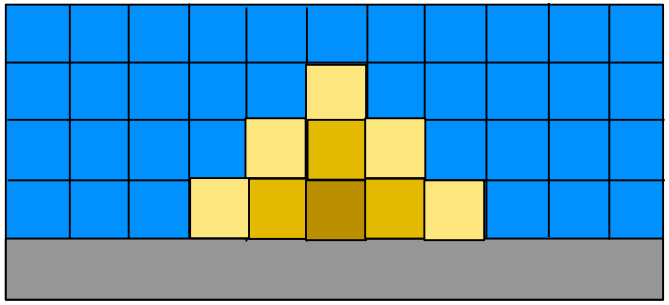


Fig. The virtual distribution of rust represented by concentration of rust

Diffusion coefficients (D_i) and electrical conductivity (κ) 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.

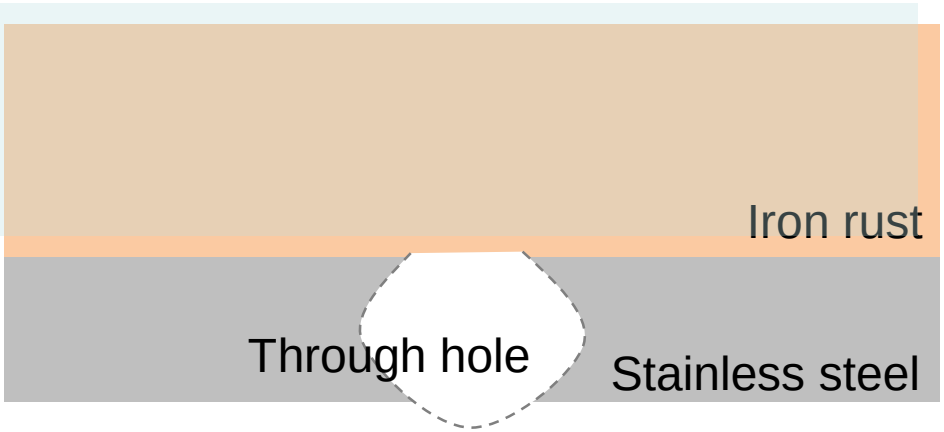
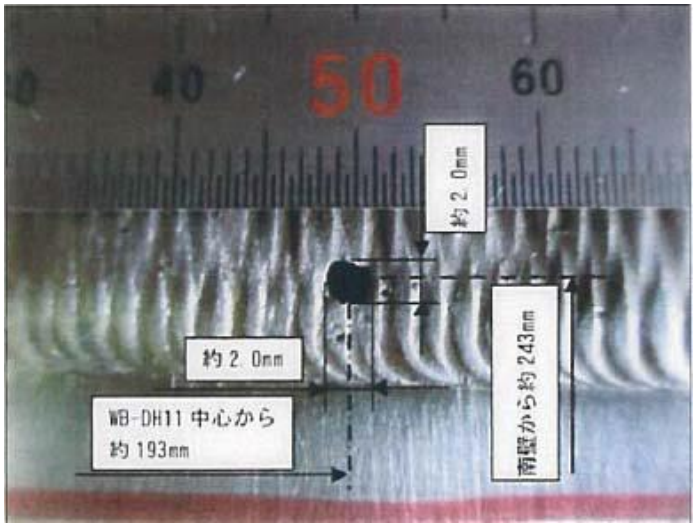


Fig. Overview of localized corrosion under accumulated rust

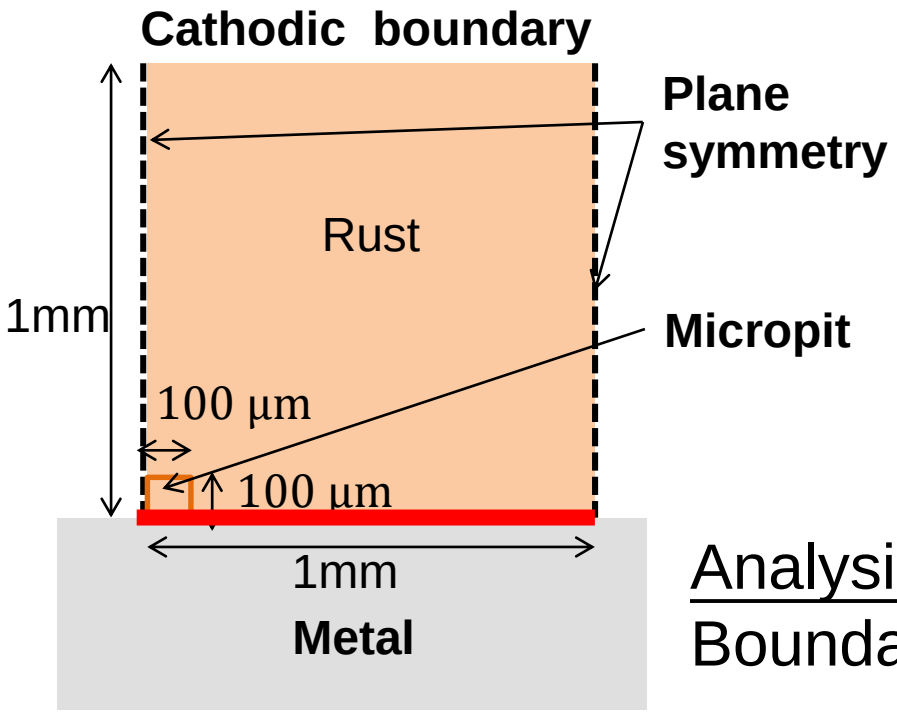


Through hole detected in Hamaoka nuclear power station[2]

[2]Ministry of Economy, Trade and Industry: Reporting causes of corrosion holes in condensate storage tank lining and Measures to prevent recurrence in Unit 5 Chubu Electric Power Co., Inc. Hamaoka Nuclear Power Station, 2012.

Analysis conditions

Configuration



Analysis conditions on metal

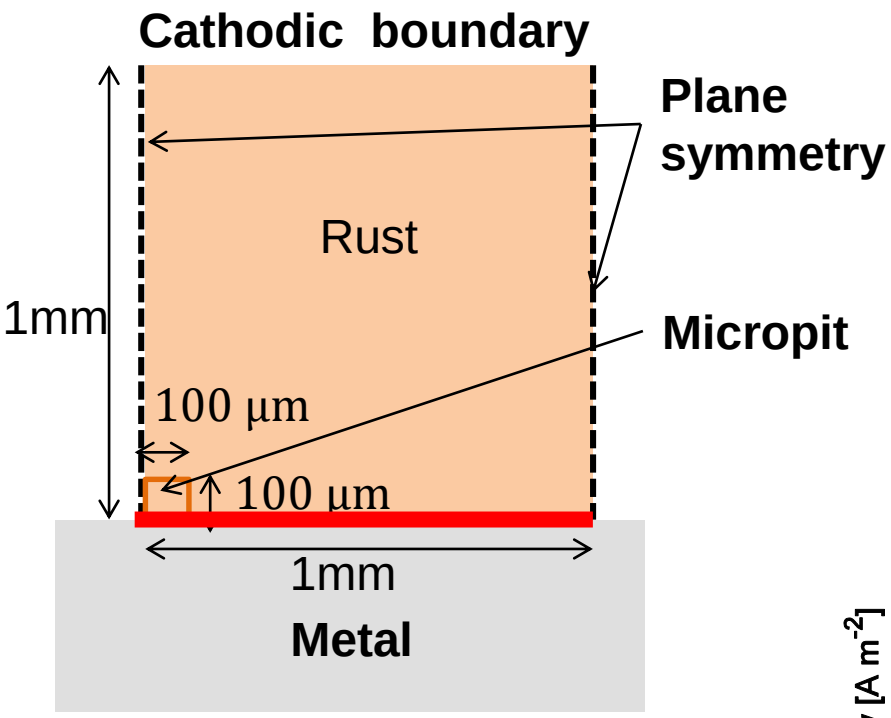
Boundary condition : Polarization curves (SUS304)

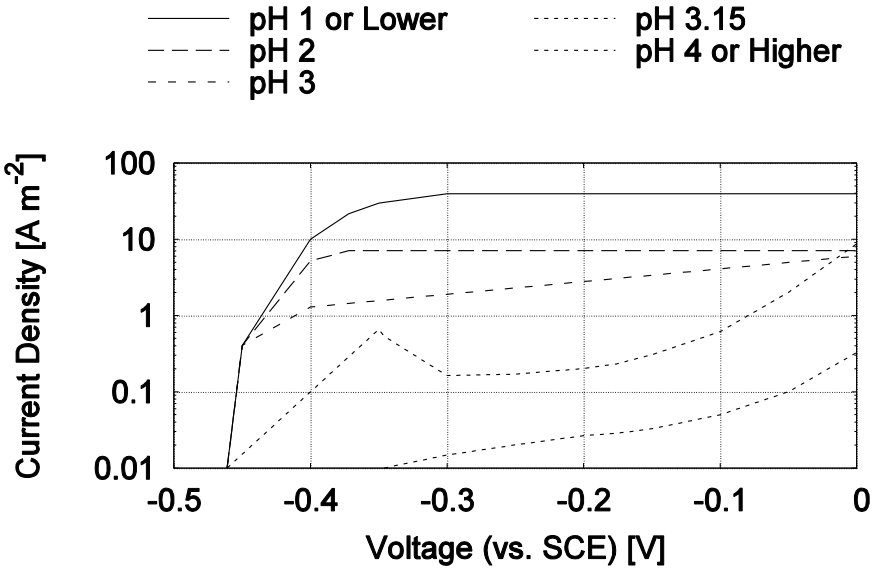
Composition ratio : Fe 80%, Cr 20%

Density : 20 [kg m^{-3}] (0.25% of the actual density to emphasize the change in shape)

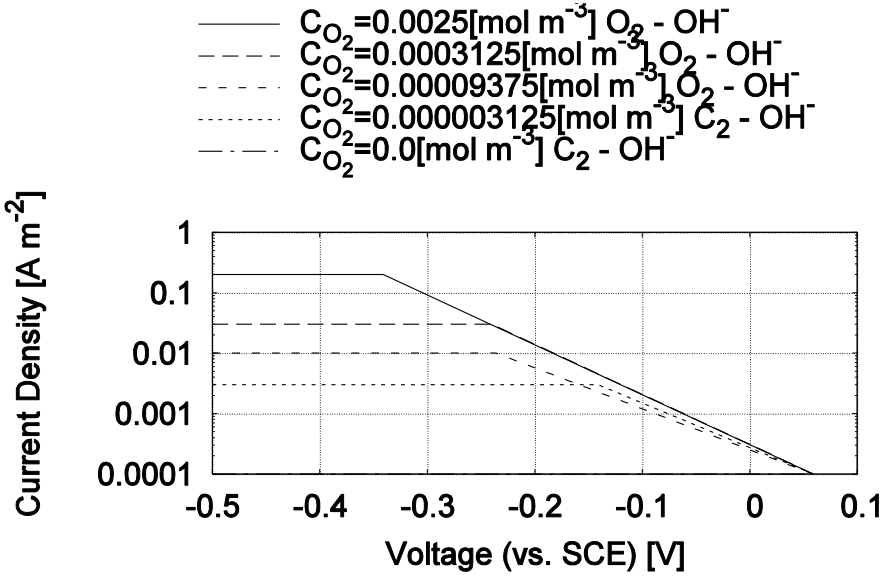
Analysis conditions

Configuration





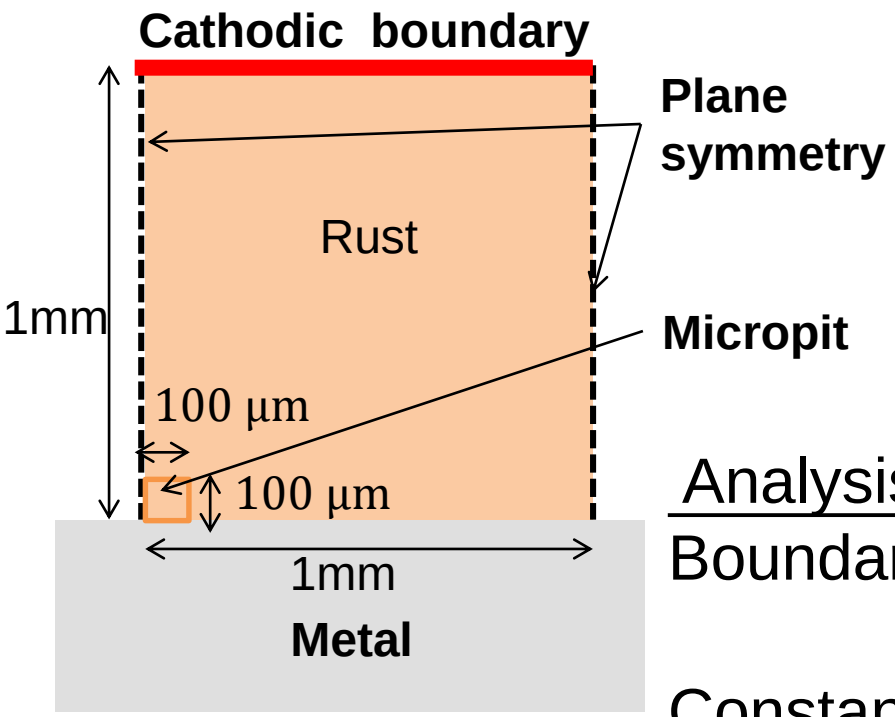
Anodic polarization curve of stainless steel

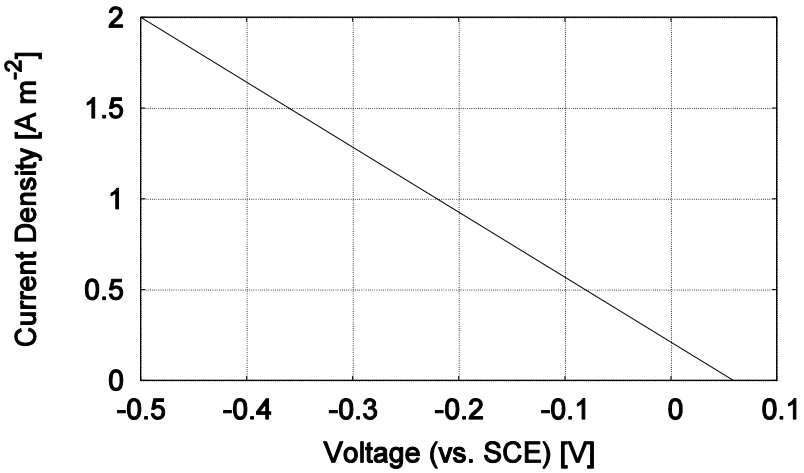


Cathodic polarization curves of stainless steel

Analysis conditions

Configuration





Polarization curve of cathodic boundary

Analysis conditions on cathodic boundary

Boundary condition : Polarization curves

$$(O_2 + H_2O + 4e^- \rightarrow 4OH^-)$$

Constant concentration

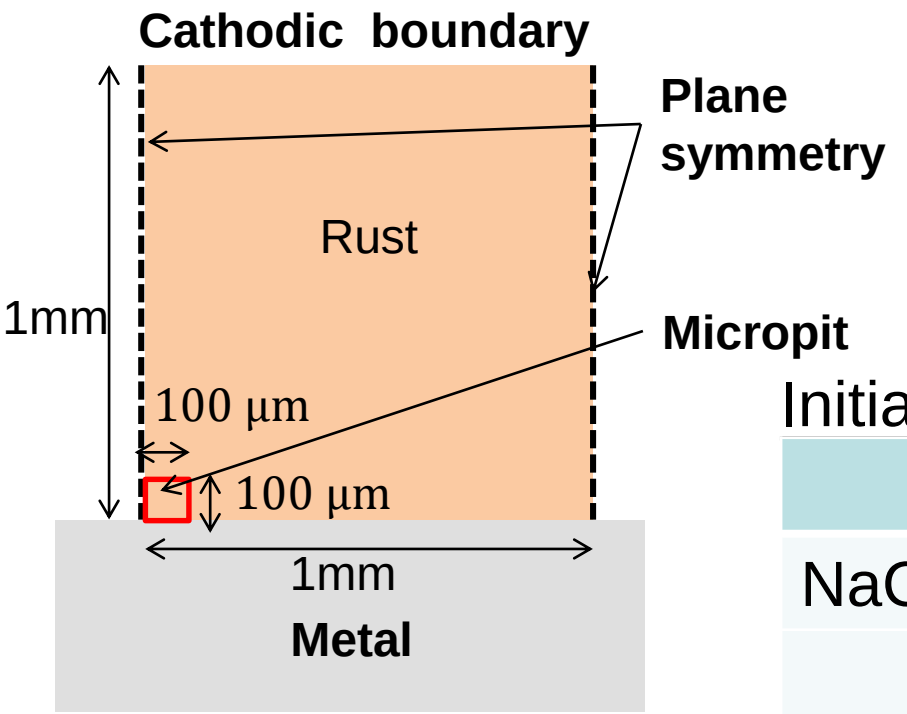
pH7 , $C_{NaCl} = 550$ [mol m^{-3}]

$C_{O_2} = 0.0025$ [mol m^{-3}]

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

Analysis conditions

Configuration



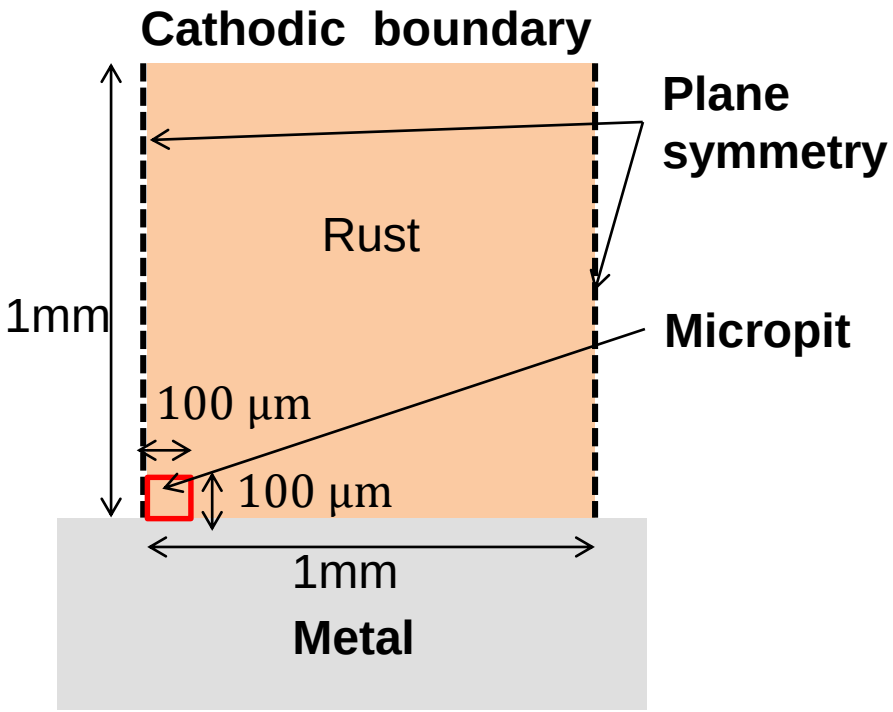
As the initial condition, we set the micropit of pH 3 in the cell of the lower left corner in the solution.

Initial concentration $[\mathrm{mol\ m^{-3}}]$ and pH

	Micropit	Rust
NaCl	550	550
O_2	2.5×10^{-3}	2.5×10^{-3}
FeOOH	1.0×10^{-3}	1.0×10^{-3}
pH	3	7

Analysis conditions

Configuration



Time step

1×10^{-2} s

Mesh size

$100\ \mu m \times 100\ \mu m$

Chemical reactions

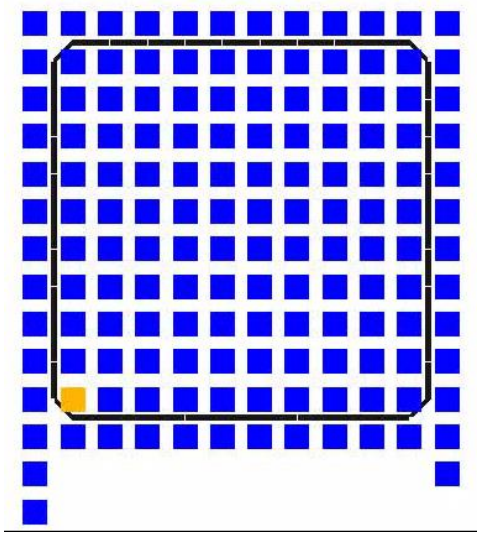
$$Cr^{3+} + H_2O \rightleftarrows CrOH^{2+} + H^+$$
$$H_2O \rightleftarrows H^+ + OH^-$$
$$Cr^{3+} + Cl^- \rightleftarrows CrCl^{2+}$$

Chemical species

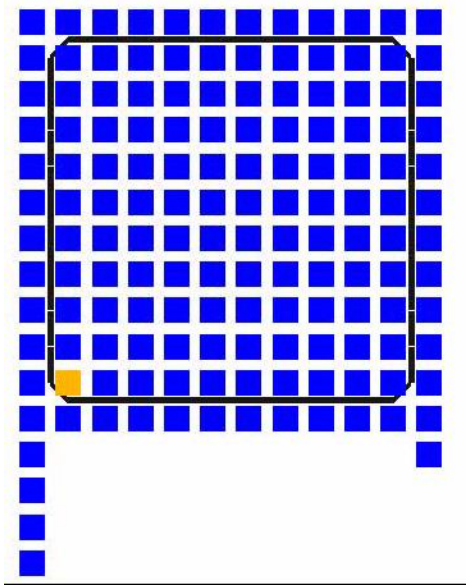
Cr^{3+} Fe^{2+} H^+ OH^- FeOOH O_2 Cl^- Na^+ $CrOH^{2+}$ $CrCl^{2+}$

Analysis results

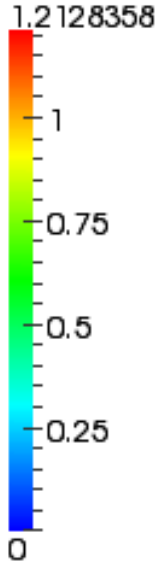
No rust



Under rust



Concentration of H+ ions



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.