Change of Chemical Species with Progress of Crevice Corrosion
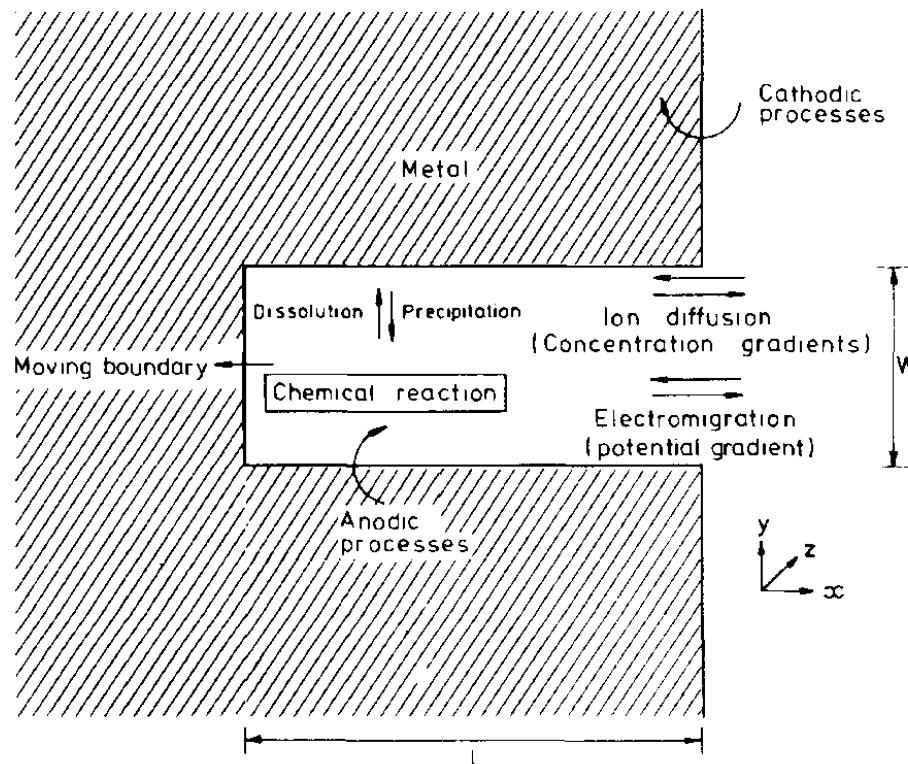
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[1] *Keisoku Engineering System Co., Ltd., Japan*

[2] Japan Atomic Energy Agency, *Japan*

Research Background

■ The narrow region in a crevice makes exchange of solution between the interior and the bulk difficult, so changes in composition of the solution in a crevice occur much more quickly than that outside the crevice.
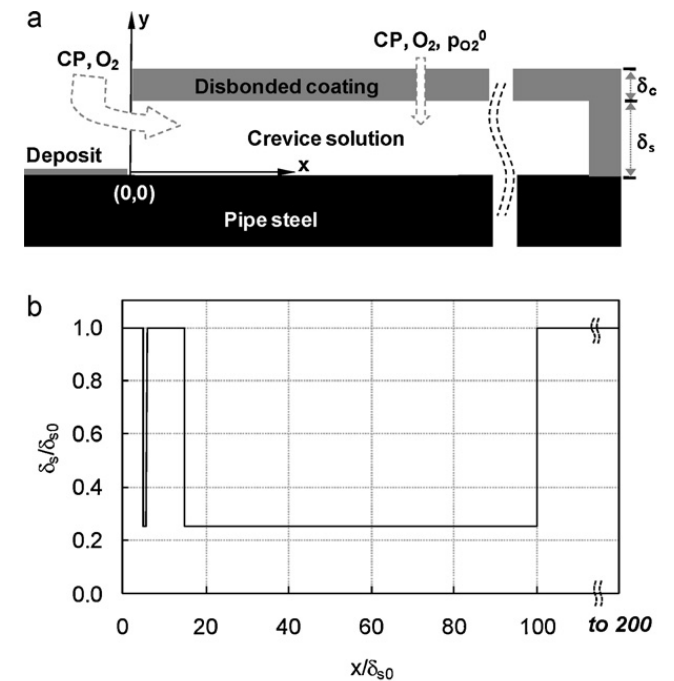

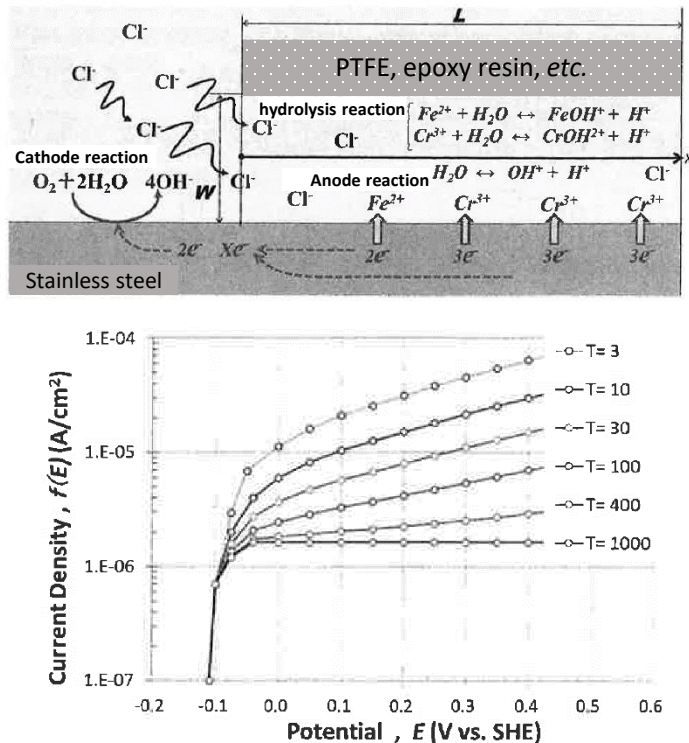Ref.: S. M. Sharland, C. P. Jackson and A. J. Diver: Corrosion Science **29** (1989) 1149-1166.
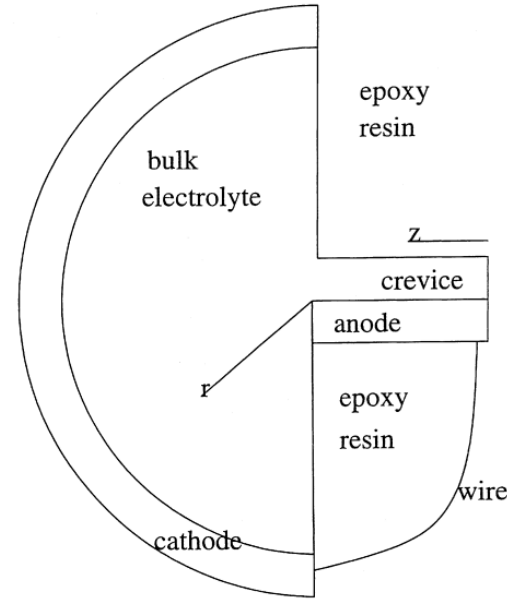
Ref.: F. M. Song: Electrochimica Acta **56** (2011) 6789– 6803

Ref.: S. P. White, G. J. Weir, N. J. Laycock: Corrosion Science **42** (2000) 605-629
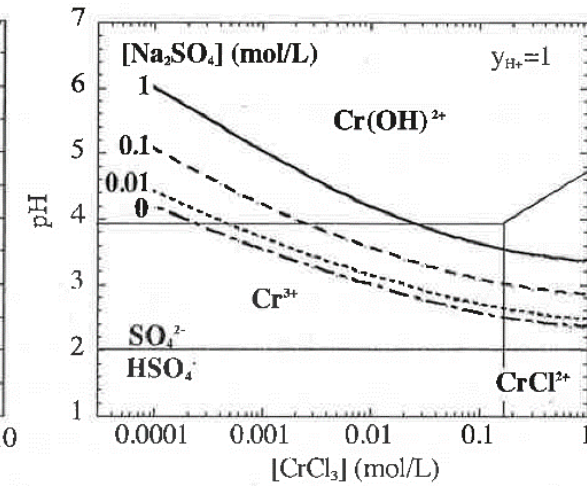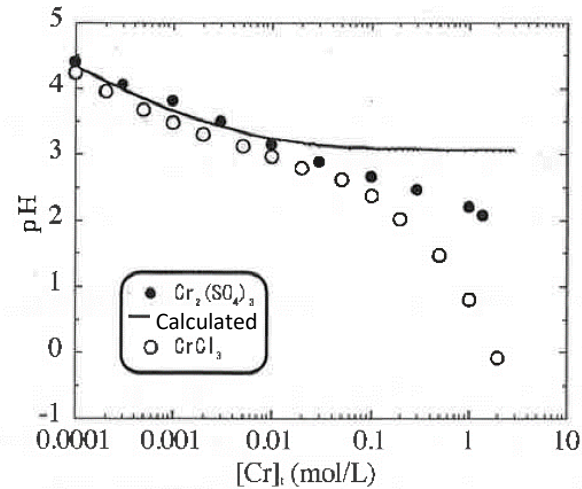
Research Background

- It is known that during crevice corrosion, metal dissolves at a large current density associated with the electrochemical reaction, which causes the solution composition, pH, and dissolved oxygen concentration to exceedingly vary.

Ref.: T. Shinohara , etc. : Proceedings of JSCE materials and environments, C-103 (2011) [in Japanese].

Ref.: K. Matsuoka, etc. : 65th Symposium of Materials and Environments in Japan, B-305 (2018) [in Japanese].

In this paper, a model research on change of chemical species with progress of crevice corrosion is performed.

Electrochemical modeling of corrosion

Electrolyte Transport

➢ Nernst–Planck equation is a conservation of mass equation used to describe the motion of a charged chemical species in a fluid medium .

• Nernst-Planck transport

$$\frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i = R_i$$

Concentration   Flow velocity   Charge
Diffusivity   Mobility

$$\mathbf{N}_i = -D_i \nabla c_i + c_i \mathbf{u} - z_i m_i F c_i \nabla \phi_l$$

Faraday's constant   Ionic potential

➢ Current density

$$\mathbf{j} = F \sum_i z_i \mathbf{N}_i \qquad \nabla \cdot \mathbf{j} = Q_l$$

Assuming electroneutrality, sum of charges = 0

$$\mathbf{j} = F \left(\sum_i -z_i D_i \nabla c_i - \nabla \phi_l \sum_i \left(z_i \right)^2 m_i F c_i \right)$$

$$\mathbf{j} = -\underbrace{\left(F \sum_i \left(z_i \right)^2 m_i F c_i \right)}_{\kappa = conductivity} \nabla \phi_l$$

Current Distribution Types

◆ Primary: Only assuming Ohmic potential drops
◆ Secondary: Adding effects of activation overpotential (Butler-Volmer kinetics or similar)
◆ Tertiary: Adding mass transport effects (concentration overpotential)
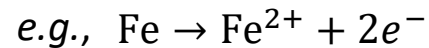
Electrochemical modeling of corrosion

Chemical and electrochemical reactions
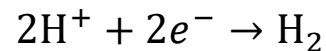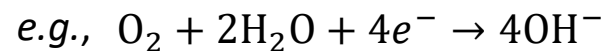
➢ Chemical reactions in solution

- Equilibrium reactions $e.g.,$ $Fe^{2+}+H_2O \leftrightarrows Fe(OH)^+ + H^+$ $Fe^{2+} + Cl^- \leftrightarrows FeCl^+$

$$Fe(OH)^+ + H_2O \leftrightarrows Fe(OH)_2 + H^+$$ $$FeCl^+ + Cl^- \leftrightarrows FeCl_2$$

$$H^+ + OH^- \leftrightarrows H_2O$$

➢ Electrochemical reactions on electrodes

- Metal dissolution reaction

$e.g.,$ $Fe \rightarrow Fe^{2+} + 2e^-$

- Cathodic reduction reactions

$e.g.,$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
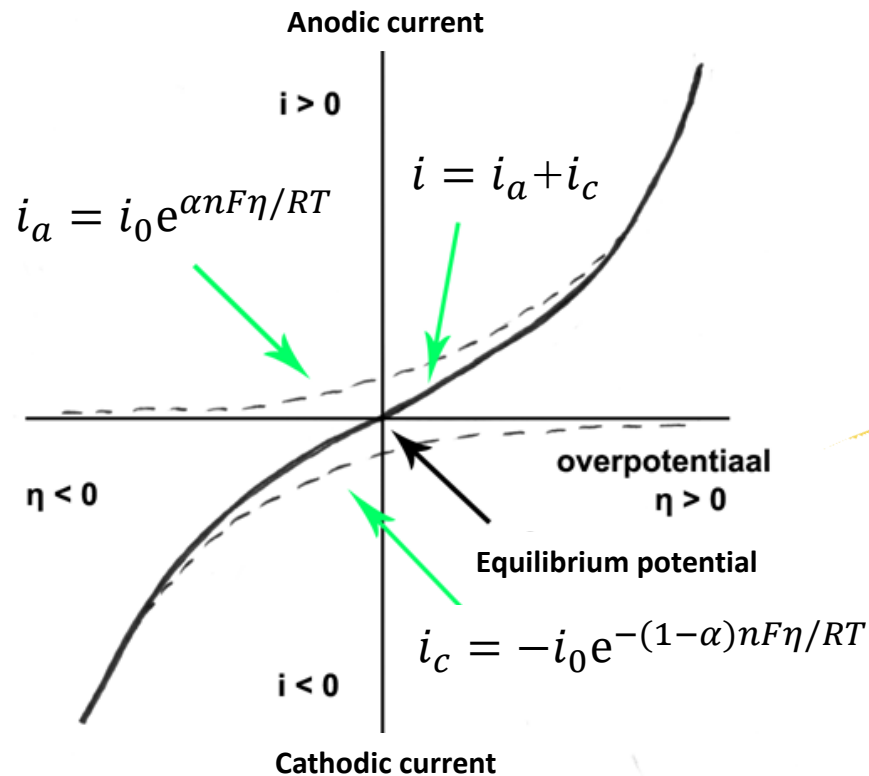
$$2H^+ + 2e^- \rightarrow H_2$$

Tertiary Current Distribution

◆ Supporting electrolyte assumption
- If conductivity is not affected by reactions

◆ Nernst-Planck (with electroneutrality)
- If mass transport = charge transport

◆ Nernst-Planck-Poisson
- If local charge neutrality cannot be satisfied

◆ Concentrated electrolyte theory
- When the charged species interact in the solution

◆ Electroanalysis
- Excess electrolyte and small current densities

Electrochemical modeling of corrosion

Electrochemical reactions: Butler–Volmer equation

Anodic current

$i > 0$

$i = i_a + i_c$

$i_a = i_0 e^{\alpha n F \eta / RT}$

$\eta < 0$

overpotentiaal

$\eta > 0$

Equilibrium potential

$i_c = -i_0 e^{-(1-\alpha) n F \eta / RT}$

$i < 0$

Cathodic current

➢ Secondary current distribution

$$i = i_0 [\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \exp(-\frac{\alpha_c F}{RT}\eta)]$$

Exchange Current Density

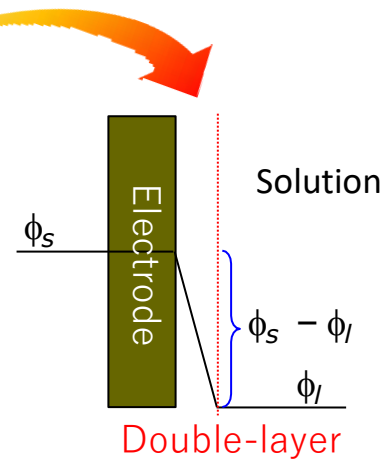- Proportional to the forward and backward reaction rates at the equilibrium potential

➢ Tertiary current distribution

$$i = i_0 [\frac{c_a}{c_b}\exp\left(\frac{\alpha_a F}{RT}\eta\right) - \frac{c_c}{c_b}\exp(-\frac{\alpha_c F}{RT}\eta)]$$

Electrode

Solution

ϕ_s

$\phi_s - \phi_l$

ϕ_l

Double-layer

Overpotential

$$\eta = \phi_s - \phi_l - E_{eq}$$

Equilibrium Potential

COMSOL Corrosion module

- ▲ Chemical Species Transport
  - Transport of Diluted Species (tds)
  - Chemistry (chem)
  - Nernst-Planck-Poisson Equations
  - Transport of Diluted Species in Porous Media (tds)
  - Electrophoretic Transport (el)
  - ▷ Reacting Flow
  - Surface Reactions (sr)
  - Transport of Diluted Species in Fractures (dsf)
- ▲ Electrochemistry
  - ▷ Primary and Secondary Current Distribution
  - ▲ Tertiary Current Distribution, Nernst-Planck
    - Tertiary, Electroneutrality (tcd)
    - Tertiary, Water-Based with Electroneutrality (tcd)
    - Tertiary, Supporting Electrolyte (tcd)
  - Electroanalysis (tcd)
  - Electrode, Shell (els)
  - ▲ Corrosion, Deformed Geometry
    - Corrosion, Primary
    - Corrosion, Secondary
    - Corrosion, Tertiary with Electroneutrality
    - Corrosion, Tertiary with Supporting Electrolyte
  - ▷ Electrodeposition, Deformed Geometry
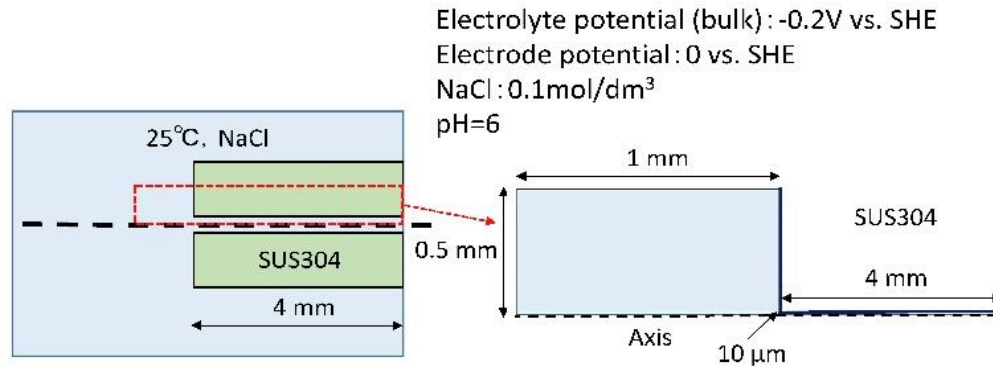
- ▲ Fluid Flow
  - ▲ Single-Phase Flow
    - Creeping Flow (spf)
    - Laminar Flow (spf)
  - ▲ Porous Media and Subsurface Flow
    - Brinkman Equations (br)
    - Darcy's Law (dl)
    - Free and Porous Media Flow (fp)
  - ▲ Nonisothermal Flow
    - Laminar Flow
- ▲ Heat Transfer
  - Heat Transfer in Solids (ht)
  - Heat Transfer in Fluids (ht)
  - Heat Transfer in Solids and Fluids (ht)
  - ▷ Conjugate Heat Transfer
  - ▷ Electromagnetic Heating
  - Heat Transfer in Porous Media (ht)
- ▷ Structural Mechanics
- ▷ Δu Mathematics

In this paper, the Chemistry interface is coupled with the Tertiary Current Distribution, Nernst-Planck interface.

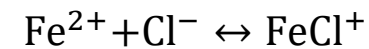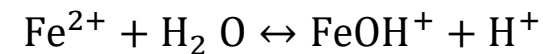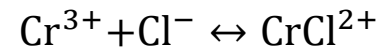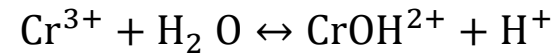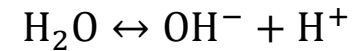# Computational model of crevice corrosion

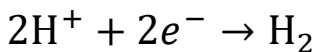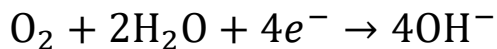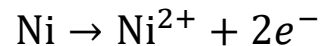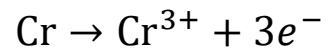## Specimen configuration of crevice corrosion and computational model

Electrolyte potential (bulk) : -0.2V vs. SHE
Electrode potential : 0 vs. SHE
NaCl : 0.1mol/dm³
pH=6

25℃, NaCl

1 mm

SUS304

SUS304

0.5 mm

4 mm

4 mm

Axis

10 μm

Chemical species in solution:

Fe^{2+}, Ni^{2+}, Cr^{3+}, H^+, OH^-, $FeOH^+$, $CrOH^{2+}$, $FeCl^+$, $CrCl^{2+}$, $CrClOH^+$, Na^+, Cl^-, O_2, H_2, H_2O

Equilibrium reactions in solution

$$H_2O \leftrightarrow OH^- + H^+$$
$$Cr^{3+} + H_2O \leftrightarrow CrOH^{2+} + H^+$$
$$Cr^{3+} + Cl^- \leftrightarrow CrCl^{2+}$$
$$CrCl^{2+} + H_2O \leftrightarrow CrClOH^+ + H^+$$
$$Fe^{2+} + H_2O \leftrightarrow FeOH^+ + H^+$$
$$Fe^{2+} + Cl^- \leftrightarrow FeCl^+$$

Electrochemical reactions on SUS304

$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Cr \rightarrow Cr^{3+} + 3e^-$$
$$Ni \rightarrow Ni^{2+} + 2e^-$$
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
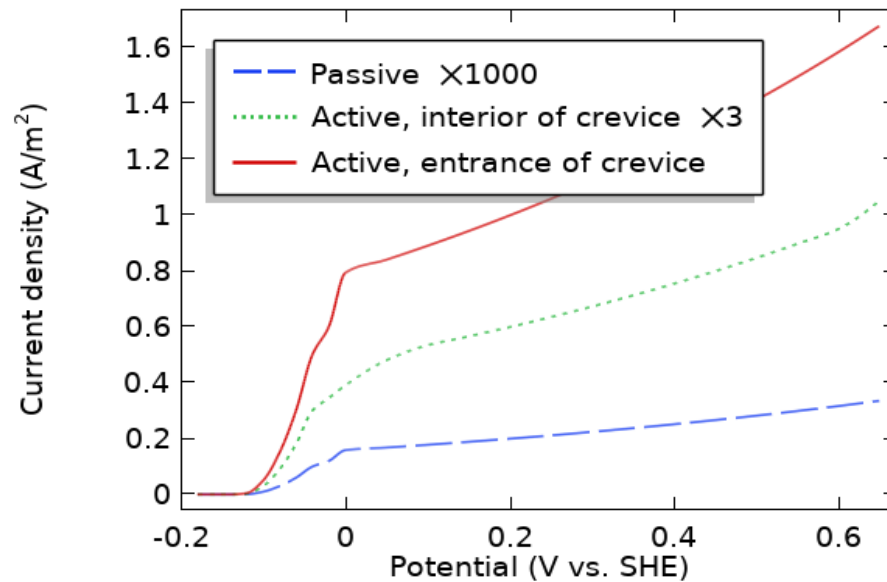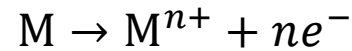$$2H^+ + 2e^- \rightarrow H_2$$
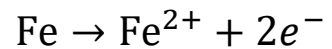
Polarization curves for SUS304

Computational model of crevice corrosion

Polarization curves for SUS304

In calculation, the three reactions of metal dissolution are replaced by the dissolution of single metal atom M

$$M \rightarrow M^{n+} + ne^-$$

Electrode Reaction

▼ Stoichiometric Coefficients

Number of participating electrons:

n	2.2	1

Stoichiometric coefficients:

ν_{cO2}	0	1
ν_{cHp}	0	1
ν_{cOHm}	0	1
ν_{cFe2p}	-0.716	1
ν_{cNi2p}	-0.087	1
ν_{cCr3p}	-0.197	1

The contents of elements in SUS304 are 0.716, 0.197 and 0.087 for Fe, Cr, and Ni, respectively.

Fe^{2+} Cr^{3+} Ni^{2+}

$$n = 2 \times 0.716 + 3 \times 0.197 + 2 \times 0.087 = 2.2.$$

Computational results

Benchmark study of equilibrium reactions

➢ The calculation is performed for a solution involving $FeCl_2 \cdot 4H_2O$, $CrCl_3 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ in a 2D area of 2 cm $\times$ 2cm, which is consistent with the experimental set-up.

➢ The simulation time considered in this work is set to 10 hours so that a complete equilibrium state can be reached.
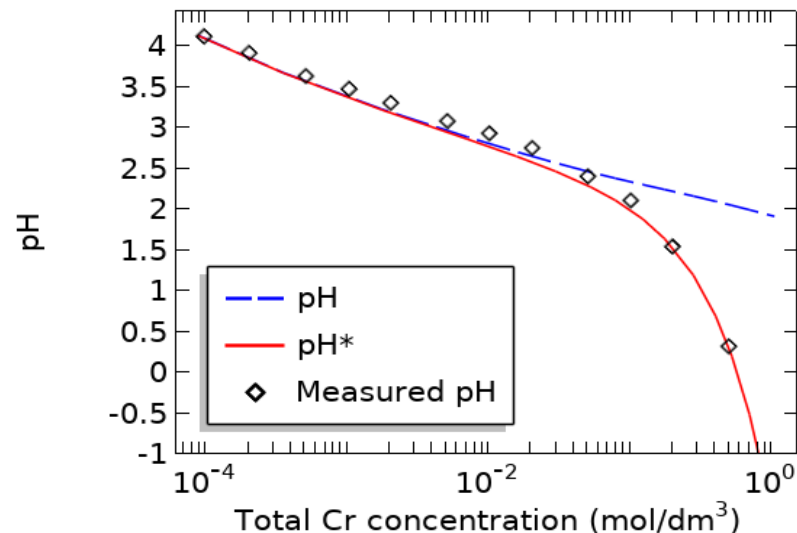
pH* is the modified pH by activity coefficient

$$logY_{all} = logY_{FeCl_2} + logY_{CrCl_3} + logY_{NiCl_2}$$

$$pH^* = -log(c_{H^+}Y_{all})$$

where Y_{FeCl_2}, Y_{CrCl_3}, and Y_{NiCl_2} denote the increasing ratios of activity coefficient of H^+ with $FeCl_2$, $CrCl_3$, $NiCl_2$ species, respectively, and Y_{all} is their sum.

Ref.: Y. Fukaya and T. Shinohara : 66th Symposium of Materials and Environments in Japan, B-107 (2019) [in Japanese].

Computational results

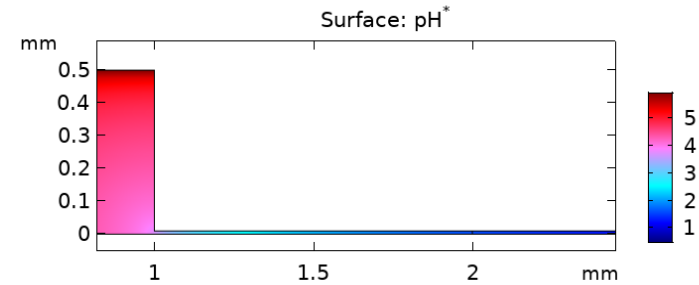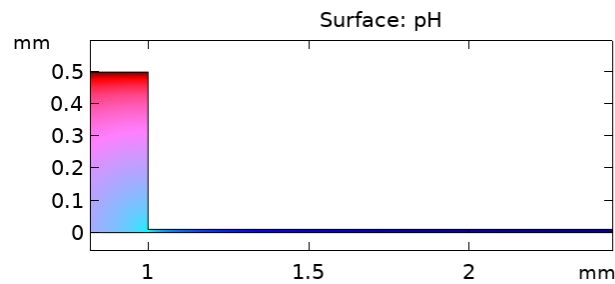## Simulation of change of chemical species with progress of corrosion

Distributions of concentrations of chemical species after 100 hours of corrosion
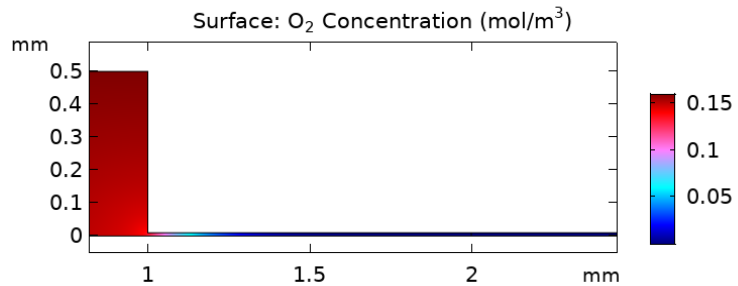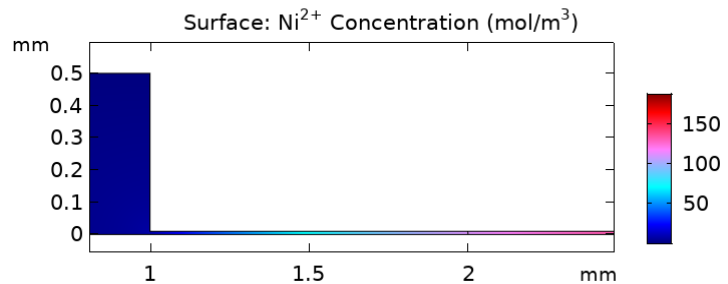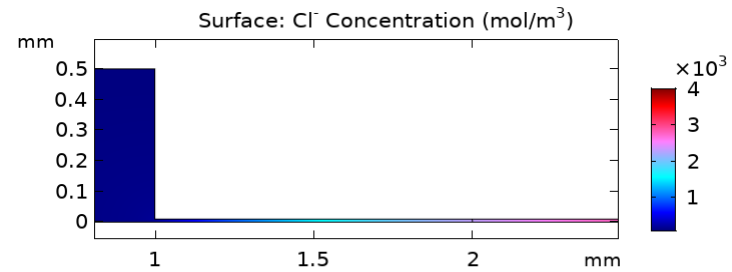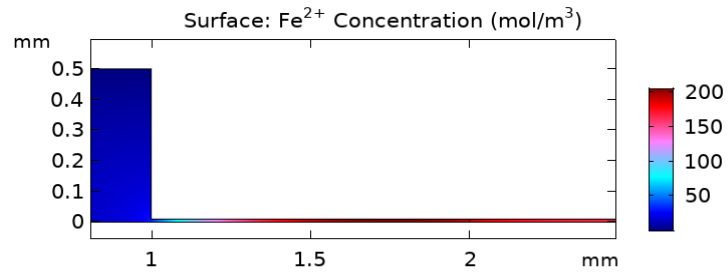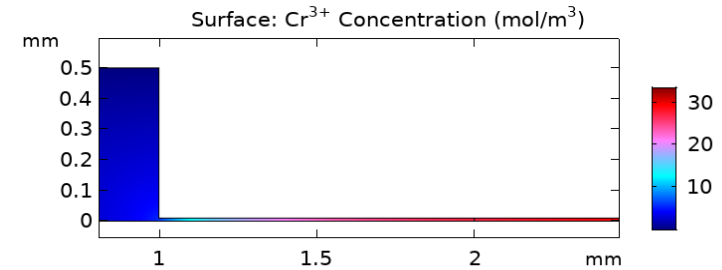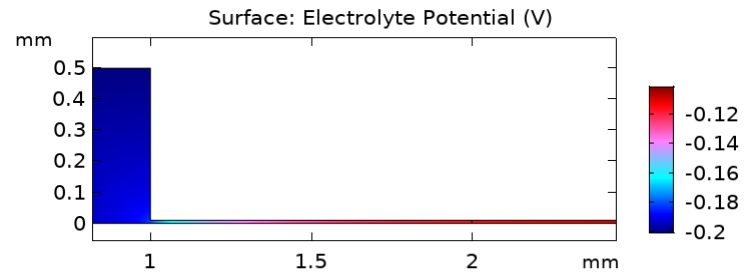
Computational results

Simulation of change of chemical species with progress of corrosion

pH and pH* after 100 hours of corrosion

$$E_{eq,O_2} = 1.228 - 0.059 \times pH$$

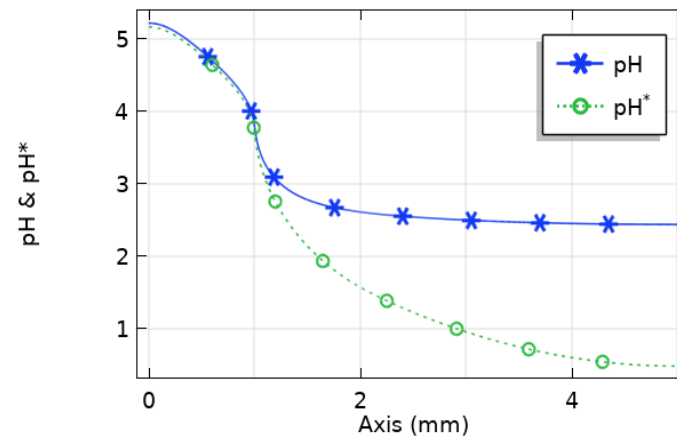$$E_{eq,H_2} = -0.059 \times pH^*$$

$$i_{loc} = -i_0 \times 10^{\eta/A_c}$$

$$\eta = V - \phi_0 - E_{eq,S} \leftarrow$$
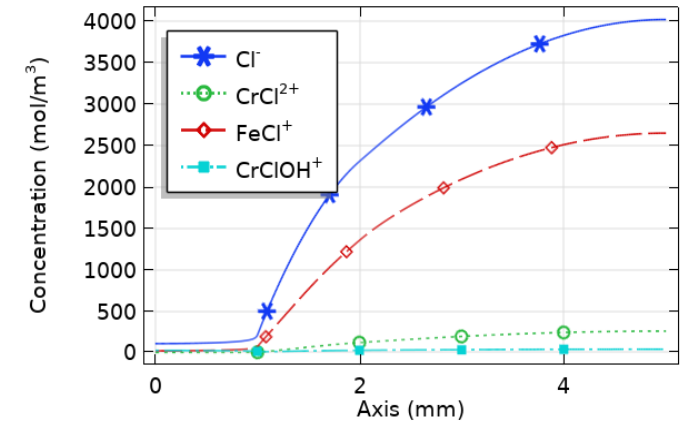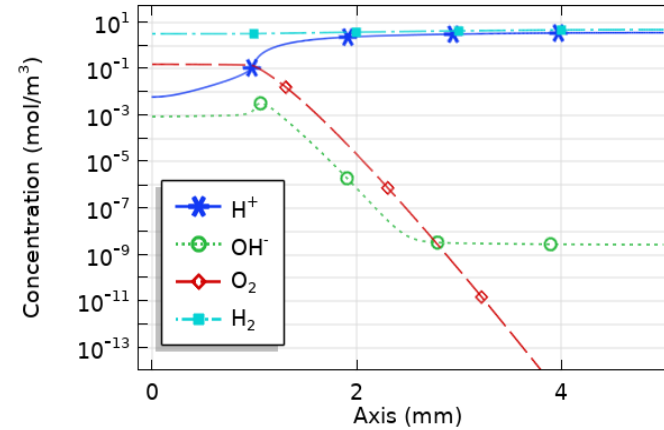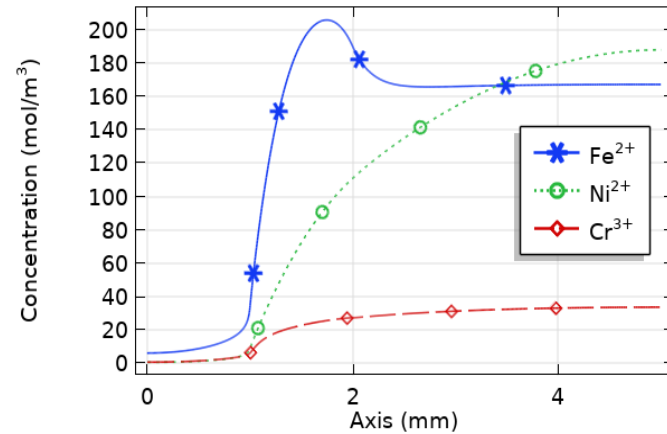
O$_2$ or H$_2$

pH decreases from the initial value of 6 to 2.5 and the modified value pH* by activity coefficient decreases to 0.5.

Computational results

Simulation of change of chemical species with progress of corrosion

Distributions of concentrations of various ions, O_2, and H_2 in the middle of a crevice


The evolved hydrogen concentration appears a quasi-uniform distribution inside the crevice, but the oxygen concentration has a dramatic decrease in the crevice, which is lower than 1×10^{-13} mol/m³ in the interior area of crevice.

Computational results

Simulation of change of chemical species with progress of corrosion

Time variation of concentrations of Cl^- ion and O_2
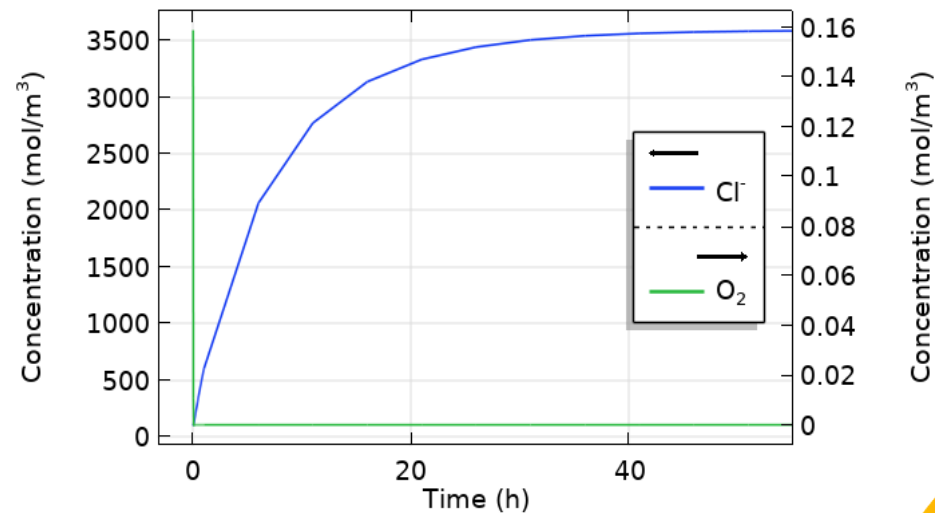
Equilibrium Reaction *(tcd)* => Chemistry *(chem)*

Conclusions

- This paper presents a simulation research based on a two-dimensional model of crevice corrosion of stainless steel SUS304 in NaCl solution.

- The concentration distributions of various ions, oxygen, and hydrogen in the crevice are obtained and the pH value in the crevice is presented and evaluated.

- The reversible reactions specifying equilibrium constants in the Chemistry interface of COMSOL Multiphysics® are used to solve the equilibrium reactions occurred in the solution, which are coupled with the Tertiary Current Distribution, Nernst-Planck interface.

- A benchmark simulation for the equilibrium reactions occurred in solution is performed. The effect of activity coefficient of H^+ on pH is verified and the calculated modified pH, *i.e.*, pH^* is consistent with the experimental data.

- It is found that it is necessary to solve the temporal change of the chemical reactions in solution for crevice corrosion until an equilibrium state is reached, which is directly related to computational convergence.

- The approach proposed in this work could be applied to further elucidate actual complex corrosion phenomena that involve various chemical reactions of solution in near future.

Thank You

For Your Attention