

## Effect of temperature on the dissipation behavior of Chloride ion within the crevice of stainless steels

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### ABSTRACT

In this study, we measured solution conductivity within crevices Type 316L stainless steels using microsensors and studied the effect of temperature on the dissipation behavior of chloride ion. Solution conductivity within crevice with dimensions of 10 mm × 23 mm × 25 μm was measured using microsensors. Assuming the purification process after seawater had flowed into the reactor facility, after chloride ions fully diffused into the crevice, the outside water was purified, and we estimated the purification behavior from the change in solution conductivity in the crevice. Tests were conducted at temperatures of 15-18°C (room temperature), 80°C and 130°C. At room temperature, the rate of decrease in conductivity was close to the rate estimated from simple concentration diffusion, but it was significantly slower at temperatures above 80°C. As an increase in temperature generally increases the diffusion coefficient of ions, we expected that concentration diffusion would be promoted by an increase in temperature, but effect of diffusion was inhibited in this study. Although localized corrosion was not observed in the crevices of the stainless steel, metal cation was generated by uniform corrosion occurred, and the corrosion rate was considered to be accelerated by increase in temperature. We assumed that the potential gradient formed in the liquid phase with generation of metal cation attracted chloride ions into the crevice and which inhibited their desorption by concentration diffusion. However, it was also possible that anions other than chloride (e.g., hydroxide ion) were also attracted into the crevice by the potential gradient.

### INTRODUCTION

In May 2011, the main condenser tubes were damaged during the cold shutdown process after the reactor shutdown at Hamaoka Unit 5, and approximately 400 m<sup>3</sup> of seawater flowed into the reactor facility. After this incident, the reactor water was purified by replacing demineralized water and other means. However, there is still a possibility that chloride ions originated from the seawater remain in the crevice structure in the reactor and they are leaching into the reactor water.

Therefore, it is necessary to directly measure the behavior of such ions in the crevices and understand the mechanism by which chloride ions remain for a long period of time, and to formulate an appropriate plan for removal of residual ions. In this study, we measured solution conductivity within crevices Type 316L stainless steels using microsensors<sup>1</sup> and the effect of temperature on the dissipation behavior of chloride ion was studied.

### EXPERIMENTAL PROCEDURE

#### *Crevice specimen with sensor*

The test material was Type 316L stainless steel, which is widely used in nuclear reactor internals and comprises many crevice structures. Figure 1 shows the crevice specimen attached to the sensors for the electrochemical measurement. The crevice specimen shown in Figure 1(a) comprised a pair of stainless steel plates with one having a machined groove and another having a flat surface with sensors. The crevice specimen assembled by the two pieces had a crevice with dimensions of 10 mm × 23 mm × 25 μm. The microsensor can measure conductivity and the specimen with the sensor was placed at three locations at

distances of 1.5 mm, 5 mm, and 21 mm from the crevice mouths. In addition, the specimen used by insulator was also prepared for comparison with the metal crevice specimens. The insulator material was polyetherketone (PEEK).

The sensor surface used for the specimen of Type 316L stainless steel is shown in Fig. 1(b) as representative. The sensor was comprised of a Type 316L electrode with a diameter of 300  $\mu\text{m}$  insulated by alumina tubing. Each component was brazed using Ag-Cu brazing filler metal. The diameter of the electrode was about 400  $\mu\text{m}$  and about 300  $\mu\text{m}$ , and were designated as specimen No. 1 and No. 2, respectively. The sensor for the specimen used by insulator is made of Pt with a diameter of 500  $\mu\text{m}$  as the central electrode, which was fixed in the PEEK with epoxy resin. The cross-section structure of the sensor is shown in Fig. 2. An alternating current was applied between the sensor electrode and the crevice specimen (in the case of insulator specimens, the sensor electrode of the same configuration) and we calculated the solution conductivity by the AC impedance method.

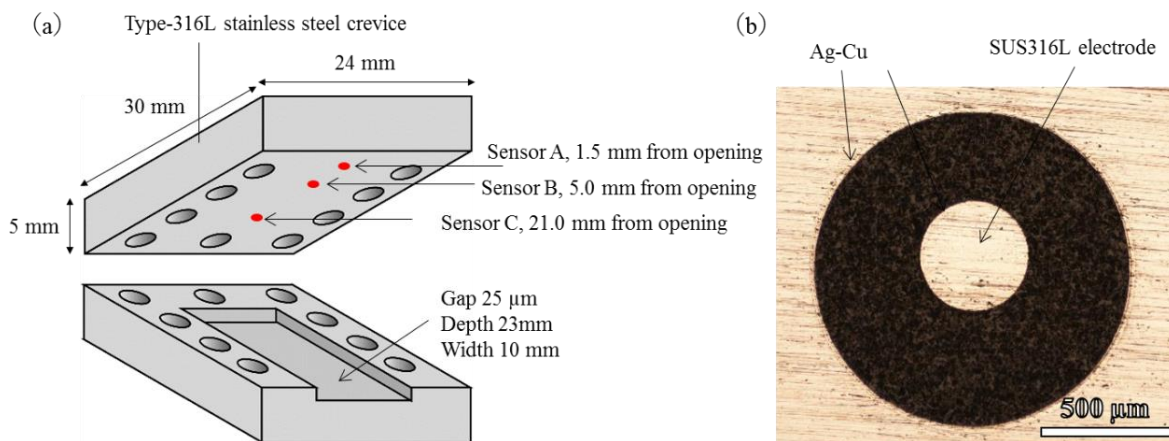


Figure 1. (a) Crevice specimen with microsensors and (b) the surface of the microsensor

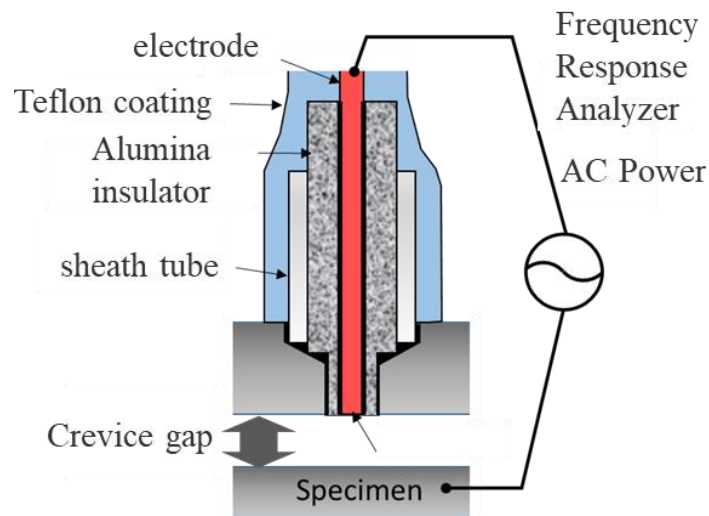


Figure 2. The structure of the sensor

**Test system**

Schematic of the water circulation system is shown in Figure 3. The system consists of autoclave made of titanium (inner diameter 40 mm, length 300 mm, volume 0.39 dm<sup>3</sup>, design temperature 300 °C, design pressure 10 MPa), pumps, temperature control systems, purification systems and measurement systems. The solution prepared in the tank is sent to the autoclave inlet, and after passing through the outlet, the loop returns to the tank via the purification system or bypass line.

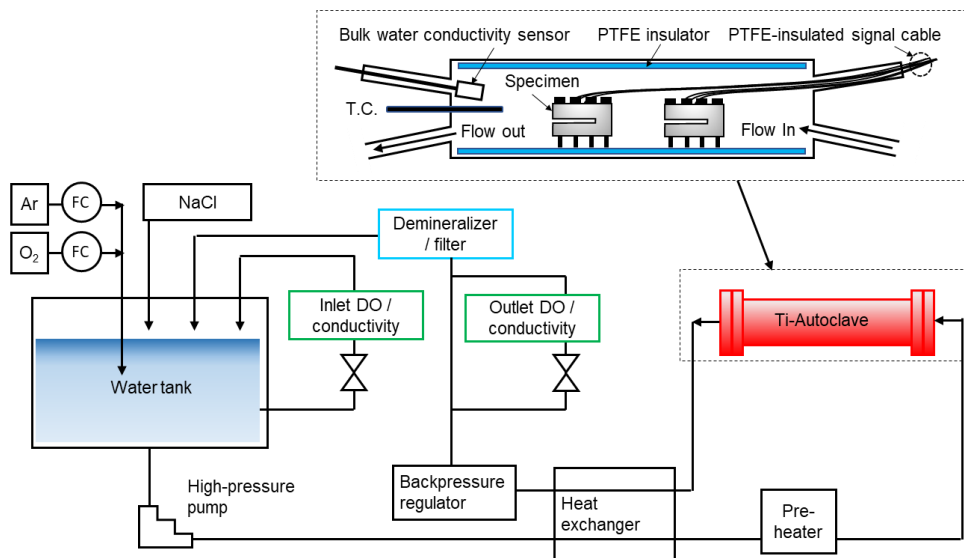


Figure 3. Schematic of the water circulation system

**Test procedure**

Figure 4 shows typical operating parameters at a temperature of 130°C. The test is divided into three stages. In the stage 1, the temperature and the concentration of dissolved oxygen were adjusted to the desired values (130°C / 8 ppm). In the stage 2, the NaCl was injected (0.01 ~ 0.02 M). In the stage 3, the bulk water was purified again by the purification system and measured solution conductivity within crevice.

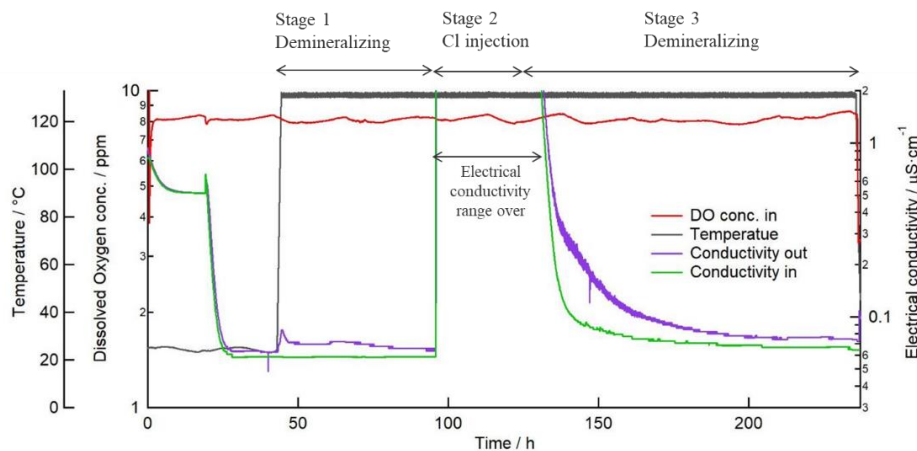


Figure 4. Typical operating parameters at a temperature of 130 °C

## SIMULATIONS

### *Simulation conditions*

The theoretical values for comparing the experimental values with the concentration-diffusion behavior was calculated by the following procedure. In this model, only the NaCl desorption behavior from the crevice due to external purification was subject to the calculation. The calculation model is shown in Fig. 5. The calculation software COMSOL Multiphysics was used. The model consists of a gap of 25  $\mu\text{m}$  and a depth of 23 mm, which simulates the cross section of the specimen, and an outer boundary. The outer boundary was 0.5 mm from the mouth in the depth direction and 1 cm in the gap direction as a diffusion layer. The specific concentration of NaCl was given to crevice and outside as an initial value. The boundary conditions for the calculation were the edge conditions drawn by the green line, referring to the experimental values. The diffusion coefficient was set to  $1.29 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ , which was corrected for the test temperature (average  $15^\circ\text{C}$ ) in reference to the literature value for NaCl in the Electrochemical Handbook ( $1.61 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$  @  $25^\circ\text{C}$ ). In the calculations, the y-axis intercepts were matched by shifting the sensor position towards the mouth by 0.8-3 mm from the actual position, which is considered to be due to the non-ideal shape of the crevice.

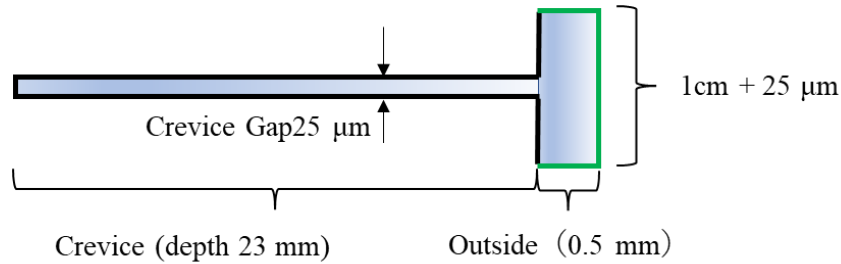


Figure 5. Simulation model

### *The diffusion coefficient for high temperatures*

The above values can be used for diffusion behavior near room temperature. But, at higher temperatures, it is necessary to know the limiting molar conductivity of the various ions and the temperature dependence of the diffusion coefficient to convert to conductivity. They were calculated in the following formula. The temperature dependence of the limiting molar conductivity of the ions was calculated using equation (1).

$$\ln \lambda(T) \eta(T) = A + B/T \quad (1)$$

where  $\lambda(T)$  is the limiting molar conductivity of each ion,  $\eta(T)$  is the viscosity of water,  $T$  is the temperature and  $A$  and  $B$  are constants specific to each ion.  $\eta(T)$  was calculated with reference to the literature.

The calculated the limiting molar conductivity of each ion was then converted into a diffusion coefficient  $D$  using equation (2) and the diffusion coefficient  $D_{\text{salt}}$  as salt (NaCl) was obtained using equation (3).

$$D = (RT/F^2)(\lambda/|z|) \quad (2)$$

$$D_{\text{salt}} = \frac{(z_+ + |z_-|)D_+ D_-}{z_+ D_+ + |z_-| D_-} \quad (3)$$

where  $R$  is the gas constant,  $z$  is the charge, and the subscripts  $+$  and  $-$  attached to  $D$  and  $z$  mean cation and anion, respectively. The diffusion coefficients were substituted into the following equation to calculate the position and time variation of conductivity.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (4)$$

$$C(x, t) = C_0 \operatorname{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \quad (5)$$

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-a^2} da \quad (6)$$

where  $C$  is the conductivity,  $C_0$  is the initial conductivity,  $x$  is the position in the crevice depth direction and  $t$  is the time.

## RESULTS

Tests were conducted at room temperature, 50, 80 and 130 °C to evaluate the temperature dependence of the dissipation behavior of Chloride ion. The results at room temperature are first shown in Figure 6. At room temperature, the crevice specimens were made of metal or insulating material (PEEK) and tested under Argon degassing or a dissolved oxygen concentration of 8 ppm (atmospheric pressure condition). The time variation of the conductivity of the solution in the crevice is expressed as  $\kappa$ . The values of  $\kappa$  are  $\kappa$  (SUS-A to C) for the SUS316L and  $\kappa$  (PEEK-A to C) for the PEEK. The calculation results from concentration-diffusion are shown as solid red, blue and black lines from the mouth. At room temperature (15-18 °C), the time variation of the conductivity of the solution in the crevice is in good agreement with the values inferred from the concentration-diffusion calculations. This suggests the effect of DO (dissolved oxygen) concentration and material (metal and insulator) on the dissipation behavior of Chloride ion within the crevice is small. At high temperatures, the specimens were made of metal and tested at a DO concentration of 8 ppm. Representative results at 80°C and 130°C are shown in Figures 7(a) and 8(a). In Stage 3, it can be seen the solution conductivity within crevices decreases with the purification of the outside water. At sensor C (the far side of the crevice mouth), the experimental value is close to the calculated value (broken line) immediately after the outside water is purified. But the rate of decrease slows down over time. It can be seen the purification in crevice is slower than calculation values. Specimens after the test are shown in Figures 7(b) and 8(b). Although no significant localized corrosion occurred, brown corrosion products were observed near the mouths. We considered that the metal cations generated by uniform corrosion of the metal surface in the crevice reacted with oxygen diffused from outside near the crevice mouth and it precipitated such corrosion products. The increase in temperature increases the diffusion coefficient, which promotes ion desorption from the crevice by concentration-diffusion during external water purified, but also increases the corrosion rate. The potential gradient formed in the crevice, driven by the combination of the corrosion reaction in the crevice and the cathodic reaction by the reduction of oxygen outside the crevice, effect of oxygen concentration cell, has the effect of attracting anions into the crevice. This effect is more active at higher temperatures, and it can be considered to inhabit the desorption of Chloride ions compared to lower temperatures. Meanwhile, hydroxide ions produced by the reduction of oxygen are also thought to migrate into the crevice in the same way as Chloride ions, which suggests that hydroxide ions may have replaced some of the Chloride ions.

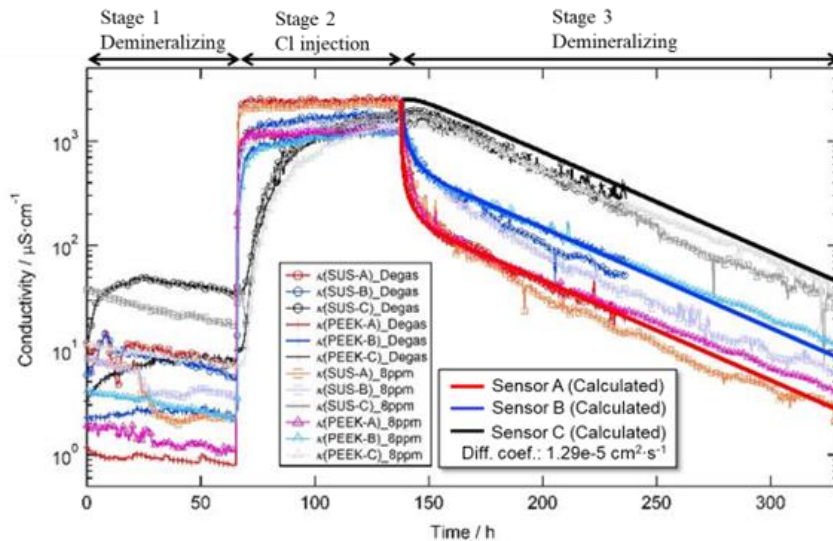


Figure 6. Conductivity in the crevice at room temperature

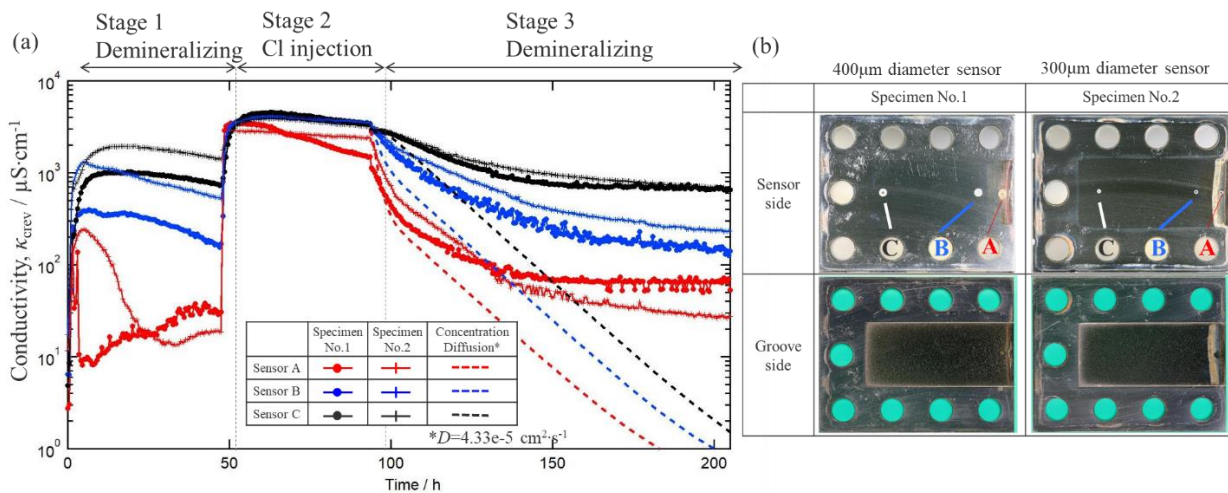


Figure 7. (a) Conductivity in the crevice at 80°C (b) the specimen after the test

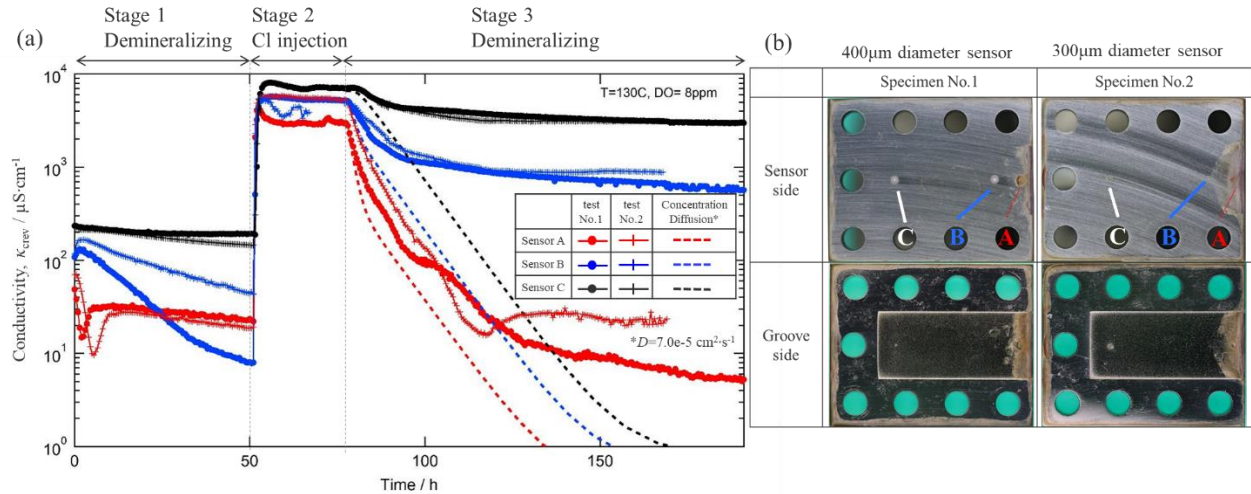


Figure 8. (a) Conductivity in the crevice at 130°C (b) the specimen after the test

## CONCLUSION

In this study, we investigated the temperature dependence of the dissipation behavior of chloride ions in stainless steel crevices. Following to the concentration-diffusion model, an increase in temperature is considered to increase the diffusion coefficient and accelerate the dissipation of chloride ions from the crevice, but the time variation of the conductivity of the solution in the crevice measured suggests the dissipation rate of chloride ions is slower than that of simple concentration-diffusion. This phenomenon was not observed in the insulating material and increase in temperature promote localized corrosion in stainless steel. It suggests that the effect of the electrical migration of Cl<sup>-</sup> into the crevices to balance the charge of metal cations generated by increasing corrosion rate is more significant than the promotion effect of ion desorption by increase in temperature. It is inferred that desorption of Cl<sup>-</sup> from the crevice in stainless steel may not be simply promoted by the increase in temperature.

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