水化学部会第18回全体会議

Contribution of Cathodic Reaction inside Crevice to development of Crevice Corrosion in 304L SS

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1. Seawater contamination in Fukushima SFP

Unit 2-4: Seawater was injected into SFP just after the accident for emergency fuel cooling.

Temperature & [Cl^-] raised up to 92°C and 1944ppm.
It was crevice corrosion possible environment[1] for 304 SS.

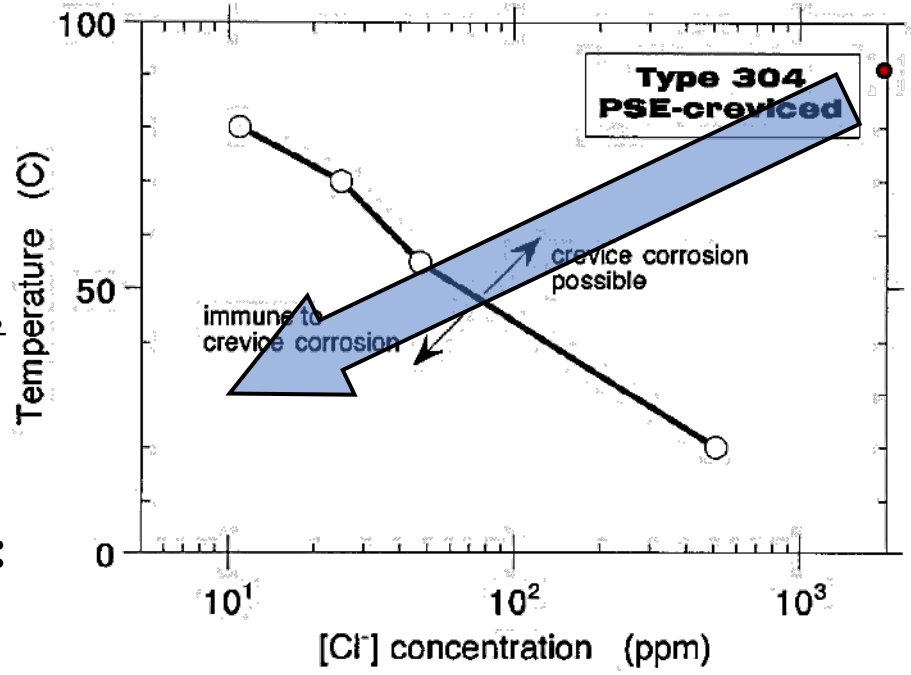
Ø Localized corrosion, especially crevice corrosion may have occured.

Environment was purified & deoxygenated.
Low possibility of another localized corrosion.

Whether localized corrosion once initiated and propagated in high temp. & [Cl^-] repassivate when environment is improved is not confirmed.

Study on crevice corrosion propagation continuity of when the environment is improved:

cathodic reaction on the surface outside no more contribute to propagation of the corrosion.



[1: M. Akashi, et al., CORROSION '98, 158, (1998)]

2. Crevice corrosion initiation and propagation

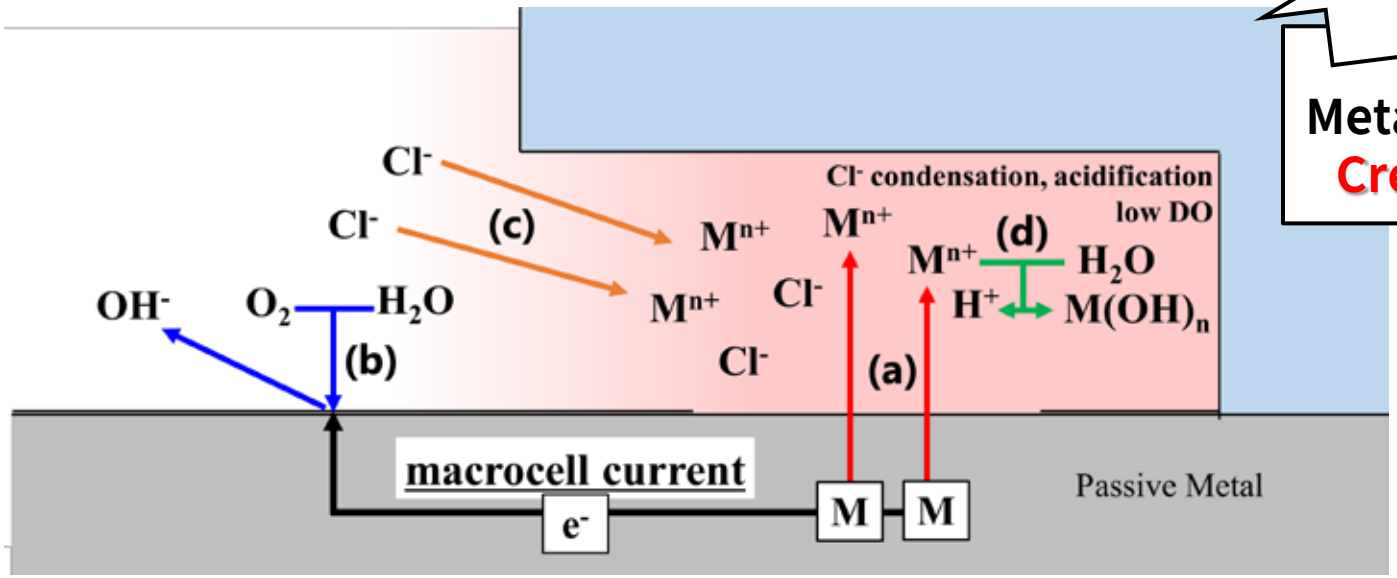
[2: M. G. Fontana, et al., *Corrosion Engineering* (New York, NY: McGraw-Hill, 1967), p. 28]

- **Oxygen reduced in/outside. → Oxygen diffusion into occluded crevice is blocked. → Oxygen deplete inside. → Cathodic reaction occur only outside crevice.**

- **Hydrolisys of dissolved metal cation → Acidification**
- **Condence of cation inside crevice → Cl^- condensation**

Aggressive solution inside crevice

Metal surface depassivation, Crevice corrosion initiation



Ø **Anodic reaction inside crevice is supported by cathodic reaction outside crevice.**[3-8]

[3: O. B. Ellis, et al., *CORROSION* 7, (1951): p. 362]
[4: Z. Y. Chen, et al., *J. Electrochem. Soc.* 155, 7 (2008): p. C360]
[5: N. Sridhar, et al., *CORROSION* 50, 11 (1994): p. 857]
[6: F. Bocher, et al., *CORROSION* 71, 9 (2015): p. 1051]
[7: J. R. Galvele, *J. Electrochem. Soc.* 123, 4 (1976): p. 464]
[8: S. Tsujikawa, et al., Corrosion Chemistry within Pits, Crevices and Cracks, paper 10 (London, Oct. 1-3, 1984), p. 171]

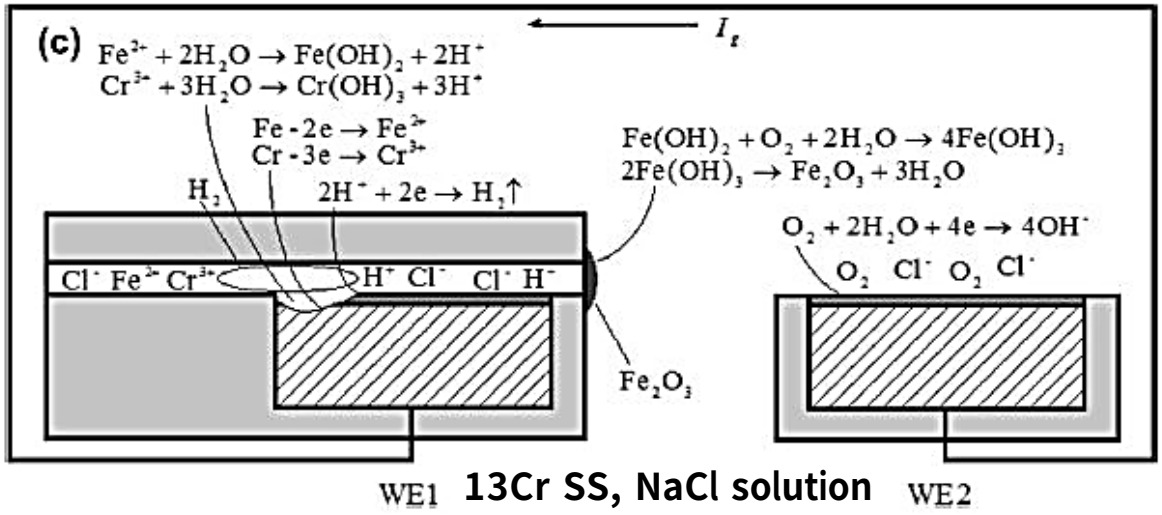
3. Cathodic reaction inside crevice

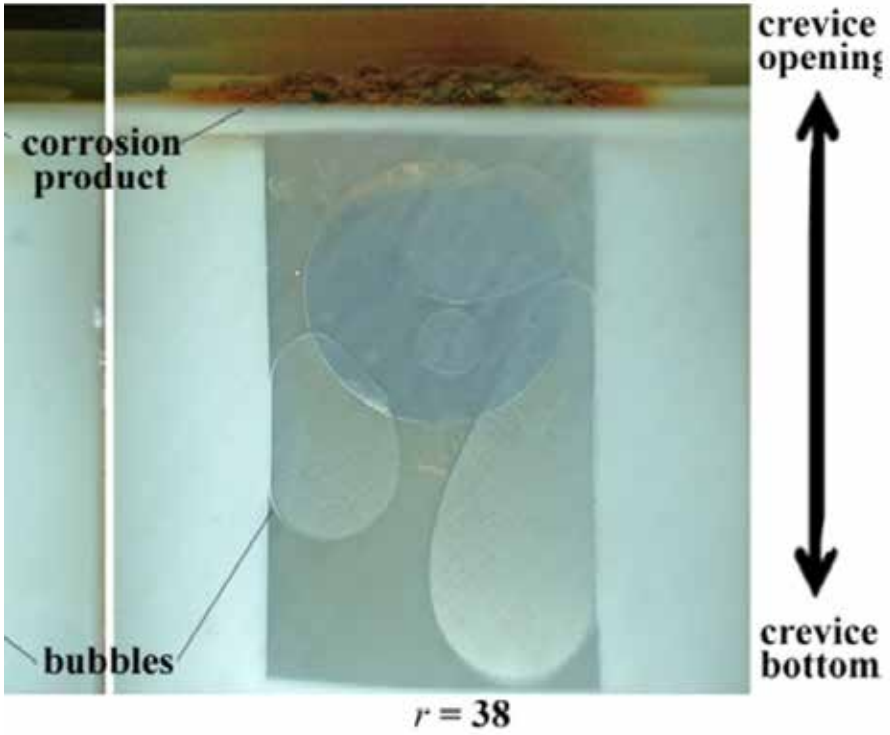
[9: Q. Hu, et al., *Corros. Sci.* 53, 12 (2011): p. 4065]

- **Generally, anodic reaction mainly occur inside crevice and cathodic reaction could be ignored.**

- **Gas generation inside crevice have been observed during crevice corrosion propagation under open circuit immersion as below.**

$$2H^+ + 2e^- \rightarrow H_2\uparrow$$



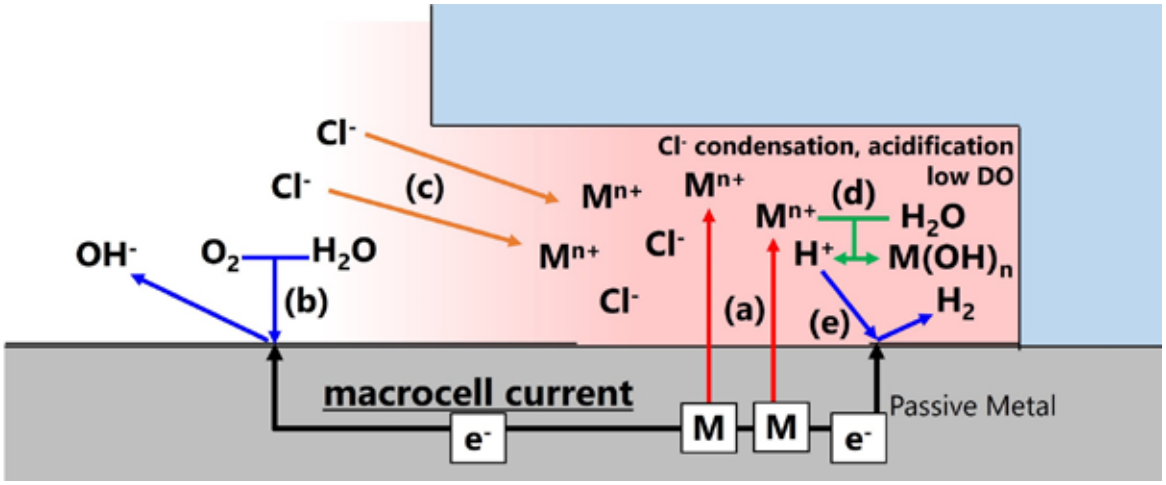


Ø **Contribution of cathodic reaction inside crevice** to propagation of the corrosion could not be ignored actually.

4. Objective of this study & Way of research

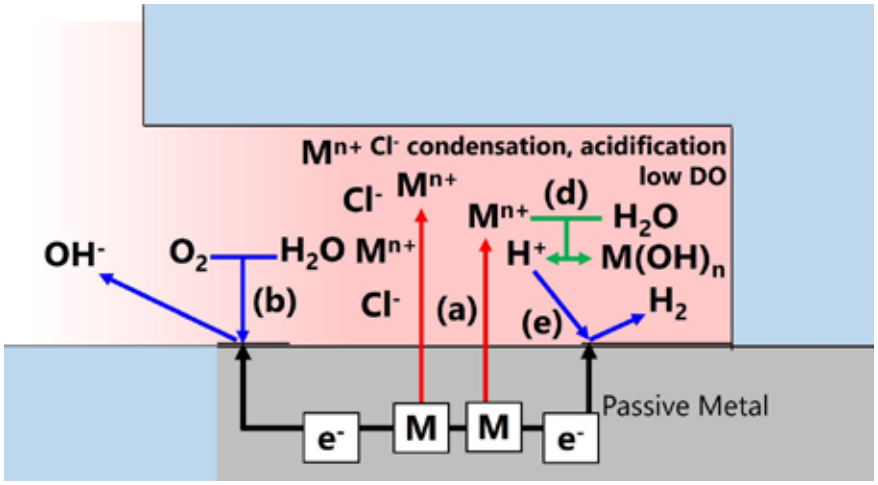
- Clarify contribution of **cathodic reaction inside and outside** crevice on propagation of crevice corrosion.

With outer cathode



(a) Anodic dissolution
(b) Oxygen reduction @outside
(c) Cl^- migration
(d) H^+ generation by hydrolysis
(e) Hydrogen gas generation

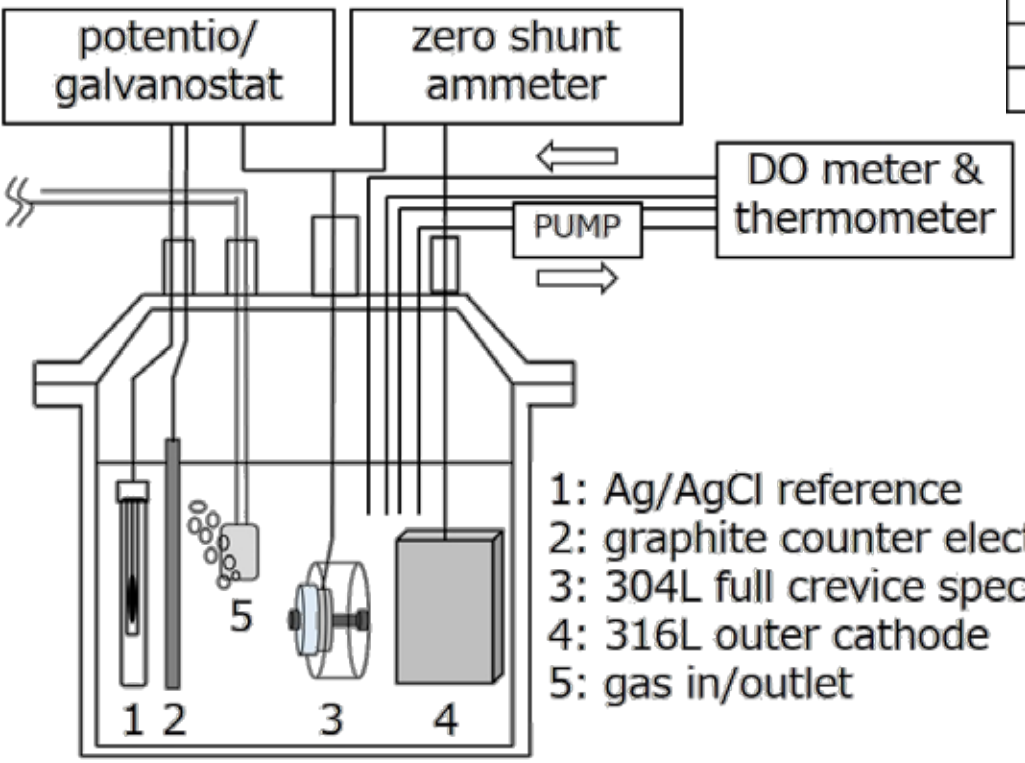
Without outer cathode

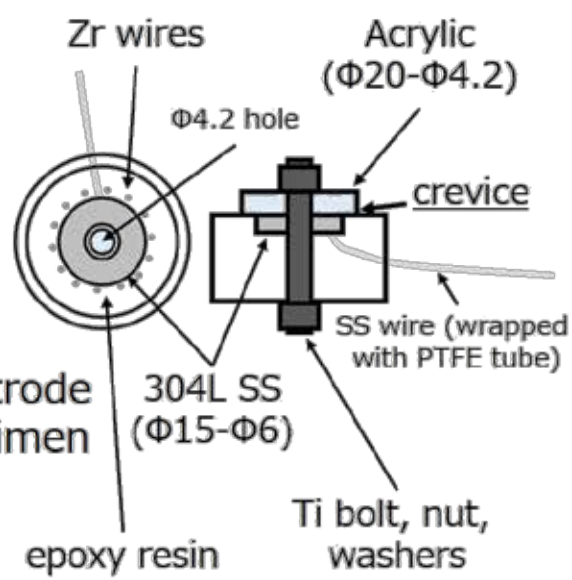


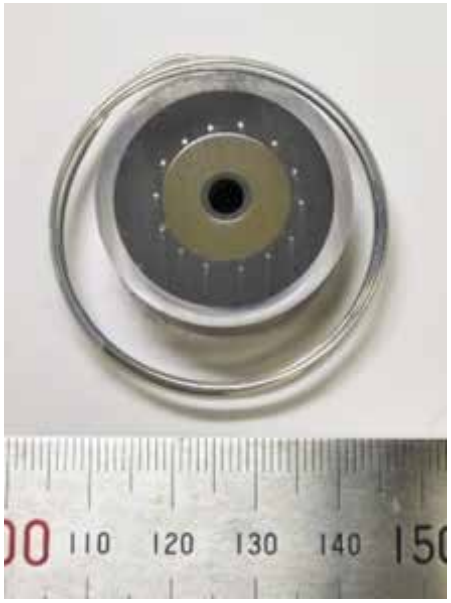
(a) Anodic dissolution
(b) Oxygen reduction @mouth
~~(c) Cl^- migration~~
(d) H^+ generation by hydrolysis
(e) Hydrogen gas generation

5. Experimental setup

wt%	C	Si	Mn	P	S	Ni	Cr	Mo	Fe
SUS304L	0.021	0.46	0.84	0.027	0.004	9.13	18.22		Bal.
SUS316L	0.009	0.60	0.89	0.018	0.005	12.26	16.31	2.10	Bal.







Specimen (P500 polished):

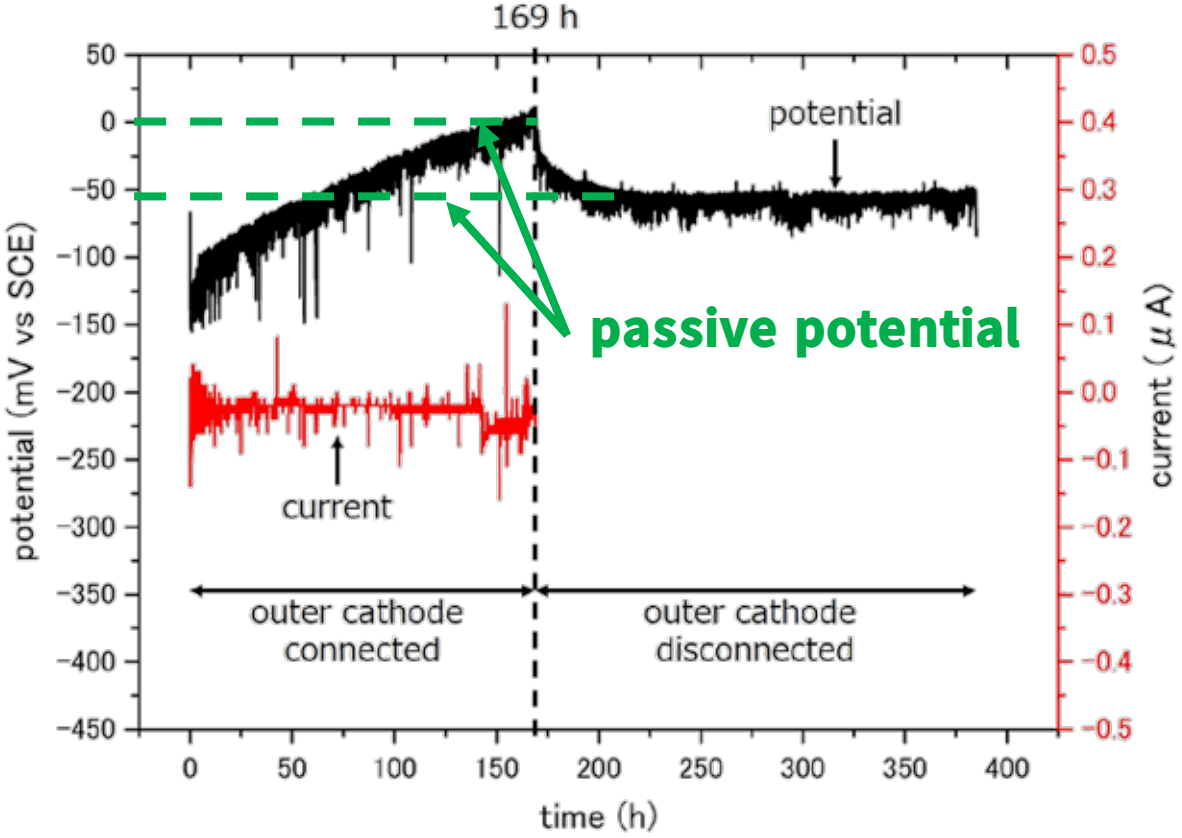
- **Full crevice specimen: 304L (Φ15-6.0=1.48mm³) - acrylic (Φ20, P2400)**
- **Outer cathode: 316L SS (H65×W50×T3.0=71.9mm³)**

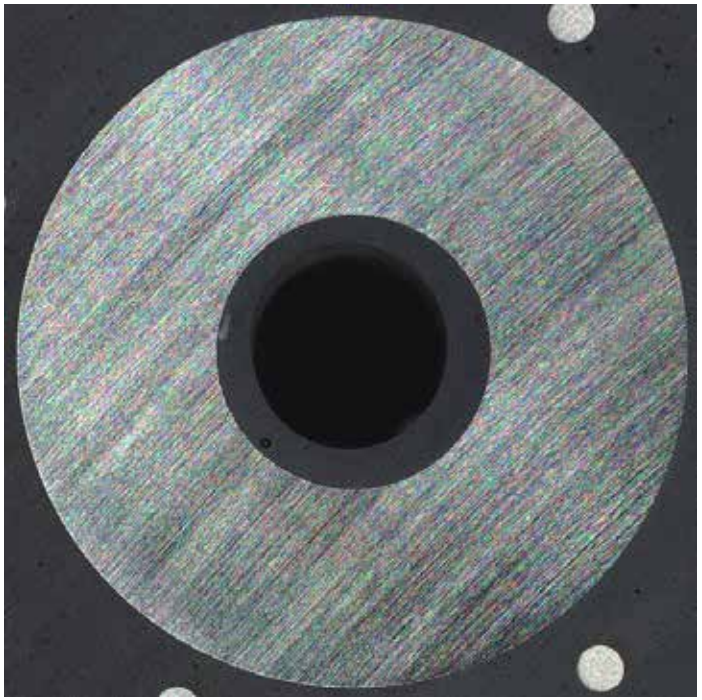
Solution • Temperature • Injected gas:

- **NaCl (Cl^-=10000ppm), 50°C, Artificial air (N_2: 80%, O_2: 20%)**

6. Passive potential: with/without outer cathode

- **To determine whether the corrosion repassivated or keep propagating, measured the potential of passive state of full crevice specimen with/without outer cathode and coupling current.**





Surface after immersion

With outer cathode: above $0V_{SCE}$, under 0.1μA
Without outer cathode: about $-60mV_{SCE}$

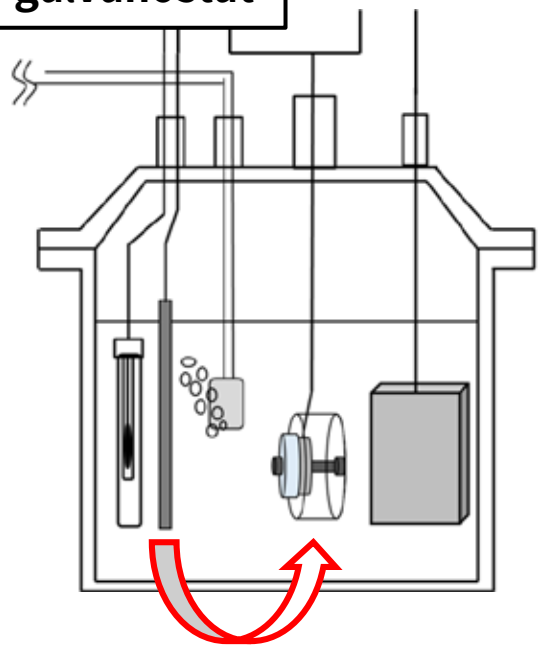
When the corrosion propagation terminated and repassivated.

7. Experimental procedure

Step ①

Electrochemical operation (polarization)

potentio/ galvanostat



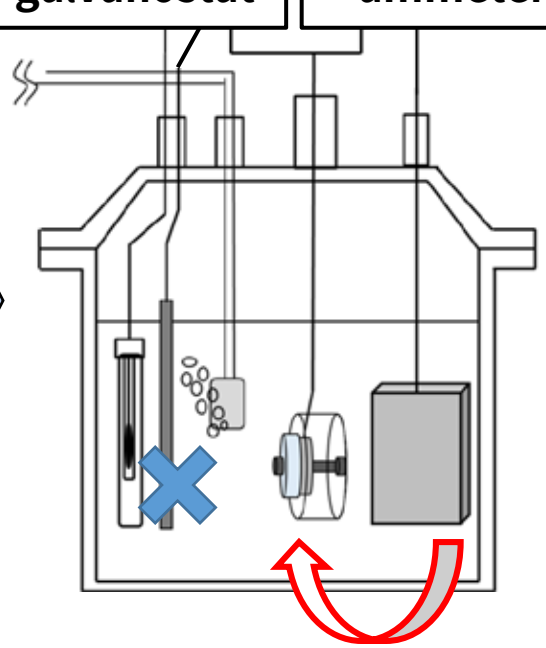
Initiate and propagate crevice corrosion on full crevice specimen.

Step ②

Open circuit immersion Outer cathode connected

potentio/ galvanostat

zero shunt ammeter

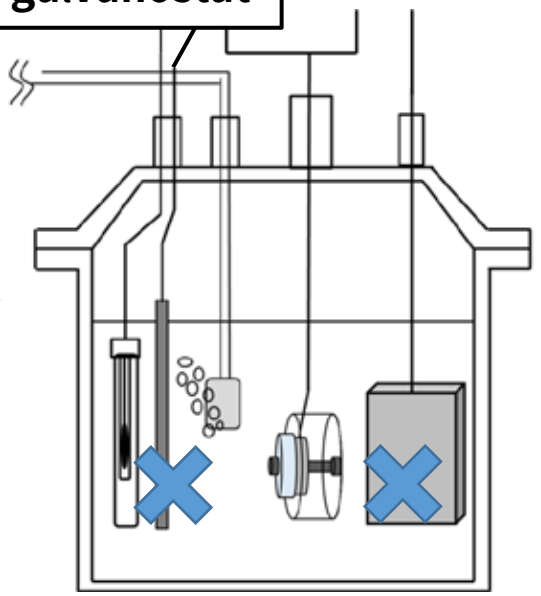


Propagate the corrosion. Measure potential and coupling current.

Step ③

Open circuit immersion Outer cathode disconnected

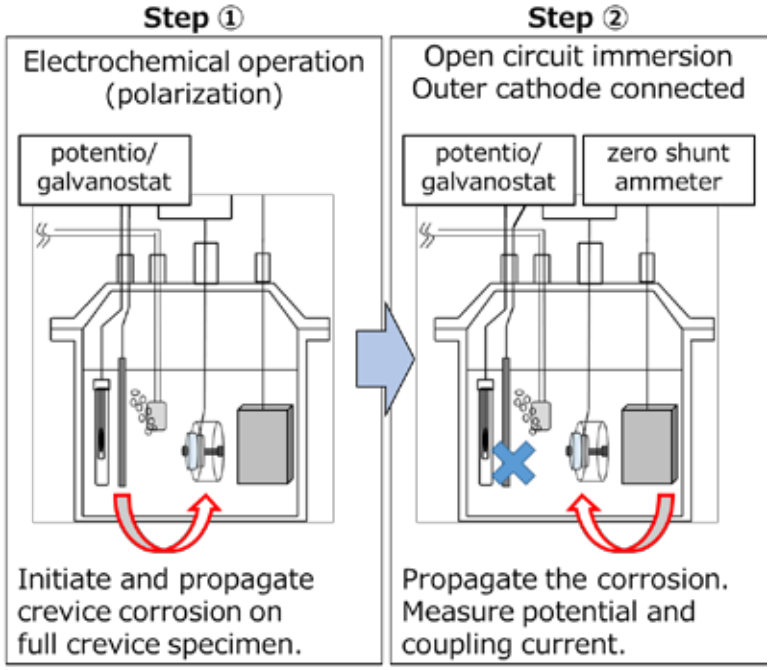
potentio/ galvanostat

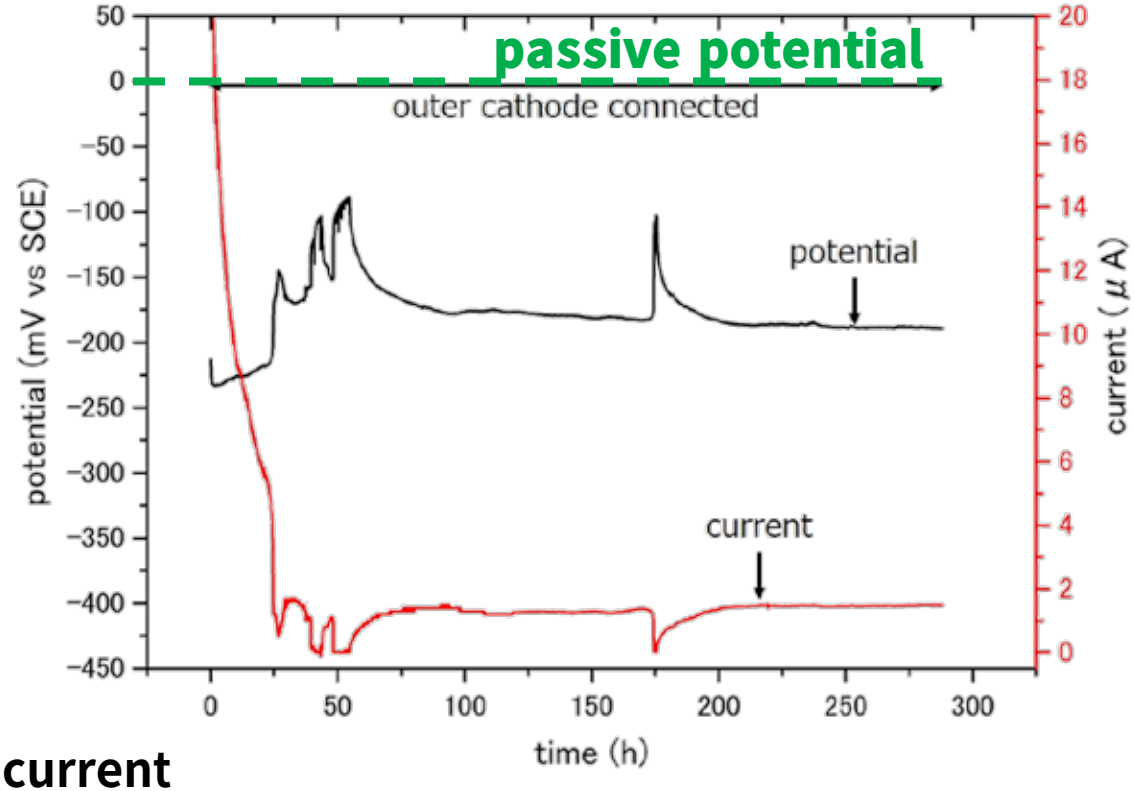


Measure potential. Consider propagating or repassivated.

8. Propagation with outer cathode

Step ① to Step ② under artificial air aerated.





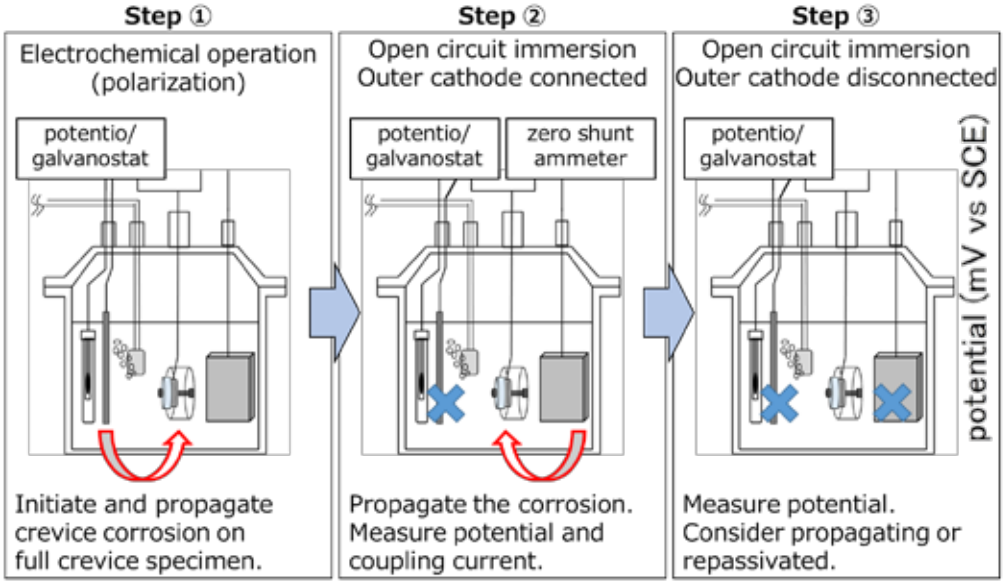
u **Corr. vol. converted from coupling current was 93.1% of actual corrosion volume.**

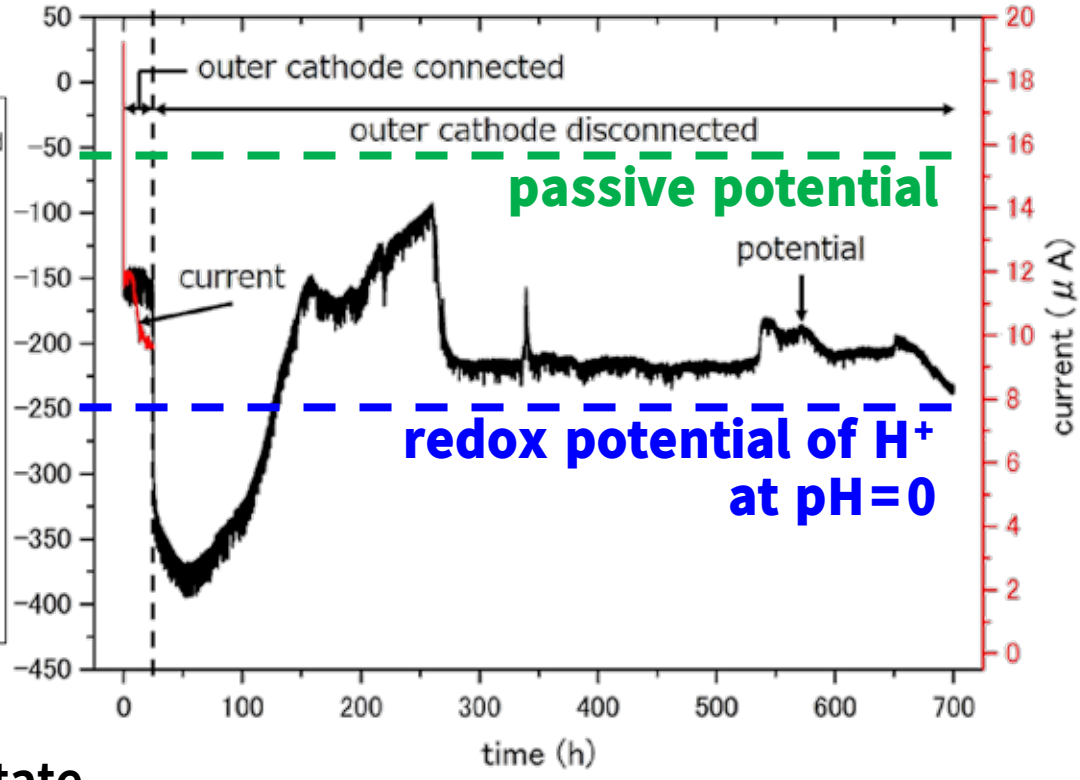
Ø **Cathodic reaction outside crevice was dominant** of cathodic reaction which support anodic dissolution inside crevice. Cathodic reaction inside was limited.

Ø **The potential may be too high for H_2 generation to occur inside crevice.**

9. Propagation without outer cathode

Step ① to Step ③ under artificial air aerated.





u **The potential was lower than passive state.**
Ø **Crevice corrosion continued propagating by only cathodic reaction inside crevice.**

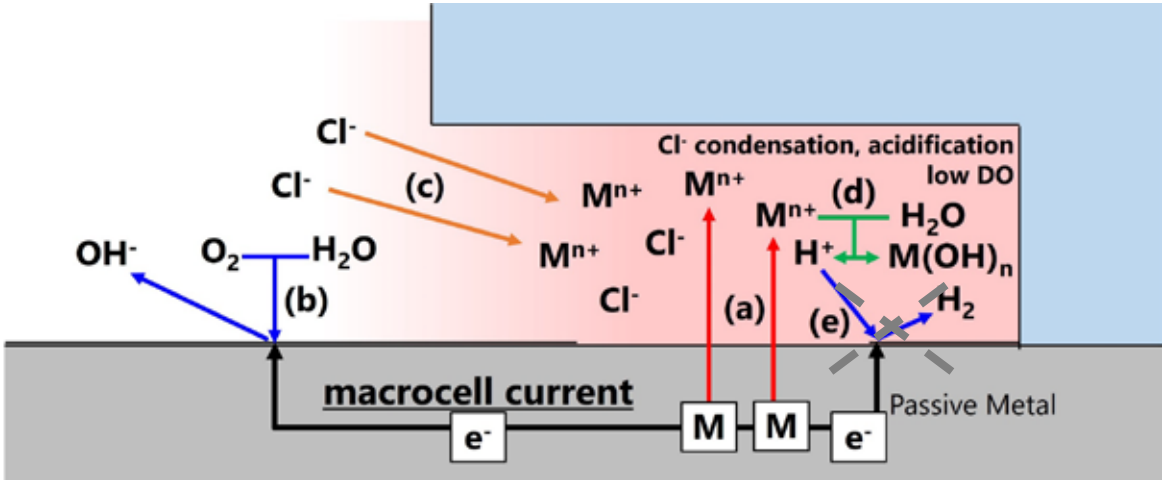
u **The potential was almost equal or higher than redox potential of H_2 generation.**
Ø **Not only H_2 generation but also O_2 reduction is required.**
Ø **It may be difficult to continue to propagate when DO outside crevice is low enough.**

10. Summary

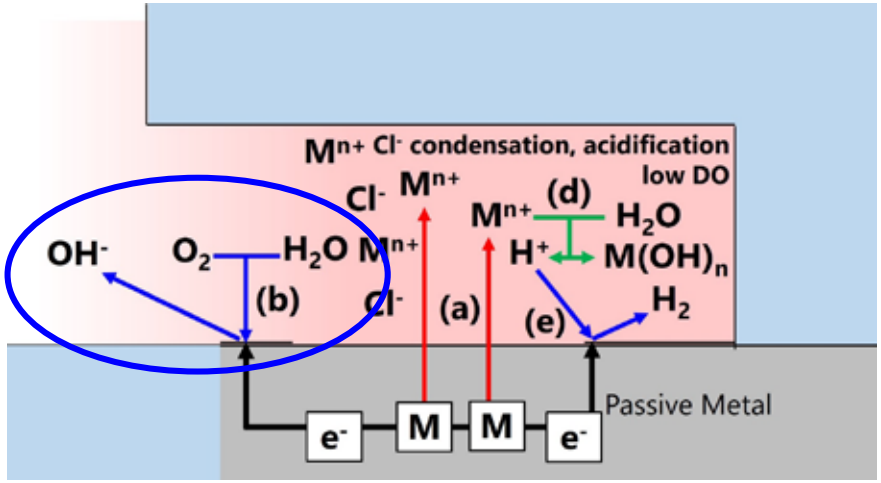
- Clarify contribution of **cathodic reaction inside and outside** crevice on propagation of crevice corrosion.

- **Outer cathode contributes mainly when it is available.**
- **Crevice corrosion is able to propagate with only cathodic reaction inside crevice, but the corrosion rate will be more than one magnitude smaller.**
- **Not only hydrogen but also oxygen reduction may play an important role.**

With outer cathode



Without outer cathode



Ø **It may be difficult to continue to propagate when DO outside crevice is low enough.**