WORLD SALT SYMPOSIUM

June 19-21, 2018 Park City UT, USA

Effect of Composition and Dissolved Oxygen of Mother Liquor on Rest Potential of Metals

The Salt Industry Center of Japan
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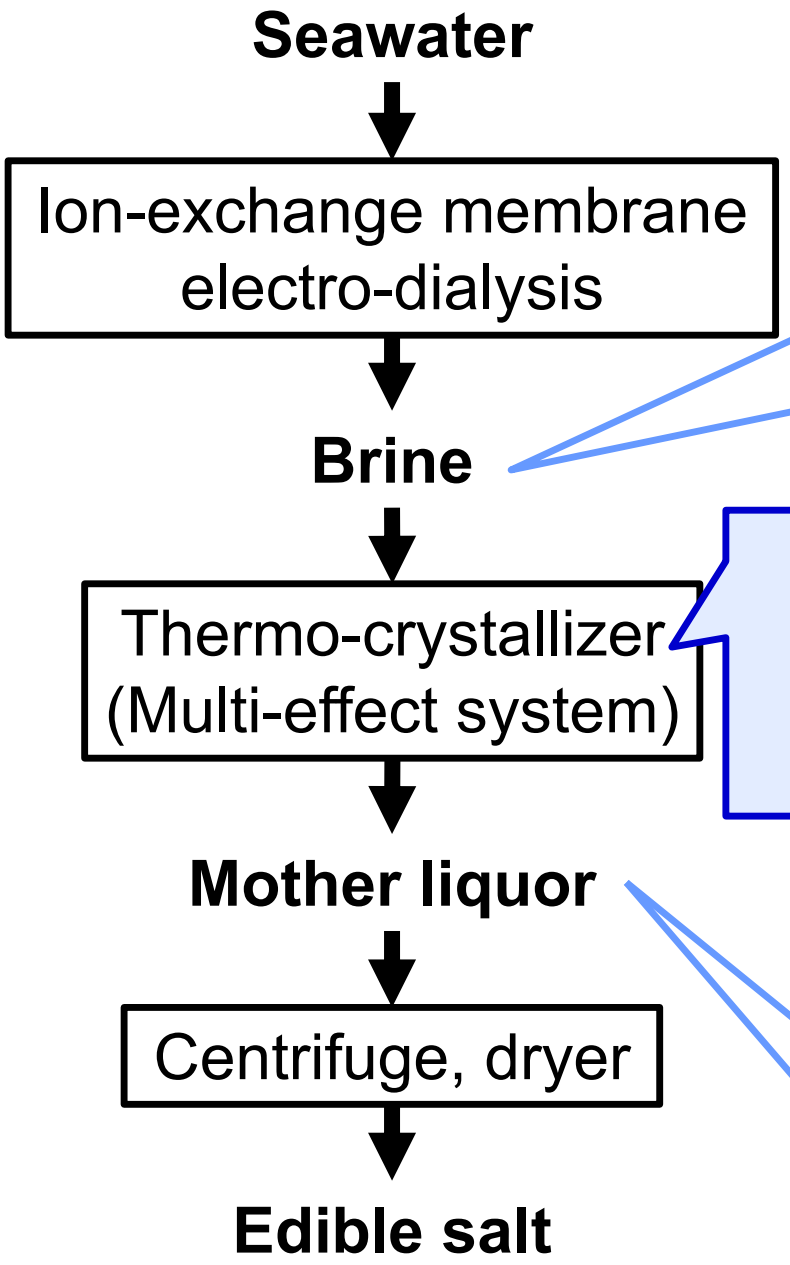
Japanese salt-production-method



Contains inorganic ions as impurity

Ions : magnesium, calcium, potassium, etc.
Concentration : ca. 1 mass%

Evaporators are fabricated using highly corrosion-resistant metals

e.g. super-austenitic stainless steels, nickel-based alloys, and titanium alloys

Very corrosive to metals

Compared to mining system:

- Chloride ion concentration is higher
- pH is lower

Heavy metal ions from the metals used to fabricate evaporators will be present

Problems and aim

Problems

1. The selection of an appropriate metal is difficult
2. The impurity concentration, temperature, and concentration of the dissolved oxygen are different in each evaporator

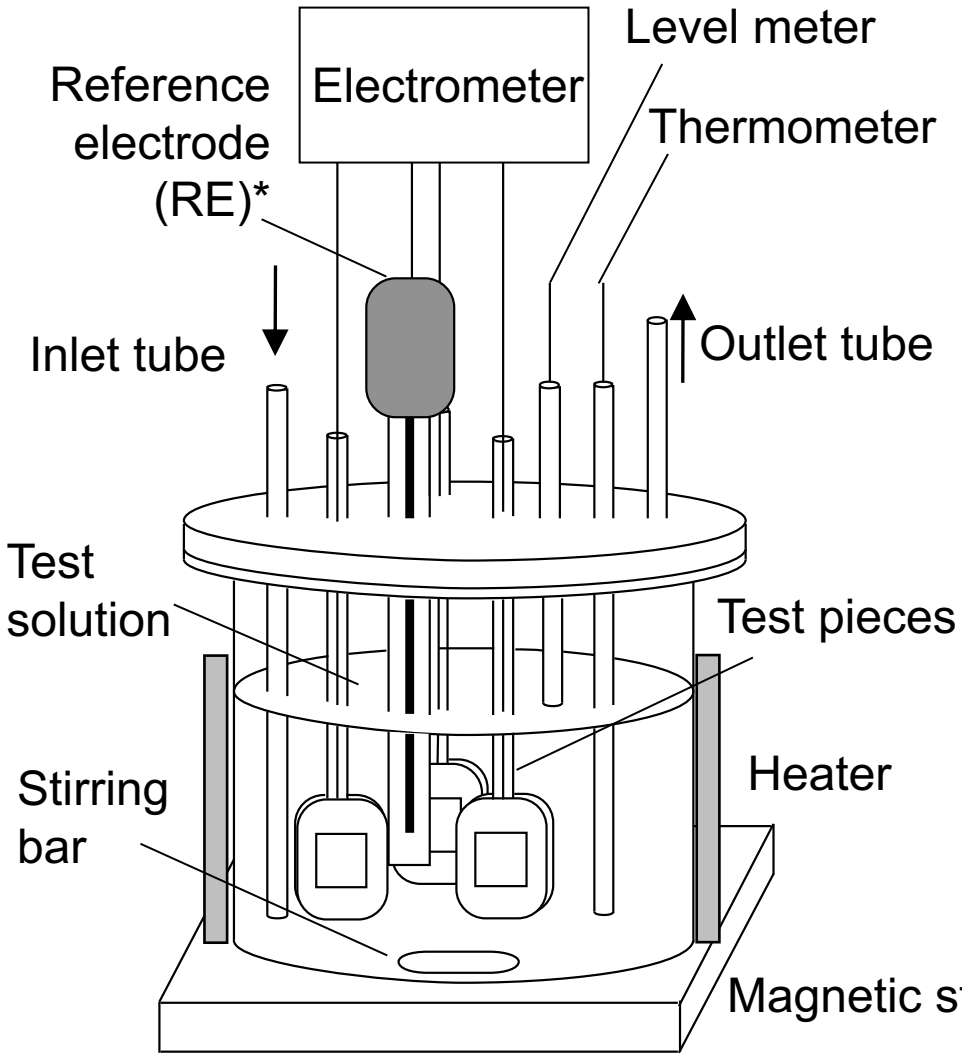
What factor associated with the mother liquor affect corrosion?

Outline

Determining the corrosion potential (rest potential), to clarify the effect of the composition of the mother liquor and the amount of dissolved oxygen on the corrosion of various metals.

Experiment

Apparatus



Method

Test pieces were immersed in test solution

⇓

Potential of test piece relative to RE was measured

- Gas: Constantly passed through inlet tube
- Duration: 30 days

*A silver-silver chloride electrode in a saturated potassium chloride solution

Test pieces

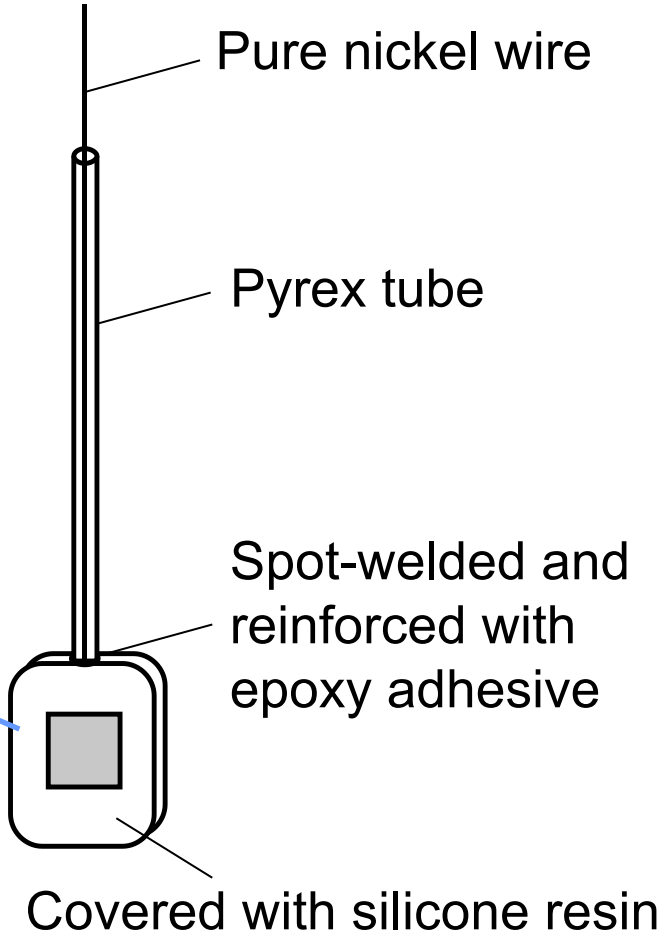
Test materials

1: Austenitic stainless steel
2-4: Super-austenitic stainless steel
5: Nickel-based alloy

No	UNS No.	Main component [%]			
		Cr	Ni	Mo	others
1	S31600	18	12	2.5	
2	S31254	20	18	16	N:0.2, Low C
3	S32053	23	25	5.5	N:0.2
4	N08354	23	35	7.5	N:0.2
5	N06022	22	57	13	W:3, Fe:4

Exposed area

- ca. 1 cm^2
- Finished with 2000-grid paper



Experimental conditions

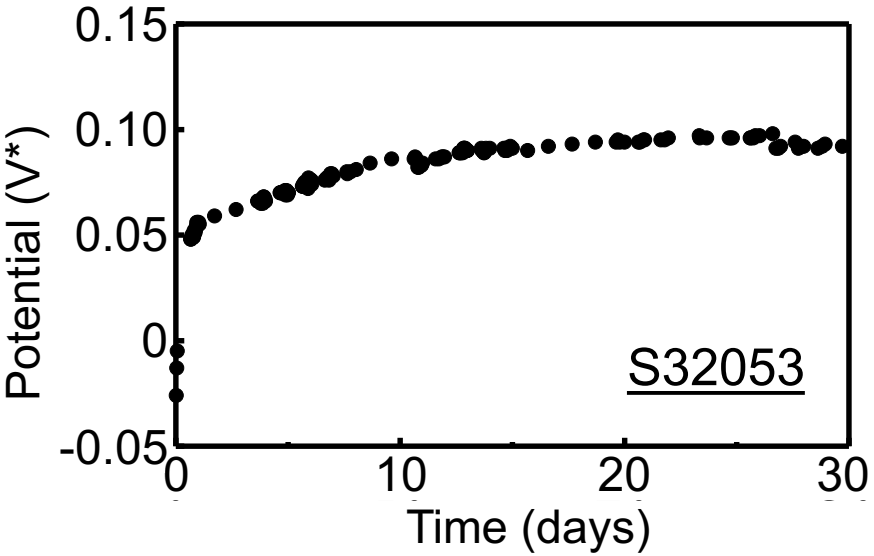
Test solutions Prepared mother liquor containing potassium, magnesium, calcium, bromide ions

Operation factor		Range
1	Dissolved oxygen (DO)	0-0.4 mg/kg (controlled by aerating the solution with air or argon-oxygen mixed gas)
2	Impurity concentration	1-11.2 mass% (Magnesium concentration C_{Mg} : 3-35 mg/kg)
3	Temperature	50-90°C (323-363 K)
4	Copper ions	C_{cu} : 0-10 mg/kg

Time histories of rest potential

1	Air aeration
2	C_{Mg} : 3.4 mg/kg

3	90°C (363 K)
4	C_{Cu} : none



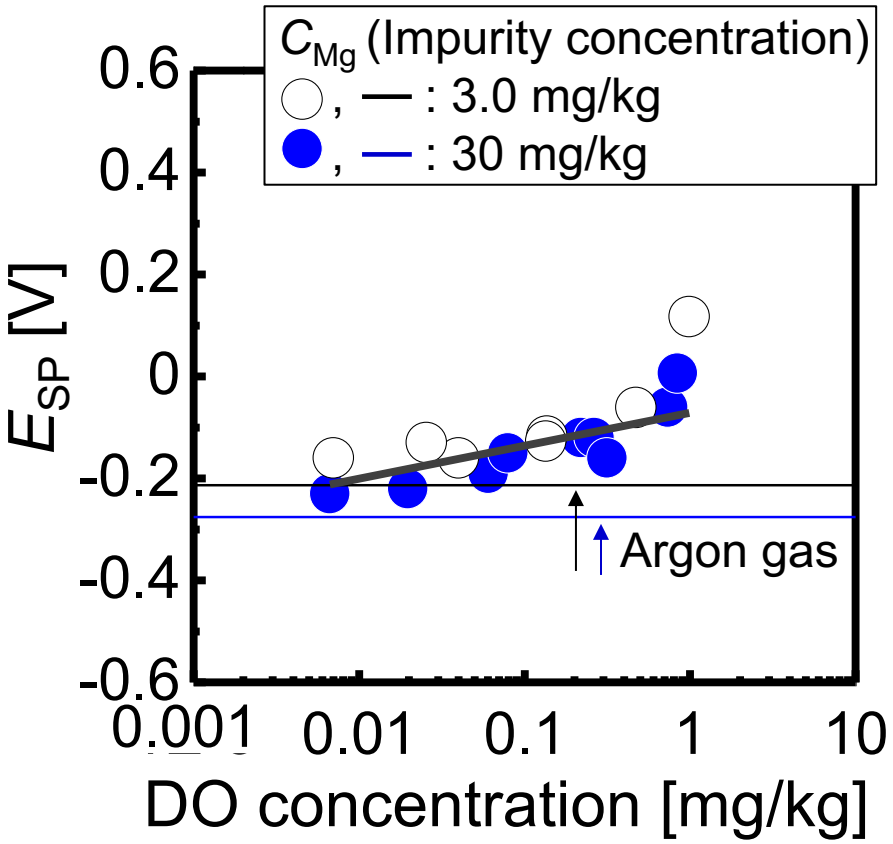
- Rest potential of test piece changed over time but stabilized after 20 days.
- Regardless of the experimental conditions, similar time histories were observed for each metal.

Rest potential measured after 30 days is defined as E_{SP} – this is used in subsequent descriptions.

*The potential is expressed as a value relative to the potential of RE at 90°C(363 K).

1 : Effect of DO

S31600 | 3 | 70°C (343 K) | 4 | C_{Cu} : none



E_{SP} value decreased with DO concentration.

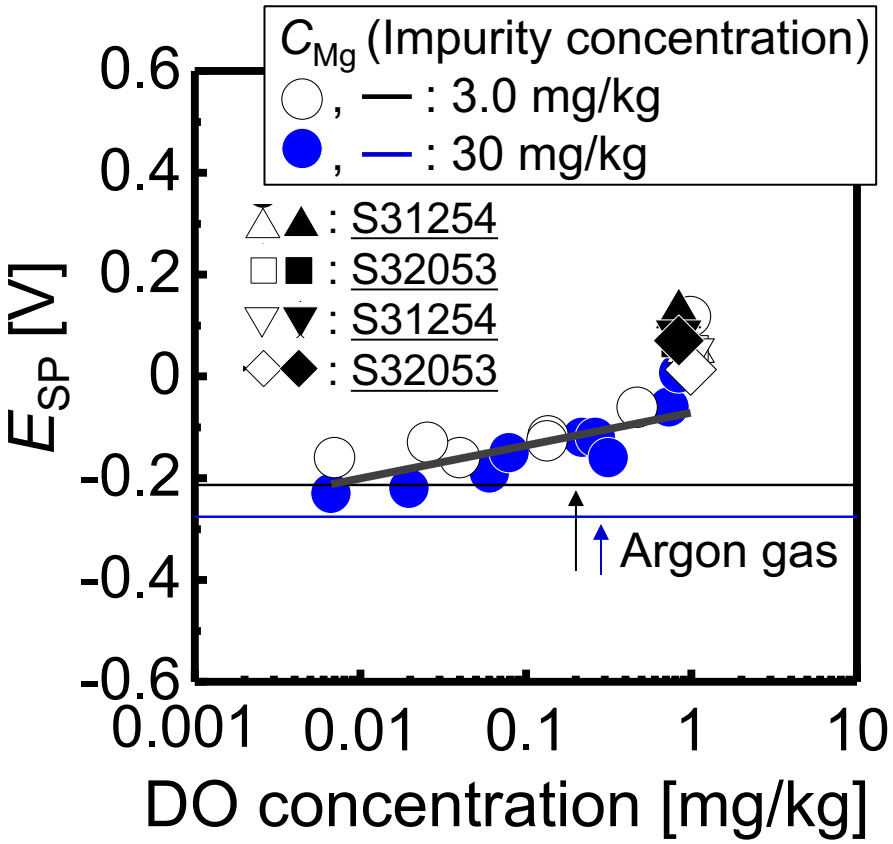
Assumed that E_{SP} for S31600 test piece could be explained by DO concentration, C_{DO} [mg/kg].

$$E_{SP} = a \times \log_{10} C_{DO} + b,\ a = 0.09,\ b = -0.02$$

1 : Effect of DO

3	70°C (343 K)

4	C_{Cu} : none



Other metals

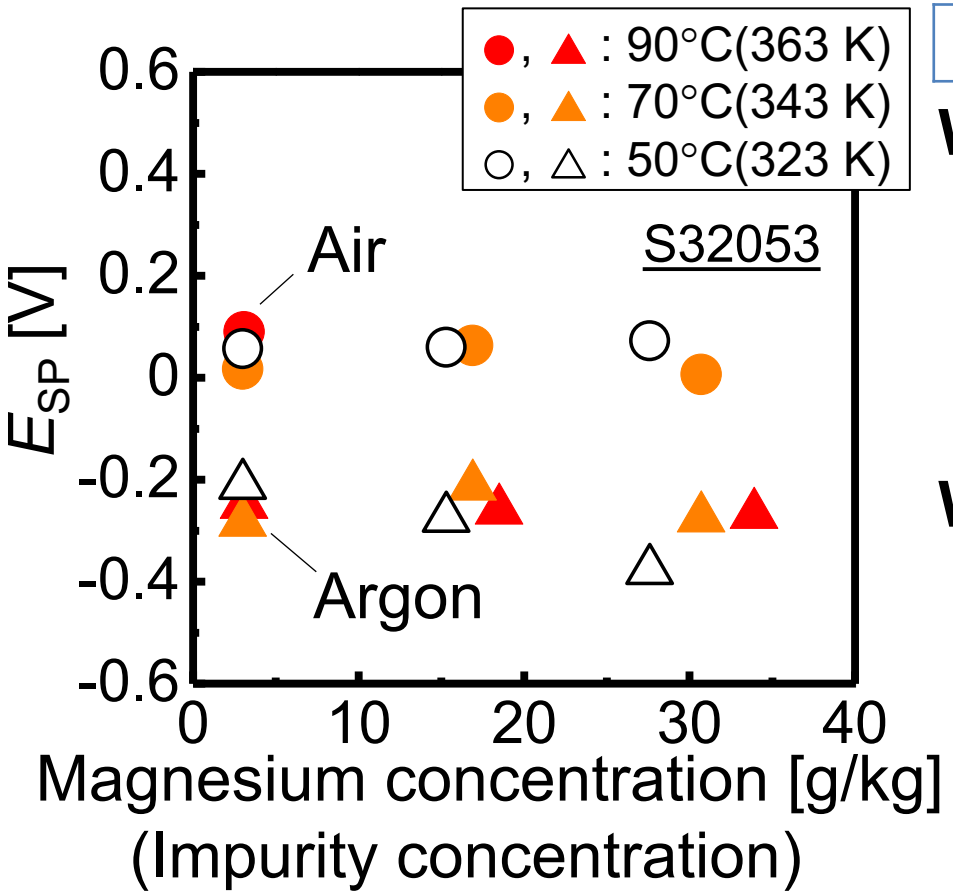
- E_{SP} values were similar to that for S31600.
- Trend in E_{SP} values was constant regardless of composition of test solution.

$$E_{SP} = a \times \log_{10} C_{DO} + b$$

a, b : varying with the metal

In the salt-producing process, we assumed that the effect of the DO concentration of mother liquor on E_{SP} value would be considerable.

2,3 : Effects of impurity concentration and temperature



4	C_{Cu} : none

With air aeration

- DO concentration : 0.6-1.0 mg/kg
- The E_{SP} value was in the range of 0.057 V to 0.117 V.

With argon gas aeration

- The E_{SP} value was in the range of -0.378 V to -0.211 V.

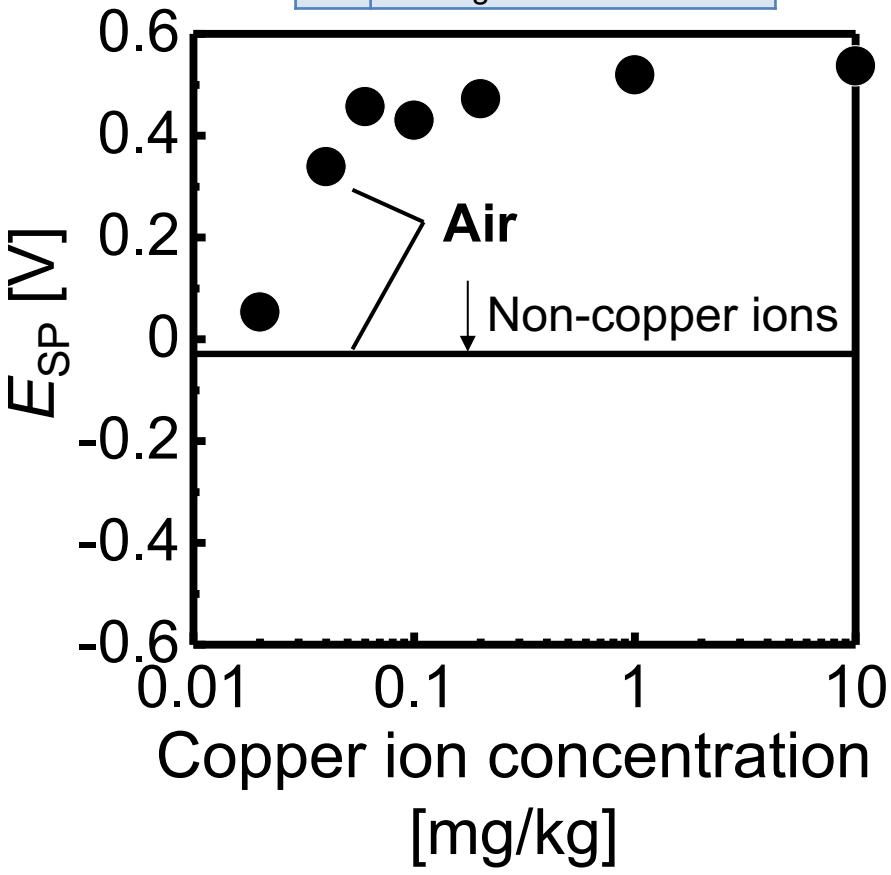
It can be assumed that the effects of the impurity concentration and temperature of the mother liquor on the E_{SP} value would be minimal.

4 : Effect of copper ions

S32053

1	Air aeration
2	C_{Mg} : 3.4 mg/kg

3	90°C (363 K)



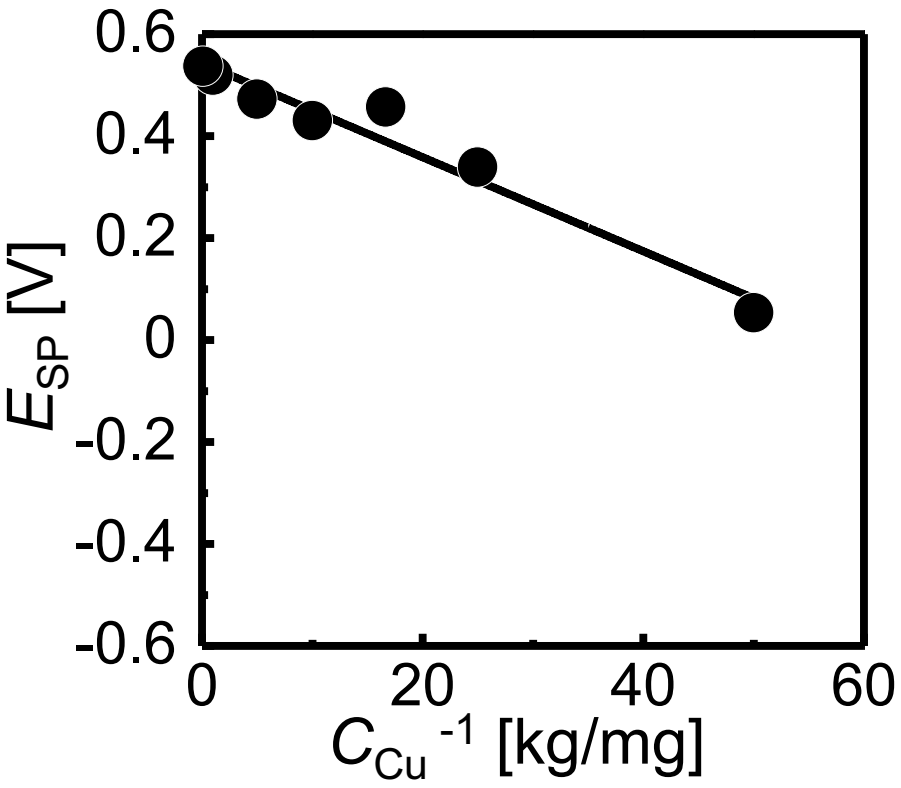
With air aeration

- With the addition of copper ions, the E_{SP} value increased with the copper ion concentration.
- Within a copper ion concentration range of 0.01-0.1 mg/kg, the E_{SP}-increase-rate increased remarkably.

4 : Effect of copper ions

S32053

1	Air aeration
2	C_{Mg} : 3.4 mg/kg
3	90°C(363 K)



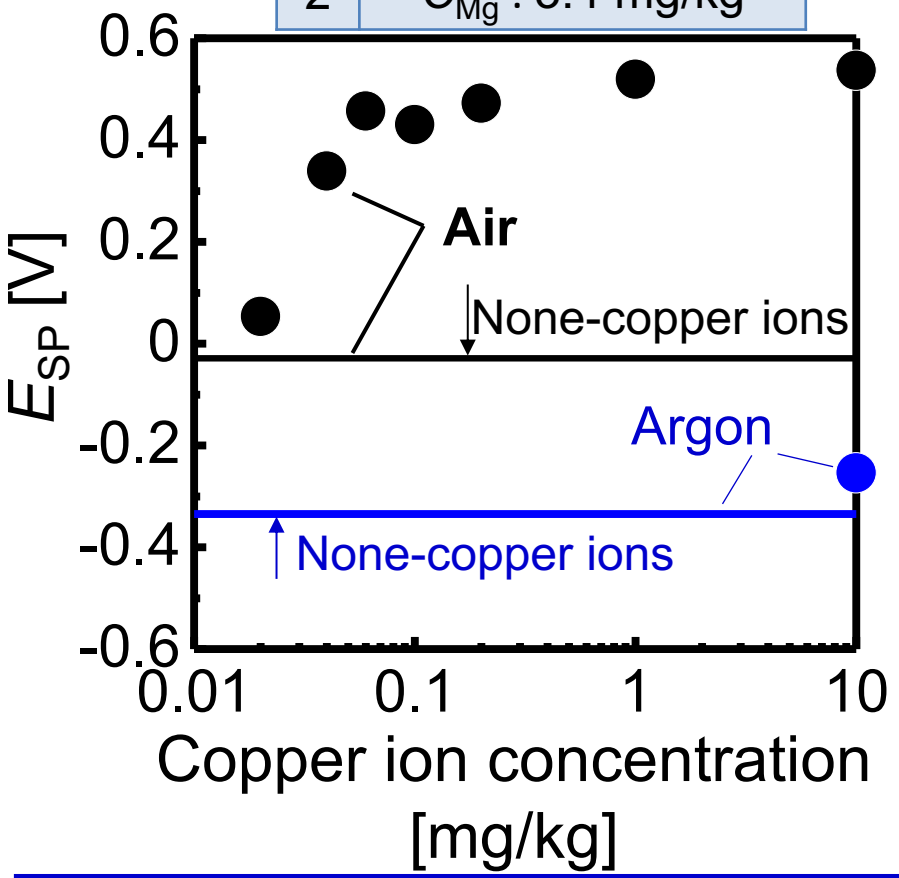
E_{SP} value was inversely proportional to the reciprocal of the copper ion concentration (C_{Cu} [mg/kg]).

$$E_{SP} = 0.092 \times C_{Cu}^{-1} + 0.543$$

4 : Effect of copper ions

S32053

1	Argon gas aeration
2	C_{Mg} : 3.4 mg/kg
3	90°C (363 K)



With argon gas aeration

- E_{SP} value differed little regardless of copper ion concentration.

DO concentration

The air aeration: 0.2 mg/kg

The argon gas aeration: < 0.01 mg/kg

- Assumed that, with a low DO concentration, effect of copper ions on E_{SP} value would be minimal.
- Suggested that copper ions were not acting as a deoxidant, but were instead accelerating the reaction $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

Conclusions

We examined the rest potential of S31600, S31254, S32053, N08354 and N06022 test pieces in solutions having the same composition as that used for salt production.

Operation factor		Effect of the mother liquor on E_{SP}
1	DO	• Decreased with the DO concentration
2	Impurity concentration	• Found to be small
3	Temperature	• Found to be small
4	Copper ions	• With air aeration, increased with the copper ion concentration • With argon gas aeration, little difference regardless of copper ion concentration

We can conclude that to effectively protect metals from corrosion, the DO and copper ion concentrations in the mother liquor should be controlled.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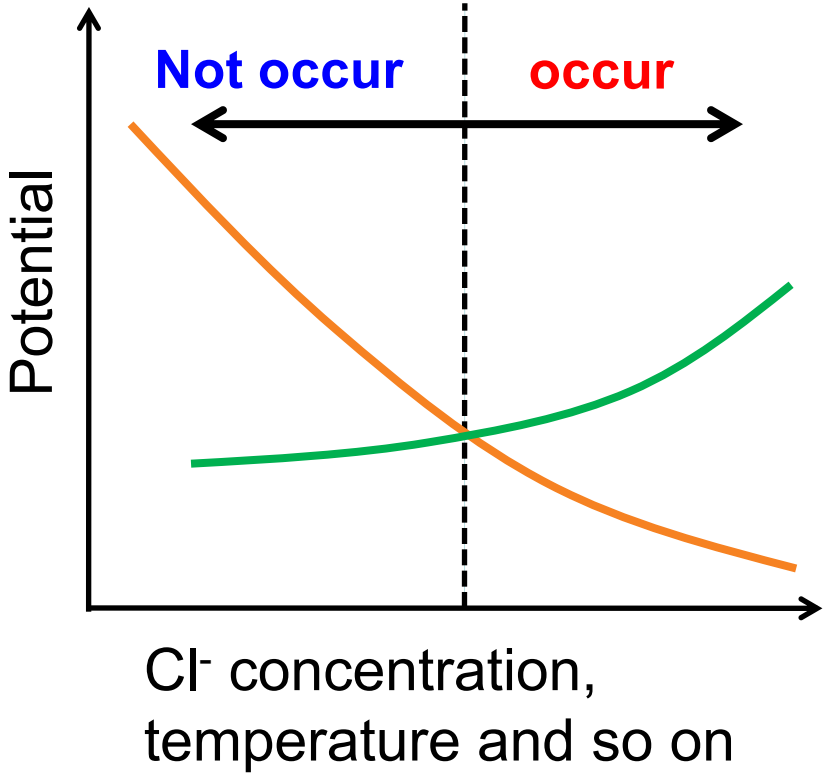
Prediction results of whether or not pitting corrosion occurs



Rest Potential

Pitting potential

critical potential of pitting corrosion

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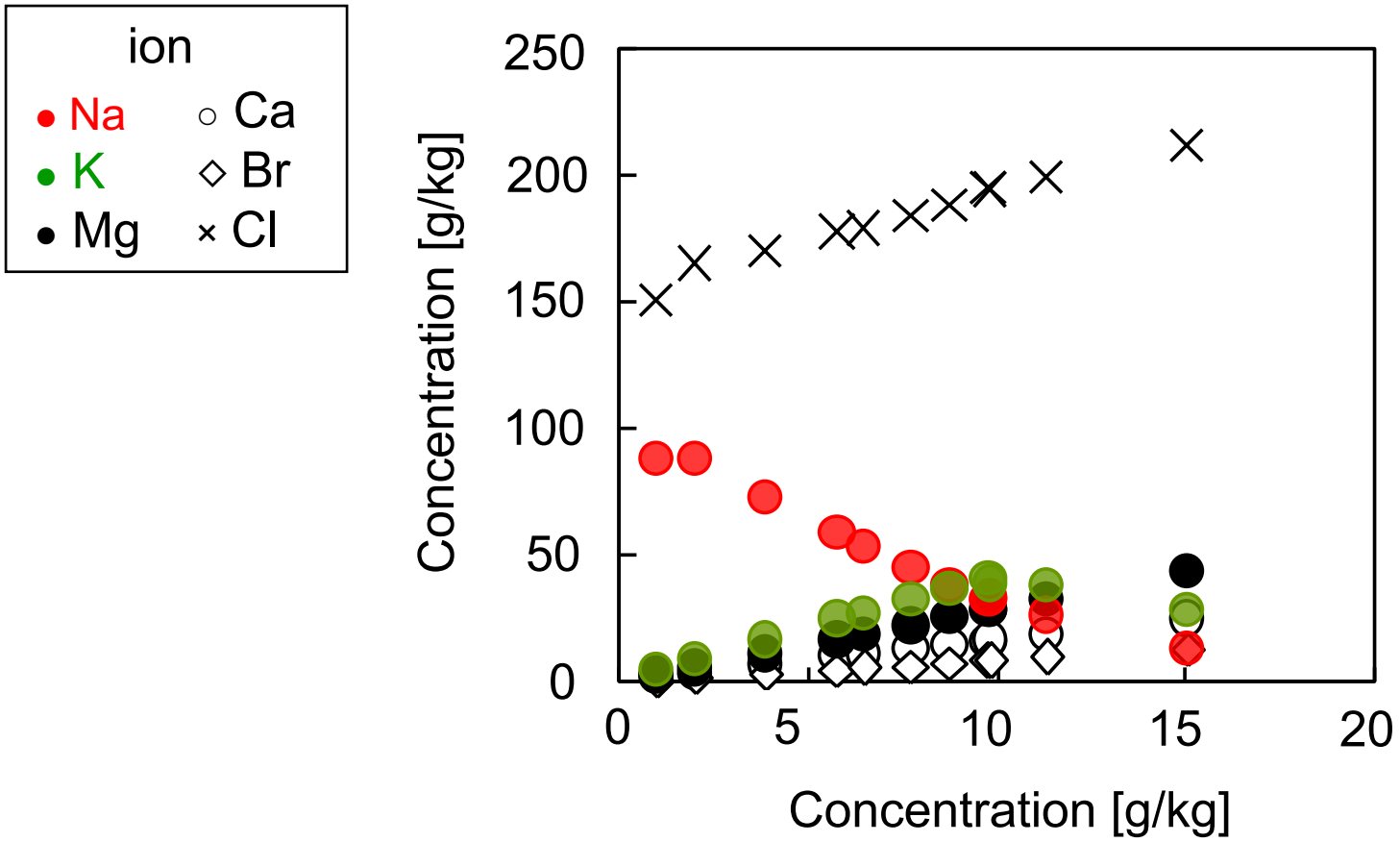
A concentration process of the brine produced by ion exchange membrane (50°C)



*The Salt Industry Center of Japan, “Data book for Seawater Science and Salt Production”, (2015)