

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

Salt Production

Keywords: Corrosion Potential, Corrosion Protection, Mother Liquor, Dissolved Oxygen, Austenitic Stainless Steel, Nickel-Based Alloy

Abstract

Most of the edible salt sold in Japan is produced by a multi-effect system using concentrated seawater and ion-exchange membranes. This Japanese system does not incorporate a means of refining the brine, so that the mother liquor contains a small percentage of inorganic ions (magnesium, calcium, potassium, etc.) as impurities from seawater. Therefore, the mother liquor has a higher concentration of chloride ions and a lower pH than a solution mining system, such that the mother liquor is corrosive to metals. Therefore, the evaporators are fabricated using highly corrosion-resistant metals; e.g. austenitic super stainless steels, nickel-based alloys, and titanium alloys. However, the choice of an appropriate metal is difficult because the impurity concentration and temperature in each evaporator is different in a multi-effect system. As a result, there are cases of local corrosion or over-performance.

In this study, we examined the effect of the composition of the mother liquor and the amount of dissolved oxygen (DO) on the corrosion of various metals by measuring the corrosion potential (rest potential).

We measured the rest potentials of different metals over 30 days at 50°C, 70°C, and 90°C, while immersed in mother liquors of varying compositions. The metals used for the test pieces were UNS S31600, S31254, S32053, N08354, and N06022, from which evaporators are typically fabricated.

Within those solutions which had the same composition as those used in salt production, the effects of the concentration and temperature of the mother liquor on the rest potentials were found to be small but the effects of the concentration of DO and copper ions in the mother liquor increased with the concentrations of DO and copper ions. A similar tendency was observed for the metals examined in this study. Thus, to effectively protect metals from corrosion, the DO and copper ion concentrations in the mother liquor should be controlled. On the other hand, when the DO concentration was greatly reduced, the effects of the copper ions on the rest potentials were minimal. Thus, we can suggest that the copper ions accelerate the redox reactions caused by DO.

1. Introduction

Most edible salt in Japan is produced by ion-exchange membrane. In this Japanese system, seawater is first filtered, fed to an ion-exchange membrane electrodialysis device and then fed to thermo-crystallizers to produce salt (NaCl). Thus, the mother liquor contains a 1-10 percentage of inorganic ions (magnesium, calcium, potassium, etc.) as impurities from the seawater, and the mother liquor is more corrosive to metals than that in the solution mining system. Furthermore, a typical plant will have 5 to 7 multi-effect type evaporators (volume: 100-700 m³/evaporator). The impurity concentration, temperature, and concentration of the dissolved oxygen (DO) are different in each evaporator. As a result, the metals from which an evaporator is fabricated should be selected based on the conditions within that evaporator. Furthermore, heavy metal ions from the

metals which the evaporators are typically fabricated will be present in the mother liquor. Copper ions, in particular, are said to accelerate corrosion¹⁾.

Evaporators are fabricated using highly corrosion-resistant metals; e.g. austenitic super stainless steels, nickel-based alloys, and titanium alloys. However, the choice of an appropriate metal is difficult since the impurity concentration and temperature in each evaporator is different. As a result, local corrosion or over-performance may occur.

In the present study, we examined the effect of the composition of the mother liquor and the amount of DO on the corrosion of the various metals from which evaporators are typically fabricated by measuring the rest potential. The results indicated that, to effectively protect metals from corrosion, the DO and copper ion concentrations in the mother liquor should be controlled.

2. Experimental

2.1 Apparatus

Figure 1 shows our rest potential measuring system. The measuring system consisted of a beaker-type vessel (volume: 1 L, internal diameter: 120 mm) surrounded by a heater, a magnetic stirrer, and an electrometer.

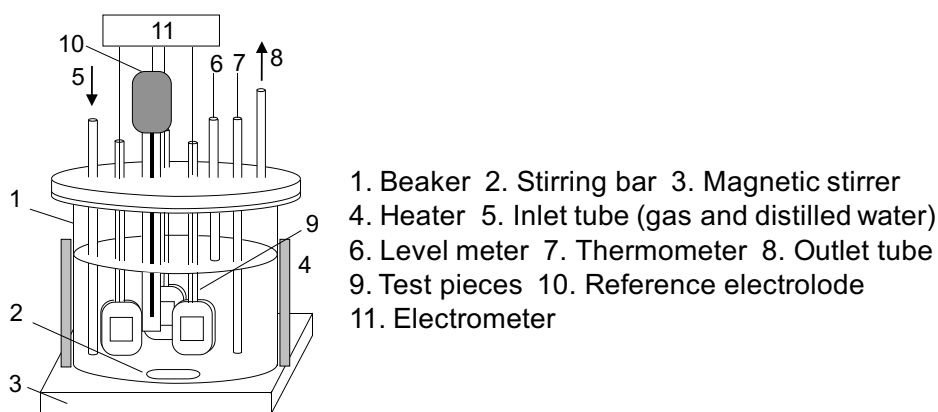


Figure 1: Experimental apparatus

The beaker-type vessel was covered with a plate, to which test pieces, such as a reference electrode, liquid-level sensor, gas outlet tube, or gas/water inlet tube, were attached. The test vessel was filled with the test solution and stirred with the magnetic stirrer while being maintained at a predetermined temperature. The concentration of DO in the test solution was maintained by constantly aerating gas through the inlet tube. Moreover, the volume of the test solution was maintained by supplying distilled water through the inlet tube when a liquid level sensor detected the liquid level falling because of evaporation. The test pieces and the reference electrode were immersed in the test solution and then connected to the electrometer to measure the potential of the test piece relative to the reference electrode (rest potential). A silver-silver chloride electrode in a saturated potassium chloride solution was used as the reference electrode.

2.2 Test pieces

The test materials used in this work were austenitic stainless steel, three kinds of super austenitic stainless steel, and a nickel-based alloy, all of which are used to fabricate evaporators. **Table 1** summarizes the chemical compositions of the test materials. Flat plates measuring 25 × 20 mm

were cut from sheets, 2-mm thick, as described in Table 1. One side of the flat plate was polished with SiC abrasive papers, finishing with 2000-grit paper. Next, the flat plate was cleaned with distilled water and doubly ethanol in an ultrasonic bath and then dried in cool air. A pure nickel wire conductor was spot-welded to the top of the flat plate and the weld point was reinforced with epoxy resin adhesive. Then, the exposed area of the polished side of the flat plate test piece was adjusted to $1.0 \times 10^2 \text{ mm}^2$ by using silicone resin.

2.3 Method

2.3.1 Test of controlling DO

We measured the rest potentials while controlling the DO in the test solution by aerating the solution with argon-oxygen mixed gas. The test vessel was filled with 1,200 g of A-70 or C-70 solution, described in **Table 2**, as a test solution at 70°C. A type S31600 test piece was immersed in the test solution and the rest potential was measured continuously for 30 days. The rest potential is expressed as a value relative to the potential of reference electrode at 25°C. Argon and oxygen gas were supplied from pure gas cylinders and mixed in an inlet tube, and the mixed gas was used to aerate the test solution. The mixing ratio of the gas was maintained to regulate the flow of the argon and oxygen gas to the inlet tube. After the test, the test piece was cleaned with distilled water and doubly ethanol and then dried in cool air. Then, the surface of the test piece was examined using a 10 x optical microscope. Furthermore, the test solution was sampled, and the DO concentration was determined by using either the Winkler²⁾ or electrochemical method³⁾.

2.3.2 Test of controlling composition and temperature

We measured the rest potentials while controlling the composition and temperature of the test solutions to imitate those used in the salt-producing process. The A-50 to C-90 solutions listed in Table 1 were aerated with air or argon gas at 50°C, 70°C, and 90°C. The type S31600, S31254, S32053, N08354, and N06022 test pieces were simultaneously immersed and their rest potentials were measured using the same method as that described in 2.3.1. After the test, the test pieces were cleaned, dried in cool air, and then examined using a 10 x optical microscope. The DO concentration in the test solution was determined using the same method as that described in 2.3.1.

2.3.3 Test of copper ions addition

We measured the rest potentials in a test solution containing copper ions. A 10-mg/kg copper standard solution, a 10-mg/kg copper solution, and a 100 mg/kg standard solution were prepared by dissolving copper chloride (II) dihydrates in distilled water. One of these standard solutions was added to the C-90 solution, described in Table 1 to obtain a test solution containing a predetermined copper ion concentration. Furthermore, the test solution was aerated with air or argon gas at 50°C, 70°C, and 90°C. Type S32053, N08354, and N06022 test pieces were simultaneously immersed and their rest potentials were measured using the same method as that described in 2.3.1. After the test, the test pieces were cleaned and then dried in cool air. They were then examined using a 10 x optical microscope. The DO concentration in the test solution was then determined using the same method as that described in 2.3.1.

Table 1: Main components of test pieces

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

Table 2: Composition of test solutions

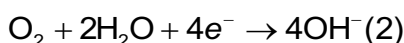
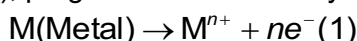
Solution	Temperature [°C]	Composition of test solution [mass%]						
		Na	K	Mg	Ca	Cl	Br	H ₂ O
A-50	50	9.5	0.5	0.3	0.2	16.2	0.1	73.2
B-50	50	6.2	2.5	1.5	1.0	17.9	0.5	70.4
C-50	50	2.9	4.5	2.8	1.9	19.6	0.8	67.5
A-70	70	9.6	0.5	0.3	0.2	16.5	0.1	72.8
B-70	70	6.1	2.7	1.7	1.2	18.6	0.5	69.2
C-70	70	2.5	5.0	3.0	2.1	20.6	0.9	65.9
A-90	90	9.8	0.5	0.3	0.2	16.8	0.1	72.3
B-90	90	5.9	3.0	1.9	1.3	19.3	0.6	68.0
C-90	90	2.1	5.5	3.4	2.3	21.7	1.0	64.0

3. Results and discussion

3.1 Time histories of rest potential

Figure 2(a) shows the time histories of the rest potential of the type S32053 test piece immersed in C-90.

With no copper ions or argon gas aeration, which was assumed to correspond to those conditions that are least likely to give rise to corrosion, the rest potential decreased with time and stabilized after 25 days. Moreover, there was no corrosion on the surface of the test piece. In neutral solution containing oxygen, it is said that an anodic reaction and cathodic reaction, described by Equations (1) and (2), progress simultaneously on a passive metal surface⁴⁾.



In the case with copper ions and argon gas aeration, the rest potential decreased with time and then stabilized after 5 days. Moreover, the surface of the test piece exhibited an interference color. Similarly, with copper ions and air aeration, the rest potential decreased with time and then stabilized after 5 days. Again, the surface of the test piece exhibited an interference color. It was thought that the interference color was caused by an increase in the passive film thickness, because the test pieces are all fabricated from passive metal.

Figure 2(b) shows the time histories of the rest potential of test pieces immersed in C-90. In the case with no copper ions and air aeration, the rest potential of the type S32053 test piece increased with time and then stabilized after 20 days. Moreover, there was no corrosion on the surface of the test piece. The time histories of the rest potential of the type S31254, N80354, and N06022 test pieces were similar to that of the type S32053 test piece. Regardless of the experimental conditions, similar time histories were observed regardless of the metal. However, the rest potential of the type S31600 test piece decreased with time and then stabilized. Pitting corrosion appeared on the surface of the test piece after the immersion test. When the corrosion was examined using an optical microscope, the value of the rest potential was excluded from the subsequent discussion.

As mentioned above, about 25 days were required for the rest potential to stabilize in this work. Following, the rest potential measured after 30 day is defined as E_{SP} and recorded.

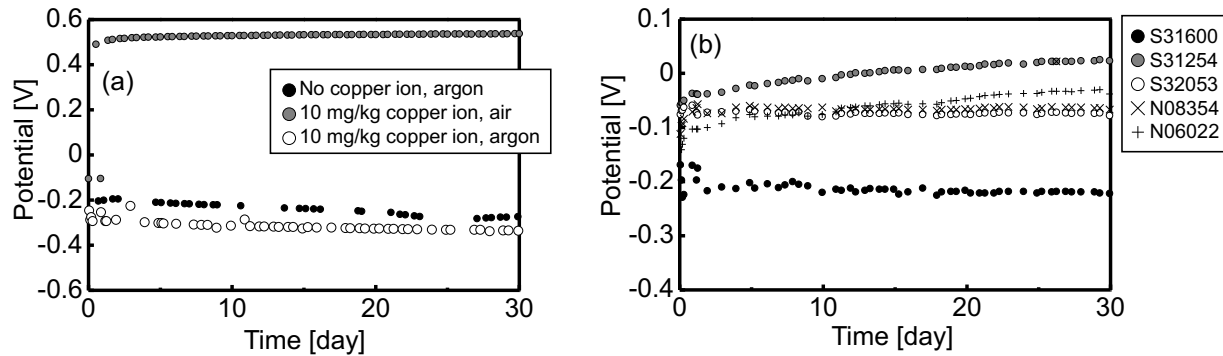


Figure 2: Time histories of rest potential

3.2 Effect of DO on rest potential

Figure 3 shows the effect of the DO concentration and the composition of the test solution on E_{SP} of the type S31600 test piece.

E_{SP} in the A-70 solution was in the range of 0.117 V to -0.284 V and decreased with the DO concentration. It was thought that the decreasing DO concentration suppressed reaction (2), thus causing E_{SP} to fall⁵⁾. For E_{SP} in the C-70 solution, a similar tendency to that in the A-70 solution was observed, within a range of 0.006 V to -0.276 V. Because the effect on reaction (1) is small even when the composition of the test solutions have changed⁶⁾, it was thought that E_{SP} for the type S31600 test piece could be explained by the DO concentration, C_{DO} [mg/kg], thus giving Equation (3), which can be used to approximate the E_{SP} and the DO concentration. Further, the correlation coefficient ($|r|$) was equal to 0.720.

$$E_{SP} = a \times \log_{10} C_{DO} + b \quad (3)$$

$$a = 0.09, b = -0.02$$

Similar to the type S31600 test piece, the E_{SP} of the type S31254, S32053, N08354, and N06022 test pieces with the argon gas aeration was lower than that with the air aeration, regardless of the composition of the test solution. Moreover, with the argon gas aeration, the effects of the metals on E_{SP} were minimal and, in the case of the air aeration, the E_{SP} value fell in the order of the S31600, S31254, S32053, N08354, and then N06022 test pieces. It is assumed that this could be attributed to reaction (2) being constant even when the metals were changed, but the variation in reaction (1) depended on the metal. Thus, it was concluded that the relationship between the DO concentration and E_{SP} of the type S31254, S32053, N08354, and N06022 test pieces could be expressed by Equation (3), with constants a and b varying depending on the metal. Given these results, we thought that, in the salt-producing process, the effect of the DO concentration of the mother liquor on E_{SP} would be considerable. Also, we can suggest that the effect was different from metals.

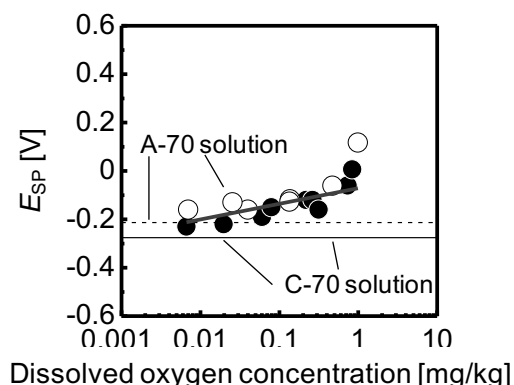


Figure 3: Effect of DO concentration and composition of test solution on E_{SP} .

The solid and dotted lines show the E_{SP} with argon gas aeration.

Metal: S31600

Immersing condition: 70°C, without copper ions

3.3 Effect of impurity concentration and temperature on rest potentials

Figure 4 shows the effect of magnesium concentration on E_{SP} of the type S31600 test piece, with either air or argon gas aeration. In the case of air aeration, the DO concentration was in a range of 0.6 mg/kg to 1.0 mg/kg. Comparing this range with that shown in Figure 3, we can see that the effect of the DO concentration on E_{SP} was minimal, hence we can conclude that E_{SP} in the case of the air aeration shown in Figure 4 represented the effects of the impurity concentration and temperature. The E_{SP} in the case of air aeration was in the range of 0.057 V to 0.117 V and there was no correlation between E_{SP} and the impurity concentration and temperature. The E_{SP} in case of the argon gas aeration was in the range of -0.378 V to -0.211 V and there was no correlation between the E_{SP} value and the impurity concentration and temperature. Similar to the type S31600 test piece, there was no correlation between the E_{SP} value for the type S31254, S32053, N08354, and N06022 test pieces, or the impurity concentration and temperature. Given these results, it can be assumed that, in the salt-production process, the effects of the impurity concentration and temperature of mother liquor on the E_{SP} value would be minimal, even when the metals are changed.

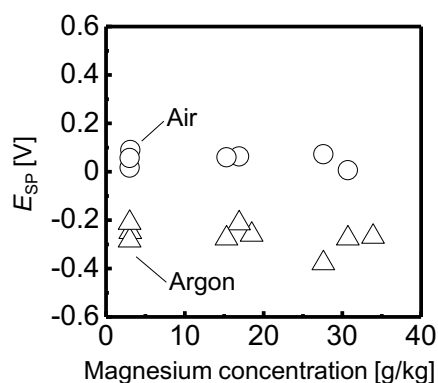


Figure 4: Effect of enrichment degree and kind of aeration gas on E_{SP} . Magnesium concentration is indicator of enrichment degree of solution.

Metal: S31600

Immersing condition: Solution C-90 at 90°C without copper ions

3.4 Effect of copper ions on rest potentials

Figure 5 shows the effect of the copper ion concentration on the E_{SP} value of the type S32053 test piece. With air aeration, the E_{SP} value with no copper ions was approximately -0.09 V (solid line) and that with the addition of copper ions (● plot) increased with the copper concentration. Within a copper ion concentration range of 0.01 mg/kg to 0.1 mg/kg, the E_{SP} -increase-rate increased remarkably with the copper ion concentration and within a range above 0.1 mg/kg, where the E_{SP} value was approximately 0.5 V and became constant. Thus, it was thought that the E_{SP} value of the type S32053 test piece was inversely proportional to the reciprocal of the copper ion concentration (C_{Cu} [mg/kg]). **Figure 6** shows the results, plotted as a function of the reciprocal of the copper ion concentration. The plot corresponds to a straight line, and can be approximately expressed by Equation (4). Note that the correlation coefficient ($|r|$) was equal to 0.946.

$$E_{SP} = 0.092 \times C_{Cu}^{-1} + 0.543 \quad (4)$$

Since E_{SP} increased with the copper ion concentration, the copper ions in the mother liquor possibly accelerated the corrosion. However, with the argon gas aeration, the E_{SP} value with the addition of copper ions to the mother liquor (dotted line) and with no copper ions (▲ plot) were approximately -0.25 V and -0.34 V, respectively, and there was a little difference between them. Since the DO concentration of the test solution was remarkably low, it was thought that with a low DO concentration, the effect of the copper ions on the E_{SP} value would be minimal. In the case of a copper ion concentration of 10 mg/kg, the E_{SP} value differed depending on the aeration gas, hence it was suggested that the copper ions were not acting as a deoxidant, but instead were accelerating the reaction (2). Given these results, we can say that the copper ions accelerated reaction (2) to increase the value of E_{SP} with the copper ion concentration.

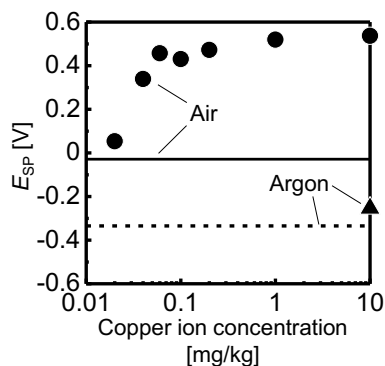


Figure 5: Effect of copper ion concentration and aeration gas on E_{SP} . The solid lines and dotted lines show the E_{SP} in solution without copper ions.
Metal: S32053
Immersing condition: Solution C-90 at 90°C

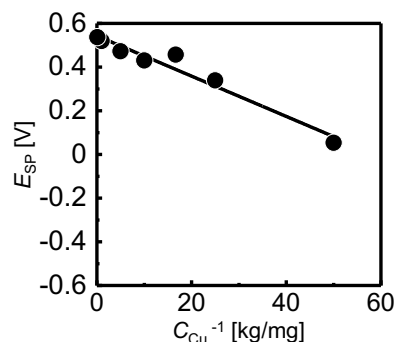


Figure 6: Relationship between E_{SP} and C_{Cu}^{-1} .
Metal: S32053
Immersing condition: Aerated air in solution C-90 at 90°C

A similar tendency was observed for the relationship between the E_{SP} value of the type N08354 and N06022 test pieces and the copper ion concentration. In the case of air aeration, the E_{SP} values of the type N08354 and N06022 test pieces increased with the copper concentration, and were similar to that of the type S32053 test piece. As mentioned in 3.2, with no copper ions or air aeration, the E_{SP} value differed depending on the metal, and it was thought that the effect of accelerating reaction (2) with the presence of copper ions made a greater contribution to the

value of E_{SP} , relative to the difference of reaction (1) with the metal. Moreover, the relationship between the E_{SP} value of the type N08354 and N06022 test pieces and the copper ion concentration could be approximated by Equations (5) and (6). The correlation coefficient ($|r|$) was equal to 0.991 and 0.836, respectively.

$$E_{SP} = 0.011 \times C_{Cu}^{-1} + 0.520 \quad (5)$$

$$E_{SP} = 0.0072 \times C_{Cu}^{-1} + 0.488 \quad (6)$$

Given these results, it was thought that copper ions in the mother liquor in the salt-producing process accelerated reaction (2) to remarkably increase the E_{SP} value.

4. Conclusion

We examined the rest potential of the type S31600, S31254, S32053, N08354, and N06022 test pieces in solutions of the same composition as that used for salt production. Under the same composition and temperature conditions as those of the salt-producing process, the effects of the concentration and temperature of the mother liquor on the rest potentials were found to be small. However, the effects of the DO and copper ion concentrations in the mother liquor were found to be significant. Moreover, it was thought that the effect of accelerating reaction (2) through the presence of copper ions made a much greater contribution to E_{SP} than the difference of reaction (1) depending on the metal. We can conclude, therefore, that to effectively protect metals from corrosion, the DO and copper ion concentrations in the mother liquor should be controlled.

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