

## Experimental Consideration of Criteria for Cathodic Protection of RC Members under High Moisture Conditions

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### ABSTRACT

The criterion of 100 mV depolarization is adopted in many cases of CP (cathodic protection) under atmospheric conditions. However, this criterion is not suitable for members under high moisture conditions. In this paper, another criterion,  $-850$  mV (less noble than  $-850$  mV vs. Saturated Copper Sulphate Electrode (CSE)), was examined for specimens. The results show that under the 100 mV depolarization criterion, corrosion can not be sufficiently controlled when the CP currents are interrupted in order to avoid hydrogen evolving, but that the  $-850$  mV criterion is more applicable under high moisture conditions.

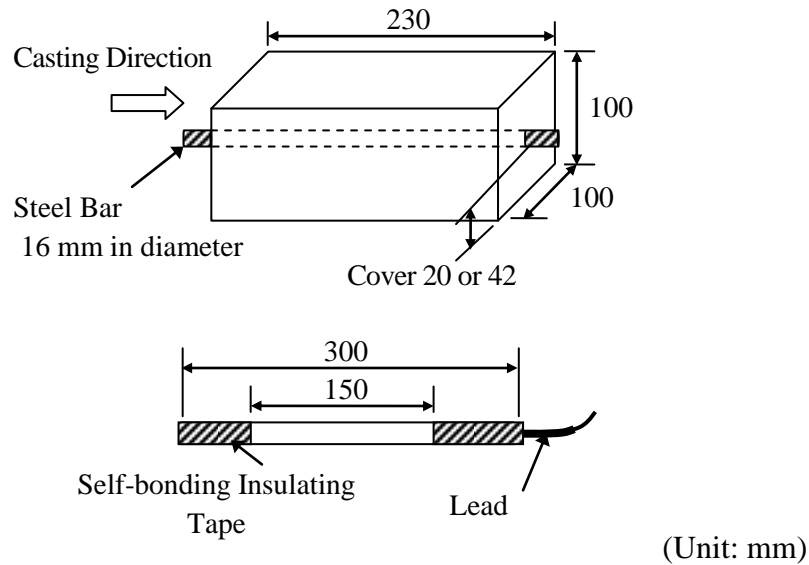
### INTRODUCTION

The criterion of 100 mV depolarization ( $\Delta 100$  mV) is adopted in many cases of cathodic protection (CP) for reinforced concrete (RC) under atmospheric conditions. This criterion is very applicable and its validity is confirmed in many cases. However, it is not suitable for members under high moisture conditions such as upper members of piers, which are exposed to splash and tidal zones. Due to poor diffusion of oxygen into the concrete, the potential of steel in the concrete does not shift to a noble value after the CP current is interrupted. In this paper, another criterion, "less noble than  $-850$  mV vs. Saturated Copper Sulphate Electrode (CSE)" ( $-850$  mV) was examined for specimens in a laboratory. The  $-850$  mV criterion has been adopted for buried pipelines as well as for concrete members submerged in sea water [NACE 1969; JCI-107 2001]. This criterion is based on electrochemical thermodynamics theory, whereas iron (Fe) can not be ionized into  $Fe^{2+}$  ions at a potential less noble than  $-850$  mV vs. CSE. Adopting this criterion, CP effect can be evaluated without respect to poor diffusion of oxygen. Also in this paper, the pH on the corroding steel surface is discussed from the viewpoint of CP current densities to achieve the stated criteria.

## EXPERIMENTAL INVESTIGATION

### Specimens

Steel bars of 16 mm diameter were weighed and shielded with tape as shown in Figure 1. The dimensions of the specimen were 100x100x230 mm. Concrete covers were 20 mm or 40 mm. Mix proportions of the concrete are shown in Table 1. Sodium chloride was added to mix water to provide a concentration of chloride ions of 10 kg/m<sup>3</sup>-concrete for chloride content specimens. Factors for tests are summarized in Table 2.



**Fig. 1. Preparation of Specimen**

**Table 1. Mix Proportions of Concrete**

| W/C (%) | Air (%) | s/a (%) | Mass per Unit Volume (kg/m <sup>3</sup> ) |     |     |     |       |       |
|---------|---------|---------|-------------------------------------------|-----|-----|-----|-------|-------|
|         |         |         | W                                         | C   | S   | G   | Ad    | AE    |
| 53      | 4.5     | 48      | 170                                       | 321 | 859 | 959 | 0.663 | 0.612 |

\*Note: s/a = Volume % of fine aggregate against total aggregates,  
 S = Mass of fine aggregate, G = Mass of coarse aggregate,  
 Ad = Water reducing agent, AE = Air entraining agent (1/100 diluted).

### Anodic dissolution Treatment

Steel bars in the concrete were corroded before CP according to the following method: an anodic current of 1.1 A/m<sup>2</sup> was applied for about 8 days. The quantity of electricity was 200 Ah/m<sup>2</sup>, which theoretically is 208.4 g/m<sup>2</sup> of iron dissolution.

### Experimental conditions

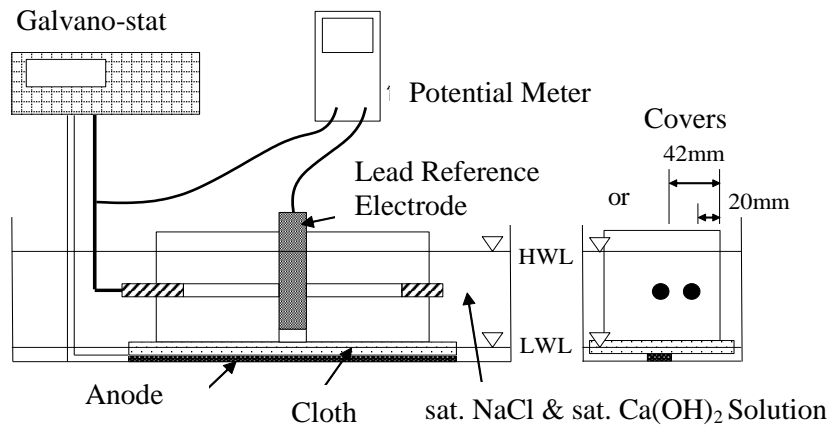
The specimens were exposed to two kinds of condition: dry/wet and submerged in a mixed solution of saturated NaCl and saturated Ca(OH)<sub>2</sub>. A schematic diagram of the experiment is shown in Figure 2 and the experimental conditions of specimens are shown in Table 2.

**Table 2. Experimental Conditions of Specimens**

| Cl (kg/m <sup>3</sup> ) | Cover (mm) | Wettig Condition              | Criterion                     | Period (year)     | Specimen No.            |
|-------------------------|------------|-------------------------------|-------------------------------|-------------------|-------------------------|
| 0                       |            | Dry/Wet                       | Δ100mV                        | 0.5               | 1                       |
|                         |            |                               |                               | 1                 | 2                       |
|                         |            |                               | - 850mV                       | 0.5               | 3                       |
|                         |            |                               |                               | 1                 | 4                       |
|                         |            | Non-protection                | 1                             | 5                 |                         |
|                         |            |                               | 0.5                           | 6                 |                         |
|                         |            | Submerged                     | - 850mV                       | 1                 | 7                       |
|                         |            |                               | Non-protection                | 1                 | 8                       |
|                         | Submerged  | Control of Anodic Dissolution | (8days)                       | 9,10,11           |                         |
| 10                      | 20         | Dry/Wet                       | Δ100mV                        | 1                 | 14                      |
|                         |            |                               |                               |                   | 15                      |
|                         |            |                               | - 850mV                       | 0.5               | 16                      |
|                         |            |                               |                               |                   | 17                      |
|                         |            | Non-protection                | 0.5                           | 18                |                         |
|                         |            |                               | 1                             | 19                |                         |
|                         |            | Submerged                     | 1                             | 20                |                         |
|                         |            |                               |                               | 21                |                         |
|                         | Submerged  | - 850mV                       | 1                             | 22                |                         |
|                         |            | Non-protection                | 1                             | 23                |                         |
|                         |            | Submerged                     | Control of Anodic Dissolution | (8days)           | 24,25,26,27,28,29,30,31 |
|                         | 42         | Dry/Wet                       | Δ100mV                        | 0.5               | 38                      |
|                         |            |                               |                               | 1                 | 39                      |
|                         |            |                               | - 850mV                       | 0.5               | 40                      |
|                         |            |                               |                               | 1                 | 41                      |
|                         |            | Non-protection                | 0.5                           | 42                |                         |
| 1                       |            |                               | 43                            |                   |                         |
| Submerged               |            | - 850mV                       | 1                             | 44                |                         |
|                         |            | Non-protection                | 1                             | 45                |                         |
|                         | Submerged  | Control of Anodic Dissolution | (8days)                       | 46,47,48,49,50,51 |                         |

Regarding dry/wet condition, the cycle was 2 days dry and 5 days wet. Regarding CP, mixed-metal-oxide (MMO) coated titanium ribbon was used as the anode. Corrosion potential and instant-off potential were measured with the Lead Reference Electrode (LRE) which is rigid and indicates a stable potential even in alkaline environments. The potential (E<sub>m</sub>) measured by LRE is converted into the potential (E) versus CSE by the formula {1} as shown below.

$$E = E_m - 800 \text{ (mV vs. CSE)} \quad \{1\}$$



**Fig. 2. Schematic Diagram of Experiment**

### Current control

CP currents were controlled based on the criterion both of  $\Delta 100$  mV and  $-850$  mV under dry/wet condition, and  $-850$  mV under submerged condition. There was a current interruption of 60 days to make the dry/wet specimens dry and the potentials of the steel bars noble. The CP test was carried out over 295 days excluding the interrupted period of 60 days.

## RESULTS AND DISCUSSIONS

### Anodic dissolution treatment

The steel bars in chloride free concrete dissolved only slightly; the average mass losses of steel bars are  $10.44 \text{ g/m}^2$ . In the chloride content specimens, the steel bars dissolved by  $266.63 \text{ g/m}^2$  and  $271.94 \text{ g/m}^2$  for covers of 20 mm and 42 mm, respectively. These values were higher than the theoretical value of  $208.4 \text{ g/m}^2$  dissolution. It may be reasoned that the mass losses include self-corrosion during the period from casting to the end of the anodic dissolution treatment. The steel bars were corroded almost evenly and the colors of corrosion products were black and brown, as shown in Figure 3.

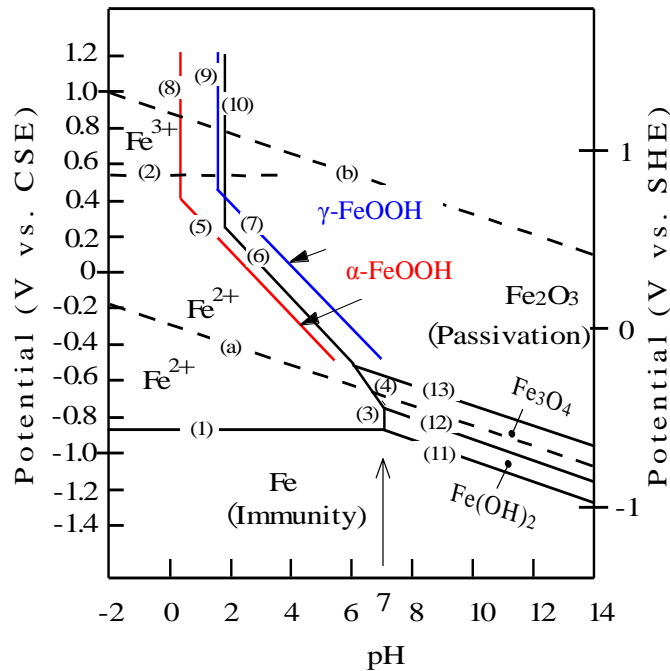


**Fig. 3. Corrosion Products on a Steel Bar after Anodic Dissolution Treatment in the Concrete**

### Potential-pH diagram

A potential-pH diagram for Fe-H<sub>2</sub>O was drawn by the author based on the formulae described by Pourbaix [Pourbaix 1974a] and Misawa [Misawa 1973], as shown in Figure 4 and in Table 3. The formation mechanism of corrosion products in concrete is not clear. The assumptions of the diagram are pH7, which is the value measured on the steel bars of

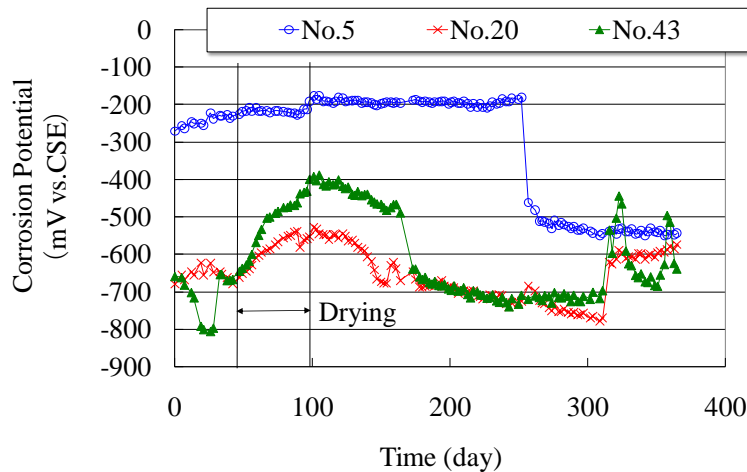
specimens (No.15, No.16, No.17 and No.22 shown afterward in Table 4), and the activity of  $\text{Fe}^{2+}$  ions is  $10^{-2.6}$ , calculated from formula (3). The  $\alpha\text{-FeOOH}$  (goethite) is assumed to be the dominant corrosion product in acidic solution. And  $\text{Fe}(\text{OH})_2$  (ferrous hydroxide),  $\text{Fe}_3\text{O}_4$  (magnetite),  $\gamma\text{-FeOOH}$  (lepidocrocite), and  $\text{Fe}_2\text{O}_3$  (hematite) are assumed to be produced with increase of oxidation potential in alkaline solution.



**Fig. 4. Potential – pH Diagram for Fe – H<sub>2</sub>O**

**Corrosion potentials under dry/wet condition**

The corrosion potentials of non-protection specimens under dry/wet condition are plotted against time in Figure 5. The potential of the chloride-free specimen with 20 mm cover



**Fig. 5. Corrosion Potentials under Dry/Wet Condition**

**Table 3. Formulae for Potential – pH Diagram for Fe-H<sub>2</sub>O**

| (No.) / [Referred Formula No.] / Reactions                     | Equilibrium Formulae                                             |
|----------------------------------------------------------------|------------------------------------------------------------------|
| (a) [P(a)] $H_2 = 2H^+ + 2e^-$                                 | $E = 0 - 0.0591\text{pH}$                                        |
| (b) [P(b)] $4OH^- = O_2 + 2H_2O + 4e^-$                        | $E = 1.228 - 0.0591\text{pH}$                                    |
| (1) [M34] $Fe = Fe^{2+} + 2e^-$                                | $E = -0.440 + 0.0296 \cdot \log [Fe^{2+}]$                       |
| (2) [M23] $Fe^{2+} = Fe^{3+} + e^-$                            | $E = 0.771 + 0.0592 \cdot \log ([Fe^{3+}] / [Fe^{2+}])$          |
| (3) [M4] $Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$                   | $\log [Fe^{2+}] = 11.36 - 2\text{pH}$                            |
| (4) [M50] $3Fe^{2+} + 4H_2O = Fe_3O_4 + 8H^+ + 2e^-$           | $E = 0.982 - 0.2366\text{pH}$<br>$- 0.0887 \cdot \log [Fe^{2+}]$ |
| (5) [M39] $Fe^{2+} + 2H_2O = \alpha\text{-FeOOH} + 3H^+ + e^-$ | $E = 0.655 - 0.1775\text{pH}$<br>$- 0.0592 \cdot \log [Fe^{2+}]$ |
| (6) [P28] $2Fe^{2+} + 3H_2O = Fe_2O_3 + 6H^+ + 2e^-$           | $E = 0.728 - 0.1773\text{pH}$<br>$- 0.0591 \cdot \log [Fe^{2+}]$ |
| (7) [M40] $Fe^{2+} + 2H_2O = \gamma\text{-FeOOH} + 3H^+ + e^-$ | $E = 0.919 - 0.1775\text{pH}$<br>$- 0.0592 \cdot \log [Fe^{2+}]$ |
| (8) [M15] $Fe^{3+} + 2H_2O = \alpha\text{-FeOOH} + 3H^+$       | $\log [Fe^{3+}] = -1.99 - 3\text{pH}$                            |
| (9) [M16] $Fe^{3+} + 2H_2O = \gamma\text{-FeOOH} + 3H^+$       | $\log [Fe^{3+}] = 2.5 - 3\text{pH}$                              |
| (10) [P20] $2Fe^{3+} + 3H_2O = Fe_2O_3 + 6H^+$                 | $\log [Fe^{3+}] = -0.72 - 3\text{pH}$                            |
| (11) [M36] $Fe + 2H_2O = Fe(OH)_2 + 2H^+ + 2e^-$               | $E = -0.104 - 0.0592\text{pH}$                                   |
| (12) [M56] $3Fe(OH)_2 = Fe_3O_4 + 2H_2O + 2H^+ + 2e^-$         | $E = -0.026 - 0.0592\text{pH}$                                   |
| (13) [P17] $2Fe_3O_4 + H_2O = 3 Fe_2O_3 + 2H^+ + 2e^-$         | $E = 0.221 - 0.0591\text{pH}$                                    |

Note : [“M” ; after Misawa & No. of the formula, “P” ; after Pourbaix & No. of the formula]

(No.5) indicated a noble value of about  $-200$  mV vs. CSE, which means the surface of the steel bar had been passivated by  $Fe_3O_4$  and/or  $Fe_2O_3$  in an alkaline environment. However, after 257 days the potential dropped abruptly to a less noble value of about  $-500$  mV vs. CSE. It is considered that chloride ions diffused into the concrete and broke the passive film. This might be a mixed potential of non-corroded area and corroded area where the potential was less noble, associated with formula (1) in Figure 4.

The potentials of specimens containing chloride with 20 mm cover (No.20) indicated less noble values in the range from  $-780$  to  $-530$  mV vs. CSE during the exposure period. This is considered that the limited oxygen supply increased the cathodic polarization and the corrosion potentials indicated a close potential of the local anode of corrosion cells on the steel bar. The pH of the surface of the corroding steel bar might be less than pH7 due to hydrolysis by iron ions according to formula (3) in Table 3. Therefore, the local anode potential seems to be close to the potential of formula (1) in Figure 4, i.e., about  $-830$  mV vs. CSE. The potential of the specimens containing chloride with 42 mm cover (No.43) indicated a less noble value of about  $-810$  mV vs. CSE in the initial stage. This means that the thicker cover made the corrosion potential less noble for the same reason stated above. On the other hand, during the drying period of 60 days, these potentials (No.20 and No.43)

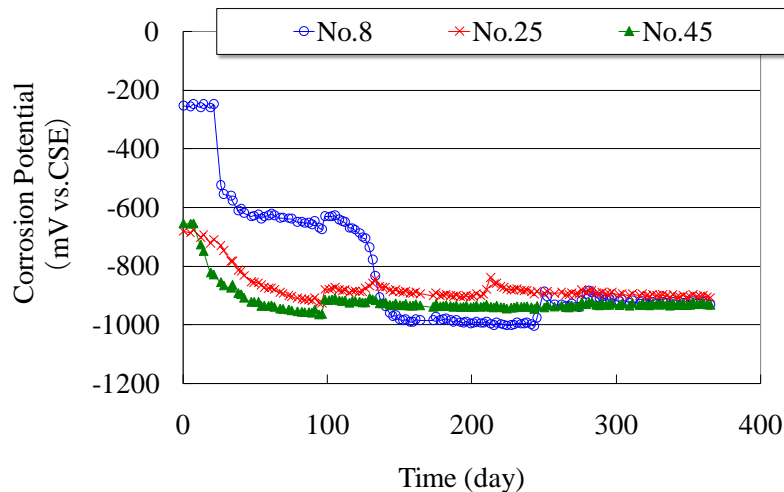
rose to noble values of  $-530$  mV vs. CSE and  $-400$  mV vs. CSE, respectively, due to a good supply of oxygen. According to Figure 4, the main cathodic reaction on the surface of the steel bar might be as given by formula (5) and (b).

### Corrosion potentials under submerged condition

The corrosion potentials of non-protection specimens under submerged condition are plotted against time in Figure 6. The potential of the chloride-free specimen with 20 mm cover (No.8) dropped from about  $-250$  mV vs. CSE to about  $-650$  mV vs. CSE after only 26 days submersion. And then after 150 days the potential dropped to  $-980$  mV vs. CSE. The steel bar corroded very slightly as shown afterward in Table 4. This means that enough hydrolysis by iron ions did not occur and the pH of the surface might remain high. Therefore, it is considered that the cathodic reaction shifted from formula (b) to formula (13) and then to formula (a) (hydrogen electrode) in Figure 4. When the potential is  $-1,000$  mV vs. CSE, the pH on the surface is calculated to be about 12 by the equation {2} as shown below. This pH12 is not far from the value which concrete normally indicates, i.e., pH13 – pH14.

$$E_{\text{CSE}} = -0.059\text{pH} - 0.316 \text{ (V vs.CSE)} \quad \{2\}$$

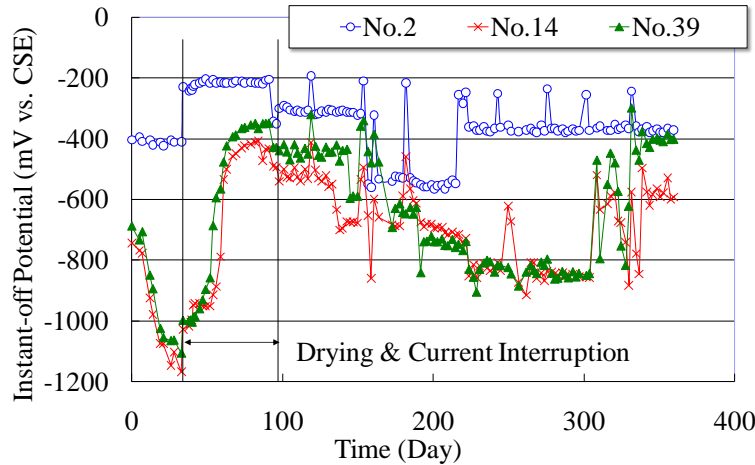
The corrosion potential of the specimen containing chloride with 20 mm cover (No.25) indicated less noble values of about  $-900$  mV vs. CSE after 67 day submersion. The corrosion potential of the specimen containing chloride with 42 mm cover (No.45) indicated a lesser noble value than that of No.25. These potentials might indicate that the surfaces of the steel bars changed their pH to higher values by the supply of hydroxyl ions from the concrete surrounding the steel bars due to the negligible corrosion shown afterward in Table 4. The equilibrium reaction might change from formula (1) to formula (11) and/or formula (12). In this case, the potential difference between anode and cathode (hydrogen electrode) is very small, so that the corrosion rate is very low [Pourbaix 1974a].



**Fig. 6. Corrosion Potentials under Submerged Condition**

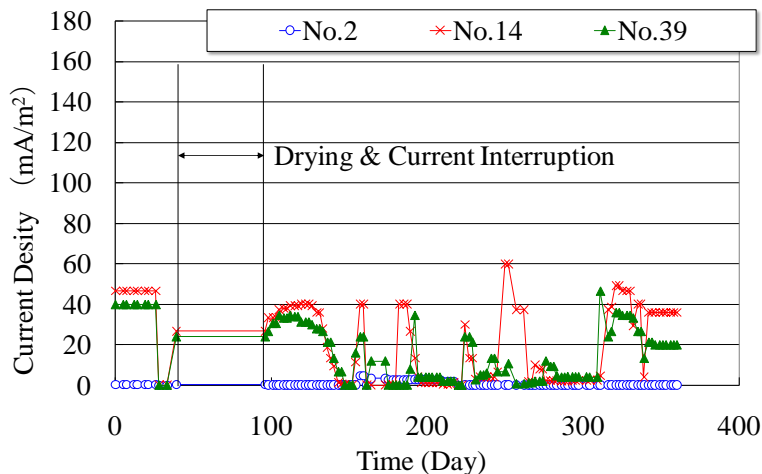
### $\Delta 100$ mV criterion under dry/wet condition

Instant-off potentials of  $\Delta 100$ mV criterion specimens under dry/wet condition were plotted against time in Figure 7. Current densities and depolarization values of the same specimens are plotted in Figure 8 and Figure 9, respectively.



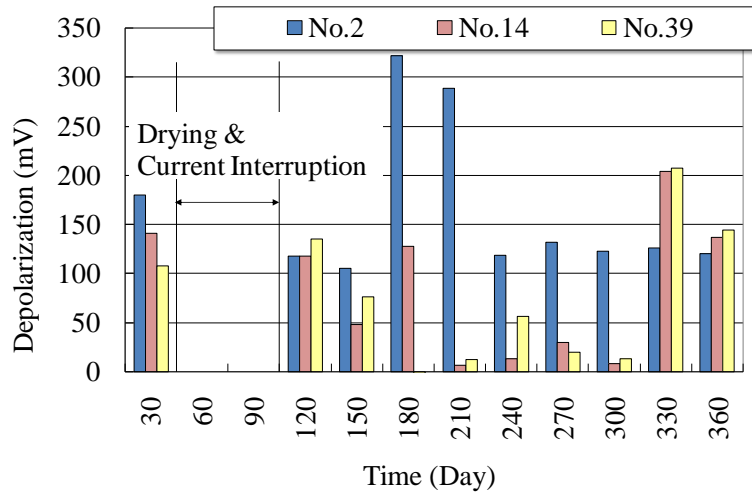
**Fig. 7. Instant-off Potentials under Dry/Wet Condition ( $\Delta 100$  mV)**

The instant-off potential of chloride free specimen of 20 mm cover (No.2) indicated noble values more than  $-420$  mV vs. CSE excluding the period from 161 days to 220 days. Regarding that the steel bar did not have corrosion products on the surface, and the instant-potential was noble, the main cathodic reaction might be oxygen reduction. And the surface condition of the steel bar might be in the region of “passivation” as shown in Figure 4. In spite of the very low current density of less than  $0.1$  mA/m<sup>2</sup>, the depolarization cleared 100 mV from the first stage as shown in Figure 9. These results imply that non-corroded steel surface needs very low current density for CP. So that installation of CP systems into a new concrete structure in a salt attack environment is expected to be very effective and the installation load (repair of concrete, electric power and anodes) is expected to be very light.



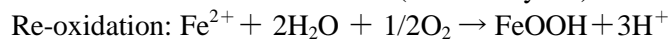
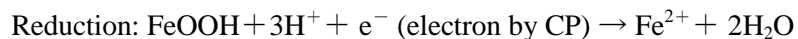
**Fig. 8. Current Densities under Dry/Wet Condition ( $\Delta 100$  mV)**





**Fig. 9. Depolarization Values under Dry/Wet Condition ( $\Delta 100$  mV)**

On the other hand, the specimens of No.14 and No.39 required high current densities from the initial stage in spite of the same moisture condition of No.2. And the current densities increased when the instant-off potentials were nobler than about  $-500$  mV vs. CSE after 96 days. It is considered that the CP current was consumed by the reduction of corrosion products on the surface of the steel bar under acidic (low pH) conditions, according to formulae (5), (6) and (7) as shown in Figure 4. The current densities of them fluctuated from  $1.0$  mA/m<sup>2</sup> to  $40$  mA/m<sup>2</sup> and to  $60$  mA/m<sup>2</sup>, respectively. It was difficult to control the current densities aiming the  $\Delta 100$  mV criterion due to the variations of the moisture conditions or of the supply of oxygen of the concrete. As a result, the  $\Delta 100$  mV criterion was not achieved for 5 months as shown in Figure 9. That is, under the dry condition, the high current density might be required by the reduction of re-oxidation products. On the other hand, under the wet condition, the low current density might be enough due to lack of the reducible products. With regard to these reactions, it should be noted that re-oxidation of reduced ions such as Fe<sup>2+</sup> can occur repeatedly until the pH of the surface changes to a stable level of about pH13 by the cathodic reactions of the CP, and until the main cathodic reaction changes to oxygen reduction. The reactions might be described as below.

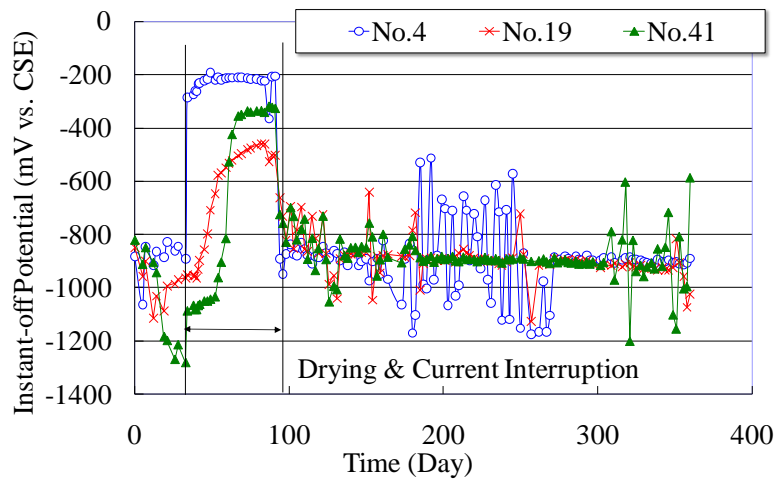


#### —850 mV criterion under dry/wet condition

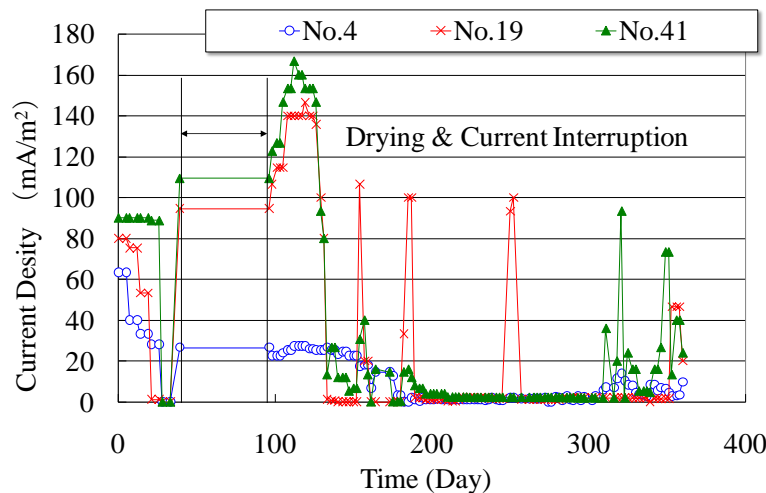
The instant-off potentials of  $-850$  mV criterion specimens under dry/wet condition were plotted in Figure 10. And current densities are plotted in Figure 11. The instant-off potential of chloride free specimen with 20 mm cover (No.4) fluctuated in the range from  $-1,170$  mV vs. CSE to  $-510$  mV vs. CSE with low current densities in the range from  $0.02$  mA/m<sup>2</sup> to  $3.3$  mA/m<sup>2</sup> in the period from 180 day to 280 day. These results imply that the pH of the surface of steel bars was about pH13 and the equilibrium reaction varied from formula (a) under wet condition to formula (b) under dry condition. In this case, a low constant or

intermittent [Glass et al. 2000] current can be applied such as  $0.5\text{mA/m}^2 - 1.0\text{ mA/m}^2$  for CP operation.

The instant-off potentials of specimens containing chloride with 20 mm cover (No.19) and with 42 mm cover (No.41) required very high current densities in the range from about  $80\text{ mA/m}^2$  to about  $170\text{ mA/m}^2$  to achieve the criterion of the  $-850\text{mV}$  in the initial period of 31 days and after the current interruption of 60 days. The reason for this can be explained by the reduction of corrosion products on the steel bars as mentioned above. However the current densities decreased down to the range from  $2\text{ mA/m}^2$  to  $20\text{ mA/m}^2$  after the operation of high current densities from 140 days. This implies that some amount of electricity is required to reduce the corrosion products to achieve the criterion. This was also experienced on the actual beam of a pier under CP operation [Yamamoto 2006]. And these current densities fluctuated in the range from  $0.07\text{ mA/m}^2$  to about  $100\text{ mA/m}^2$ . This might be reasoned that re-oxidation and reduction occurred as mentioned in Figure 8.



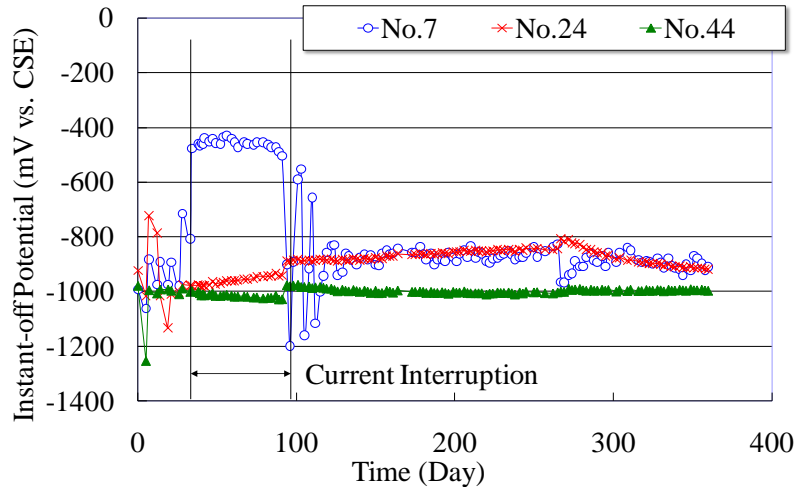
**Fig. 10. Instant-off Potentials under Dry/Wet Condition ( $-850\text{ mV}$ )**



**Fig.11. Current Densities under dry/wet condition ( $-850\text{ mV}$ )**

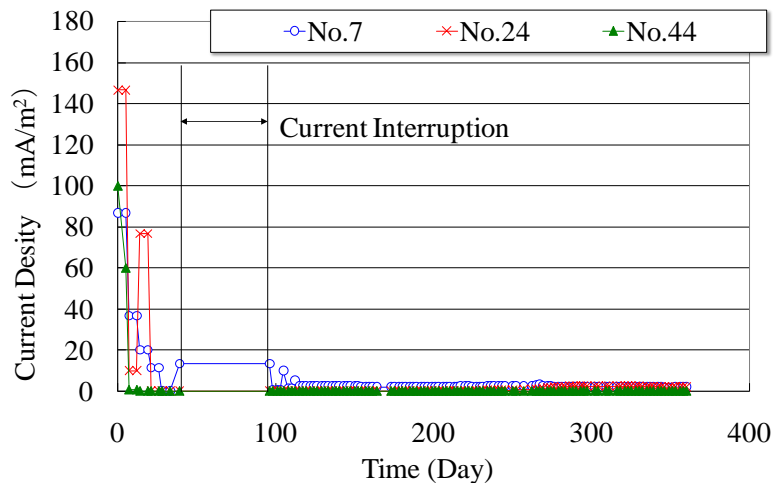
### –850 mV criterion under submerged condition

The instant-off potentials of –850 mV criterion specimens under submerged condition were plotted in Figure 12. And current densities are plotted in Figure 13.



**Fig. 12. Instant-off Potentials under Submerged Condition (–850 mV)**

The instant-off potentials of chloride free specimen with 20 mm cover (No.7) and the potential of specimen containing chloride with 20 mm cover (No.24) fluctuated in the range from about –1,200 mV vs. CSE to about –500 mV vs. CSE in the initial period of 31 days and after the current interruption of 60 days. These two specimens required relatively high current densities in the initial period. The reason why No.7 specimen required the high current density is supposed that the passive film on the surface of the steel bar was weakened by the reductive environment under the submerged condition. And No.24 specimen might require the high current density for reduction of the corrosion products on the surface as mentioned above. And after that period, very low current densities of about 2 mA/m<sup>2</sup> were required by No. 7 and No.24. And No.44 required very slight current density of that under 0.05 mA/m<sup>2</sup>. This might be considered that the supply of oxygen was too poor to oxidize the corrosion products on the surface of the steel bar.



**Fig.13. Current Densities under Submerged Condition (–850 mV)**

## Steel bar observation

Specimens were split and observation of the steel bars and pH measurement by universal pH test paper (measuring range is from pH1 to pH11) were carried out. The results including mass losses are shown in Table 4.

**Table 4. Observation Result and pH on Steel Bars of Specimens**

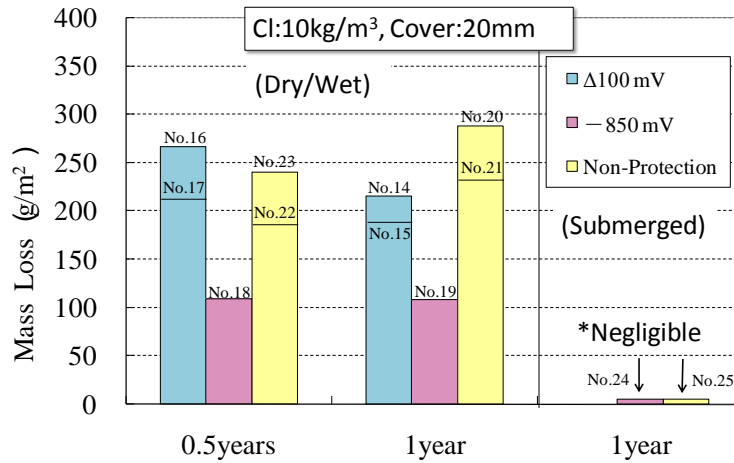
| Cl<br>(kg/m <sup>3</sup> ) | Cover<br>(mm) | Wettig<br>Condition | Criterion             | Period<br>(year)      | Specimen<br>No. | Mass<br>Loss<br>(g/m <sup>2</sup> ) | Corrosion<br>Area<br>(%) | Color of Rust | pH on Surface of Steel Bar |                 |                   |    |
|----------------------------|---------------|---------------------|-----------------------|-----------------------|-----------------|-------------------------------------|--------------------------|---------------|----------------------------|-----------------|-------------------|----|
|                            |               |                     |                       |                       |                 |                                     |                          |               | Corrosion<br>Spot          | General<br>Area | Non-<br>corrosion |    |
| 0                          |               | Dry/Wet             | $\Delta 100\text{mV}$ | 0.5                   | 1               | Neg.                                | —                        | —             | —                          |                 | over 10           |    |
|                            |               |                     |                       | 1                     | 2               | Neg.                                | —                        | —             | —                          |                 | over 10           |    |
|                            |               |                     | - 850mV               | 0.5                   | 3               | Neg.                                | —                        | —             | —                          |                 | over 10           |    |
|                            |               |                     |                       | 1                     | 4               | Neg.                                | —                        | —             | —                          |                 | over 10           |    |
|                            |               | Non-protection      | 1                     | 5                     | 3               | —                                   | —                        | —             |                            | over 10         |                   |    |
|                            |               |                     | 0.5                   | 6                     | 11              | —                                   | —                        | —             |                            | over 10         |                   |    |
|                            |               | Submerged           | - 850mV               | 1                     | 7               | Neg.                                | —                        | —             | —                          |                 | over 10           |    |
|                            |               |                     | Non-Protection        | 1                     | 8               | 5                                   | —                        | —             | —                          |                 | over 10           |    |
| 10                         | 20            | Dry/Wet             | $\Delta 100\text{mV}$ | 1                     | 14              | 215                                 | 83.8                     | Br / Bl       | 4~5                        | 9               | 10                |    |
|                            |               |                     |                       |                       | 15              | 198                                 | 87.6                     | Br / Bl / Gr  | 5                          | 7~8             | 10                |    |
|                            |               |                     |                       | 0.5                   | 16              | 267                                 | 87.0                     | Br / Bl / Gr  | 4                          | 7               | 10                |    |
|                            |               |                     |                       |                       | 17              | 213                                 | 89.3                     | Br / Bl / Gr  | 5                          | 7               | 10                |    |
|                            |               |                     | - 850mV               | 0.5                   | 18              | 109                                 | 86.9                     | Br / Bl       |                            | 8~9             | 10                |    |
|                            |               |                     |                       | 1                     | 19              | 108                                 | 80.2                     | Br / Bl       |                            | 8               | 10                |    |
|                            |               |                     | Non-protection        | 1                     | 20              | 288                                 | 80.8                     | Br / Bl / Gr  | 4~5                        | 9~10            | 9~10              |    |
|                            |               |                     |                       |                       | 21              | 235                                 | 85.2                     | Br / Bl / Gr  | 4~5                        | 9               | 9                 |    |
|                            | 0.5           | 22                  |                       | 196                   | 82.0            | Br / Bl / Gr                        | 4                        | 6~7           | 10                         |                 |                   |    |
|                            |               | 23                  |                       | 240                   | 87.6            | Br / Bl / Gr                        | 4                        | 5~6           | 10                         |                 |                   |    |
|                            | Submerged     | - 850mV             | 1                     | 24                    | Neg.            | 83.4                                | Bl / Gr                  | 7             | 8~9                        | —               |                   |    |
|                            |               | Non-protection      | 1                     | 25                    | Neg.            | 85.3                                | Bl / Gr                  | 6             | 8~9                        | —               |                   |    |
|                            | 42            |                     | Dry/Wet               | $\Delta 100\text{mV}$ | 0.5             | 38                                  | 165                      | 92.4          | Br / Bl / Gr               | 4               | 5                 | 10 |
|                            |               |                     |                       |                       | 1               | 39                                  | 162                      | 95.0          | Br                         | —               | 8                 | 10 |
|                            |               |                     |                       | - 850mV               | 0.5             | 40                                  | 140                      | 88.5          | Br / Bl                    | 8~9             | 8~9               | 10 |
|                            |               |                     |                       |                       | 1               | 41                                  | 144                      | 90.7          | Br / Bl                    | 7               | 8                 | 10 |
| Non-protection             |               |                     | 0.5                   | 42                    | 208             | 92.0                                | Br / Bl / Gr             | 4             | 8~9                        | —               |                   |    |
|                            |               |                     | 1                     | 43                    | 127             | 90.0                                | Br / Bl / Gr             | 5~6           | 8                          | 9~10            |                   |    |
| Submerged                  |               |                     | - 850mV               | 1                     | 44              | Neg.                                | 87.0                     | Bl / Gr       | 5                          | 7               | 10                |    |
|                            |               |                     | Non-protection        | 1                     | 45              | Neg.                                | 89.1                     | Bl / Gr       | —                          | 8~9             | 8~9               |    |

Note) Neg. = < 0 g/m<sup>2</sup> (Negligible), Colors = Br ; brown , Bl ; black, Gr ; green

The colors of corrosion products were brown, black and green. Brown one was not observed on the steel bars under submerged condition. Generally brown one is observed under aerated condition, it was found that the supply of oxygen to the steel bar was limited under the submerged condition. On the other hand, it was confirmed that oxygen was supplied to the steel bar under the dry/wet condition. The pHs on the corrosion spots were in the range from 4 to 9, and low pHs of about pH4 were mainly measured on the corrosion spots of the non-protection specimens.

### Mass losses of steel bars with 20 mm cover under dry/wet condition, $\Delta 100$ mV criterion

The mass losses of steel bars of dry/wet specimens containing chloride with 20 mm cover are shown in Figure 14. After 0.5 years (No.16 and No.17) the mass losses were 267 g/m<sup>2</sup> and 213 g/m<sup>2</sup> respectively, and after 1 year (No.14 and No.15) the mass losses were 215 g/m<sup>2</sup> and 198 g/m<sup>2</sup>, respectively. These mass losses did not depend on time. However, the mass losses



**Fig. 14. Mass Losses of Steel Bars of Cover 20 mm**

of non-protection specimens after 1 year (No.20 and No.21) increased. From these results, it is considered that corrosion of steel bars during the period from 0.5 years to 1 year was curbed by CP under the  $\Delta 100$  mV criterion. The mass losses of No.16 and No.17 were almost the same as that of non-protection (No.22 and No.23). It may be reasoned that the corrosion during non-operation of CP of “23 day preparation” and “60 day drying” occurred (the corrosion rate is designated as “BLANK20”, below). Furthermore, current interruption and insufficient current densities to achieve  $\Delta 100$  mV criterion might make mass losses larger during the period of 0.5 years. The actual cathodic operation was carried out for 155 days. The BLANK20 is calculated from the mass loss of non-protection of No.23, it is assumed that the corrosion continued at a constant rate during the periods, as follows,

$$240 \text{ g/m}^2 \times (23 + 60) \div (23 + 60 + 155) = 240 \text{ g/m}^2 \times 0.35 = 84 \text{ g/m}^2.$$

And the mass loss of No.16 during CP operation may be estimated,

$$267 \text{ g/m}^2 - 84 \text{ g/m}^2 = 183 \text{ g/m}^2.$$

and this is calculated into a corrosion rate as follows,

$$183 \text{ g/m}^2 \div 1.042 \text{ g/Ah} \div (155 \text{ day} \times 24 \text{ h/day}) \times 10^3 \text{ mA/A} = 47 \text{ mA/m}^2.$$

This  $47 \text{ mA/m}^2$  is very high corrosion rate compared with the CP current densities in the range of  $5 \text{ mA/m}^2$ —  $30 \text{ mA/m}^2$  which compensate the corrosion rates of the rebar in actual concrete structures. This means that the  $\Delta 100$  mV criterion is inadequate in the early stage for the CP of severely corroded steel bars in the concrete with 20 mm cover.

#### **Mass losses of steel bars with 20 mm cover under dry/wet condition, $-850$ mV criterion**

The mass losses of steel bars of dry/wet specimens under  $-850$  mV criterion were  $109 \text{ g/m}^2$  after 0.5 years (No.18) and  $108 \text{ g/m}^2$  after 1 year (No.19), as shown in Figure 14. These values can be calculated as  $25 \text{ g/m}^2$  and  $24 \text{ g/m}^2$ , respectively, if the BLANK20 is  $84 \text{ g/m}^2$ . It is considered that the  $-850$  mV criterion is adequate for CP operation, especially in the early stage under such a severe condition. The reason why the  $-850$  mV criterion is adequate in the early stage may be explained by the fact that the steel bars were polarized to near the potential of immunity (about  $-850$  mV vs. CSE, as shown in Figure 4), and sufficient current densities (up to  $140 \text{ mA/m}^2$  as shown in Figure 11) are applied, followed by increase of pH, as shown in Table 4.

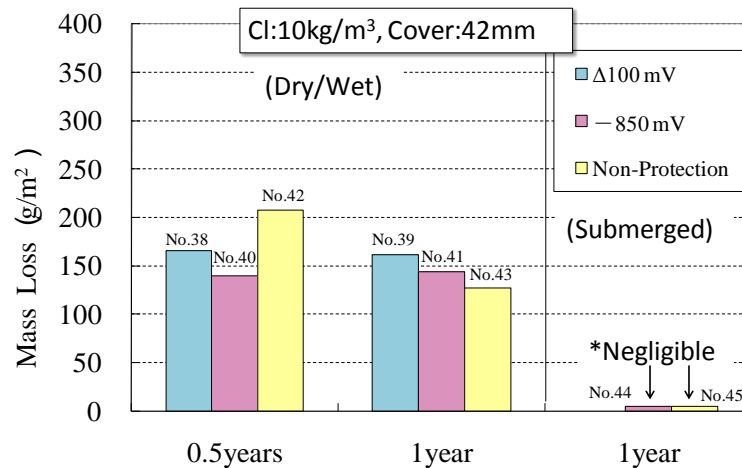
**Mass losses of steel bars with 20 mm cover under submerged condition,  $-850$  mV criterion**

The mass loss of the steel bar of submerged specimen under  $-850$  mV criterion was negligible as shown in Figure 14. And that of non-protection was also negligible. These results mean that the corrosion rate is controlled by the rate of the oxygen supply (diffusion) as mentioned above. However, it should be noted that when these steel bars connected with the steel bars of the nobler potentials, these steel bars corrode severely by composing a macro cell without CP operation.

**Mass losses of steel bars with 42 mm cover under dry/wet condition,  $\Delta 100$  mV criterion**

The mass losses of steel bars of specimens containing chloride with 42 mm cover are shown in Figure 15. The mass losses under  $\Delta 100$  mV criterion were  $165 \text{ g/m}^2$  after 0.5 years (No.38) and  $162 \text{ g/m}^2$  after 1 year (No.39), respectively. These mass losses did not depend on time. This means that CP operation curbed the corrosion of the steel bars in the period of from 0.5 years to 1 year. The mass losses of non-protection specimens were  $208 \text{ g/m}^2$  after 0.5 years (No.42) and  $127 \text{ g/m}^2$  after 1 year. These values were smaller than that of specimens with 20 mm cover. It can be reasoned that the thicker cover deterred the diffusion of oxygen to the surface of the steel bar. The BLANK42 is calculated from the mass loss of non-protection of No.42, it is assumed that the corrosion continued at a constant rate during the non-operation periods, in the same manner mentioned above,

$$208 \text{ g/m}^2 \times 0.35 = 73 \text{ g/m}^2.$$



**Fig. 15. Mass Losses of Steel Bars of Cover 42 mm**

**Mass losses of steel bars with 42 mm cover under dry/wet condition,  $-850$  mV criterion:** The mass losses of steel bars of dry/wet specimens under  $-850$  mV criterion were  $140 \text{ g/m}^2$  after 0.5 years (No.40) and  $144 \text{ g/m}^2$  after 1 year (No.41), respectively. And these values can be calculated as  $67 \text{ g/m}^2$  and  $71 \text{ g/m}^2$  respectively, if the BLANK42 is  $73 \text{ g/m}^2$ . These mass losses were larger than those of specimens with 20 mm cover under  $-850$  mV criterion. It may be reasoned that the dry condition was continued for about 30 days after interruption of 60 days as shown in Figure 11, so that the oxygen was sufficient to corrode for the steel bars. It is assumed that if there were not the interruption and drying operation, the mass losses would be lesser than those of cover 20 mm, due to poor supply of oxygen.

**Mass losses of steel bars with 42 mm cover under submerged condition,  $-850$  mV criterion:** The mass losses of steel bars of submerged specimens under  $-850$  mV criterion was negligible. And that of non-protection was also negligible. These results means that the corrosion rate is controlled by the rate of the oxygen diffusion as mentioned above.

## CONCLUSIONS

The criteria of CP of steel bars in concrete were examined for specimens under dry/wet condition and submerged condition. The results show that when the steel bar in the concrete is severely corroded under high moisture conditions, the criterion “less noble than  $-850$  mV vs. CSE” is more adequate than “100 mV depolarization” in the early stage of CP operation. The results of these examinations are as follows:

- The potential variations of the steel bars in specimens are explained by the potential-pH diagram, which is based on electrochemical thermodynamics theory.
- The corrosion potentials of the steel bars under the submerged condition indicated less noble values in the range from  $-1,000$  mV vs. CSE to  $-830$  mV vs. CSE. It may be considered that the potentials correspond to hydrogen electrode potential and the local anode potential.
- The steel bars in the specimens under the submerged condition corroded negligibly. This means that the corrosion is controlled by the rate of oxygen diffusion.
- The current densities to achieve the criteria were very high when corrosion products existed on the steel bars. It is considered that cathodic currents might be consumed by the reduction of corrosion products on the steel surface.
- The pH on the surface of the corroded steel bars was less than pH4, but the current of CP increased the pH up to more than pH10. These variations of pH seemed to affect the current densities of CP.
- It was difficult to control the potential of severely corroded steel bars to achieve the criteria under high moisture conditions. Thus, it seemed to be better to apply sufficient current densities to the corroded steel bars until the surface will be improved, without regard to the potentials in RC structures.

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