Verification of Cathodic Protection Criteria for Chloride Attacked Members of a RC Pier

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ABSTRACT

The members of a pier, which had been repaired by mortal and epoxy resin coating repeatedly, were deteriorated by chloride attack from the sea water. Cathodic protection of impressed current system (ICCP) was installed to the members, and adjusted the protection current in order to satisfy more than one of three criteria, which are "A. polarization 100 mV", "B. depolarization 100mV" and "C. potential -850mV vs.CSE". After 5 years of ICCP operation, it is verified that "A.100mV polarization criterion should be applied in the initial stage of ICCP", "B. depolarization 100mV" criterion is suitable for aerated members and "C. potential -850mV vs.CSE" criterion is adaptable for members in the splash zone where the concrete absorbs the sea water, and ICCP is very effective to suppress the re-deterioration of concrete structures in severe chloride attack environments.

Keywords. Cathodic Protection, Criteria , RC members, Re-deterioration, Chloride Attack

INTRODUCTION

The RC members of a pier under sever chloride attack environment deteriorated due to corrosion of steel bars in the concrete after 20 years from the construction. The members had been repaired with mortar and epoxy resin coating. However, after 4 or 5 years the members deteriorated again. In order to prevent the re-deterioration, ICCP (Impressed Current Cathodic Protection) was installed. In this paper, mechanism of corrosion and cathodic protection are described, and criteria for cathodic protection are discussed based on the ICCP data of the pier under the sever chloride attack environment.

MECHANISM OF CORROSION AND CATHODIC PROTECTION

Equilibrium Theory of Corrosion Mechanism of Steel in Concrete.   Potential-pH diagram is shown in Fig.1, which is drawn based on thermodynamic theory. With this

diagram, states of surface of the steel in aqueous solutions are estimated. The main formulas are shown below, expressed by Pourbaix (Pourbaix, 1997a) and by Misawa (Misawa, 1973). These formulas were described in the author's paper (Yamamoto, 2010). In Fig.1, the pH of corroding surface of the steel in concrete is assumed 7.0, according to the experimental results, which are in the range of pH4 to pH10 (Yamamoto, 2010). The axis on the left side indicates potentials referred to "Saturated Copper-Copper Sulphate Electrode" (vs.CSE).

Oxidation-reduction equation (Oxy-Red) of hydrogen: (P) : $H_2 = 2H^+ + 2e^-$ (1)

    Formula [a] in Fig.1 (Formula [a]) : $E = 0.0 - 0.0591pH$ (2)

Oxy-Red of oxygen: (P) : $4OH^- = O_2 + 2H_2O + 4e^-$ (3)

    Formula [b] : $E = 1.228 - 0.0591pH$ (4)

Oxy-Red of iron (M) : $Fe = Fe^{2+} + 2e^-$ (5)

    Formula [1] : $E = -0.440 + 0.0296 \cdot \log [Fe^{2+}]$ (6)

Equation of ferrous hydroxide (M) : $Fe^{2+} + 2H_2O = Fe(OH)_2 + 2H^+$ (7)

    Activity of iron ions in Fig.1 : $\log [Fe^{2+}] = 11.36 - 2pH$ (8)

Oxy-Red of lepidocrocite (M) : $Fe^{2+} + 2H_2O = \gamma\text{-}FeOOH + 3H^+ + e^-$ (9)

    Formula [7] : $E = 0.919 - 0.1775pH - 0.0592 \cdot \log [Fe^{2+}]$ (10)

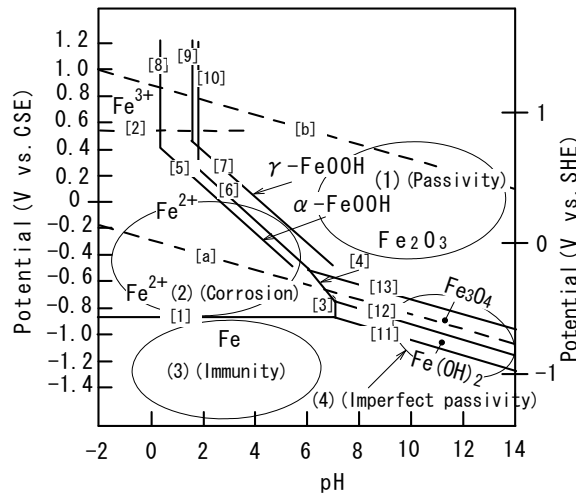   Note: [P]; after Pourbaix, [M]; after Misawa

Figure 1. Potential-pH Diagram of Iron

Some substance such as oxygen is necessary, which reacts with electrons(e^-) evolved by the reaction, so that steel keeps the passive film on its surface in concrete. This substance is called "oxidant". As shown in Fig.1, oxygen[b] is oxidant in the (1) passivity zone and oxygen[b], ferric ions[2], rust such as [5], [6], [7] and hydrogen ions[a] are assumed as oxidants in the (2) corrosion zone (Pourbaix, 1972).

In this paper, corrosion reaction is called "anodic reaction", corrosion current is "anodic current", corroding area is "anode" respectively. On the other hand, the reaction where oxidant is reduced is called "cathodic reaction", the current is "cathodic current" and the area where oxidant is reduced is "cathode" respectively.

Change of the State of Steel Surface in Concrete by Cathodic Protection. Steel surface in concrete is protected by passive film formed by alkalinity of the concrete, as shown in (1) passivity zone of Fig.1. However, when chloride ions intrude into the concrete and the concentration increases higher than the threshold, the passive film breaks and the state of the steel shifts to the (2) corrosion zone. When the steel corrodes, the pH of the surface decreases as low as pH3-pH4 (Yamamoto, 2006), due to hydrolysis of iron ions. When cathodic protection is applied, the potential of the surface shifts to negative direction and the state shifts to the (3) immunity zone, where corrosion is unable to occur. And furthermore cathodic protection is continued, the pH of the steel surface increases, subsequently the state of the steel surface shifts to the (4) imperfect passivity zone, where corrosion rate is negligible. And if the supply of the oxygen is enough to make passive film in the concrete, the state of the steel surface shifts back to the (1) passivity zone.

KINETIC THEORY OF CORROSION MECHANISM OF STEEL IN CONCRETE

Micro Cell. An illustration of corrosion of steel in concrete ("steel bar in concrete" is mentioned as "steel bar", below) is shown in Fig. 2. It is characterized that corrosion of steel bars are composed of micro cell and macro cell. The anodes of micro cells develop at the defective area such as bleeding affected area, or area of that concrete cover is insufficient. At the anodic area, micro cells propagate, replacing the micro anodes and the micro cathodes in turn.

At the micro anode, iron(Fe) releases two electrons(e^-) into the steel, and dissolves itself as a iron ion(Fe^{2+}) into the solution. These iron ions(Fe^{2+}) react with water(H_2O) to make ferrous hydride ions($Fe(OH)^+$) and hydrogen ions. Consequently, hydrogen ions increase so that the pH of the solution decreases. For example, low pH was measured on a corroded steel bar as shown Fig. 2. On the other hand cathodic reaction occurs on the cathode reducing oxidant such as oxygen, balancing with the anodic reaction.

In general, the rate of corrosion is expressed as current density (i (A/m^2)) , the current value divided by the area, according to the Faraday's laws. In Fig. 3 the micro cell current is expressed as current (I_{mic}).

Macro Cell. In general sound steel bars indicate positive potentials higher than -350mV vs.CSE, and act as cathodes of macro-cells, in combination with the anodic area in the concrete. In Fig. 3 the macro cell current is expressed as I_{mac}, which flows from the anode to the cathode through the concrete. It is reported that macro cell accelerates the micro cell corrosion (Yamamoto, 2012a).

Explanation of Corrosion Mechanism by Polarization Curbs. In Fig. 4 anodic and cathodic polarization curbs are illustrated, where both reactions are controlled by activation, in other words, the rates of the reactions depend on the potential. Both polarizations are expressed by the Tafel's formula (11) , where potential is proportional to the logarithm of the
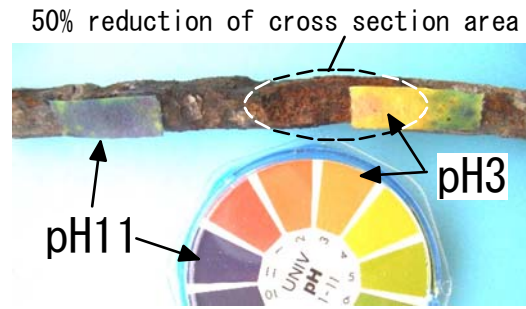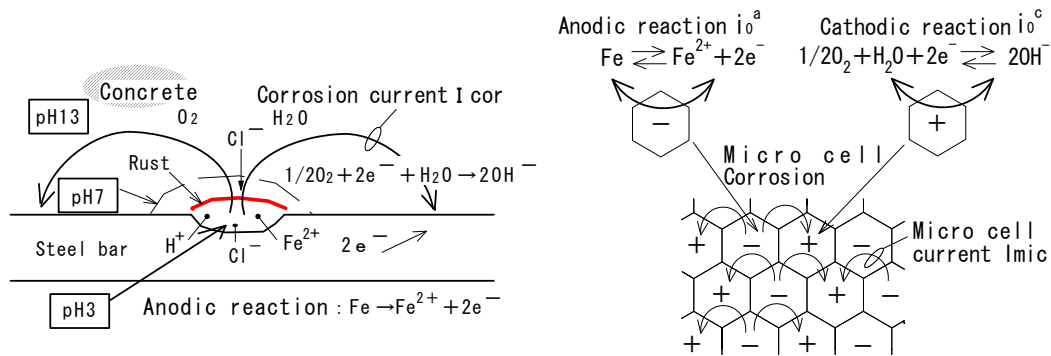
Figure 2. The pH of a corroded Steel in Concrete

Figure 3. Macro Cell (Left) and Micro Cell (Right)

current density. In formula (11), "i_0 " is called exchange current density which flows in opposite directions at an equilibrium state. In Fig. 4, horizontal axis is expressed as current I, on the condition that the corrosion occurs in the same area of the steel, which is composed of anode and cathode. The "β" is called "Tafel slope" expressed by the formula (12). Here "α" is "transference rate" of the reaction, which is 0.5 generally, "n" means the atomic value in the reaction, "F" is Faraday constant (9.6485×10^4 Coulomb/mol），"R" is gas constant (8.314 J/mol・K), "T" is absolute temperature.

$$E＝E_0＋β×\log(i/i_0) \tag{11}$$

$$β＝2.303×RT/(αnF)×10^3 \tag{12}$$

In the reaction of formula (5), Tafel slope $β_a$ is 59mV from the calculation of formula (11) at 25 degrees Celsius. However in general, actual slopes acquired from polarization curbs are in the range of 120 to 400 mV (Yamamoto, 2012). The reasons for this are that transference rate α is smaller than 0.5 and/or atomic value n is smaller than 2. The reactions of corrosion in concrete are so complicated that Tafel slope is expressed as an apparent value as β ' in Fig. 4.

In Fig. 4 (Left), anodic potential shifts in positive direction from the equilibrium potential E_0^a in accordance with the current I_a increase so that the anodic current balances with the cathodic current of I_c at the corrosion potential E_{cor}. And the cathodic potential shifts to the opposite direction. When the concrete is submerged in water, the pores of concrete are filled with water. In this case the oxidant is only dissolved oxygen. Because the rate of the oxygen
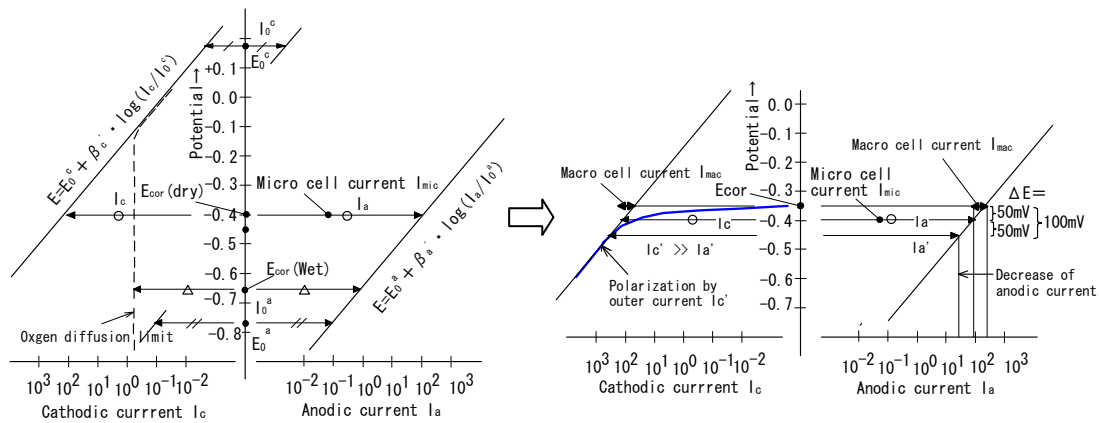
Figure 4. Polarization Curbs of Micro Cell (Left) and Macro Cell (Right)

supply is very poor, the corrosion rate is very low and the potential is very negative, shown as dotted line in Fig. 4.

Macro cell corrosion is illustrated in Fig. 4(Right). The corrosion potential of the anode of the micro cell changes in positive direction, the anodic current I_a increases. For example, if the potential changes 50 mV, the micro cell current increase 2.6 times (260÷100, in Fig. 4(Right)) in case of the Tafel slope βa' is 120mV, according to the formula (11).

On the contrary the anode potential changes in negative direction of 100 mV from the corrosion potential E_{cor} by cathodic protection, the anodic current decreases from 260 to 38 in Fig. 4(Right). In this way cathodic protection controls both of micro cell and macro cell. Furthermore continuous cathodic protection causes chloride ions to migrate away from the steel surface, and also causes hydroxide ions to accumulate on the surface. As the result of that, cathodic protection suppressed the corrosion of steel completely.

Criteria for Cathodic Protection. In general, the criterion of "more than 100 mV negative than corrosion potential" (A. polarization 100 mV), and "more than 100 mV of depolarization" (B. depolarization 100 mV) are adopted in many cases of cathodic protection for reinforced concrete under atmospheric conditions.

Furthermore "maintaining the potential more negative than -850mV vs.CSE" (C. potential -850 mV) is applicable under high moisture conditions. These three criteria are practical and confirmed their validities (Yamamoto, 2010).

The principles and characteristics of the three criteria are summarized in Table 1. Here, E_{cor} is for "corrosion potential", E_{ins} is for "instant off potential" and E_{off} is for "off potential".

The Procedures of the Tests. The criterion "A. polarization 100 mV" is mainly adopted at the initiation of ICCP to determine the current density to be supplied. The procedure to confirm the criterion is as follows.

(1) measure the E_{cor}, (2) apply current for 15 minutes, (3) cut the power source and measure the E_{ins}, (4) repeat (2) and (3) increasing the current such as 1, 2, 5, 10, ・, ・ mA/m^2 step by step, (5) calculate the polarization value by subtracting E_{ins} form E_{off}, (6) set the current of power source at the value of that the polarization is more than 100 mV.

The criterion "B. depolarization 100 mV" is mainly adopted at the time of confirming the effect of ICCP during the operation. The procedure to confirm this criterion is as follows.

(1) measure the E_{ins} , (2) cut the power source for 24 hours for example, (3) measure E_{off} and calculate the depolarization value by subtracting E_{ins} form E_{off}, (6) adjust the current of power source to the value of depolarization is expected to be more than 100 mV.

Furthermore, under high moisture condition, if the steel bars corroded in a member they need a high current density to clear criterion of "A. polarization 100 mV". It is because that the corrosion products such as ferric oxides or hydrogen ions on the steel surface are reduced (react as oxidant) by cathodic protection (Yamamoto, 2011). In this case, "C. potential -850 mV" is considered most suitable (Yamamoto, 2011) for the criterion.

Table 1. Principles and Characteristics of the Three Criteria

Criteria	Calculations	Principles	Characteristics	
			Environments	Stages
A. Polarization 100mV	$\Delta E \geq E_{cor} - E_{ins}$	Shift the Potential More Negative Than 100 mV	・Dry ・High Moisture	・Initial
B. Depolarization 100mV	$\Delta E \geq E_{off} - E_{ins}$	Ditto	・Dry	・Periodic Check
C. Potential -850mV	E＝-850mV vs.CSE	・Maintain the Potential at the Immunity Zone	・High Moisture	・Initial ・Periodic Check

VERIFICATION OF CATHODIC PROTECTION CRITERIA

In order to verify the three criteria for cathodic protection, ICCP currents were adjusted based on the criteria and the members of a pier were examined if the ICCP was effective to suppress the re-deterioration of the pier.

OVERVIEW OF A RC PIER

Structure. A shelf type pier was repaired. The superstructure is composed of 6 spans of RC members. Dimensions of a span are 17.5 m by 35.0 m. Because the bottom of the beam is near to the sea level, the bottom comes in contact with seawater twice a day at the time of high tide.

Salt Attack Environments. This pier is located under severe chloride attack environment. At the time of stormy weather, the waves hit the slabs of the pier. Furthermore when rock salt is unloaded, the salt spreads over the slab. The chloride concentrations of concrete at the depth of 50 mm are 5 to 8 kg/m^3 in the beam, 5kg/m^3 in the top side of the slab and 3 to 6

kg/m^3 in the bottom side of the slab respectively (Takeda, 2007).

History of Repairs. The construction of the pier was completed in 1968. In the period of 1991 to 1993, because the beams and slabs were deteriorated, the members of the pier were repaired by mortal and epoxy resin coating. However 4 to 5 years after the repair, the members of the pier deteriorated again. After repeated repairs, ICCP was installed in 2006. The area ratios of the repaired with mortar were 80 % for bottom side of slabs, 30 % for side of beams, almost 100 % for bottom of beams respectively.

CATHODIC PROTECTION

Installation of ICCP. ICCP was installed after the mortar repair of delaminated concrete of the members of all 6 spans. Tray shaped titanium anode system was installed on the surfaces of the members. Considering that the steel bars had the corrosion products on their surface, and the members were exposed to various moisture conditions, the ICCP circuit of each span was divided into 4 circuits, which were No.1 for beam bottom ($226m^2$), No.2 for land side of beam (339 m^2), No.3 for sea side of beam (480 m^2) and No.4 for bottom side of slab (333 m^2). The idea of the circuit division is illustrated in Fig. 5. Here, in order to measure the potentials of steel bars, four lead reference electrodes were installed to each circuit, as shown in Fig. 5. And in order to monitor the potential of the upper steel bars, reference electrode No.1 is buried near the upper steel bars of the slab. The lead reference
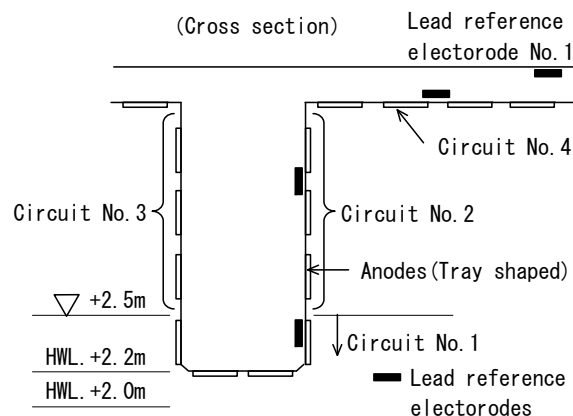

Figure 5. Circuits of ICCP

electrode indicates the most stable potential compared with the other reference electrodes in concrete for many years.

Corrosion Sensors. Tow corrosion sensors were installed in the concrete both in areas of protected and un-protected. The corrosion sensor shown in Fig. 6 has thin (diameter is 0.1 mm) steel wires. When the wire corrodes and lost its continuity, some voltage (potential difference) is generated, so that the corrosion is detected by measuring the voltage at the both sides of the wire.

Criteria for Cathodic protection. Considering that the steel bars might have corrosion products on the surfaces in the concrete and the members were exposed to various moisture conditions, the three criteria mentioned before were adopted.
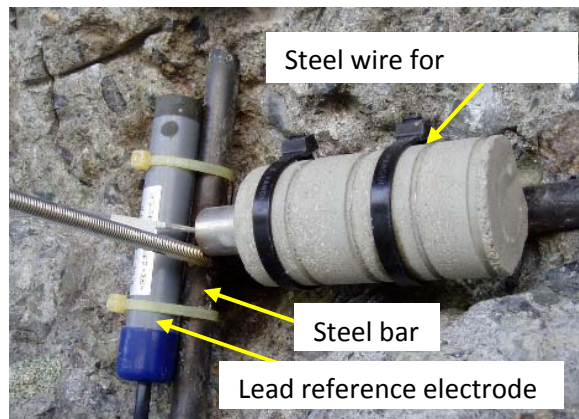
Figure 6. Corrosion Sensor

Current Adjustment. At the initial stage the current was adjusted based on the criterion "A. polarization 100 mV", by the procedure mentioned before. And at the periodic check afterwards, the current was adjusted based on the three criteria.

Measured Items. Corrosion potential E_{cor}, current, instant off potential E_{ins} and off potential E_{off} of 24 hours were measured.

RESULTS AND DISCUSSION

Circuit No.1 (Bottom of Beam). In this paper the data of span No.5 were only discussed. It is the reason why the data of the other spans indicted the same tendencies as those of this span. And because the results of this span is described in the paper (Yamamoto, 2012b), the outlines are shown below.

Current Density of Circuit No. 1 (Bottom of Beam). Current density of circuit No.1 was plotted in Fig. 7-a. Considering that the bottoms of beam contact with the sea water, the current of ICCP was adjusted based on the criterion "C. potential -850 mV".
As the result of that, although the current densities were in the range of 40 to 58 mA/m^2 at the initial stage, they decreased to 20 mA/m^2 after 372 day operation. This means the current density of ICCP decreases after a continuous operation, even if the initial current density is very high, under moisture conditions as reported by Yamamoto et al. (Yamamoto, 2010).

Potentials of Circuit No. 1 (Bottom of Beam). Instant off potentials, polarization and depolarization data of circuit No.1 are plotted in Fig. 7-b, in Fig. 7-c and in Fig. 7-d, respectively.

The instant off potentials indicated negative values in the range of -800 to -600 mV vs.CSE from the initial stage and stabled at negative value of -1,000 mV vs.CSE . Regarding to the Fig. 7-a, it is clear that continuous cathodic protection makes the potentials more negative and the current densities lesser under high moisture conditions.
At the position of reference electrode No.3 the potential of the steel bar did not satisfy the criterion "C. potential -850 mV" after 1,845 day operation. On the other hand the criterion "B. depolarization 100 mV" was cleared as shown in Fig. 7-d. This reason is that the surface conditions of the steel bars are improved by accumulation of hydroxide ions and reduction of chloride ions during ICCP operation (Yamamoto, 2011). It is assumed that the state of steel
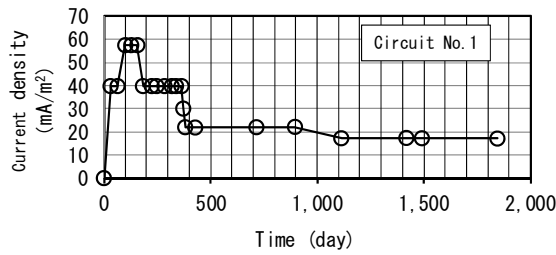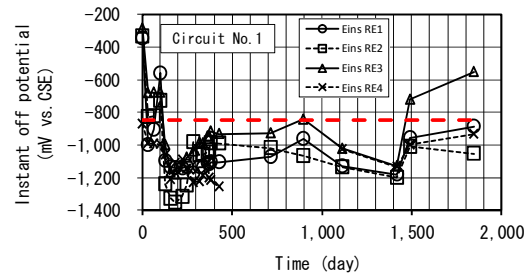
Figure 7-a. Current Density
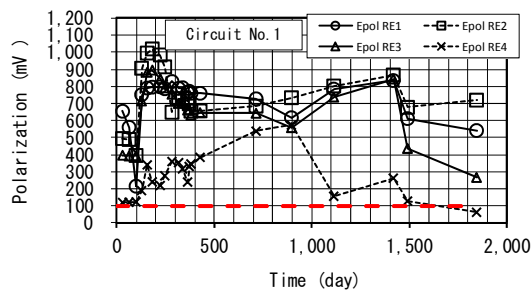

Figure 7-b. Instant Off Potentials

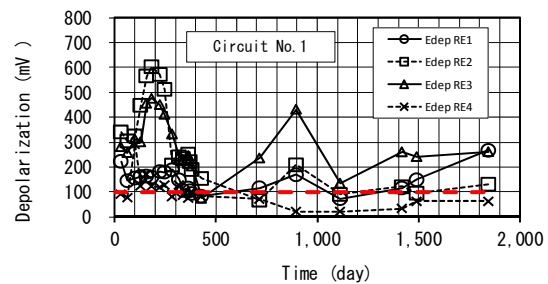**Figure 7-c. Polarizations**

Figure 7-d. Depolarizations

surface changed from (3) immunity zone to (4) imperfect passivity zone or (1) passivity zone as shown in Fig. 1.

Current Density of Circuit No.2 (Land Side of Beam). Current density of circuit No.2 was about 20 mA/m^2 at the initial stage, but they decreased to 5 mA/m^2 after 300 day operation.

Potentials Circuit No.2 (Land Side of Beam). The instant off potentials of circuit No. 2 indicated in the range of -800 to -600 mV vs.CSE during the operation. It is considered that the side of bean was under drier condition comparing with the bottom of the beam. From the results, it was found that at the all positions of reference electrode satisfied the criterion "B. depolarization 100". And the data of circuit No.3 (sea side of beam) indicated the same tendency with those of circuit No. 2 mentioned above.

Current Density of Circuit No.4 (Bottom Side of Slab). The current density of circuit No.4 was 45 mA/m^2. It was very high due to the polarization of the steel bars had been very small.

Potentials of Circuit No.4 (Bottom Side of Slab). The instant off potentials, except reference electrode No.3, indicated more noble values in the range of -800 to -400 mV vs.CSE compared with those of bottom of the beam. It is considered that the slab is drier than the bottom of the beam. At the position of reference electrode No. 1 (near the upper steel bars of the slab), the polarization exceeded 100 mV after 400 day operation. It is

considered that the ICCP current reached the upper steel bars.

Observations. Observations and hammering tests of the members were conducted every year. The areas where ICCP were installed showed no deterioration such as rust stain, cracks and delaminations of concrete.

Results of Corrosion Sensor. Tow corrosion sensors were installed in the concrete in both areas of protected and un-protected. The corrosion sensor in the protected area did not detected corrosion of steel. On the other hand the sensor in un-protected area detected corrosion. From this result it is clear that the pier had been protected by ICCP for 5 years to suppress the deterioration of the RC pier.

SUMMARY

In order to prevent the re-deterioration of a pier, ICCP (Impressed Current Cathodic Protection) of tray shaped titanium anode system was installed and the currents of ICCP were adjusted based on three criteria which are "A. polarization 100 mV", "B. depolarization 100 mV" and "C. potential -850 mV". As the result of this, it is found that adjusting the ICCP current based on the three criteria is rational and practical.

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