

강의 음극방식에 미치는 표면상태와 유속의 영향

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The Effects of Surface Condition and Flow Rate to the Cathodic Protection Potential and Current on Steel

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Abstract : Cathodic protection is being widely used to protect steel structures in sea water environment. In order to protect steel structures completely, the flow condition of sea water surrounding with this structures and the surface condition of the structures must be considered for a desirable design of cathodic protection. In this study, the optimum protection potential and current density were investigated in terms of cathodic current density, surface condition and a flow condition of sea water. The optimum protection potential of the cleaned specimen was -770 mV(SCE) and below. However in the case of the rusted specimen, its potential was -700 mV(SCE) and below, which was somewhat positive than the cleaned one irrespective of flow condition. The optimum cathodic protection current density for both the cleaned and rusted specimens was 100 mA/m², however, on the flow condition, 200 mA/m² to be supplied for cathodic protection of steel structures completely for both cleaned and rusted specimens.

Key words : Cathodic Protection Potential, Corrosion Potential, Current Density, Polarization, Surface Condition, Flow Rate.

1. Introduction

Recently with the rapid development of industry, the corrosion of steel structures exposed to the severe detrimental envi-

ronment has generated numerous social problems in the economical point of view.

Furthermore, it has been revealed that the economical damage by corrosion of steel structures was approximately 4~5%

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of GNP in the USA in 1998⁽¹⁻²⁾. Although the economical damage due to corrosion in Korea was not clearly verified, it was assumed that the damage of Korea would be much greater than that of USA. Therefore, a corrosion control is being generally accepted an important issue not only in economical but also in safety point of view.

There are a lot of kinds of protection techniques to control corrosion. Cathodic protection, one of which is being mainly used for steel structures in marine environment⁽³⁻¹¹⁾. Furthermore sacrificial anode method, one of the cathodic protection techniques is being widely used in port and/or offshore structures. And then for the optimum design of sacrificial anode method, size, weight consumption rate, life time, number of anodes should be varied with some parameters such as degree of contamination, temperature and velocity (flow rate) of the sea water and soon. These parameters have been investigated in some countries for a desirable protection design⁽¹²⁾. In the previous paper⁽¹³⁾ it was examined that flowing current, consumption rate and polarization behavior of sacrificial anode could be varied with some parameters discussed above.

In this study, the optimum protection potential and the protection current density were investigated with some parameters such as cathodic current density, surface condition of specimen and flow condition.

2. Experimental Procedure

2.1 Test specimen

Two kinds of specimens were made for

all experiments, one of which was polished with #2000 emery paper and the other one was the rusted specimen corroded purposely at the roof of building for 3 months after immersion for 5 minutes in sea water. The size of specimen was 100 cm² (10cm×10cm) as shown in Photo. 1.

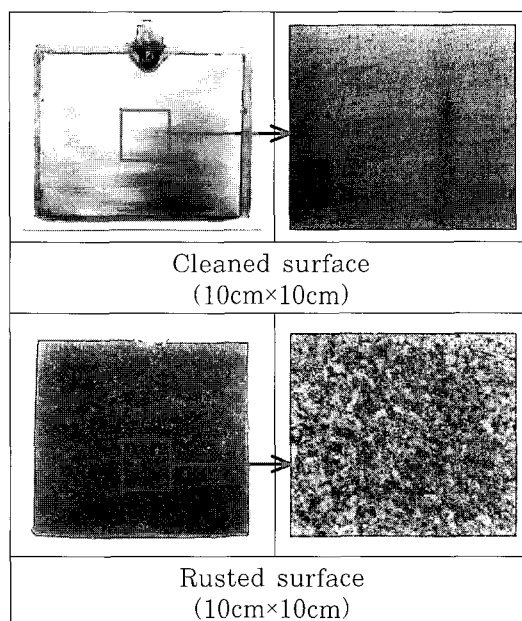


Photo. 1 Photographs of specimens' surface

2.2 Experimental method

Variation of corrosion potential measured with time. In addition cathodic and anodic polarization curves was measured with CMS-100 system and corrosion rate was computed by Tafel extrapolation technique from polarization curve. Cathodic polarization potential was evaluated for cleaned and rusted specimens at the flow or non-flow condition of sea water under a constant applied current density, which was measured for 9 days. The velocity of sea water was 3cm/s and it was measured by PIV (particle image velocimetry)

apparatus. The constant current density was supplied by D.C power supplier(JI SANG ELECTRIC CO., LTD. 15V, 1000mA). Carbon bar (Ø 0.5 cm) was used as an insoluble anode, and sea water solution was changed every day.

3. Results and Discussion

Fig. 1 shows the variation of corrosion potential with immersed time in sea water. The corrosion potential of rusted surface is more positive than that of the cleaned one, which is suggested that the oxide film deposited on the rusted surface is stronger than the cleaned one. Therefore, the corrosion potential of rusted surface was the higher potential compared to the cleaned one because of the increasing of anodic polarization by the oxide film.

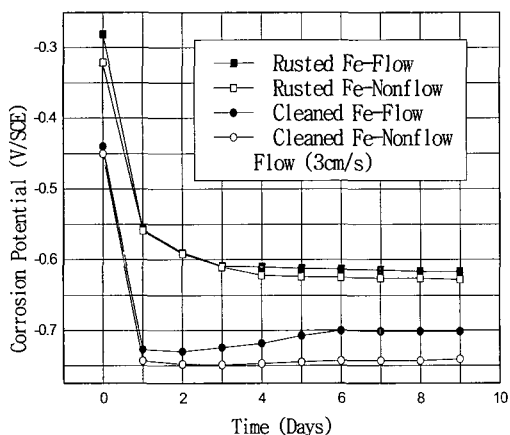


Fig. 1 Variation of corrosion potential with time for cleaned and rusted specimens at non flow and flow (3cm/s) condition in sea water

When the sea water is flowing, the corrosion potential showed the trend shifting from negative to positive

potential. However, variation range of corrosion potential in the rusted surface was about 5 mV, which was far less than that of the cleaned one of 50 mV. The corrosion potential in the neutral solution is generally decided with anodic reaction ($Fe \rightarrow Fe^{2+} + 2e$) and cathodic reaction ($O_2 + 2H_2O + 4e \rightarrow 4OH^-$) Furthermore, diffusion limiting current density (i_L)

$$(i_L = \frac{nFDC}{f}, n: \text{ionic number, F: Farady}$$

constant, D: diffusion coefficient, C: dissolved oxygen concentration, f: diffusion layer) with dissolved oxygen reduction reaction is increased with moving solution^[14-15]. Therefore it is considered that the corrosion potential of the cleaned surface is closely associated with diffusion limiting current density due to concentration polarization with dissolved oxygen reduction reaction in cathodic reaction, while in the case of rusted one, its potential is somewhat related to the activation polarization due to reduction reaction of the oxide film on the surface.

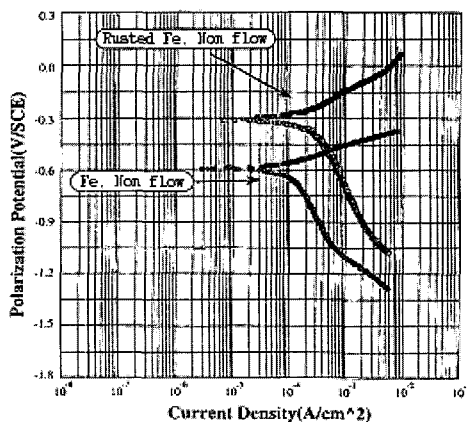


Fig. 2 Cathodic and anodic polarization curves for cleaned and rusted specimens in non-flow of sea water

Fig. 2 is the polarization curves for the cleaned and the rusted specimens. Activation polarization was occurred at the anodic polarization curves and cathodic polarization shows both an activation polarization and a concentration polarization due to dissolved oxygen reduction reaction.

It is generally accepted that corrosion current density in the neutral solution is nearly the same as diffusion limiting current density due to concentration polarization with dissolved oxygen reduction reaction^[16]. However in the rusted surface, diffusion limiting current density may not be regarded as a corrosion current density because the corrosion potential is directly associated with the activation polarization due to reduction reaction of the oxide film on the surface.

Table 1 shows the corrosion property obtained from Fig. 1, which is computed by the Stern-Geary equation $\left\{ i_{cor} = \frac{1}{2.3} \frac{i}{n} \left(\frac{\beta_a \cdot \beta_c}{\beta_a + \beta_c} \right) \right\}$ through CMS-100 system.

In Table 1 the corrosion current density of the cleaned surface is larger than that of the rusted one. This is probably that the oxide film already existed on the rusted surface acts as the barrier not only to interrupt the oxygen diffusion to

the cathode surface but also to inhibit anodic reaction. The corrosion current density of the rusted surface, therefore, is considerable lower than that of the cleaned one.

Fig. 3 shows the variation of cathodic polarization potential of the cleaned and rusted surfaces with flow and non-flow conditions at applied cathodic current density of 100 mA/m².

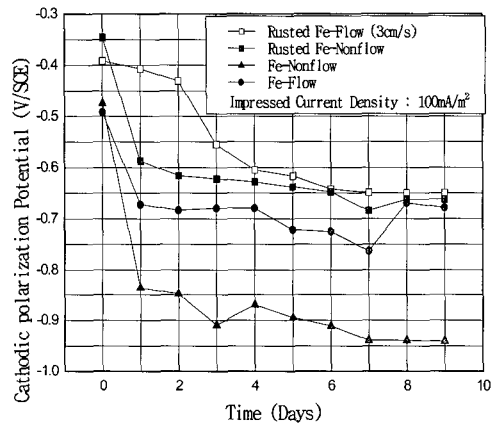


Fig. 3 Variation of cathodic polarization potential with time as a function of non-flow and flow (3cm/s) at the impressed current density of 100 mA/m²

The most negative polarization potential was observed at the cleaned surface with non-flow of sea water solution, however, the rusted surface with flow condition showed the most positive polarization potential.

Table 1 The data of corrosion properties of cleaned and rusted Fe

| 구 분 | β_a (mV/dec) | β_c (mV/dec) | Rp ($\Omega \cdot \text{cm}^2$) | i_{corr} ($\mu\text{A}/\text{cm}^2$) | Remark |
|------------|-----------------------|-----------------------|--------------------------------------|---|--|
| Cleaned Fe | 13.3 | 16.5 | 2.93×10^2 | 10.91 ($i_L : 20$) | Ecorr : -0.698V Tafel region -0.702V ~ -0.691V |
| Rusted Fe | 6.1 | 3.7 | 1.85×10^2 | 5.40 | Ecorr : -0.410V Tafel region -0.411V ~ -0.406V |

And also cathodic polarization potential of both cleaned and rusted specimens were shifted to noble direction with changing from non-flow to flow condition. Especially the potential variation range between non-flow and flow of the cleaned surface was about 265 mV after 9 days, while the rust specimen's value was about 13 mV.

The reason of these results is considered that the polarization potential of cleaned specimen was mainly controlled by concentration polarization with a reduction reaction of dissolved oxygen ($O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$)^[17] significantly associated with moving condition of solution, although in the case of rusted one, its reaction was controlled by the activation polarization with oxide film's reduction reaction^[15] little related to flow condition.

The cathodic polarization potential of cleaned specimen with non-flow condition showed more negative potential than -770 mV(SCE) which is known to be a theoretical protection potential. However, in flow condition indicated the positive value than -770 mV(SCE). In the rusted specimen, irrespective of flow and non-flow of solution, the polarization potential showed more noble potential than -700 mV(SCE).

Fig. 4 shows the variation of cathodic polarization potential at the applied cathodic current density of 150 mA/m². The cathodic polarization potential at 150 mA/m² shows negative value compared to 100 mA/m². The polarization potential of the cleaned specimen in flow condition after 9 days is about -730 mV(SCE) and that of

the rusted specimen indicated more positive potential than -730 mV(SCE) irrespective of flow and non-flow of solution.

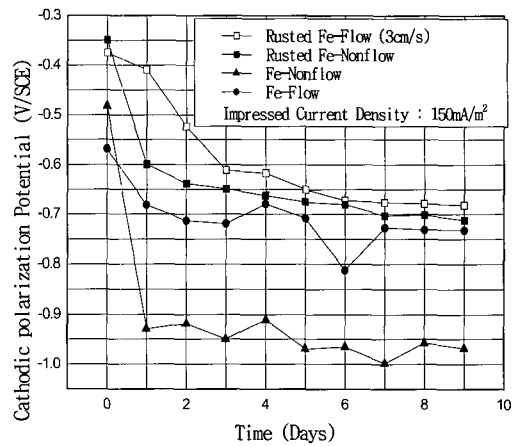


Fig. 4 Variation of cathodic polarization potential with time as a function of non-flow and flow (3cm/s) at the impressed current density of 150 mA/m²

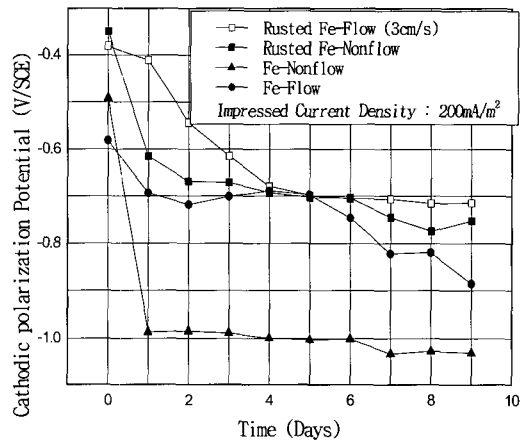


Fig. 5 Variation of cathodic polarization potential with time as a function of non-flow and flow, (3cm/s) at the impressed current density of 200 mA/m²

Fig. 5 shows the variation of cathodic polarization potential at applied cathodic current density of 200mA/m². After 6 days, the potential of the cleaned specimen in

flow condition was shifted to the more negative value than $-770\text{mV}(\text{SCE})$, and also in the case of rusted specimen, the polarization potential irrespective of flow and non-flow of solution indicated negative value than $-700\text{ mV}(\text{SCE})$.

Fig. 6 shows the variation of cathodic polarization potential at the applied cathodic current density of $250\text{ mA}/\text{m}^2$. Although solution was in a flow condition, the more negative polarization potential than $-770\text{ mV}(\text{SCE})$ was observed in the cleaned specimen from after 4 days. And the cathodic polarization potential of rusted specimen in non-flow condition was shifted to the protection region below $-770\text{ mV}(\text{SCE})$ after 6 days, and in the case of flow condition the cathodic polarization potential of more negative than $-700\text{ mV}(\text{SCE})$ was observed in the rusted specimen after 3 days.

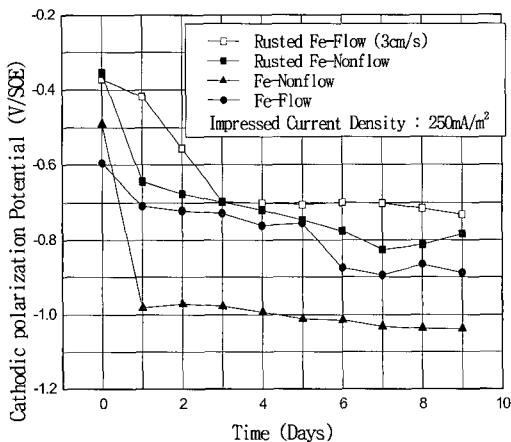


Fig. 6 Variation of cathodic polarization potential with time as a function of non-flow and flow (3cm/s) at the impressed current density of $250\text{ mA}/\text{m}^2$

From the results discussed above, it is suggested that the cathodic polarization potential was shifted to negative direction

with increasing of applied cathodic current density. And although under a constant current density, the polarized potential value also can be changed by surface condition as well as solution condition.

Futhermore, it was generally known that protection potential for all kinds of materials would be different respectively. Therefore, it is thought that the protection potential and protection current density can be dissimilar with some parameters such as the surface condition of cleaned or rusted, the solution condition of non-flow or flow.

Photo. 2 shows the surface morphology for cleaned specimens observed after 9 days, which was exposed at non-flow and flow condition of sea water at the applied cathodic current density of $100\text{mA}/\text{m}^2$ and $150\text{mA}/\text{m}^2$.

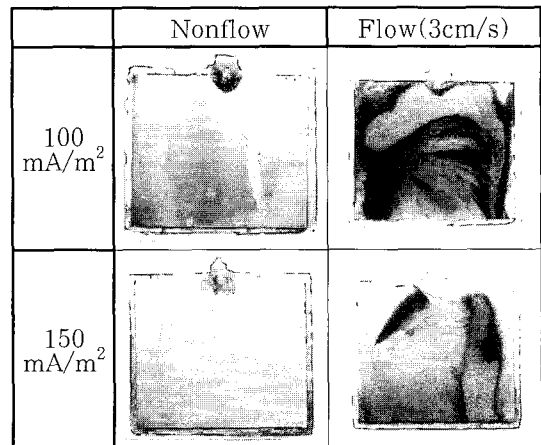


Photo. 2 Photographs of cleaned specimens' surface as a function of cathodic current density

The surface of cleaned specimen was completely protected at non-flow condition of $100\text{mA}/\text{m}^2$, however, in the case of flow condition the surface was somewhat

corroded with a red color. At 150mA/m², the surface of flow condition was not completely protected as indicated a small part of oxide film with red color

Photo. 3 shows the surface morphology at the applied cathodic current density of 200mA/m² and 250mA/m². The most area of surface with flow condition was well protected except the small part of edge area.

As shown in Fig. 3 and 4 the polarization potential at the flow condition with 100 mA/m² and 150 mA/m² after 9 days was -675 mV(SCE), -725 mV(SCE) respectively more positive potential than theoretical protection potential of -770 mV(SCE).

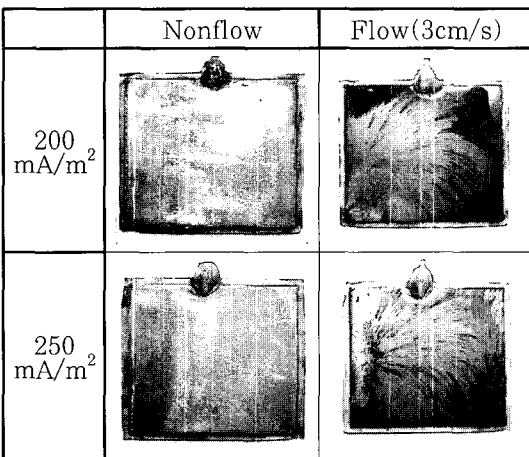


Photo. 3 Photographs of cleaned specimens' surface as a function of cathodic current density

At 200 mA/m², 250 mA/m² as shown in Fig. 5 and 6, however, the polarization potential were -880 mV(SCE), -895 mV(SCE) respectively.

Therefore, it is thought that in the case of cleaned surface the cathodic protection potential to protect the steel surface completely must be maintained with more negative potential than -770 mV(SCE), and

the protection current density should be larger than 200 mA/m² at flow condition.

Photo. 4 shows the surface morphology of the rusted specimens after 9 days at applied cathodic current density of 100 mA/m² and 150 mA/m². In the condition of non-flow at 100 mA/m², the surface was generally mixed mode of red oxide and black oxide film. Especially at 150 mA/m² it is indicated that the surface was nearly covered with black oxide film, even though its polarization potential was about -700 mV(SCE) which was more positive than the theoretical protection potential of -770 mV(SCE). However, in the flow condition a small portion of red oxide film has been observed at the upper edge of specimen. And also their cathodic polarization potential were about -650mV(SCE), -675mV(SCE) respectively.

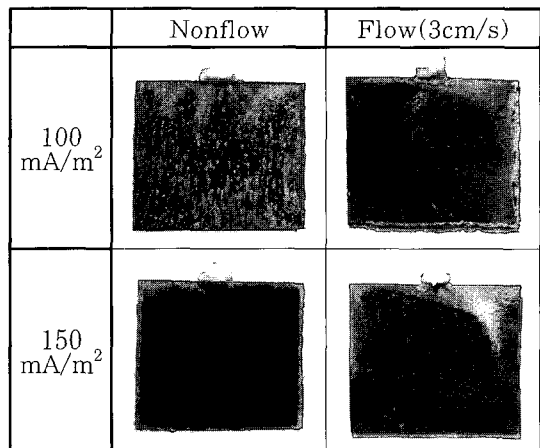
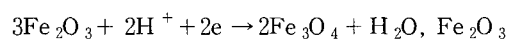


Photo. 4 Photographs of rusted specimens' surface as a function of cathodic current density

From these results it is suggested that the phenomenon of the color change of oxide film from red to black was why the reduction reactions of oxide film, namely,



$+2H^+ + 2e \rightarrow 2FeO + H_2O$ and $Fe_3O_4 + 2H^+ + 2e \rightarrow 3FeO + H_2O$ in potential-pH diagram⁽¹⁸⁾ as well as the dissolved oxygen reduction reaction ($O_2 + 2H_2O + 4e \rightarrow 4OH^-$) occurred together at the rusted surface.

Photo. 5 shows the surface morphology at the applied cathodic current density of 200 mA/m² and 250 mA/m². All area of the surface was covered with black and blue oxide films. It was revealed that the rusted surface was being clearly protected irrespective of flow condition of sea water. And their potentials were also more negative potential than -700 mV (SCE) as represented in Fig. 5 and 6.

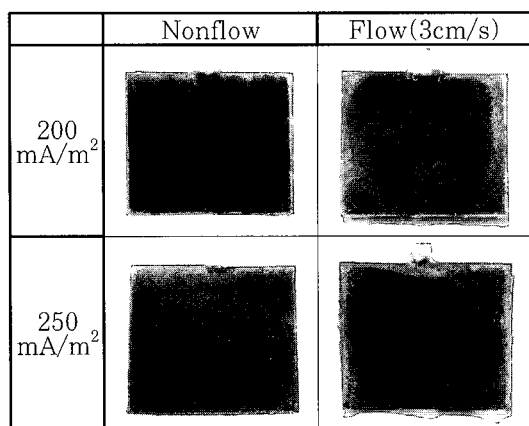


Photo. 5 Photographs of rusted specimens' surface as a function of cathodic current density

4. Conclusions

The optimum protection potential and current density were investigated in terms of several parameters i.e. the solution condition of non-flow and flow, the surface condition of cleaned and rusted, and the variation of applied cathodic current density.

The results obtained were as follows:

1. The corrosion current density of the rusted surface was considerably low compared to the cleaned one. It is considered that the oxide film already existed on the rusted surface acts as the barrier not only to interrupt the oxygen diffusion to the cathode surface but also to inhibit anodic reaction.

2. The cathodic polarization potential of cleaned specimen was more negative than that of the rusted specimen at the same applied cathodic current density because the cathodic polarization potential of cleaned specimen was controlled by the concentration polarization due to dissolved oxygen reduction reaction, while the rusted specimen was somewhat influenced by activation polarization due to reduction reaction of oxide film on the surface.

3. The protection potential of cleaned specimen was below of -770 mV(SCE), on the other hand its potential of the rusted specimen was lower than -700 mV(SCE) irrespective of solution flow condition. This is probably because the corrosion potential of rusted surface was already positive value than the cleaned one and its cathodic polarization was controlled by activation polarization by the oxide film.

4. In the case of non-flow condition, protection current density was 100 mA/m² at both cleaned and rusted specimen. However, it is accepted that in flow condition was about 200 mA/m² due to the increasing of oxygen diffusion to the cathode surface.

5. It is suggested that the optimum protection potential and current density should be controlled by the surface condition of steel structures as well as the flow condition of solution

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