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Influences of Coatings and Solution Corrosivity on Cathodic Protection of Metallic Materials

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Painting has protected metallic stack but the paint films may be degraded and corrosion problem can be arisen. To protect the painted metal stack, cathodic protection can be applied. If cathodic protection is applied to bare metal, only small area may be protected. However, if cathodic protection is applied to painted metal surface, large area can be protected and the lifetime of paint films can be extended. High corrosion resistant alloys were corroded at a Flue Gas Desulfurization (FGD) facility of power plant within a short period and thus cathodic protection can be used to protect these metals. On the base of computer simulation, if cathodic protection is applied to bare metal in a FGD environment, it was estimated that applied current could almost be spent to protect area near the anode. However, if cathodic protection is applied to high resistant-coated metal, the much larger area from the anode could be effectively protected.

Keywords : *painting, coating, cathodic protection, solution resistivity, protection voltage, computer simulation*

1. Introduction

The exhausted flue gas by the combustion of oil *etc.* contains usually many contaminated species. The environmental protection law has limited sulfur-content in the exhausted flue gas strictly and thus FGD facility should be installed in every fossil fired power plant. During the desulfurization processes of exhausted gas, highly corrosive environment including sulfuric acid can be formed in cooling zone of FGD facility and severe corrosion damage has been reported in this zone.[1)~3)] Several grade alloys for FGD facility have been used depending upon the corrosivity of the environment and the corrosion resistance of alloys. Corrosion damages, which occurred frequently in FGD facility, are pitting corrosion and thinning from the highly concentrated sulfuric acid and chloride ion.[1),2)] Pitting corrosion was usually occurred on the Heat Affected Zone (HAZ) following the weldment lines of duct metals and thinning was mostly concentrated on the local area in which gas flow hit on and condensed into acidic liquid. Because of high corrosion rate, corrosion resistant alloys should be used for FGD facility. Representative alloys for FGD facility are super stainless steel including 6Mo stainless steel and expensive Ni-base super alloy *etc.*[4)~10)] These alloys show very high corrosion resistance in most environments. However, large hole was formed by pitting corrosion in the Ni-base super alloy (thickness 6 mm) after 1-year operation in cooling zone of FGD facility of power plant.[1)] Pitting corrosion made large holes and thus highly corrosive solution penetrated even the external protection floor steel and was leaked.

On the other hand, materials for the stack are metals and ceramics. In special, metallic stacks should be painted to protect it from the corrosion of base metal, usually the carbon steel. However, even though the steel is painted, painted film may gradually be degraded with time, and thus the base metal may be exposed and corroded, and thus should be repaired frequently. Recently, cathodic protection is applied to protect the painted steel structure.[11)~14)]

Corrosivity of FGD facilities and stacks are totally different. In case of FGD facilities, the solution was highly acidic, very low pH, high conductive and corrosive. In case of the stack, the corrosion medium is usually rain and flue gas and wetted water film has the polluted contaminants as like NO_x^-, SO_x^-, dirt, and salts and it shows relatively low conductivity.

In this study, cathodic protection to metal in different

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corrosion environments, which are the cooling zone of FGD facilities and the painted stack of fossil fired power plants, was applied and the influence of its corrosivity on the cathodic protection was investigated. This work focused on the computer simulation for cathodic protection when the metals were in bare state or coated state in two environments.

2. Experimental methods

2.1 Solution analysis

Solutions were collected in cooling zone of FGD facilities and in painted metallic stack of power plants. Those solutions were analyzed using a Bio-LC Dx-300 (Dionex) for anions and ICP-AES (Spectro) for cations.

2.2 Anodic polarization test

Plain carbon steel specimens were cut in 2 x 2 cm and then connected to a rubber-coated wire by soldering for electric connection and they were insulated using an epoxy resin. Its surface was polished using an emery paper to #600. 1 cm^2 of the surface area was exposed and the other parts were insulated using an epoxy resin. They were kept in desiccator until the test starts. For anodic polarization test, the Potentiostat (Gamry DC105) was used. A high-density graphite electrode was used as a counter electrode, and a Saturated Calomel Electrode (SCE) as a reference electrode. Scanning rate was 1 mV/sec.

2.3 Computer simulation on cathodic protection

The boundary element method (BEM) has been proved to provide the optimum solutions to problems associated with corrosion simulation. The BEM requires the user to describe the boundary conditions and surfaces of the objectives to be modeled thus simplifying the modeling process. To model CP problems the computer model must simulate the IR drop through the electrolyte and the electrochemical electrodes kinetics on the metallic surfaces. In this study, modeling works were performed with a commercial program "BEASY 9.2".

3. Results and discussion

3.1 Corrosion damage and corrosivity of FGD facilities and stack of power plants

It was reported that large hole formed by pitting corrosion in the high Ni super alloy (thickness 6 mm) occurred after 1-year operation in cooling zone of FGD facility of power plant #U.[1)] Pitting corrosion made a large hole and thus high corrosive solution penetrated to even the external protection floor steel. Contaminated solution was leaked. The structural material was the high nickel super alloy, which has been shown an excellent corrosion resistance. Table 1 shows the result of analysis on the solution collected in gas cooling zone. As shown in Table 1, the solution of plant #U contains 386,918 ppm of SO_4^{2-} ion and large amount of metallic ions by severe corrosion and shows very low pH (-0.9), which it is extremely acidic solution. On the other hand, Fig. 1 shows the degradation of painted stack (painted by polyurethane) and steel corrosion of the stack of power plant #S. Coated paint failures can result from two basic causes; 1) poor or inadequate surface preparation and/or application of the paint to substrate, 2) atmospheric effects. In this case, it is considered that the latter is more possible reason. By the Table 2, painted surface was wetted by acidic solution and thus flue gas from the stack and flying salt from the sea may be deposited on the surface. It means that this corrosive environment could make the degradation of the paint film and corrosion of the steel.

Fig. 2 shows the polarization curves of the alloys in

Table 1. Analysis on the solution collected in the cooling zone of FGD facility of power plant #U

Species	Concentration, ppm
SO_4^{2-}	386,918
Cl^-	2,478
F^-	505
Ni	13,385
Cr	4,564
Fe	1,244
Cu	11.6
Co	33.3
pH	-0.9

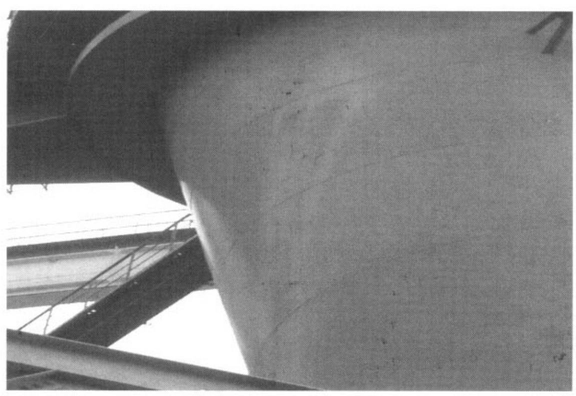

Fig. 1. Degraded paint film and corrosion of painted metallic stack of power plant #S

Table 2. Analysis on the solution collected in the outer surface of the stack of power plant #S

Species	Concentration, ppm
SO_4^{2-}	318.8
NO_3^-	10.5
Cl^-	2.1
Ca	14.1
Na	7.2
Fe	7.3
Mg	1.4
Zn	0.8
pH	2.5

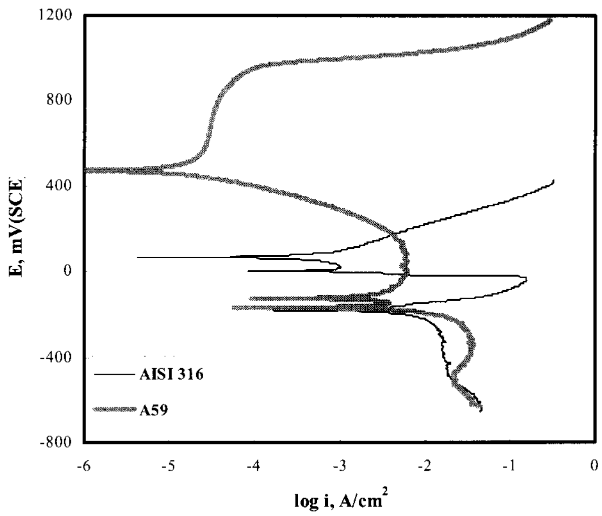

Fig. 2. Polarization curves of AISI 316 stainless steels and Ni-base super alloy, A59 in 70℃ green death solution

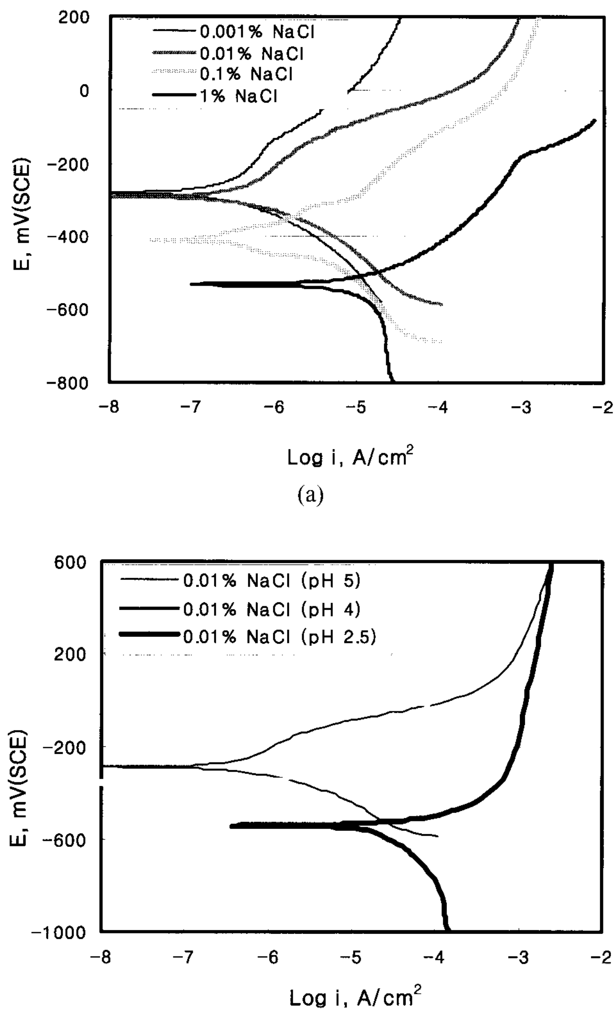

Fig. 3. Polarization curves of carbon steel in NaCl solutions at room temperature with different pH

70 ℃, 'Green death solution'. As shown in figure, AISI 316 shows low corrosion potential, and its passivity is destroyed and then pitting corrosion occurs. Its current sharply increases by anodic polarization. However, Ni-base super alloy- A59 shows unstable active-passive polarization curve. The curve has low corrosion potential, cathodic current loop and low passive current density and also the increased current density over 1V(SCE) is attributed to oxygen evolution but not pitting corrosion. The corrosion environments of the cooling zone of FGD facility are cyclic wet-dry, cyclic thermal change, and highly fast windy. As shown in figure, even high corrosion resistant alloys suffered severe corrosion damage due to highly variable corrosive conditions.

Fig. 3 shows the polarization curves of carbon steel in NaCl solutions with different pH. With increasing NaCl concentration, corrosion potential was greatly decreased and passive current density was increased (Fig. 3a). In 0.01% NaCl solution, corrosion potential was lowered and current density was greatly increased with decreasing pH by sulfuric acid. Corrosion behavior of carbon steel was affected by salt content and pH and therefore if the corrosion environment of outer surface of the painted stack may have salts and acidic contaminations, the painted stack can be degraded and corroded.

3.2 Calculation of cathodic protection conditions in two environments

There are abundant research results on the corrosion problem using BEM but only a few could be found that deal with the corrosion problems due to formation of the acidic thin layered electrolytes. To avoid inaccuracy from the large aspect ratio difference of elements and boundaries, the model was approached to bulk spaces divided into several zones. Instead, each zone was hypothetically

Table 3. Boundary conditions and initial condition used in the simulation

Factors	Outer surface condition of Stack	Duct Bottom condition of FGD
Resistivity	1,050.4Ωcm pH 2.5(0.01%NaCl)	21.8Ωcm(Green death solution)
Thickness of electrolyte	5mm	5mm
Anode area	16.95cm^2	16.95cm^2
Cathode area	Bare metal (5m × 5m) Painted metal (5m × 5m)	Bare metal (5m × 5m) Coated metal (5m × 5m)
Transfer coefficient	From Anodic Polarization Test data	From Anodic Polarization Test data
Polarization data	Experimented data	Experimented data

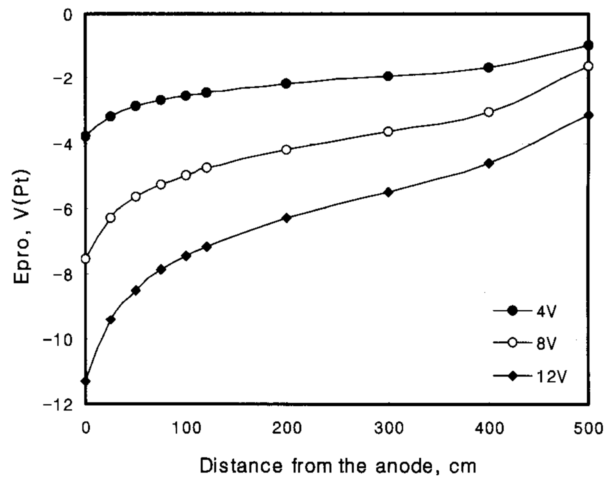

Fig. 4. Calculated protection potential for bare metal, A59 in green death solution using a BEASY program

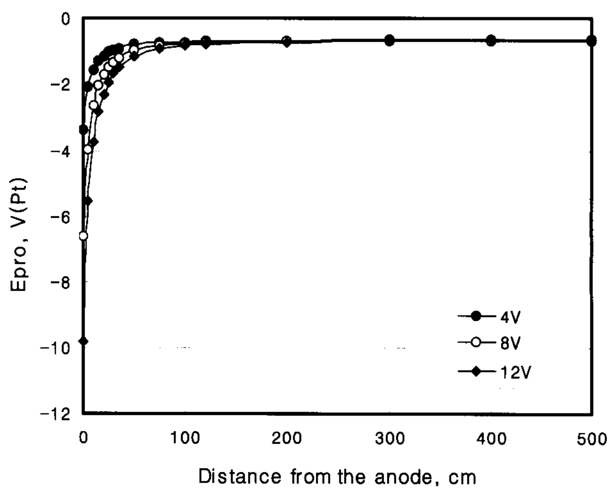

Fig. 5. Calculated protection potential for bare metal, carbon steel in 0.01%NaCl solution (1,050.4Ωcm, pH 2.5) using a BEASY program

described as thin-layered or thick bulk electrolyte solution with varying of conductivity, polarization resistance, and transfer coefficient with variants of resistivity, electrolyte thickness, distance between anode and cathode, and radius of anode and cathode. Table 3 shows boundary conditions and initial condition used in simulation for two environments.

In the previous result,[2] advanced cathodic protection system was shown to control the corrosion and degradation of coating on the metal surface for FGD facilities and stacks. This system is composed of protective coat on the metal and insoluble anodes and reference electrodes on the coating. This cathodic protection system uses telecommunication method like an Internet to monitor the information *in-situ* such as protection potentials, protection current densities, on-off potentials and depolarization potentials.[15] Both the variable input potential method and the variable input current method are applied to supply protection current on the protected metals exactly. When this system is applied to low-grade metals like carbon steel that needs a high protection current density, special kind of heat-resistant and acid-resistant coating is complementarily applied to decrease system construction cost and increase economical efficiency in operation of the E-Protec™ system.[15] It can be achieved from the fact that the protection current concentrates on the defects and pinholes of the coating materials on the metals.

Fig. 4 shows the calculated cathodic protection potentials for the bare metal, A59 in 'Green death solution' using the Beasy program. Because green death solution shows high conductivity, the large area from the anode can be protected. Cooling zone of FGD facility shows highly changeable corrosive environment and thus the water film couldn't form uniformly over the whole surface. There fore, cathodic protection system needs the resistant coatings in the changeable corrosion environments that are cyclic wet-dry, cyclic thermal change, and highly fast wind. As shown in figure, even high corrosion resistant alloys suffered severe corrosion damage due to highly changeable corrosive conditions.

Fig. 5 shows the calculated cathodic protection potential for the bare carbon steel in acidic rain using the Beasy program. Because acidic rain shows a relatively low conductivity, the protection potential increased drastically from the anode and thus only small area from the anode can be cathodically protected.

Fig. 6 shows the simulation result of cathodic protection for the coated metal, A59 in 'Green death solution'. Because high resistant coating is formed on the metal surface

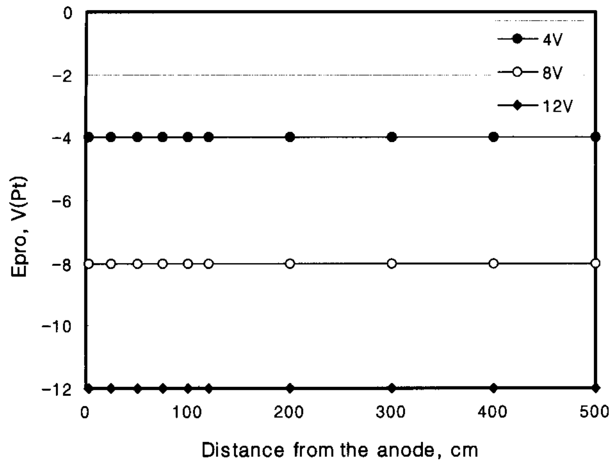

Fig. 6. Calculated protection potential for the coated metal, A59 in green death solution using a BEASY program

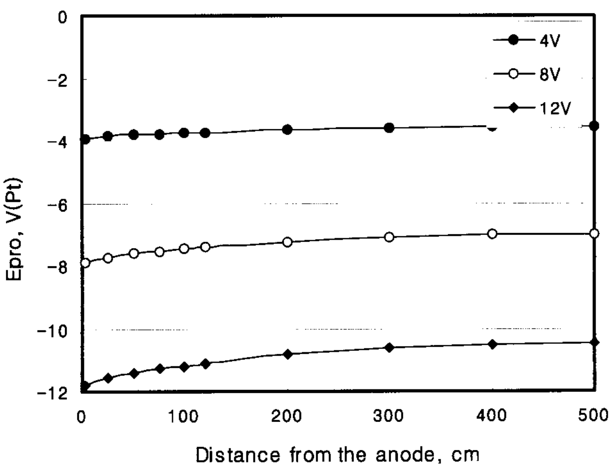

Fig. 7. Calculated protection potential for painted metal, carbon steel in 0.01%NaCl solution (1,050.4Ωcm, pH 2.5) using a BEASY program

and the exposed metal surface to highly acidic thin-layered solution having high conductivity is extremely small, the large area from the anode can be protected. If the coating may be degraded and metal surface be exposed to corrosive environment, only small current would be needed to prevent the corrosion of metal. The protection potential and current can be used to monitor the coating failure and the protection voltage can be increased depending upon the exposed metal area by coating failure.[15]

Fig. 7 shows the simulation result of cathodic protection for the painted carbon steel in acidic rain. Because the painted layer was formed on the metal, the current was less consumed and could reach to longer distance from the anode. The lifetime of painted layer can be extended by cathodic protection.[14] With increasing protection voltage, protected area can be increased. However, high protection voltage may give the coating failure, thus it should be carefully controlled. Also, it should be noted that cathodic protection to outdoor exposure painted structures might be less effective since water film from the anode would be not continuous and not uniform. Therefore, using automatic monitoring and controlling cathodic protection system,[15] the protected structures should be controlled precisely. Using the protection system, the protection voltage will be increased to feed the current when the coated surface may be failed, and thus the protection potential and current can be used to monitor the coating failure.

4. Conclusions

1) Corrosion environment of cooling zone of FGD facilities of power plants was very aggressive and showed very low pH. If cathodic protection is applied to bare metal in this FGD environment, protection system was less effective. However, if cathodic protection is applied to high resistant-coated metal, the wide area from the anode can be protected.

2) Corrosion environment of outer surface of metallic stack of power plant was still acidic but showed a relatively low conductivity than a FGD condition. If cathodic protection is applied to bare metal in this environment, only small area can be protected. However, if cathodic protection is applied to painted metal surface, wide area can be protected.

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