Application of Cathodic Protection on Metallic Structure in Extremely Acidic Fluids

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Fossil fired power plant produces the electric energy by using a thermal energy by the combustion of fossil fuels as like oil, gas and coal. The exhausted flue gas by the combustion of oil *etc.* contains usually many contaminated species, and especially sulfur-content has been controlled strictly and then FGD (Flue Gas Desulfurization) facility should be installed in every fossil fired power plant. To minimize the content of contaminations in final exhaust gas, high corrosive environment including sulfuric acid (it was formed during the process which SO_2 gas combined with $Mg(OH)_2$ solution) can be formed in cooling zone of FGD facility and severe corrosion damage is reported in this zone. These conditions are formed when duct materials are immersed in fluid that flows on the duct floors or when exhausted gas is condensed into thin layered medium and contacts with materials of the duct walls and roofs. These environments make troublesome corrosion and air pollution problems that are occurred from the leakage of those ducts. The frequent shut down and repairing works of the FGD systems also demand costs and low efficiencies of those facilities. In general, high corrosion resistant materials have been used to solve this problem. However, corrosion problems have severely occurred in a cooling zone even though high corrosion resistant materials were used. In this work, a new technology has been proposed to solve the corrosion problem in the cooling zone of FGD facility. This electrochemical protection system contains cathodic protection method and protection by coating film, and remote monitoring-control system.

Keywords *: fossil-fired power plant, FGD, pitting, CPT, cathodic protection*

1. Introduction

Fossil fired power plant produces the electric energy by using a thermal energy by the combustion of fossil fuels as like oil, gas and coal. The exhausted flue gas by the combustion of oil etc. contains usually many contaminated species, and especially sulfur-content has been controlled strictly and then FGD facility should be installed in every fossil fired power plant. During a desulfurization process, high corrosive environment including sulfuric acid can be formed in cooling zone of FGD facility and severe corrosion damage is reported in this zone. Sulfuric acid was formed during the process which SO_2 gas combined with $Mg(OH)_2$ solution

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 because of highly concentrated sulfuric acid and chloride ion.[1)] Pitting corrosion was usually occurred on the HAZ (Heat Affected Zone) following the weldment lines of duct metals and thinning was mostly concentrated on the local area in which gas flow hit and condensed into acidic liquid. Because of the highly corrosive environment, corrosion resistant alloys should be used for the FGD facility. Representative alloys are super stainless steel including 6Mo stainless steel and expensive Ni-base super alloy etc.[2)~8)] Large hole was formed by pitting corrosion in Alloy C276 (thickness 6 mm) after 1-year operation in cooling zone of FGD facility of power plant as shown in the results. Pitting corrosion made a large hole and thus highly corrosive solution penetrated the external protection floor steel and was leaked.

In this study, we investigated the corrosivity of cooling zone and dilution tank of the FGD facility of a fossil fired power plant and corrosion behavior of several alloys in 'Green death solution' and proposed the advanced corro-

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sion control system for the FGD facility.

2. Experimental

2.1 Pitting corrosion test

Specimen was cut by 2x2 cm and then was polished using an emery paper (#120) and were kept in desiccator until the test starts. A glass cell having 1-liter volume was used and a vaporization of solution was prohibited using a condenser. Specimen was installed into solution using a rubber-coated wire and testing solution was replaced with new one everyday. Testing was conducted on the base of ASTM G48[9),10)] and the testing solutions were 6% $FeCl_3$ and green death solution (11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$). Corrosion rate was determined at every 24hrs. CPT (Critical Pitting Temperature) means the temperature exceeding 5 mg of accumulated weight loss at each test temperature. After weighing, specimen surface was examined by optical microscope to confirm the occurrence of any pits.

2.2 Polarization test

Specimen was cut by 2x2 cm and then connected to a rubber-coated wire by soldering for electric connection and specimen was insulated using an epoxy resin. Specimen surface was polished using an emery paper to #600. 1 cm^2 of the surface area was exposed and an epoxy resin insulated the others. They were kept in desiccator until test starts. Polarization test used a Potentiostat (Model EG&G 273A) and a high-density graphite electrode was used as a counter electrode, and a SCE (Saturated Calomel Electrode) as a reference electrode. Scanning rate was 1 mV/sec. Test temperature was 70 ℃.

2.3 Solution analysis

Solutions were collected in cooling zone of the FGD facility of U#4, 5, 6 power plants. Those solutions were analyzed using a Bio-LC Dx-300 (Dionex, Sunnyvale, CA, USA) for anions and ICP-AES for cations.

2.4 Cathodic protection

To control the corrosion of metallic materials in the FGD, cathodic protection was applied to non-coated metals and coated metals. This protection was performed in a laboratory scale at 80 ℃ and a pilot scale in the range from room temperature and 150 ℃.

2.5 Computer simulation

The boundary element method (BEM) has been proved to provide an optimum solution to problems associated with corrosion simulation. The BEM requires the user to only describe the boundary or surface of the objective to be modeled thus simplifying the modeling process. To model a cathodic protection problem the computer model must simulate the IR drop through the electrolyte and the electrochemical electrode kinetics on the metallic surfaces. In this study, BEM method was introduced with a widely known commercial program, BEASY.

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

3. Results and discussion

Corrosion resistance of several alloys for a FGD: Several grade alloys for FGD facility have been used depending upon the corrosiveness of the environment. Corrosion damages, which occurred frequently in FGD facility, are pitting problem and thinning because of highly concentrated sulfuric acid and chloride ion. Because of high corrosion rate, high corrosion resistant alloys should be used for FGD facility. Representative alloys are super stainless steel including 6Mo stainless steel and expensive Ni-base super alloy etc. Fig. 1 shows critical pitting temperature (CPT) of high corrosion resistant alloys. An evaluation is based on the ASTM G48 specification, and corrosion solutions are 6% $FeCl_3$ and 'Green death

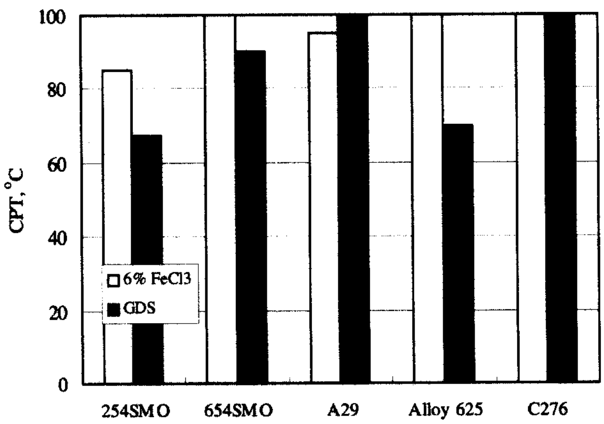


Fig. 1. Critical pitting temperature (CPT) of high corrosion resistant stainless steels and Ni-base super alloy by ASTM G48

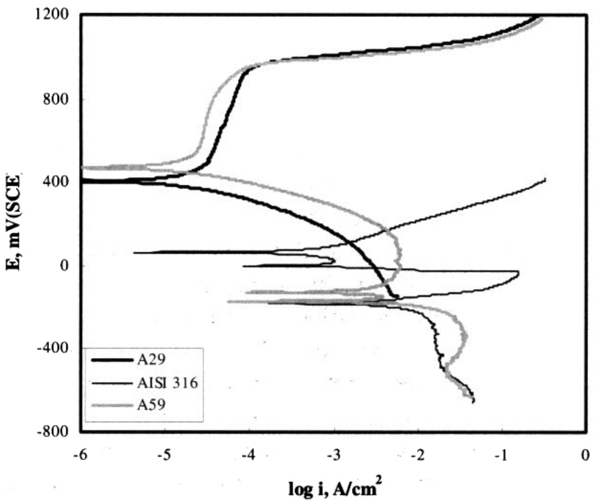


Fig. 2. Polarization curves of stainless steels and Ni-base super alloy in 70 ℃ green death solution

Fig. 3. Pitting corrosion in Alloy C276 (thickness 6 mm) occurred after 1-year operation in cooling zone of FGD facility of power plant U#4

solution'. As shown in Fig. 1, CPT of super stainless steel - 254SMO is 85 ℃ in 6% $FeCl_3$, but 67.5 ℃ in 'Green death solution'. Super stainless steel - 654SMO and A29 of which corrosion resistance is better than 254SMO, CPT over 90 ℃ is shown in both environments. Ni-base super alloy - Alloy 625 shows high CPT over 100 ℃ in 6% $FeCl_3$, but relatively low CPT of 70 ℃ in 'Green death solution'. However, Ni-base super alloy - C276 shows the best pitting resistance of 100 ℃ and over in both environments. As like these results, the reason for high corrosion resistance of these alloys is attributed to the synergistic effect of Cr, Mo, W, and N in alloy. The effect of alloying element is formulated as pitting resistance equivalent (PRE) and one of the equations is as below.[11)-13)]

$$PRE = \%Cr + 3.3(\%Mo + 0.5\%W) + 30\%N \qquad (1)$$

Fig. 2 shows the polarization curves of the alloys in 70 ℃, 'Green death solution'. As shown in the figure, AISI 316 shows a low corrosion potential, and its passivity destroys and then pitting corrosion occurs and its current sharply increases by polarization. However, super stainless steel - A29 and Ni-base super alloy - A59 show high corrosion potential of + 400 mV(SCE) over and low passive current density, and these results mean corrosion resistance of two alloys very high. Also, the increased current density over 1V(SCE) is attributed to oxygen evolution but not pitting corrosion. It should be noted that the above alloys except AISI 316 are high corrosion resistant alloys.

Corrosion damage and corrosivity of FGD facility of power plant U#4, 5, 6: Fig. 3 shows large hole (and sunlight) formed by pitting corrosion in Alloy C276 (thickness 6 mm) occurred after 1-year operation in cooling zone of FGD facility of power plant U#4.[1)] Pitting corrosion made a large hole and thus high corrosive solution penetrated the external protection floor steel and was leaked. The used material was Alloy C276, which showed the best corrosion resistance. However, only 1-year operation corrodes Alloy C276 and makes pitting corrosion, but this result is not coincident to the above lab-scale experiments.

Corrosivity of cooling zone of FGD facility of power plants U#4, 5, 6: In case of fossil fired power plants, electric energy can be produced by using a thermal energy by the combustion of fossil fuels as like oil, gas and coal. The exhausted flue gas by the combustion of oil etc. contains usually many contaminated species, especially sulfur-content has been controlled strictly, so FGD facilities have been installed in most fossil fired power plants.

During a desulfurization process, high corrosive environment including sulfuric acid can be formed in cooling zone of FGD facility and severe corrosion damage is reported in this zone. Table 1 shows the result of solution analysis on solutions collected in gas cooling zone and dilution tank for disposal.

U#4-315 means the result on the solution collected on March 15, 2002 in gas cooling zone of FGD facility of power plant #4, and U#5-422 and U#6-422 mean the results on the solutions collected on April 22, 2002 in dilution tank of power plant #5 and #6. Also, U#6-422 is in the case that MgO in desulfurization process was not added, but U#6-615 is in the case that MgO in desulfurization process was added.

As shown in Table 1, the solution of U#4-315 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,

Table 1. Result of solution analysis on 5 solutions in cooling zone and dilution tank for disposal of power plants U#4, 5, 6

Ions, ppm	Cooling zone in U#4-315	Dilution tank for disposal			
		U#5-422	U#5-615	U#6-422	U#6-615
SO_4^{2-}	386,918	38,184	19,487	18,778	892
F^-	505	-	-	-	-
Cl^-	2,478	137	707	143	92
Ni	13,385	164	14.3	153	11.3
Cr	4,564	1.1	1.4	1.4	0.3
Fe	1,244	76.8	46.8	91.2	13.4
Cu	11.6	0.2	0.9	0.2	0.14
Co	33.3	2.2	0.2	1.9	0.1
Mo	-	2.7	0.84	3.1	0.3
Mg	-	6.9	3.8	440	61.4
pH	-0.9	+1.22	+0.68	+1.24	+1.87

Remarks :-(not detected), 422 and 615 mean the date collecting solutions

the solutions of dilution tank have relatively low amount of several ions and high pH range of 0.68~1.87, but it is also acidic solution.

Advanced method for corrosion control of FGD facility of power plant: Power plant U#4 has experienced severe corrosion damage in cooling zone of FGD facility after only 1-year operation even though Ni-base super alloy C276 was used. To solve the problem, the plant changed the material of cooling zone from Alloy C276 to A59, which is more corrosion resistant than Alloy C276. However, another corrosion control method is needed since super alloy having good corrosion resistance might be corroded in the FGD environment. Fig. 4 shows the

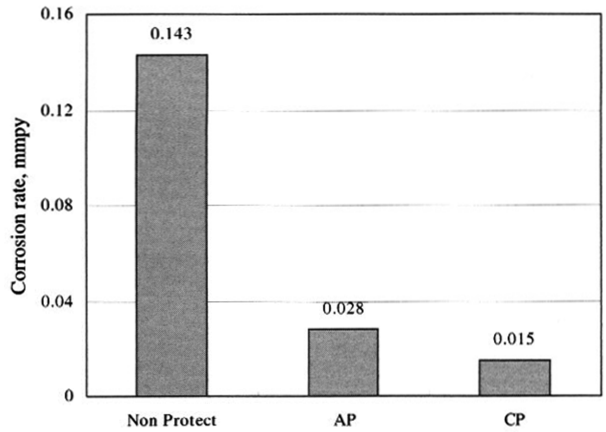


Fig. 4. Effects of cathodic protection (CP) and anodic protection (AP) on corrosion rate of Ni-base super alloy A59 tested for 40 days in green death solution at 80 ℃

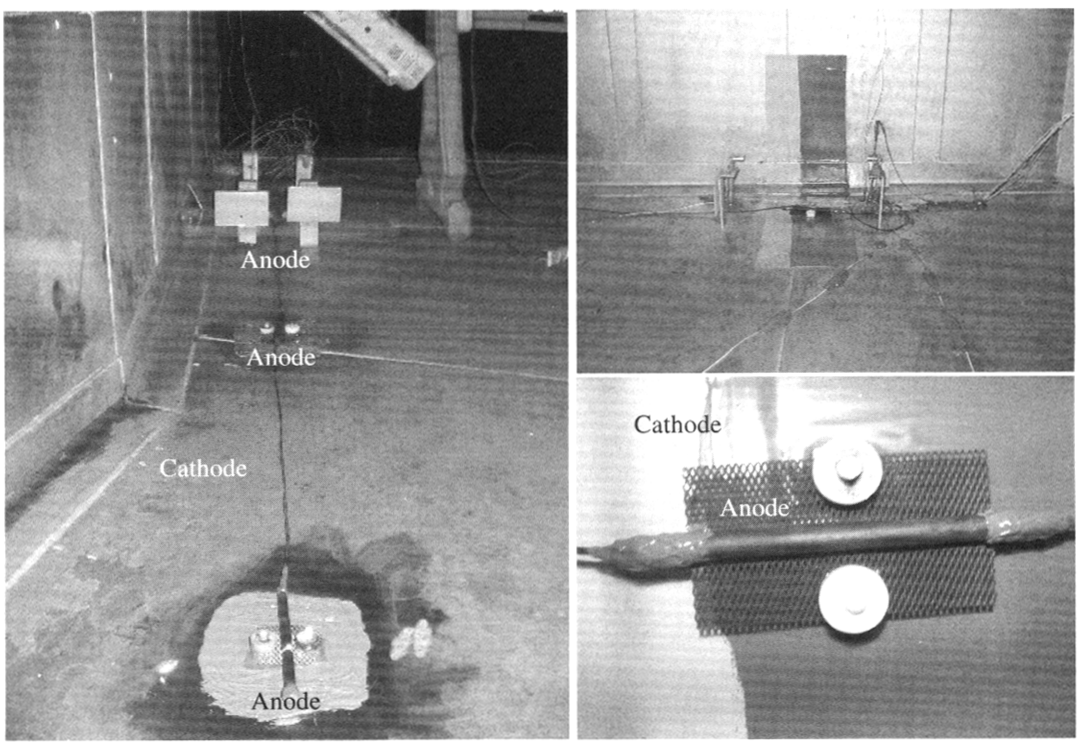


Fig. 5. Photos that show arrangement of CP system and electrode in real FGD inlet cooler.

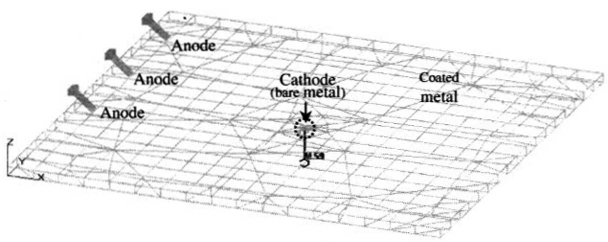
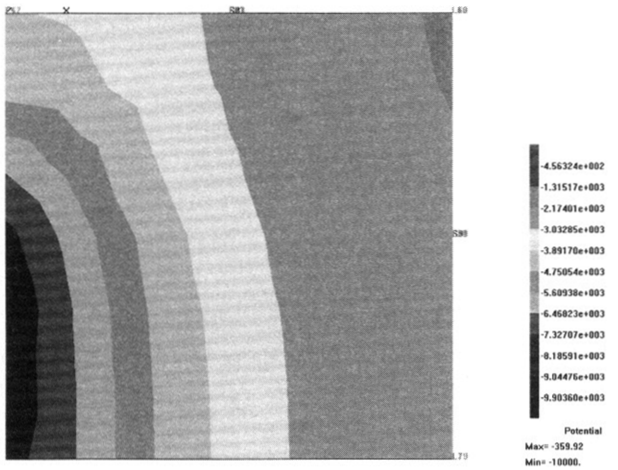
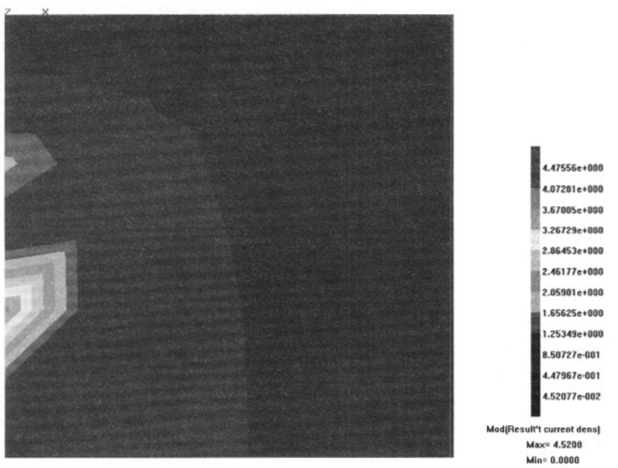


Fig. 6. 3-D BEM mesh element for CP model in FGD inlet cooler.



(a)

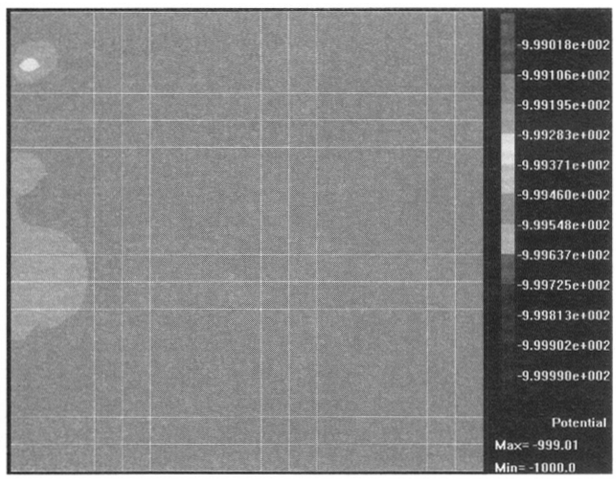


(b)

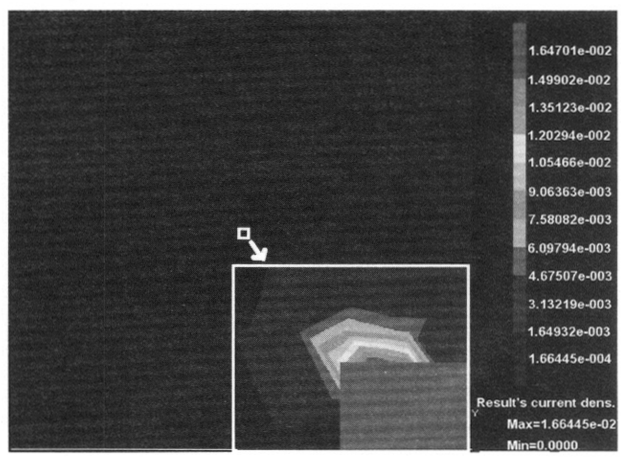
Fig. 7. Simulation results of CP on the bare metal (Alloy 59). (a) Potential distribution (b) Protection current density distribution

effect of an electric protection of A59 for 40 days in 80 ℃, 'Green death solution'. Two methods were applied. As shown in the figure, corrosion was depressed by the electric protection regardless of the protection methods. Anodic protection can reduce the corrosion rate from 0.143 mmpy to 0.028 mmpy and cathodic protection can decrease the rate to 0.015 mmpy. However, as shown in Table 1, chloride and fluoride ions in addition to sulfuric ions were detected in the cooling zone and thus it should be noted that the cathodic protection is more efficient and safer than the anodic protection.

Computer simulation of CP system for real FGD system: The extent of cathodic protection (CP) was simulated when the CP system was applied to a real FGD system. Fig. 5 shows the arrangement of CP system in the FGD system on site and Fig. 6 shows the 3-dimensional BEM mesh element for this model. As shown in Fig. 7, a proper protection range was very narrow when the cathodic protection was applied to a bare surface of alloy. That means that very high conductivity of FGD slurry solution limits protection range making most applied



(a)



(b)

Fig. 8. Simulation results of CP on the flaw of coated metal. (a) Potential distribution (b) Protection current density distribution (profiles are magnified near flaw)

Table 2. Boundary conditions and initial condition used in the simulation

Factors	Duct Bottom(FGD slurry) conditions
Resistivity	21.834Ωcm
Thickness of electrolyte	10cm
Anode area	$16.95 cm^2$
Cathode area	Bare metals(5m × 5m) $1 mm^2$ of coating flaw
Conductivity	0.005859
Transfer coefficient	From APT data
Polarization data	Experimented data
Protection potential	10V
Initial potential	0V

Fig. 9. Advanced corrosion protection system for FGD facility

current consumed near the anode. Furthermore, CP for the whole FGD system seems to be inappropriate method because metal surfaces exposed to FGD solution demand enormous protection current (even thousands amperes). Therefore, in order to overcome this problem, simulation was carried for the case of insulated coat existing on the surface of protection objects. The results are shown in Fig. 8. The figure shows that when a flaw exists on the coating, only a small exposed area of metal needs very low protection current stretching protection current very widely. It can be an effective corrosion protection method over wide range of metallic objects. This procedure brings the additional benefit that the appropriate repair schedules can be noticed because the damage condition and protection level can be detected simultaneously from the continuous monitoring of protection current and potential. It is difficult to properly distribute cathodic current over the metals that should be protected in high temperature and extremely acidic thin-layered environment with currently commercialized anodes. This is due to the fact that thin-layered corrosive medium has a high resistance and an insufficient contact with metals. A special kind of anode and its holders applied are designed to supply enough cathodic current to and maintain uniform contact with thin-layered corrosive medium on the protected metals. The specially designed grip type connector inside anodes between the power supply lead and anodes is also applied to prevent being damaged in an immersion condition like a duct floor as well as in an thin-layered condition like a duct wall.

Fig. 9 shows an advanced cathodic method to control the corrosion and degradation of coating on the metal surface for FGD facility. This system is composed of protection coating on the metal and insoluble anode and reference electrode 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. 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 and acid resistant coat is complementarily applied to decrease system construction cost and increase economical efficiency in operation of the E-Protec™ system. It can be achieved from the fact that the protection current concentrates on the defects and pin holes of the coating materials on the metals.

4. Conclusions

1. Corrosion damages, which occurred frequently in FGD facility, are pitting problem and thinning because of highly concentrated sulfuric acid and chloride ion. Ni-base super alloy - Alloy 625 shows high CPT over 100 ℃ in 6% $FeCl_3$, but relatively low CPT of 70 ℃ in 'Green death solution'. However, Ni-base super alloy - C276 shows the best pitting resistance of 100 ℃ and over in both two environments. As like these results, the reason for high corrosion resistance of these alloys is attributed to the synergistic effect of Cr, Mo, W, and N in alloy.

2. Pitting corrosion in Alloy C276 (thickness 6 mm) occurred after 1-year operation in cooling zone of FGD facility. This result is not coincident to the lab-scale experiments. It suggested that green death solution cannot exactly describe the FGD environment of the examined fossil power stations and it should be modified.

3. From the results of computer simulation, CP for the bare metals of FGD system seems to be inappropriate method because metal surfaces exposed to FGD solution demands enormous protection current (even thousands amperes). In case of CP for insulated coat existing on the surface of protection objects that has a flaw exists on the coating, it is judged to be an effective corrosion protection method over wide range of metallic objects. This pro-

cedure brings the additional benefit that the appropriate repair schedules can be noticed because the damage condition and protection level can be detected simultaneously from the continuous monitoring of protection current and potential.

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