CORROSION SCIENCE AND TECHNOLOGY, Vol.4, No.6(2005), pp.242~249

Influences of Cathodic Protection and Coating Properties on the Corrosion Control of Metallic Structure in Extremely Acidic Fluids

H. Y. Chang, Y. R. Yoo[1], T. E. Jin, and Y. S. Kim[1,†]

Korea Power Engineering Company Inc. 360-9 Mabuk, Guseong, Yongin, Gyeonggi, 449-713, Korea
[1]Department of Materials Science and Engineering, Andong National University,
388 Songcheon, Andong, Gyeongbuk, 760-749, Korea

A lot of parts in FGD (Flue Gas Desulfurization) systems of fossil-fuel power plants show the environments in which are highly changeable and extremely acidic corrosive medium according to time and locations, *e.g.* in duct works, coolers and re-heaters *etc.* These conditions are formed when system materials are immersed in fluid that flows on them or when exhausted gas is condensed into thin layered acidic medium to contact materials of the system walls and roofs. These environments make troublesome corrosion and air pollution problems that are occurred from the leakage of the condensed solution. To cathodically protect the metallic structures in extremely acidic fluid, the properties of the protective coatings on the metal surface were very important, and epoxy Novolac coating was applied in this work. On the base of acid immersion tests, hot sulfuric acid decreased the hardness of the coatings and reduced greatly the content of Na_2O, Al_2O_3, and SiO_2 among the main components of the coating. A special kind of CP(Cathodic Protection) system has been developed and tested in a real scale of the FGD facility. Applied coating for this CP system was peeled off and cracked in some parts of the facility. However, the exposed metal surface to extremely acidic fluid by the failure of the coatings was successfully protected by the new CP system.

Keywords *: FGD, cathodic protection, coatings, BEASY simulation, remote monitoring-controlling.*

1. Introduction

The exhausted flue gas from the fossil-fuel power stations contains usually many contaminated species. Sulfur-content has been strictly controlled from the FGD facility installed in almost all fossil-fuel power plants. From the processes to minimize the content of sulfur contaminations in exhausted gas, high corrosive environments including sulfuric acid can be formed in some parts in FGD facility and severe corrosion damages are reported in those areas (Fig 1). To mitigate corrosion problems, many efforts have been done on the development and improvement of cathodic protection system.[1)-8)] In the previous paper,[9)] from the results of computer simulation, CP for the bare metals of FGD facility seemed to be inappropriate method because metal surfaces exposed to FGD solution demands enormous protection current (even thousands amperes). In case of CP for insulated coating existing on the surface of protection objects that have flaws exist on the coating, it is judged to be an effective corrosion protection method over wide range of metallic objects. This procedure brings an 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.[9)]

This specially designed cathodic protection system has been developed and tested in a real scale of FGD system. This CP system is one of the economical technologies that can effectively prevent corrosion of plant, from the merits of easy maintenance and of being replaced by expensive stainless steels or super alloys. This system that consists of coating technology, the design technology of CP and a communication technology has shown excellent corrosion control performances in FGD system. However, the coatings have been peeled off and cracked in some parts of facility that exceeded the service temperature of the coating, which made protection currents wasted and made

† Corresponding author: yikim@andong.ac.kr

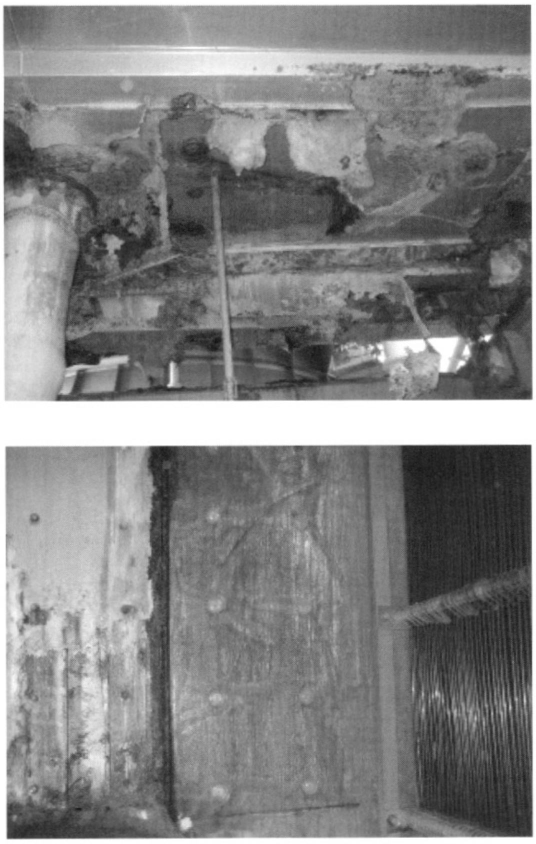


Fig. 1. Severe corrosion damages in FGD facilities

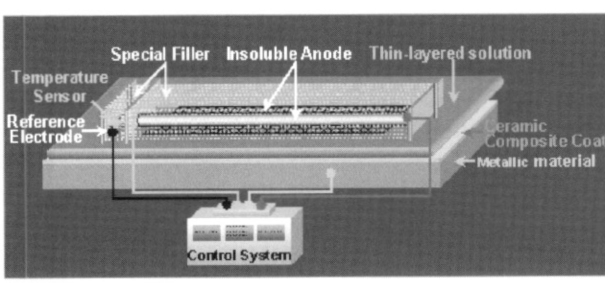


Fig. 2. Schematic diagram of electrode system

CP control difficult. Therefore, it was needed for the service temperature of coating to increase in the environment of extremely acidic solution. This paper dealt with the application of this CP system to a real scale of power plant #Y-1 and the evaluation of coating's properties and cathodic protection efficiency.

2. Experimental

2.1 Corrosion rate measurement in FGD

In the previous paper,[9] the corrosivity of FGD was revealed to be very high acidic and changeable and high temperature. Several metallic materials were tested in the cooling zone of the FGD, power plant #Y-1 and corrosion rate was measured as weight loss. Tested alloys were 12 austenitic stainless steels, 2 ferritic stainless steels, and 1 carbon steel.

2.2 Acid immersion test for coated specimen

To evaluate the resistance of coated specimen to concentrated sulfuric acid, acid immersion test was performed. The concentrations of the acid were 30, 50, 80, 97 wt% and test temperature was 100 ℃. After immersion test, the surfaces of the coated specimens were analyzed by AFM (Atomic Force Microscope) and SEM (Scanning Electron Microscope).

2.3 Cathodic protection system for the FGD facility

Fig. 2 shows the layout of electrode system and CP system used in this study. This system has been under evaluation of its performance since it was applied to 900 m^2 in one unit of the real-scale FGD system, and the study of its optimization has been carrying out.

2.4 Computer simulation for cathodic protection

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 modelled thus simplifying the modelling 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

Table 1. Boundary condition for cathodic protection simulation using BEASY program

Factors	Duct Bottom(FGD slurry) conditions
Resistivity	21.8 Ωcm
Thickness of electrolyte	5 mm
Anode area	16.9 cm^2
Cathode area	236.1 m^2
Conductivity	0.00458
Transfer coefficient	From APT data
Polarization data	Experimented data
Protection potential	8V

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. Table 1 is boundary condition for cathodic protection simulation using a BEASY program.

3. Results and discussion

Table 2 indicates the composition of the condensed solution in the cooler of FGD system in which the newly developed CP system is installed.[1] The solution has pH -1, sulfuric acid concentration of about 20% and chloride ion concentration of above 2,500 ppm in ambient temperature.[2] However, when the temperature increases above the boiling point, it's really impossible to measure the activities of the species in the solution. Corrosion rates of several metallic coupons are shown in Fig. 3 that were exposed for 92 days in this environment. The corrosion rate of carbon steel is 33mm/yr, and it seems not reasonable to use it as a construction material in this environment.

In the other paper we reported,[9] 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 have flaws exist on the coating, it is judged to 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. Namely, protective coating on the metallic structure is one of the most important factors in cathodic protection to metals in extremely acidic environment

The purposes of using coating in this CP system are that firstly it protects metals under coating by separating them to acidic solution, and secondly it provides the rich

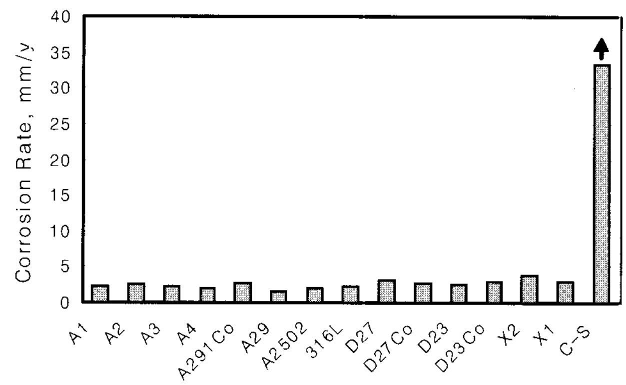


Fig. 3. Corrosion rates of several metallic coupons in the FGD system

paths of protection current to reach farther coating damages, otherwise most of the current would be consumed near the anodes from the fact that even though the solution of the FGD systems has a very high conductivity (>80 mS/cm), it forms very thin layer of fluid with a high electrical resistance. Furthermore, thousands A/m^2 of protection current may be consumed without coatings because the extremely acidic solution has a high dissolution rates of metal ions as well as a high conductivity. The consumption rate of protection current would be even increased with increasing temperature. Therefore, coating is indispensable for CP system to protect metallic structures of FGD system economically and effectively.

There are very restricted numbers of coatings that can be served in extremely acidic solution of high temperature (above boiling point).[10] There is a series of epoxy Novolac system[11] and fluoric system coatings[12] that can endure 60~70% of sulfuric acid under the temperature of 150 ℃. These coatings also showed good stability against CP current from their excellent adhesiveness with metals. Being considered workability and mechanical properties epoxy Novolac coating was applied in this study.[13] The main components of this coating are phenolic epoxy Novolac as a resin and Nepheline Seyenite as a reinforcement with minor additives such as $Na(AlSi_3O_8)$ and $K(AlSi_3O_8)$. As a pre-treatment of metal surfaces, de-scaling and cleaning were performed. After blasting the surface of metal surfaces(roughness: 75~125㎛), the coating materials were sprayed in the thickness of 40mils as a primer and 60mils as a top coat.

Table 2. The composition of the condensed solution in the cooler of FGD facility, #Y-1

Chemicals	SO_4^{2-}	F^-	Cl^-	Ni	Cr	Fe	Cu	Co	Mo	Mg
Concentration (mg/L)	206,800	505	2478	466	4.39	1060	0.945	2.68	3.99	21.6

This coating showed a good performance in 60~70 wt% of sulfuric acid and 150 ℃ of gas temperature. However, when it locally contacted with over 180 ℃ of gas, some of peel-offs and cracks were occurred. Therefore, the heat resistance needed to be strengthened in highly concentrated sulfuric acid for this coating. Immersion tests were performed[14] with the condition of solutions as follows, in order to investigate the deterioration mechanism of coating in highly acidic solution of high temperature:

- Sulfuric acid: 30wt%, Solution temperature: 100℃ for 5 days
- Sulfuric acid: 50wt%, Solution temperature: 100℃ for 3 days
- Sulfuric acid: 80wt%, Solution temperature: 100℃ for 1 day
- Sulfuric acid: 97wt%, Solution temperature: 100℃ for 3 hrs

Fig. 4 and Fig. 5 show the microstructures of coatings with variation of acid concentrations.[15] As the concen-

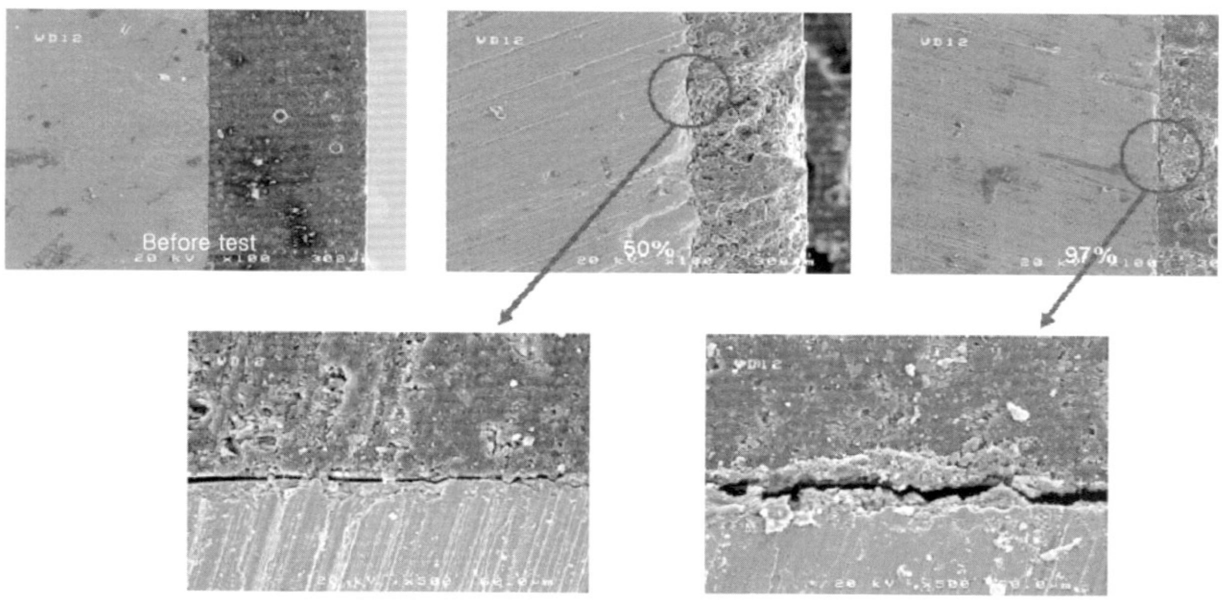


Fig. 4. Delamination between metal and coating with variation of acid concentrations

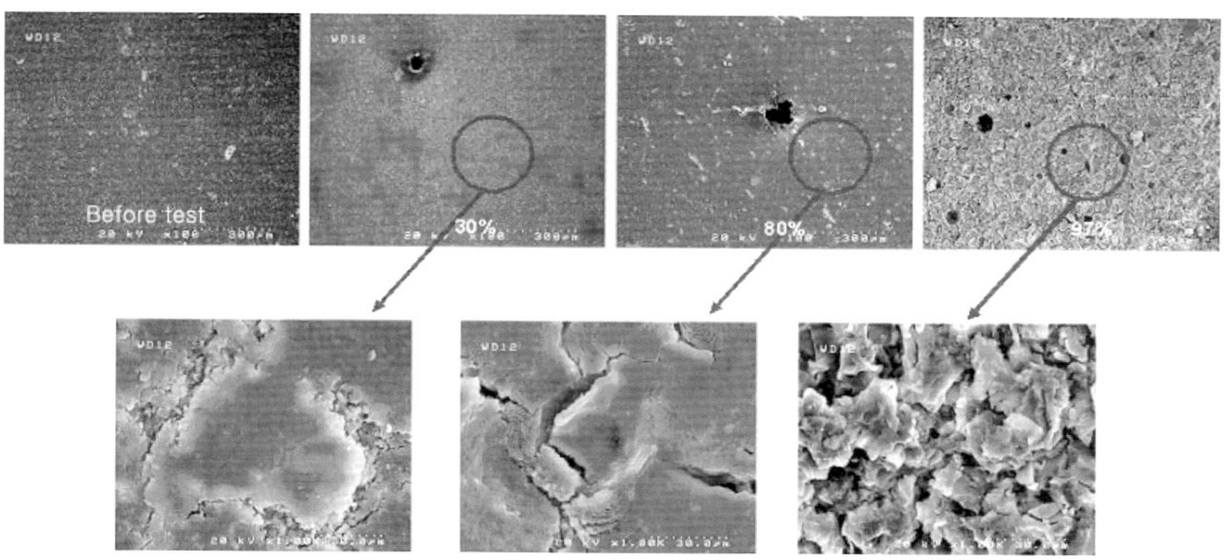


Fig. 5. Degradation of coating surface with variation of acid concentrations

tration of sulfuric acids increased, the thickness of coating decreased and the separation between interfaces became worse. The surface of the coating showed much more cracks increasing with acid concentration. In the 97 wt% of sulfuric acid, it was estimated that acid penetrated into the coating layer through the numerous cracks and voids.

The results of AFM are shown in Fig. 6 and Fig. 7. These diagrams indicate that as the concentration of acids increased fine indents were disappeared and bigger indents were smoothened. It was likely that as the concentration went up, some compositions forming the fine dents in coating might be dissolved to be cut out. It was impossible to perform AFM analysis of specimen in 97 wt% sulfuric acid because the specimen in that solution had too rough surfaces.

Table 3 summarizes the results of micro-Vickers hardness test.[16] As shown in the table, the hardness of coating decreased with increase of acid concentration. The coating specimen maintained in 30 wt% sulfuric acid for a month showed 115 Hv, and the decreasing rate of hardness was reduced as time went by. However, the specimens in over 50 wt% sulfuric acids showed rapid decrease of hardness, and especially the hardness became under 30 Hv in 80 wt% sulfuric acid after only 3 days.

The variations of composition in coatings are represented in Table 4.[17] It can be found that the composition

Table 3. Micro-Vickers hardness results of the damaged coating with variation of acid concentrations

	Average Hardness, Hv
Before test	140.6
Sulfuric acid 30 wt%	124.6
Sulfuric acid 50 wt%	94.6
Sulfuric acid 80 wt%	69.9
Sulfuric acid 98 wt%	57.6

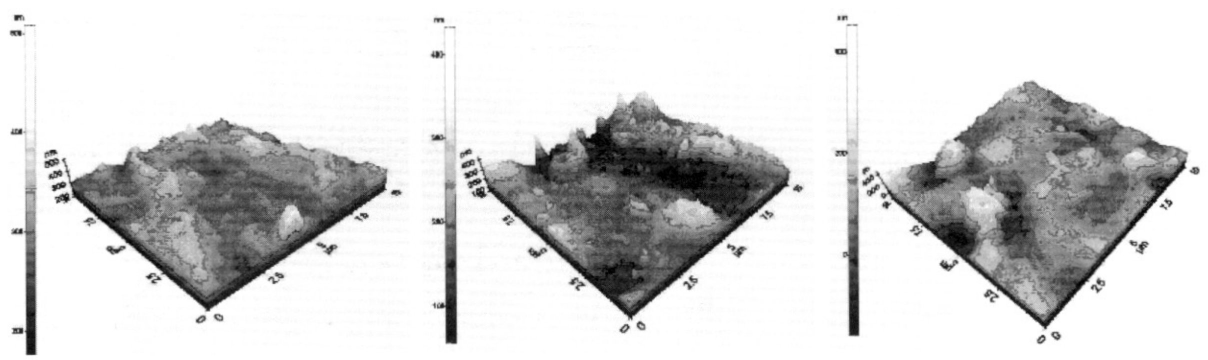


Fig. 6. Surface analysis of the coatings damaged by sulfuric acid (AFM) - 3D

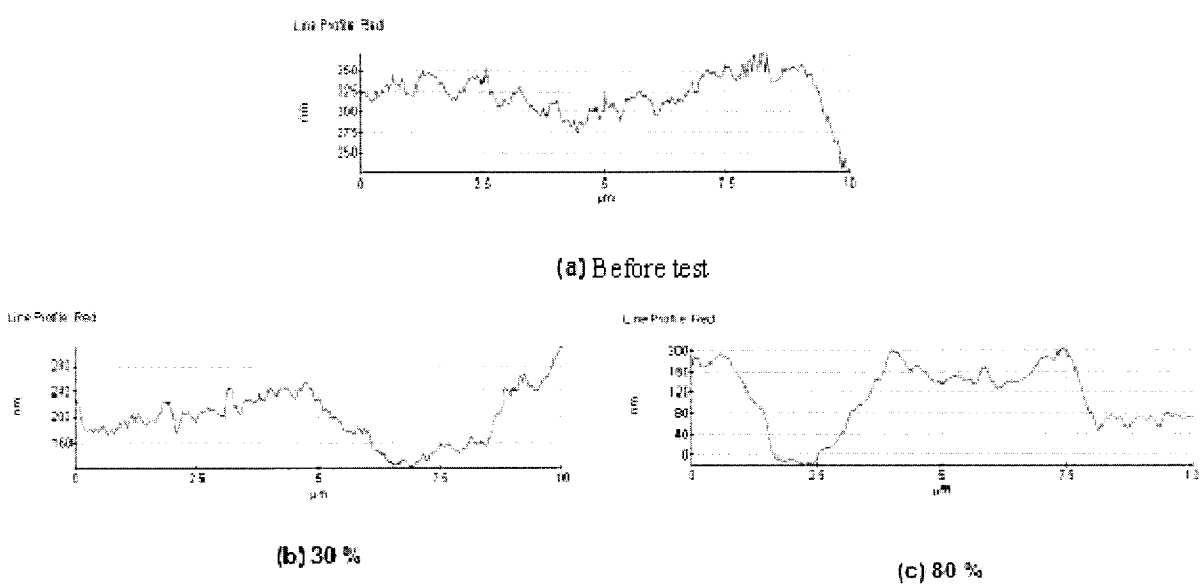


Fig. 7. Surface analysis of the coatings damaged by sulfuric acid (AFM) - 2D

Table 4. The variation of composition of the coatings before/after acid immersion tests

	Na_2O	Al_2O_3	SiO_2	K_2O	SO_3
Before test	15.13	18.44	53.48	4.75	0.03
30% H_2SO_4	2.49	11.11	43.11	4.48	24.47
50% H_2SO_4	2.40	10.92	43.49	4.28	24.42
80% H_2SO_4	2.21	9.19	35.19	3.91	36.92
97% H_2SO_4	2.28	10.49	30.55	2.72	34.59

of SO_3 increased and the others of oxides were reduced with being dissolved as the solution was becoming saturated with sulfuric acid.[18]

Even though the solution in this environment includes a highly concentrated sulfuric acid, the anodic protection can not be applied instead of the cathodic protection. The main reason is that it is almost impossible to draw the exact condition to produce passive film on the metals of whole area in this system. It has the environment that is highly variable quantities and concentrations of the condensed solution in the form of thin layer. The temperature of this system is also highly variable by times and locations. The aims of applying this CP system are (1) to monitor the corrosion status of facilities using communication technology remotely in real time, (2) to prevent corrosion of the metals under the damaged coating area with protection current, (3) to make it easy to repair the corrosion damaged FGD system in short periods of overhaul (4) eventually to decrease construction and maintenance costs of FGD system.

Fig. 8 shows the cathodic protection system developed in this work.[1] This system can be monitored and controlled from the remote places using wire and/or wireless communication networks including an artificial satellite, LAN, radio communication *etc.* The software that monitors and controls the CP system through the internet was installed in a FGD facility of commercial power plant.

The zone, outlet hood of cooler of power plant #Y-1, was originally made of super alloy clad (Alloy C-276, 1 mm) on carbon steel (6 mm). The CP system and coatings were applied to carbon steel's area of this zone, after the damaged clad materials by corrosion were removed. However, after the CP system was applied to this area for 6 months, it is obvious from the Fig. 9 that the failed surface (25 cm length, 10 cm width) of carbon steel was not damaged.

In order to identify the performance of CP system on the coated surface of the outlet hood of cooler of power plant #Y-1, protection current and protection potential were visualized by the computer simulation using BEASY software when a coating flaw was introduced into outlet

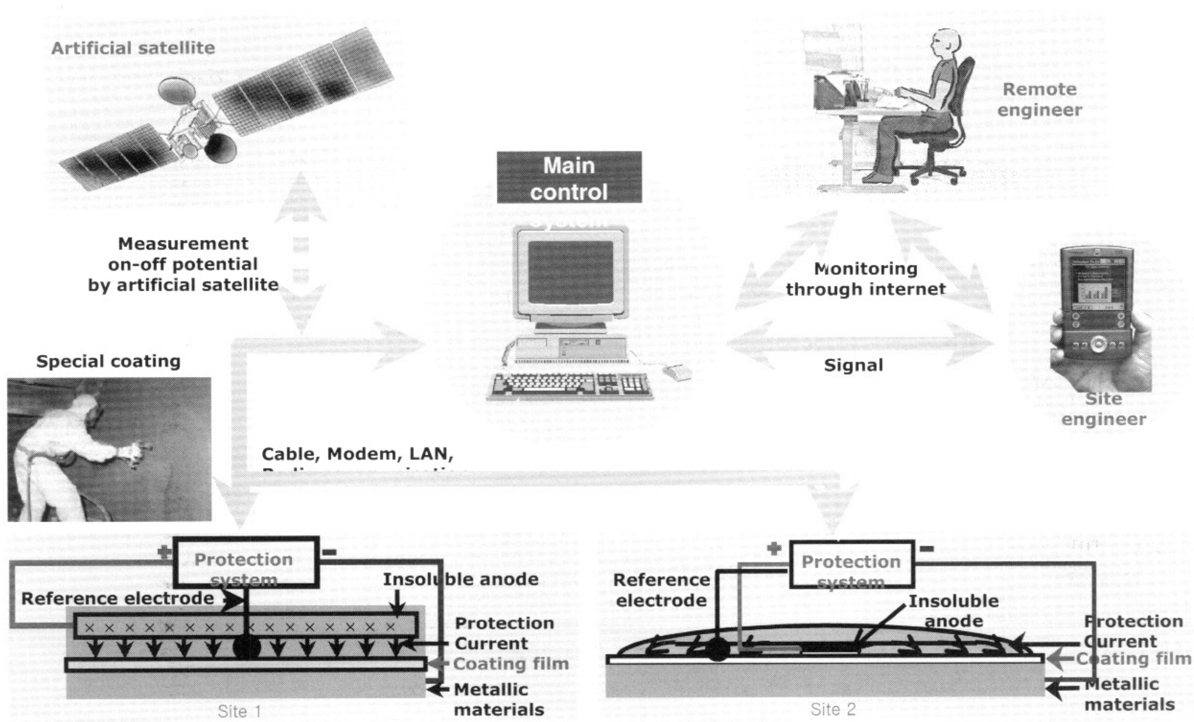


Fig. 8. Schematic diagram of CP system[1]

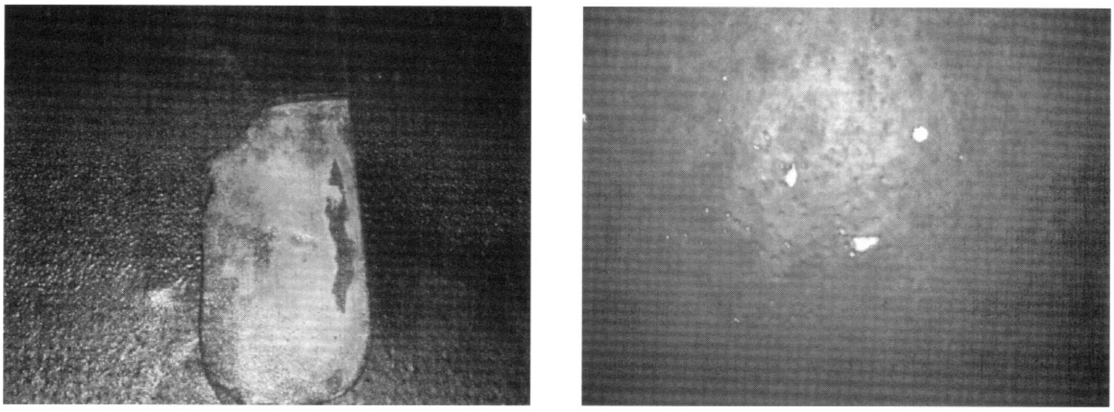
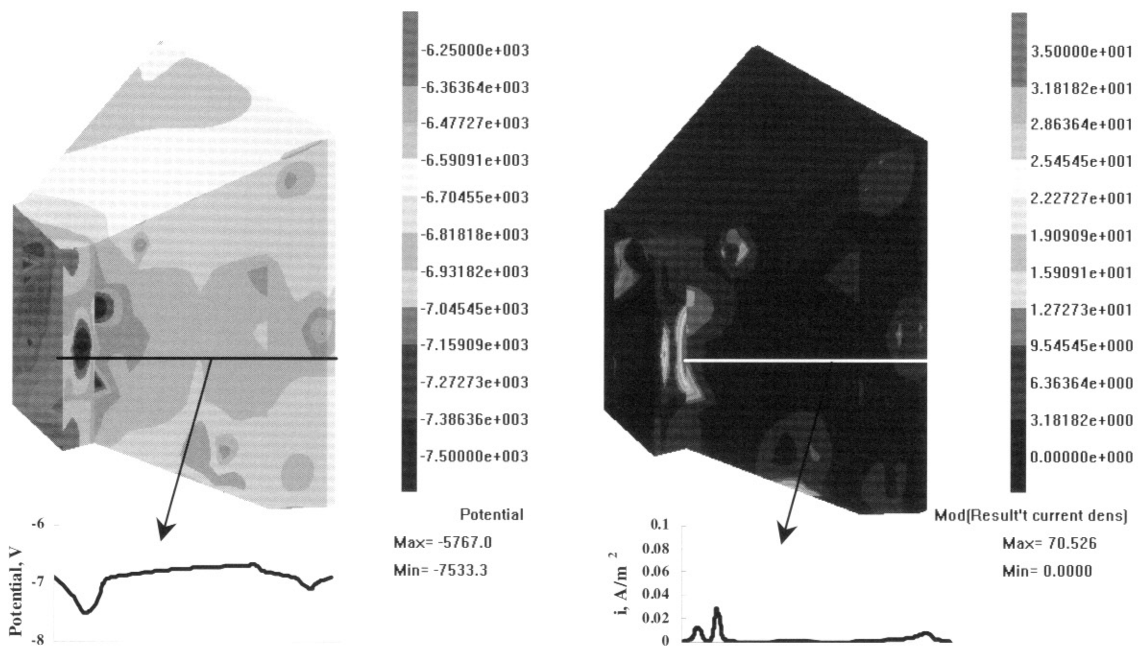


Fig. 9. Effect of cathodic protection on failed surface of carbon steel of outlet hood, the FGD facility



(a) (b)

Fig. 10. Simulation result for cathodically protected area of outlet hood which it was coated ; (a) Protection potential, (b) Protection current density

hood of cooler (6 m width between 8*8 m and 10*10 m) as shown in Fig.10. Fig.10 (a) shows cathodic protection potential between -7.5 and -6.8 V when cathodic protection voltage of -8 V was applied and Fig.10 (b) shows cathodic protection current density. If any flaws were formed at cathodic protected area, the exposed metallic area can be protected since the electric field was formed through the whole coated area.

4. Conclusions

1. To cathodically protect the metallic structures in extremely acidic fluid, the properties of the protective coatings on the metal surface were very important, and epoxy Novolac coating was applied in this work. On the base of acid immersion tests, hot sulfuric acid decreased the hardness of the coatings and reduced greatly the content of Na_2O, Al_2O_3, and SiO_2 among the main components of the coating.

2. A special kind of CP system has been developed and tested in a real scale of the FGD facility. Applied coating for this CP system was peeled off and cracked in some parts of the facility. However, the exposed metal surface to extremely acidic fluid by the failure of the

coatings was successfully protected by the new CP system.

References

1. Y. S. Kim, "Remote monitoring and controlling system of corrosion and corrosion protection using wire and/or wireless communication networks," Korea Patent Number - 0405590
2. H. Y. Chang and G. Hwangbo, "The application of EP system for FGD in power stations", Interim report, KOPEC (2002).
3. H. Y. Chang, S. H. Hong, and Y. S. Kim, *Corrosion Science and Technology*, **31**(1), 70 (2002).
4. H. Y. Chang, G. Hwangbo, Y. R. Yoo, and Y. S. Kim, "8th International symposium on the electrochemical methods in corrosion research," EMCR 2003, P-12, 4-9 May, Ysermonde, Nieuwport, Belgium (2003).
5. H. Y. Chang, G. Hwangbo, T. E. Jin, Y. R. Yoo, J. K. Yoo, Y. S. Kim, and M. C. Shin, Advanced Corrosion Protection by Organic Coatings, p.230, 20-25, September, Christ's College, Cambridge, UK (2004).
6. K. C. Sohn, H. Y. Chang, and Y. S. Kim, *Corrosion Science and Technology*, **4**(2), 56 (2005).
7. H. Y. Chang, K. C. Sohn, S. J. Hong, and Y. S. Kim, 201st Meeting of the Electrochemical Society, p.342, May 12-17, Philadelphia, PA, USA (2002)
8. H. Y. Chang, G. Hwangbo, T. E. Jin, Y. R. Yoo, and Y. S. Kim, 13th Asian-Pacific Corrosion Control Conference, Paper C-303, 16-21, November, Osaka University, Osaka, Japan (2003)
9. H. Y. Chang, Y. R. Yoo, T. E. Jin, and Y. S. Kim, "Application of cathodic protection on Metallic Structure in extremely acidic fluids", *Corrosion Science and Technology*, **4**(4), 140 (2005).
10. R. G. Schmidt and J. P. Bell, 'Advanced in Polymer Science', *Springer-Verlag*, **75**, 33 (1986).
11. 'Studies on the adhesive properties of solid elastomer-modified novolac epoxy resin', *International Journal of Adhesion & Adhesives*, **20**, 305 (2000).
12. G. Hougham, P. E. Cassidy, K. Johns, and T. Davidson, 'Fluoropolymers', Kluwer Academic/plenum Publishers, **2**, 647 (1999).
13. 'Epoxy Resins, Chemistry and Technology' 2^{nd}., C. A. May, Marcel Dekker Inc. New York. Chap. 1, 1988
14. 'Laboratory Methods for the Evaluation of Protective Coatings Lining Materials in Immersion Service', NACE TM0174 (1996)
15. 'Metallic coatings - Measurement of coating thickness - Scanning electron microscope method', ISO 9220 (1988).
16. 'Standard Test Method for Micro-indentation Hardness of Materials', ASTM E384 (1999)
17. 'Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders', ASTM D5381 (1998).