Coatings for Cathodic Protection Systems in Flue Gas Desulphurisation Equipment

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Abstract

Many locations in the FGD (Flue Gas Desulphurization) systems of fossil-fuel power plants have environments which are highly changeable and extremely acidic and thus vary according to time, position and corrosivity; e.g. in duct work, coolers and re-heaters etc.. These conditions are formed when the system materials are exposed to dripping fluids or when exhausted gas is condensed into a thin layered medium on system materials; e.g. walls and roofs. Such environments give rise to extremely troublesome corrosion and air pollution problems. The frequent shut down and repair of FGD systems due to corrosion also increases costs and decreases efficiency of these facilities. In general, highly corrosion resistant materials have been used to solve this problem. However, even such alloys and/or Teflon linings sometimes have not been sufficiently good to prevent this corrosion. Furthermore, they are expensive and not easily repairable during short maintenance downtime periods. In this work, new technology that is effective, economical and easily repairable is proposed to solve corrosion problems in FGD facilities. This technology comprises cathodic protection, coatings and remote monitoring and controlling systems.

Keywords: FGD, Cathodic Protection, Coatings, Remote monitoring.

Introduction

The exhausted flue gas from fossil fuel power stations contains a large number of contaminant species. However, the sulphur content in flue gases is strictly controlled by the FGD systems installed in almost all fossil fuel power plants in Korea. From the processes to minimize the content of sulphur contaminations in exhausted gas, a highly corrosive environment including sulphuric acid can be formed in some parts of the system, consequently severe corrosion damage can be reported in those areas (Fig 1). A special kind of CP (Cathodic Protection) system has been developed and tested in a full-scale FGD system. Cathodic protection is one of the economic technologies that can effectively prevent corrosion of plant and has the merits of being low maintenance and cost compared with replacement of the relevant FGD components by corrosion resistance alloys. This system, consisting of the coating technology, the design technology of the CP system and a communication technology has shown excellent corrosion control performances in FGD plant. However, coatings peeled off and cracked in some parts of the plant where the critical operating temperature of the coating was exceeded. Therefore, a new coating system with a higher service temperature is required. This paper is intended as an investigation in the improvement of the heat resistance of coatings for the FGD system under study, as well as a brief explanation about the new type of CP system applied in the full-scale FGD system.

CP systems for FGD Facilities

Fig. 2 and Fig. 3 show the CP system and electrodes used in this study. This system has been under evaluation for its performance since it was initially applied over a $900m^2$ area in one unit of a full-scale FGD system. Even though the solution in this environment includes a highly concentrated sulphuric acid (i.e. at the sulphuric acid dewpoint), anodic protection cannot be applied. The main reason is that it is almost impossible to draw the exact condition to produce passive film on the metals over the whole area in this system. Thus a cathodic protection system must be used instead.

The environment is highly variable in the quantities and concentrations of the condensed solution, which is in the form of thin layer. The temperature of this system is also highly over times and by location. 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 a cathodic protection current, (3) to make it easy to repair the corrosion damaged FGD system in a short period

of overhaul, and (4) eventually to decrease overall construction costs and maintenance costs of FGD systems.

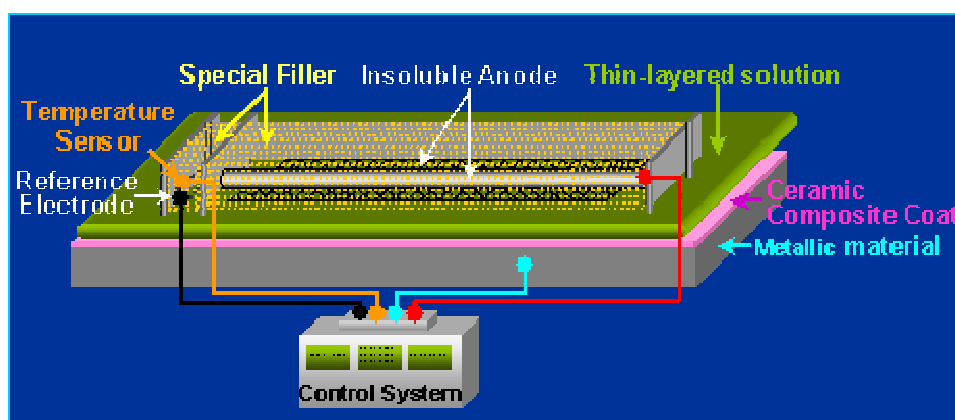Figure 1: Severe corrosion damages in FGD systems
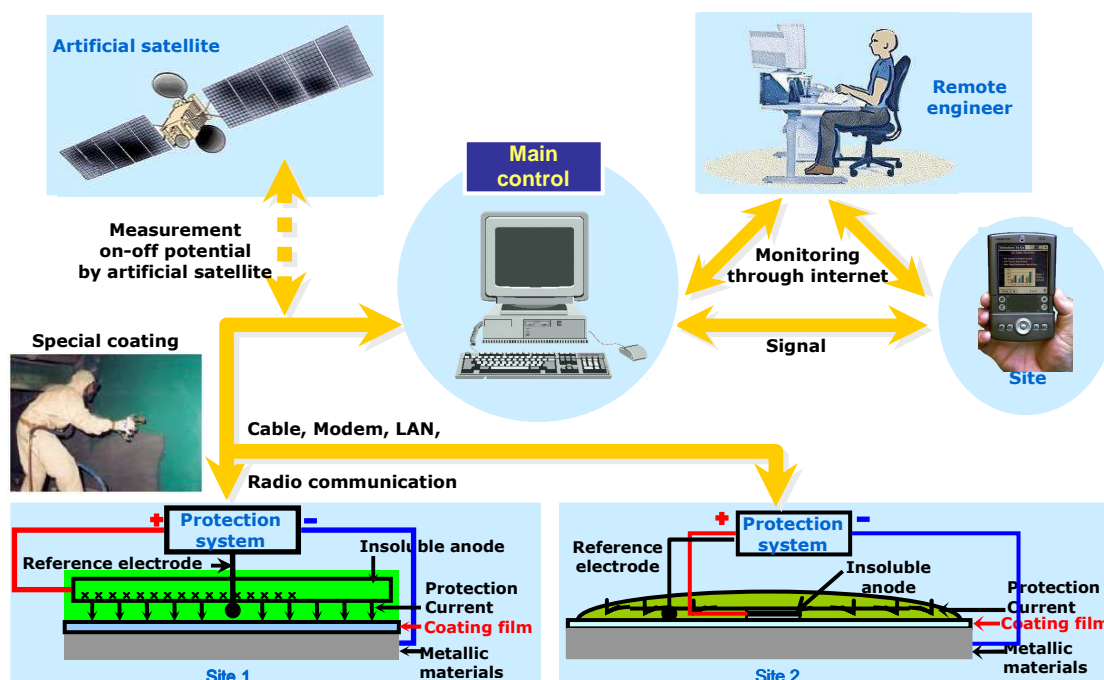

Figure 2: Schematic diagram of electrode system

Figure 3: Schematic diagram of CP system

The Effectiveness of the CP System

Table 1 indicates the composition of condensed solution in the gas-to-gas heater (GGH) of the FGD system in which the newly developed CP systems are installed [1]. The solution has pH of 1 with a sulphuric acid concentration of about 20% and a chloride ion concentration of about 2,500 ppm at 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. The corrosion rates of several metallic coupons are shown in Fig. 4 that were exposed for 92 days in this environment. The corrosion rate of carbon steel is 33 mm/yr, and it seems not reasonable to use it as a construction material in this environment.

Table 1: The composition of condensed solution in GGH of FGD system

Chemicals	SO_4^{2-}	F^-	Cl^-	Ni	Cr	Fe	Cu	Co	Mo	Mg
Concentration (mg/L)	207000	505	2480	470	4.4	1060	0.94	2.7	4.0	22.0

In order to see the performance of the CP system the protection currents and potentials were monitored by the computer when a coating flaw was introduced into the outlet hood

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of the GGH (Fig. 5). This zone was originally made of super alloy clad (1 mm) on carbon steel (6 mm). The CP system and coating were applied to carbon steels in this zone, after the corrosion-damaged clad materials were removed. It is obvious, from observing Fig. 6, that the carbon steel exposed at the coating failure (25 cm length, 10c m width) remained undamaged corrosion after 6 months service.
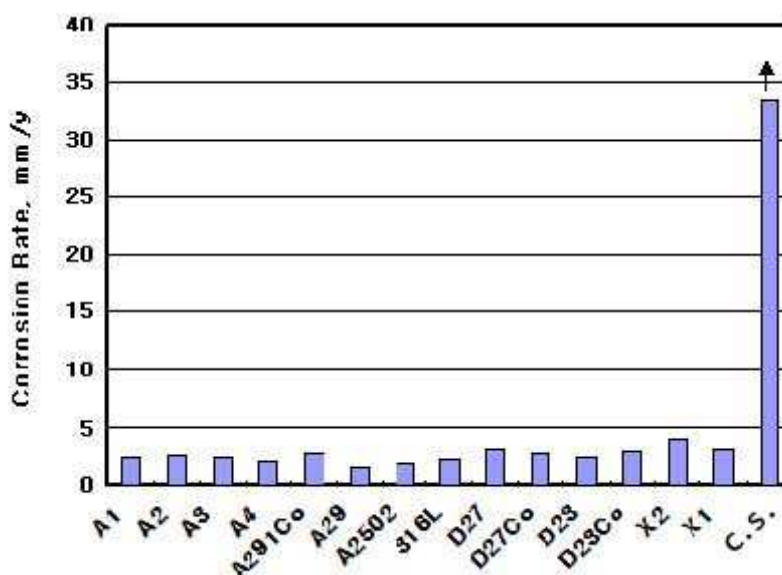

Figure 4: Corrosion rates of several metallic coupons in FGD system
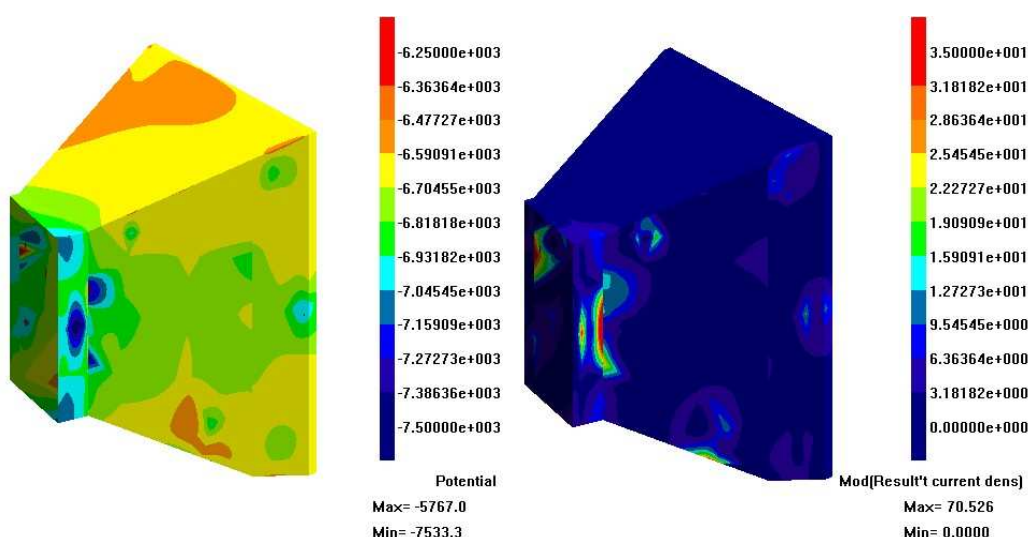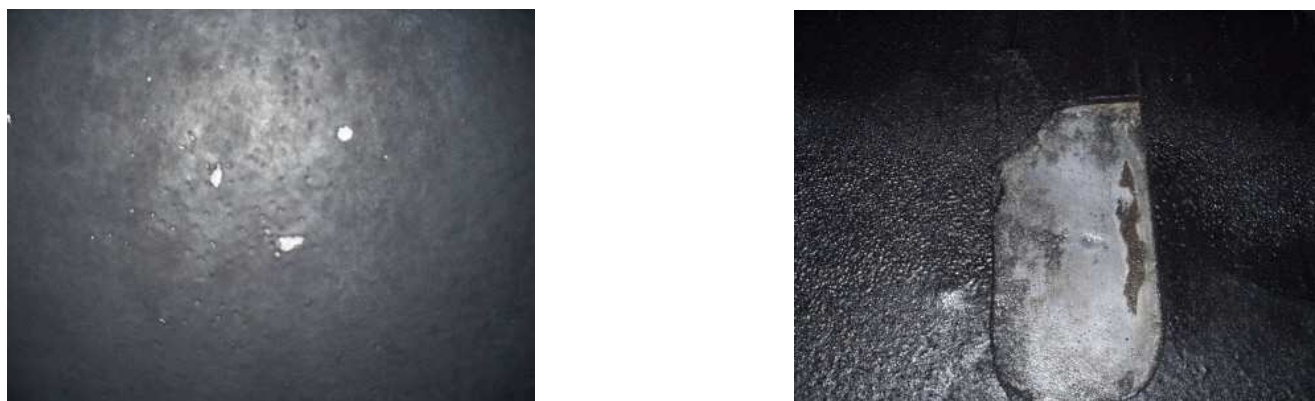

Figure 5: Simulation results of CP system in FGD system

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Figure 6: Surface of carbon steel exposed by the coating failure (cathodically protected)

Coating Requirements

The aims of using coatings in this CP system are that, firstly it protects the material under the coating by separating them from the acidic solution, and secondly it provides a high electrical resistance that permits the protection current to reach remote areas of coating damage, otherwise most of the current would be consumed near the anodes. Given the extremely corrosive fluid at the sulphuric acid dewpoint, uncoated material would require uneconomically large protection currents to counter the high dissolution rates. Therefore, an effective coating is indispensable for this CP system to protect the FGD system economically and effectively.
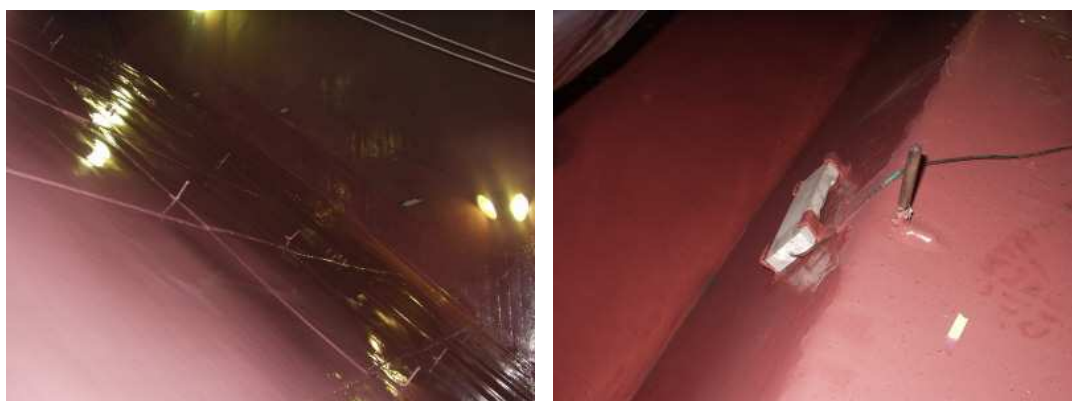

Figure 7: Application of epoxy Novolac coating with CP anodes in FGD system

There are very limited number of coatings that might be of use in extremely acidic solutions of high temperature (above boiling point) [3]. For example, there are a series of epoxy Novolac resins [4] and fluorinated coatings [5] that can endure 60–70% of sulphuric acid at

up to 150℃. These coatings also showed good stability against the CP current and had excellent adhesion to metal substrates. The epoxy Novolac coating was applied in this study for its workability and mechanical properties [6] (Fig. 7). The main components of this coating are Phenol Epoxy Novolac as a resin and Nepheline Seyenite as a reinforcement with minor additives such as $Na(AlSi_3O_8)$ and $K(AlSi_3O_8)$.

The Analysis of Coating Properties

This coating showed a good performance in the condensed sulphuric acid (60-70%) at a gas temperature of 150℃. However, when the local temperature rose to 180℃, some disbonding and cracking occurred (Fig. 9). Therefore, the heat resistance of this coating needed to be improved. Immersion tests were therefore performed [7] as follows:

Sulphuric acid : 30wt%, Solution temperature : 100℃ - 5 days

Sulphuric acid : 50wt%, Solution temperature : 100℃ - 3 days

Sulphuric acid : 80wt%, Solution temperature : 100℃ - 1 day

Sulphuric acid : 97wt%, Solution temperature : 100℃ - 3hrs

Fig. 10 and Fig. 11 show the microstructures of coatings after immersion in varying concentrations of acids as above [8]. As the concentration of sulphuric acids increased, the thickness of coating decreased and the separation between interfaces became worse. The surface of the coating showed that cracking increased with the acid concentration. In the 97wt% sulphuric acid, acid had penetrated into the coating layer through the numerous cracks and voids.

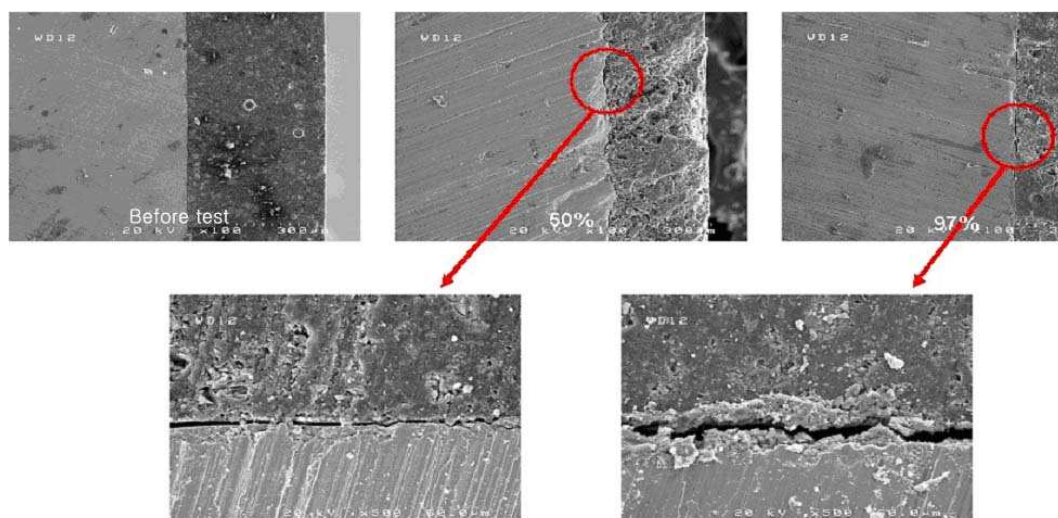Figure 8: Local disbonding and cracking occurred in high temperature gas

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Figure 9: Microstructure of coatings after exposure in various acid concentrations

The results of AFM (Atomic Force Microscopy) are shown in Fig.11 and Fig. 12 [9]. These indicate that as the concentration of acid increased fine indents disappeared and bigger indents were smoothed. It was likely that as the concentration went up, some compositions in coating forming the fine dents might be dissolved out. It was impossible to perform AFM analysis of specimen in 97wt% sulphuric acid because the surface of the specimen in that solution was too rough.
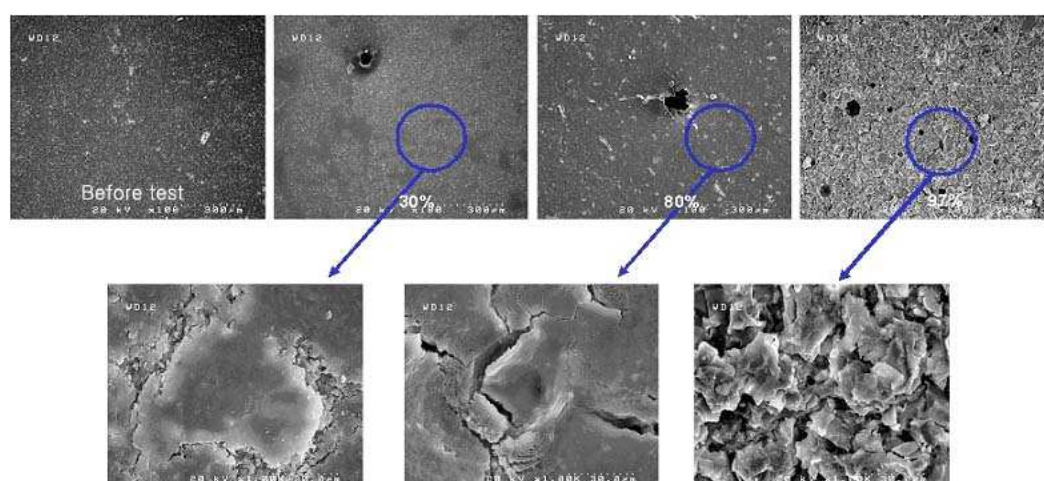

Figure 10: Micro-structure of coatings with variation of concentration of acids
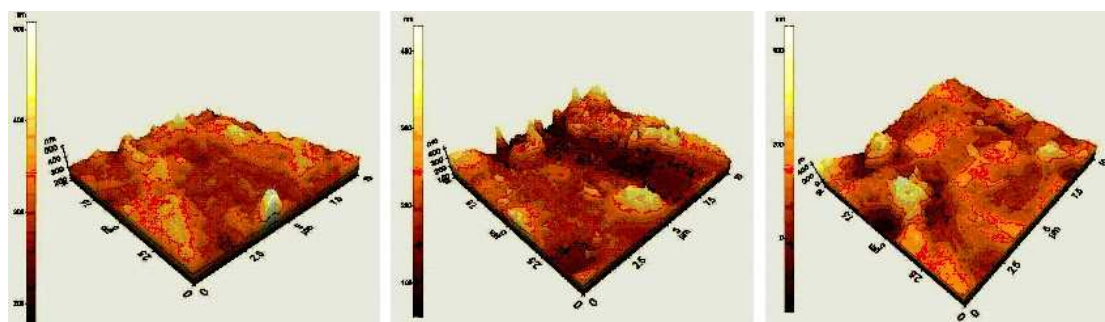
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Figure 11: Surface analysis of damaged coatings by sulphuric acid (AFM) – 3D

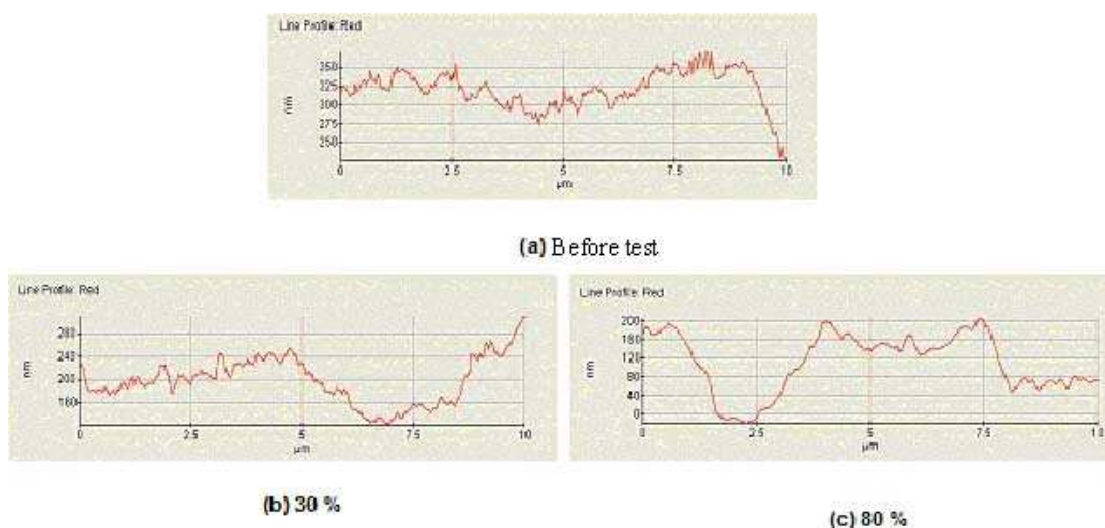(a) Before test

(b) 30 %

(c) 80 %

Fig. 12 Surface profile of coatings damaged by sulphuric acid (AFM) – 2D

Table 2 summarizes the results of micro-Vickers hardness test [10]. As shown in the table, the hardness of the coating changed as a function of acid concentration. The coating specimen immersed in 30wt% sulphuric acid for a month showed 115Hv, with slowly decreasing hardness as time went by. However, the specimens in over 50wt% sulphuric acids showed a rapid decrease of hardness, and especially the hardness became under 30Hv in 80wt% sulphuric acid after only 3 days.

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Table 2: Micro-Vickers hardness results of damaged coating with variation of acid concentration

	Average Hv [kg/mm2]
Before test	140.6
Sulphuric acid 30wt%	124.6
Sulphuric acid 50wt%	94.6
Sulphuric acid 80wt%	69.9
Sulphuric acid 98wt%	57.6

The variations of composition in coatings are represented in table 3 [11]. It can be seen that the composition of SO_3 increased, and that of the other ceramics fillers were reduced, as the sulphuric acid concentration increased [12].

Table 3: The variation of composition in coatings according as acid concentrations

	Na_2O	Al_2O_3	SiO_2	K_2O	SO_3
Before test	15.1	18.4	53.5	4.7	0.03
30%	2.5	11.1	43.1	4.5	24.5
50%	2.4	10.9	43.5	4.3	24.4
80%	2.2	9.2	35.2	3.9	37.0
97%	2.3	10.5	30.6	2.7	34.6

Improvement of Coating Properties

The epoxy Novolac used in this study has a mean available functionality of 3.6 epoxide groups, which gives it a high reactivity and high cross-linking density (Fig. 13). Therefore it has superior adhesive property and chemical resistance to traditional epoxy resins [13].
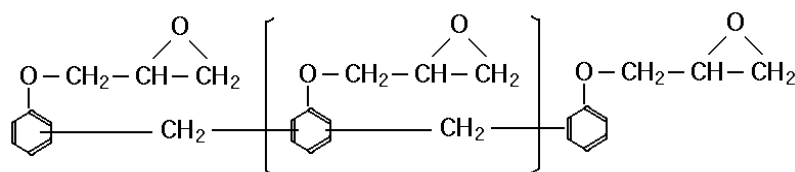

Figure13: The structure of epoxy Novolac (functionality of 3.6 epoxide groups)

This coating has a wide range of curing properties and adhesive properties with various substrates according to the selection of the epoxides or modifying reagents because epoxides located in both the sides and center of the molecules have high reactivity. The phenol structure in the molecules allows it to have high strength and high temperature properties. This resin has also excellent chemical resistance from the fact that it is mainly composed of aromatic compound linkage with ether linkages [14]. The ether bond in the main chain allows rotation for some plasticity and chemical resistance [15]. Amine compounds with an average of 6 activated sites are used for curing 16].

In order to ensure the epoxy Novolac for serviceability in the environment of 60~70% sulfuric acid at the higher gas temperature of 200℃, a modified phenol epoxy Novolac has been developed and tested where the heat resistance is strengthened [17]. The main ingredients of the additive mixture for heat resistance are organopolysiloxane, toluene and barium sulphate.

The heat resistance was the best without deterioration of acid resistance when epoxy Novolac coating was mixed with the additive mixtures in a 50:50 ratio. Fig.14 shows that this new formulation was heated up to 210℃ for 12 hours and 4 days but it had no cracks and disbonding [18]. Furthermore Fig.15 shows that this modified coating has an equivalent acid resistance to the original epoxy Novolac coating with only small cracks initiated in 80wt% sulphuric acid solution at100℃ after at least 6 days had passed.

This modified phenol epoxy Novolac has been showing excellent performance without any cracks and peel-offs since it was applied to the region in which the original one had been damaged (Fig.17).
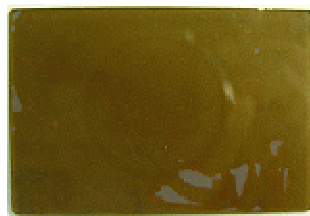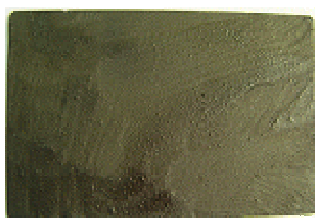
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| 12 hours passed | 4 days passed |

Figure 14: Heat resistance of modified epoxy Novolac coatings (210℃)

| Before Test | 1 hour passed |

| 12 hours passed | 6 days passed |

Figure 15: Acid resistance of modified epoxy Novolac coatings (100℃, 80wt% sulphuric acid)

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Figure 16: Application of modified phenol epoxy Novolac coatings on damaged region

Conclusions

1. A novel CP (Cathodic Protection) system has been developed and tested in a full-scale FGD system. This CP system is one of the economic technologies that can effectively prevent corrosion of plant, and has the advantages of easy maintenance and replacing by expensive corrosion resistant alloys.

2. Coatings for this CP system were based on an epoxy Novolac system and were stable against CP current and sulphuric acid strength. However, they were subject to disbonding and cracking where the local temperature exceeded 150℃; this made CP control difficult.

3. In order to ensure the epoxy Novolac for serviceability in the environment of 60~70% sulfuric acid at up to 200℃, a modified phenol epoxy Novolac has been developed and tested where the heat resistance is improved. The additive ingredients providing this heat resistance are organopolysiloxane, toluene and barium sulphate.

4. This modified phenol epoxy Novolac has been shown to give excellent performance without any cracks and disbonding since it was applied to the region in which the original one had been damaged.

References

1. 'Standard Test Method for Determination of Impurities in Plutonium: Acid Dissolution, Ion Exchange Matrix Separation, and Inductively Coupled Plasma-Atomic Emission Spectroscopic(ICP/AES) Analysis', *ASTM C1432*, 2003

2. 'Standard Practice for Describing and Specifying a Wavelength-Dispersive X-ray Spectrometer', *ASTM E1172*, 2001

3. 'Advanced in Polymer Science', R. G. Schmidt, J. P. Bell, *Springer-Verlag*, 75, pp33, 1986

4. 'Studies on the adhesive properties of solid elastomer-modified novolac epoxy resin', *International Journal of Adhesion & Adhesives*, 20, pp305-314, 2000

5. 'Fluoropolymers', G. Hougham, P. E. Cassidy, K. Johns, T. Davidson, Kluwer Academic/plenum Publishers,2, pp647-65, 1999

6. 'Epoxy Resins, Chemistry and Technology' 2nd., C. A. May, Marcel Dekker Inc. New York. Chap. 1, 1988

7. 'Laboratory Methods for the Evaluation of Protective Coatings Lining Materials in Immersion Service', *NACE TM0174*, 1996

8. 'Metallic coatings – Measurement of coating thickness – Scanning electron microscope method', *ISO 9220*, 1988

9. 'Standard Practice for Measuring and Reporting probe Tip Shape in Scanning Probe Microscopy', *ASTM E1813*, 1996

10. 'Standard Test Method for Microindentation Hardness of Materials', *ASTM E384*, 1999

11. 'Standard Guide for X-Ray Fluorescence (XRF) Spectroscopy of Pigments and Extenders', *ASTM D5381*, 1998

12. 'Standard Test Method for Identification of crystalline Pigments and Extenders in Paint by X-Ray Diffraction Analysis', *ASTM D5380*, 1998

13. 'Free-Volume Characteristics and Water Absorption of Novolac Epoxy Resins Investigated by Positron Annihilation', T. Suzuki, Y. Oki, M. Numajiri, T. Miura, Y. Shiomi and Y. Ito, *Polymer*, 37, 14, pp3025-3030, 1996

14. V. Bellenger and W. Dhaoui, *J. Appl. Polym. Sci.*, 35, PP563, 1988

15. C. C. Riccardi and R. J. J. Williams, *J. Appl. Polym. Sci.*, 32, pp3445, 1986

16. J. S. Shim, W. Lee, and J. Jang, *Polymer Journal*, 23, 7, pp911, 1991

17. 'Standard Test Methods for Heat Resistance of Polymer Linings for Flue Gas Desulfurization', *ASTM D5499*, 1999

18. 'Standard Test Method for Chemical Resistance of Protective Linings', *ASTM C868*, 1995