CORROSION SCIENCE AND TECHNOLOGY, Vol.5, No.1(2006), pp.5~14

A Study on the Coatings for CP System in the Environment in which Thin Layer of Extremely Acidic Fluids are Formed

† H.Y.Chang, I.S.So, T.E.Jin, Y.S.Kim[1], Y.R.Yoo[1], and M.S.Kang[2]

Korea Power Engineering Company Inc., 360-9, Mabuk, Guseong, Yongin, 449-713, South Korea
[1]Andong National University, 388, Songchun, Andong, 760-749, South Korea
[2]DAION Co. Ltd, 33BL-4LT, 613-3, Namchon-dong, Namdong-Gu, Incheon, 405-846, South Korea

A lot of parts in FGD (Flue Gas Desulphurization) 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 medium to contact materials of the system walls and roofs. The environments make troublesome corrosion and air pollution problems that are occurred from the leakage of the condensed solution. The frequent shut-down and repairing works of 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, even the super alloys and Teflon linings sometimes have not been good enough to preventing corrosion. Further more, they are expensive and not easily repairable in short periods of operation stops. In this work, new technology that is effective, economical and easily repairable has proposed to solve the corrosion problems in FGD facilities. This technology contains cathodic protection, coatings and remote monitoring-controlling systems.

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

1. Introduction

The exhausted flue gas from the fossil-fuel power stations contains usually many contaminated species. Sulphur-content has been strictly controlled from 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, high corrosive environment including sulphuric acid can be formed in some parts in FGD systems and severe corrosion damages are reported in those areas (Fig. 1). A special kind of CP (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 being replaced by expensive stainless steels or super alloys. This system consisting of coating technology, the design technology of CP and a communication technology has shown excellent corrosion control performances in FGD system. However, coatings were peeled

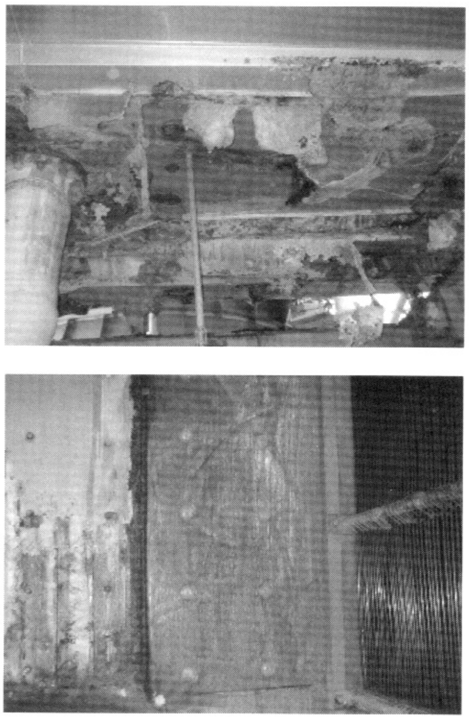


Fig. 1. Severe corrosion damages in FGD systems

† Corresponding author: hyjang@kopec.co.kr

off and cracked in some parts of facility that exceeded the service temperature of coating, which made protection currents wasted and made CP control difficult. Therefore, it was needed for the service temperature of coating to be increased in the environment of extremely acidic solution. This paper is intended as an investigation of improvement in heat resisting performance of coating for FGD system as well as a brief explanation about the new type of CP system applied in a real-scale FGD system.

2. The CP system for FGD facilities

Fig. 2 and Fig. 3 show the structures of CP system and electrodes 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 real-scale FGD system, and the study of its optimization has been carrying out. Even though the solution in this environment includes a highly concentrated sulphuric acid, Anodic Protection can not be applied instead of 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,

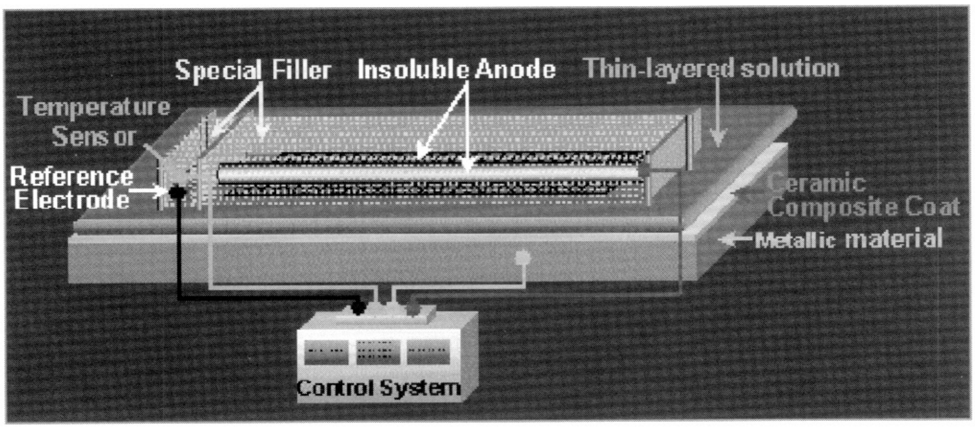


Fig. 2. Schematic diagram of electrode system

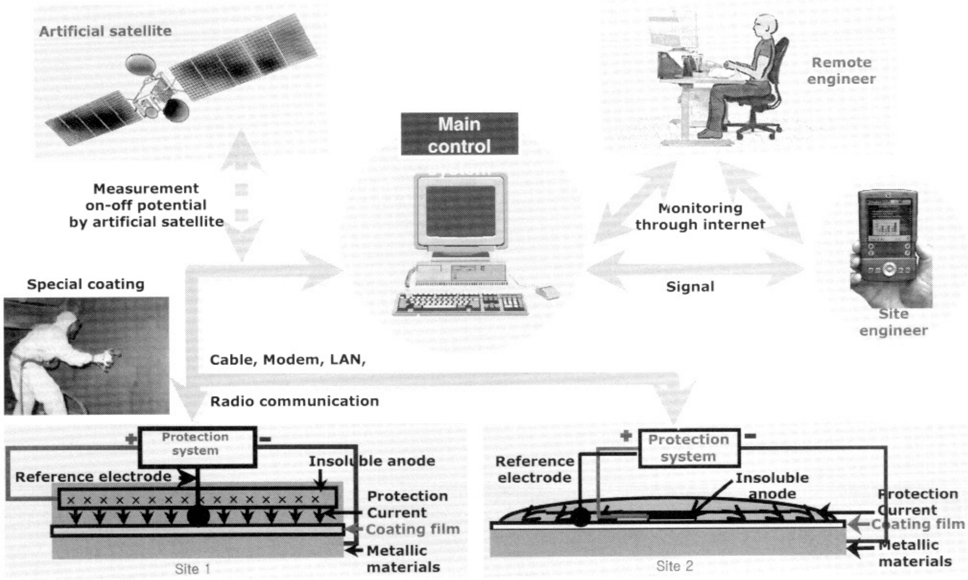


Fig. 3. Schematic diagram of CP system

(3) to make it easy to repair the corrosion damaged FGD system in a short period of overhaul (4) eventually to decrease construction and maintenance costs of FGD system.

3. The effectiveness of CP system

Table 1 indicates the composition of condensed solution in Cooler of FGD system in which the newly developed CP systems are installed.[1] The solution has pH-1, sulphuric 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. 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.

Fig. 5 shows the software that monitors and controls through the internet the CP system installed in the FGD system of commercial power plant. In order to see the performance of CP system, protection currents and protection potentials were visualized by the computer simulation when a coating flaw was introduced into outlet hood of Cooler(Fig. 6). 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 of this zone, after the damaged clad materials by corrosion were removed. It is obvious from the Fig. 7 that the surface of carbon steel exposed by the coating failure (25 cm length, 10 cm width) was not damaged at all by corrosion after

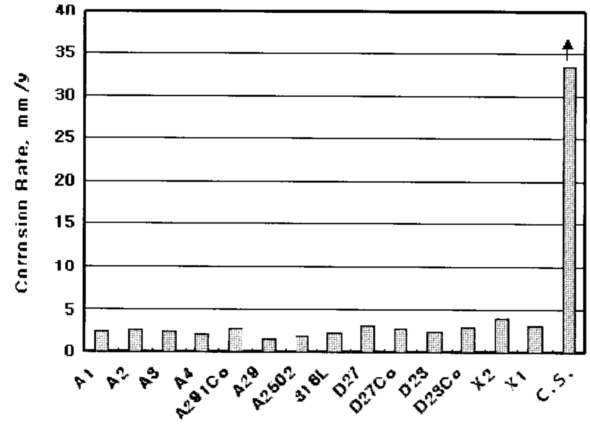


Fig. 4. Corrosion rates of several metallic coupons in FGD system

Table 1. The composition of condensed solution in Cooler of FGD system

Chemicals	SO_4^{2-}	F^-	Cl^-	Ni	Cr	Fe	Cu	Co	Mo	Mg
Concentration (mg/L)	206800	505	2478	466	4.39	1060	0.945	2.68	3.99	21.6

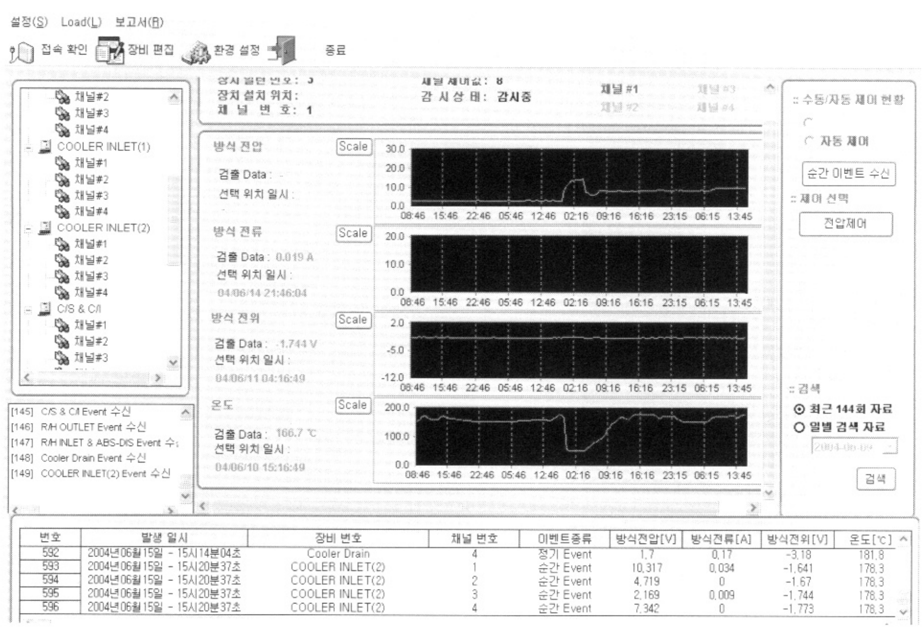


Fig. 5. Monitoring and controlling software of CP system installed in the FGD system

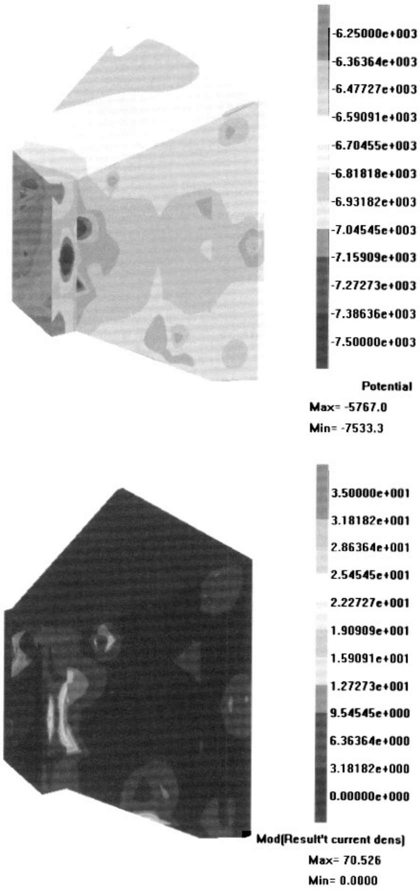


Fig. 6. Simulation results of CP system in FGD system

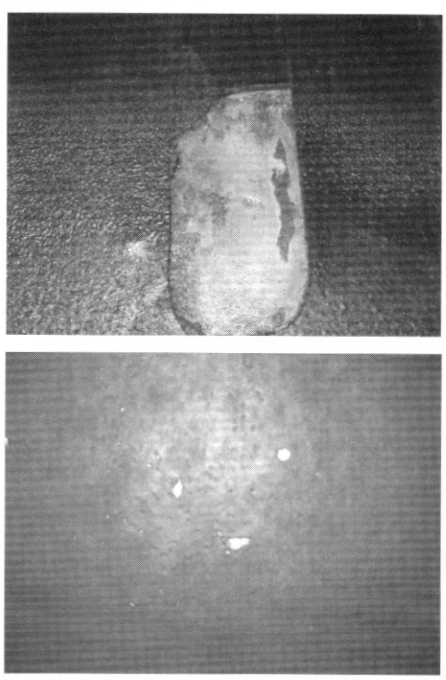


Fig. 7. Surface of carbon steel exposed by the coating failure (cathodically protected)

service in no less than 6 months.

4. The needs for coating properties

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 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 if it flows on the metal surface without coating because the extremely acidic solution has a high dissolution rates of metal ions as well as a high conductivity. The consumption rate of protection currents would be 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).[3] There are a series of epoxy Novolac system[4] and fluoric system coatings[5] that can

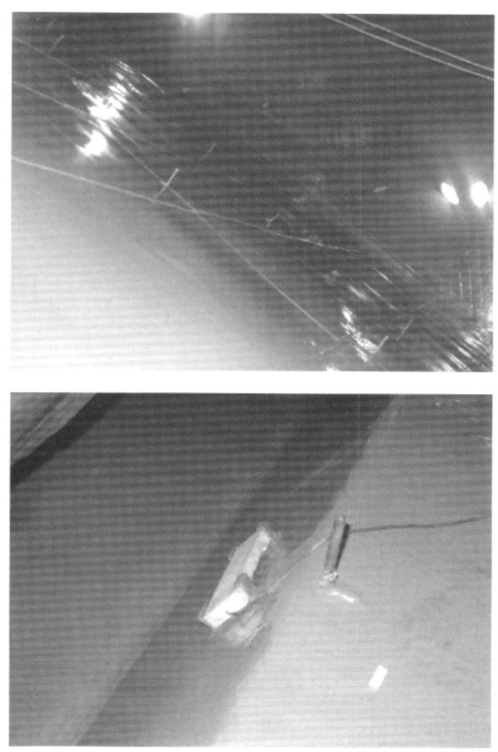


Fig. 8. Application of epoxy Novolac coating with CP anodes in FGD system

endure 60~70% of sulphuric 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[6](Fig. 8). 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 40 mils as a primer and 60 mils as a top coat.

5. Development of high performance coatings

This coating showed a good performance in 60~70 wt% of sulphuric acid and 150℃ of gas temperature. However, when it locally contacted with over 180℃ of gas, some of peel-offs and cracks were occurred (Fig. 9). It was analyzed that coating failure came from collision of the hot gas including highly concentrated gas phase sulphuric acid. It could be confirmed from the numerous crater shaped damages on the coating surface. Therefore, it was impossible to make the exact same environment that the coating was subjected to only with the immersion test in sulphuric acid.[7)-9)] New experimental methods were introduced such as the heat flux oven test, the dropping and the spraying test of hot sulphuric acid. Fig. 10 shows the

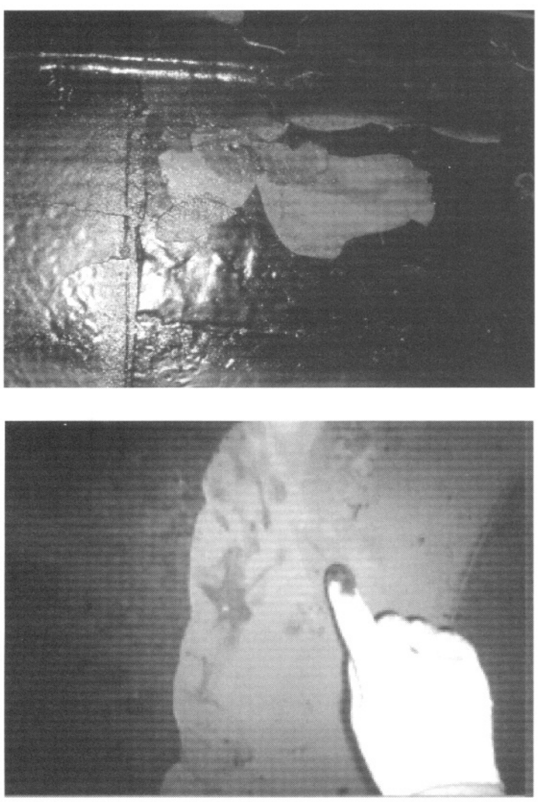
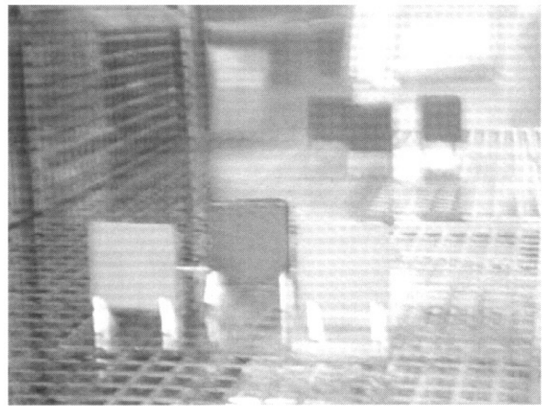
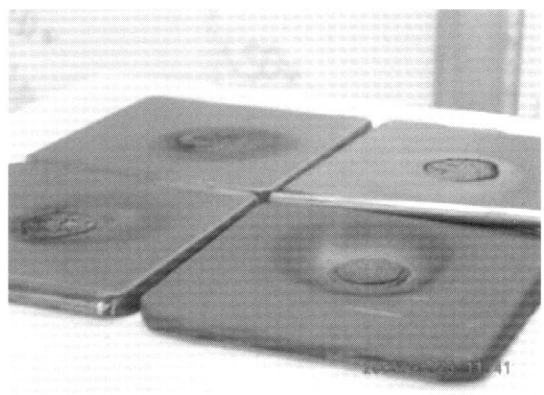


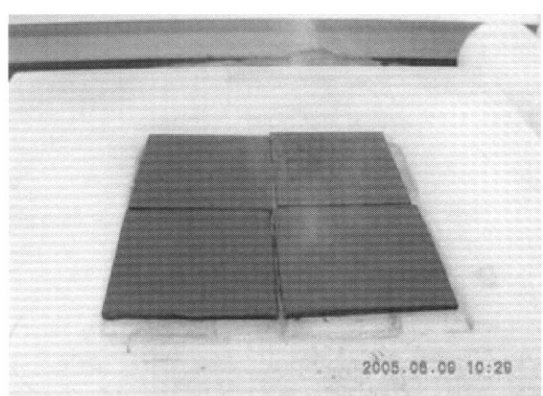
Fig. 9. Locally peel-offs and cracks occurred in high temperature gas



(a)



(b)



(c)

Fig. 10. New experimental methods: (a) heat flux oven test, (b) dropping test of hot sulphuric acid, (c) spraying test of hot sulphuric acid

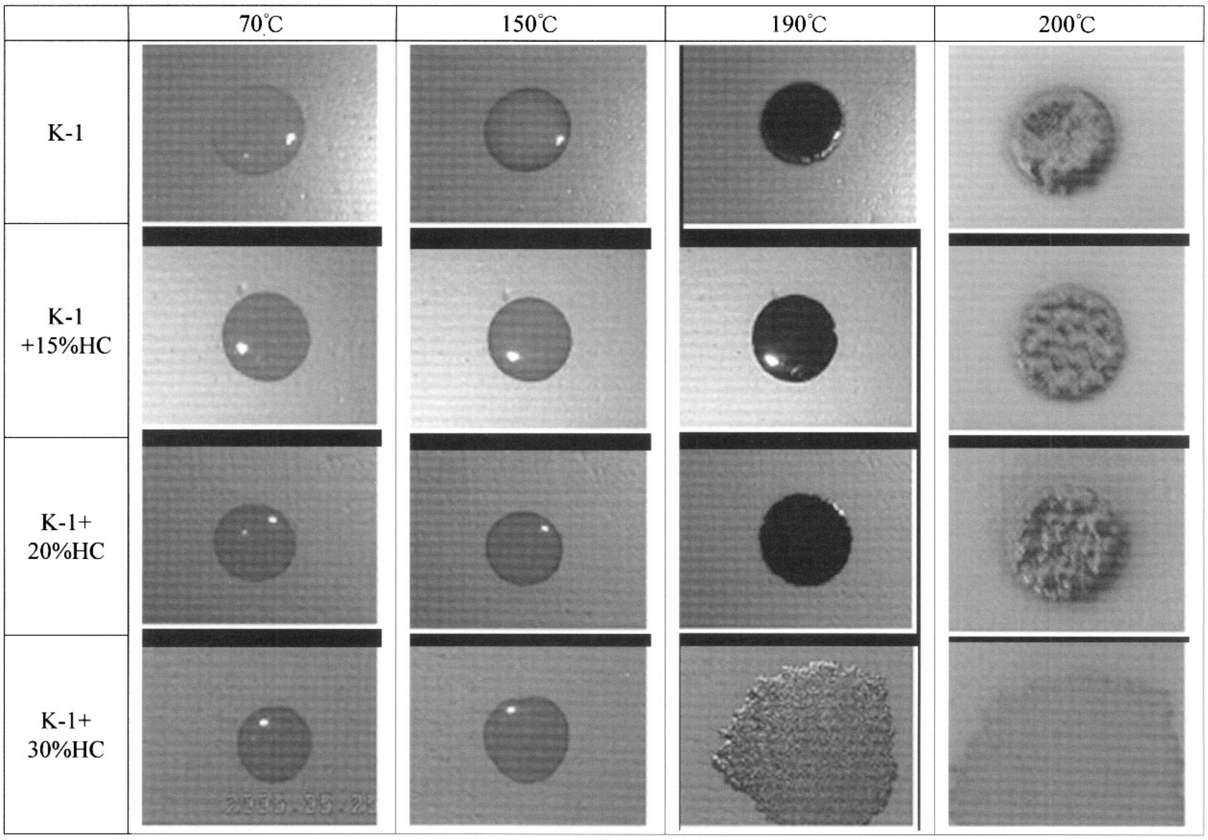


Fig. 11. The H_2SO_4(20%, up to 200℃)dropping test results of various newly developed epoxy Novolac coating materials varying with HC concentration.

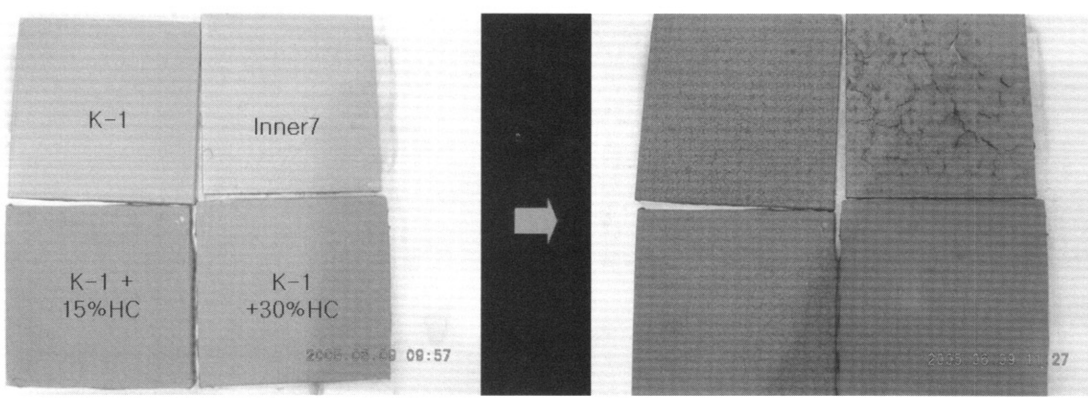


Fig. 12. The H_2SO_4(20%, 250℃) spraying test(1hour) results of various newly developed epoxy Novolac coating materials and commercial coating.

experimental apparatus of those new experiments.

Fig. 11 shows the result from the dropping test of various newly developed epoxy Novolac coating materials. K-1 is the originally developed epoxy Novolac coating and the others are modified ones with additives. As shown in this figure, the higher increases HC concentration, the lesser coating damages are occurred in high temperature. Especially the wettability of solvent is remarkably increased and the concentrated sulphuric acid is well dispersed on the coating surface. In Fig. 12, the results of spraying tests are shown for the newly developed epoxy Novolac coatings and the other commercial coating. The commercial coating(Inner 7) shows severe damage, but new coatings show better performances. The damage

Table 2. The summery of compositions and characteristics of newly developed fluoric composite coatings

	Compositions	Characteristics
FSP-1	Added silicon resin to improve adhesiveness	· Adhesiveness >100 kg/cm^2
FLC-1 FLC-2 FLC-3	Added mixed fluoric composite resin, Latex resin, and inorganic or organic fillers	· Hardening Temp. < 200°C · Similar heat and acid resistance properties with Teflon · Easy coating formation with heat flux
FRC-1	High content of fluoric resin	· Highest heat and acid resistance property · Needed hardening Temp. above 300°C and long hardening time

Table 3. The results of acid dropping test for newly developed fluoric composite coatings

Sample	Hardening	Results of acid dropping(60% H_2SO_4)			
		130°C	150°C	180°C	200°C
FC-1	OK	OK	Failed	-	-
FLC-1	OK	OK	OK	OK	OK
FLC-3	OK	OK	OK	OK	OK
FRC-1	OK	OK	OK	OK	OK

appearances are nearly same as those can be seen in the FGD system. However, in the long period of spraying test, it was concluded that epoxy Novolac coating was not appropriate for use in the temperature above 150°C of the FGD environment.

In order to endure above 180°C in this environment, new types of coating materials were formulated. The fluoric composite coating is composed of fluoric resin such as PTFE, PFA, FEP and inorganic or organic fillers. Brief composition and characteristics are summarized in Table 2.

The results of acid dropping test for newly developed fluoric composite coatings are listed in Table 3. These tests were performed using 60% sulphuric acid in various temperatures.

A couple of new coatings showed very high acid and heat resistance even in cyclic acid dropping of which time interval was 10 seconds. There was not any damage on the coating surface after the tests were performed, only showing white stains(Fig. 13)

For the proof of integrity in real time operation, these new coatings should have been tested in more severe environments. A pilot FGD plant was designed and manufactured for this purpose(Fig. 14).

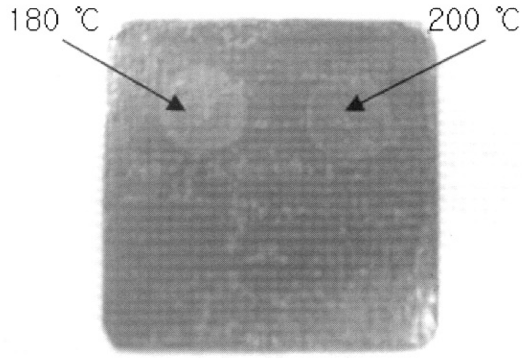
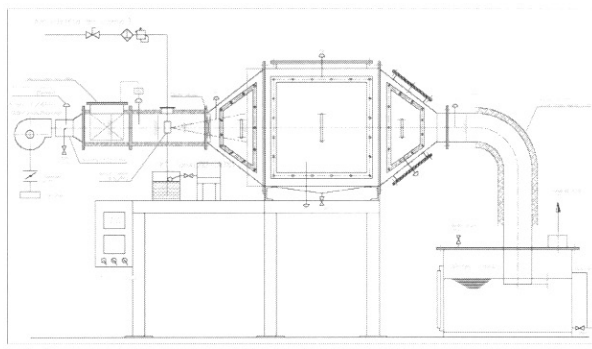


Fig. 13. Coating surface of fluoric composite coating(FLC-1) after acid dropping test in high temperature.



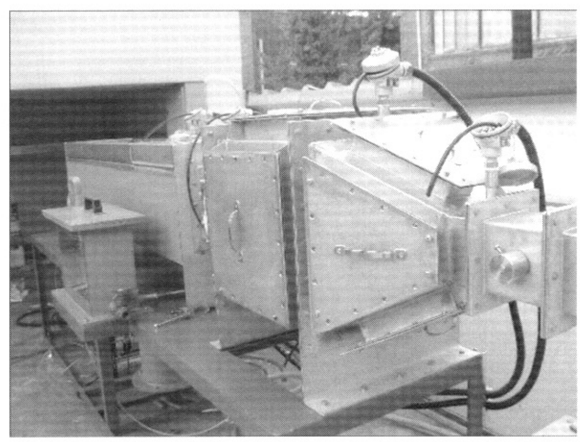
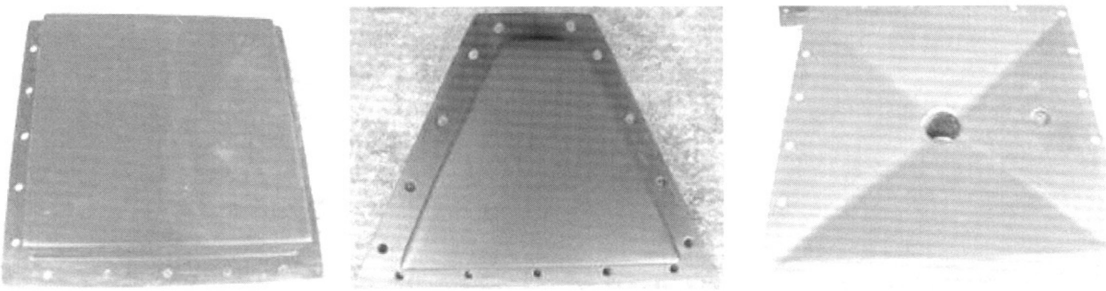


Fig. 14. Pilot FGD system for accelerated testing of coating deterioration.

In this experimental apparatus, 8 sides of reactor walls are designed to coat being used as specimens(Fig. 15). Spraying condition of sulphuric acid is shown in Fig. 16 and tests can be continued a few weeks to a few months.

Fig. 17 shows the pilot plant test result after 250 hours of epoxy Novolac coating comparing with that in the real FGD system. The damage patterns are similar to each other.



(a) (b) (c)

Fig. 15. Reactor walls coated with new coatings in pilot FGD system for accelerated testing of coating deterioration. (a) Side wall, (b) Hood bottom, (c) Drain bottom.

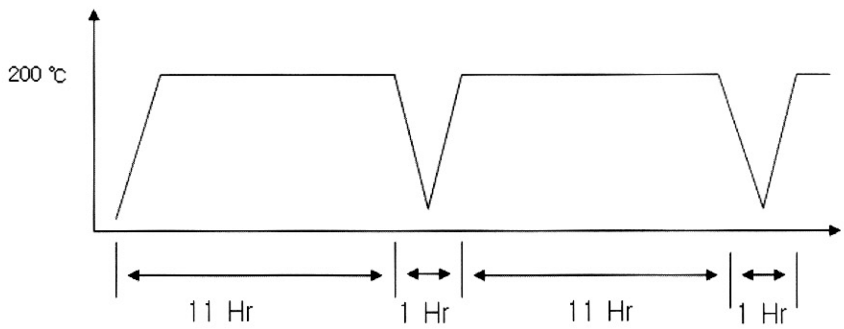
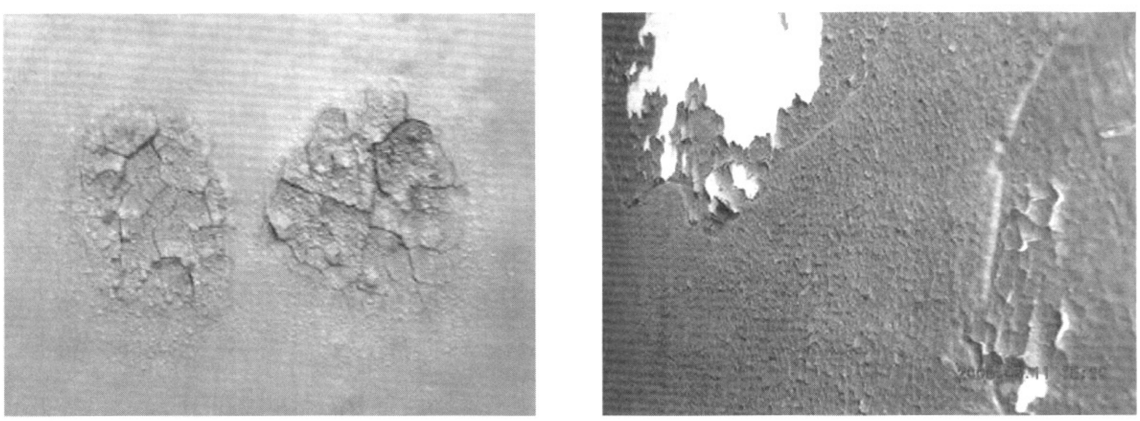


Fig. 16. Spraying condition of 20% sulphuric acid in pilot FGD system.



(a) (b)

Fig. 17. Result in pilot FGD plant test of epoxy Novolac coating((a) pilot FGD, (b) real FGD plant)

Pilot plant test results of FRC-1 after 250 hours are shown in Fig. 18. The coating was applied 3 times and the final thickness was 25~30 μm. White dots in this figure are sulphuric acid precipitates and no cracks and swellings are can't be seen. However, the edge close to bottom(drain side) is attacked by sulphuric acid and bare metal is exposed. The drain side coating is swelled. This is the result from the insufficient coating thickness and highly concentrated acid gathering in drain part.

Fig. 19 shows the comparing test results between FRC-1 and FLC-1. Half of the reactor's hood bottom side was applied by FRC-1 and the other by FLC-1. As can be seen in this figure, the bottom edge of FRC-1 is damaged and FLC-1 seems to be more resistant to acid and heat in this environment. The white sulphuric acid precipitates could be easily removed by scrubbing.

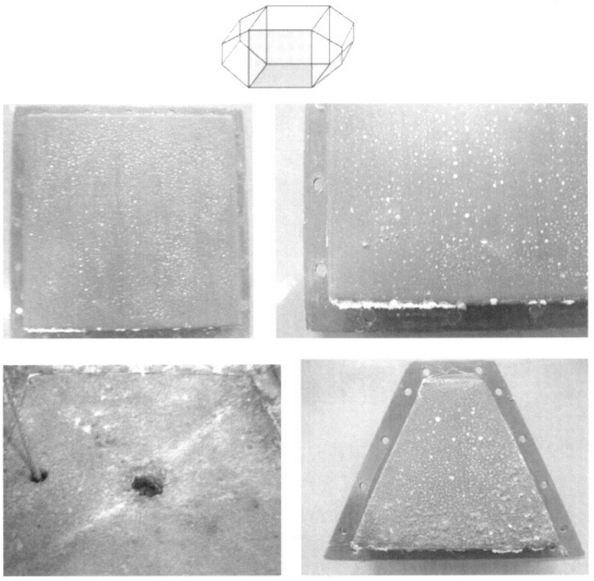


Fig. 18. Results in pilot FGD plant test of FLC-1 coating (Thickness = 25~30μm, 250 hours)

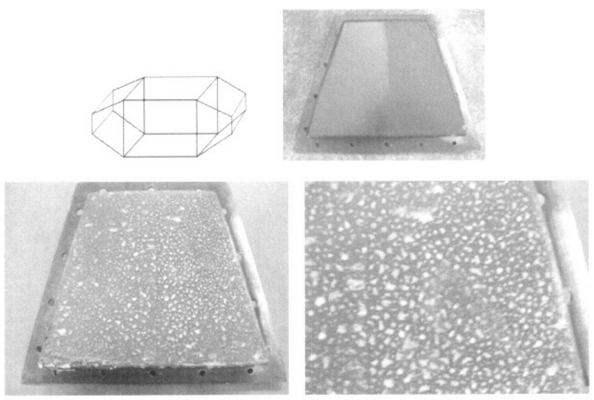
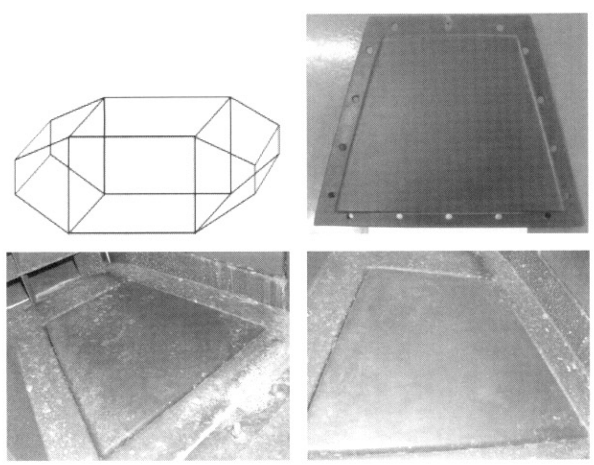
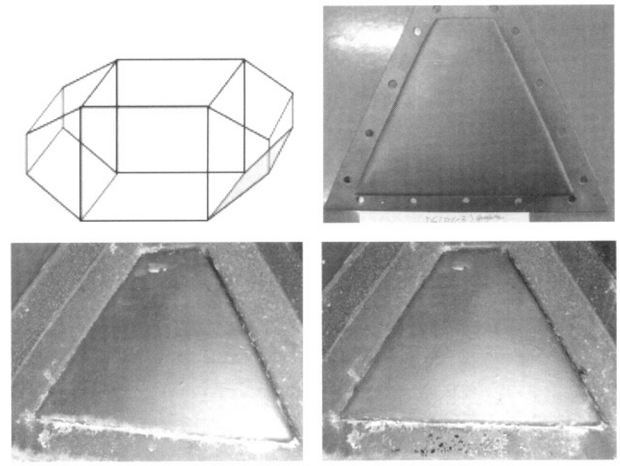


Fig. 19. Result in pilot FGD plant test of FRC-1 & FLC-1 (Thickness = 25~30μm, 250 hours)



(a) (b)

Fig. 20. Result in pilot FGD plant test of FLC-2 (carbon added, (a) 300 hours passed (b) 400 hours passed)



(a) (b)

Fig. 21. Result in pilot FGD plant test of FLC-3 (graphite added, (a) 300 hours passed (b) 400 hours passed)

FLC-2 and FLC-3 coating systems were developed in which carbon or graphite was added to FLC-1 in order to improve wettablitiy, acid and heat resistance. After testing total 400 hours, results are shown in Fig. 20 and Fig. 21. Thickness of these coating were also increased up to 220 μm to avoid the edge damage from thinning effect on edges. As shown in this figures, the surface of these coatings are clean and safe. It is expected that these coatings can serve over 2 years in the real FGD system environment.

In order to prove the integrity of FLC-2 and FLC-3 coating system, bench scale experiments are planning to perform soon, where these coatings will be applied to the some severest corrosive parts of the real scale FGD plant in power plants.

6. Results

1. A special kind of CP (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 being replaced by expensive stainless steels or super alloys.

2. Coatings for this CP system which was very stable against CP current were peeled off and cracked in some parts of facility that exceed the critical temperature of coatings, which made protection currents wasted and made CP control difficult.

3. Being considered workability and mechanical properties epoxy Novolac coating was applied in this study. 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 sulphuric acid for this coating.

4. In the long period of spraying test, it was concluded that epoxy Novolac coating was not appropriate for use in the temperature above 150℃ of the FGD system environment.

5. In order to endure above 180℃ in this environment, new types of coating materials were formulated. The fluoric composite coating is composed of fluoric resin such as PTFE, PFA, FEP and inorganic or organic fillers.

6. For the proof of integrity in real time operation, these new coatings should have been tested in the pilot FGD plant to simulate more severe FGD environment than real one. FLC-1 showed best performance in this environment. FLC-2 and FLC-3 were developed from FLC-1, and it was found that their performances were improved much.

7. It is concluded that the most important factor for FLC system to succeed in service for the real FGD plant during the required life time are the thickness of coating and satisfying the exact coating procedures.

References

1. ASTM C1432, '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', (2003).
2. ASTM E1172, 'Standard Practice for Describing and Specifying a Wavelength-Dispersive X-ray Spectrometer', (2001).
3. R. G. Schmidt and J. P. Bell, 'Advanced in Polymer Science', *Springer-Verlag*, **75**, 33 (1986).
4. R. G. Schmidt 'Studies on the adhesive properties of solid elastomermodified novolac epoxy resin', *International Journal of Adhesion & Adhesives*, **20**, 305 (2000).
5. G. Hougham, P. E. Cassidy, K. Johns, and T. Davidson, 'Fluoropolymers', Kluwer Academic/plenum Publishers, **2**, 647 (1999).
6. C. A. May, 'Epoxy Resins, Chemistry and Technology' 2nd., Marcel Dekker Inc. New York. Chap. **1**, (1988).
7. NACE TM0174, 'Laboratory Methods for the Evaluation of Protective Coatings Lining Materials in Immersion Service', (1996).
8. ASTM D5499, 'Standard Test Methods for Heat Resistance of Polymer Linings for Flue Gas Desulfurization', (1999).
9. ASTM C868, 'Standard Test Method for Chemical Resistance of Protective Linings', (1995).