
Using Electrochemical Protection to Prolong Service Life of Scrubbers and Associated Equipment

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Presented at the NACE CORROSION/98 Conference (Paper No. 477)
San Diego, California, March 1998

Austenitic chromium-nickel-molybdenum-iron alloys (904L, 316L, 317L, etc.) used to construct Flue Gas Desulfurization (FGD) scrubbers and associated equipment in coal fired generating stations can experience localized corrosion. The problem may be alleviated by using more costly materials such as higher grades of stainless steel or high nickel alloys. An alternative and more cost-effective method of prolonging equipment service life is the use of Papritection[®], an electrochemical protection system (EP). Weight-loss coupon results in environments similar to FGD scrubbers have shown that the use of electrochemical protection prolongs the life of stainless steels in oxidizing acid-chloride environments by an average of 3 to 5 times.¹

This paper discusses an EP system that was recently supplied to an electric power utility company to protect a 316L thin metallic lined (wallpapered) FGD scrubber reaction tank. Acidic effluent from the absorber section of the scrubber is piped into this reaction tank for limestone neutralization and hence formation of calcium sulfate. Inspection of the protected reaction tank after one year of operation as well as in-situ coupon test results indicated that the EP system was very effective in mitigating localized corrosion of the scrubber reaction tank. The results are presented in this paper.

Stainless steels owe their corrosion resistance primarily to chromium alloying. These alloys form a layer of protective oxide in oxidizing environments which prevents further rapid corrosion. The formation and domains of stability of the

protective layer on stainless steel may be determined by potentiodynamic polarization testing. The passive zone on the polarization curve represents the electrochemical conditions where neither localized corrosion nor active dissolution will occur (Figure 1). The

addition of molybdenum expands the passive zone thereby improving resistance to crevice corrosion and pitting although the cost of these higher alloys dramatically increases the price of construction.

Acid-chloride environments break down the passive layer and destroy the corrosion resistant property of stainless steel. The damage is usually in the form of pitting and crevice corrosion.² In extremely acidic (pH <1.5) and high chloride (Cl⁻ >5000 ppm) conditions, however, general corrosion may occur also.³ This attack may be more pronounced at or near weld areas due to the metallurgical changes associated with welding. Stainless steel with less than 4.7% Mo are more prone to this acid-chloride attack than those with greater than 6% Mo.⁴

In oxidizing acid chloride environments, the polarization curve of stainless steel changes as follows (Figure 1):

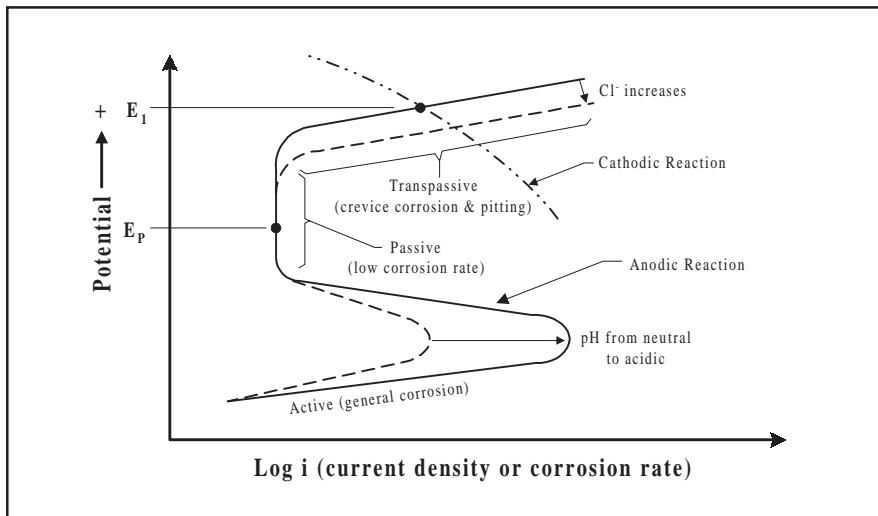


FIGURE 1 • Typical polarization curve showing the effects of pH and chloride. E_p is the protected potential and E_i is the potential where crevice corrosion and pitting occur.¹

- i) as chloride concentration increases, the width of the passive zone decreases and
- ii) as pH decreases from neutral to acidic, the active-passive transition becomes more pronounced.

Stainless steel in oxidizing acid-chloride environments will normally develop a solution potential (E_i) as depicted in Figure 1. By using a DC power supply, the potential of the metal can be moved electronegatively from its naturally occurring potential (E_i) to the passive region (E_p), repairing the passive layer and resulting in a reduction in localized corrosion.

Electrochemical Protection (EP) should be differentiated from conventional cathodic protection (CP) systems as the structure potential is shifted to the passive zone not to the immunity region as is required for cathodic protection. The amount of current required to apply conventional CP on stainless steel in oxidizing acid-chloride environments renders it impractical in most cases.

Experience in applying this technology in over 100 bleach plant washers in the pulp and paper industry indi-

cates that this method of prolonging FGD equipment is viable. Results using weight-loss coupons⁵ at Laramie River Station of the Missouri Basin Power Project indicate that EP is effective in virtually eliminating corrosion of stainless steel in FGD scrubber applications.

SPECIFICS OF THE PROTECTED REACTION TANK

The protected reaction tank is 19.5 m (64 feet) in diameter and 10.7 m (35 feet) high. The tank is carbon steel construction with a 1.6 mm (1/16 inch) thick 316L stainless steel thin metallic lining (wallpaper) installed on the

C	03 max
Mn	2.0
Cr	16-18
Ni	10-14
Mo	2-3
Si	0.1

TABLE 1 • Typical Percent Composition of Austenitic 316L Stainless Steel

inside wall. The floor is acid brick lined. The typical alloy composition of 316L stainless steel is listed in Table 1. The tank operates under slight positive pressure. The thickness of the four course carbon steel tank varies from 9.5 mm (3/8 inch) on the lowest course, to 7.9 mm (5/16 inch) on the second course and 6.3 mm (1/4 inch) on the third and fourth courses. The tank was constructed in the mid 1980's. Repairs were made recently due to corrosion perforation of the liner. The chemistry and operating conditions of the reaction tank are listed in Table 2.

The reaction tank receives an acidic feed from the absorber section of the FGD scrubber. Limestone (calcium carbonate) is added to the reaction tank to allow for the oxidation of calcium sulfite to calcium sulfate.⁶ Two agitators in the tank ensure rapid reaction between the limestone and the adsorbed sulfur compounds.

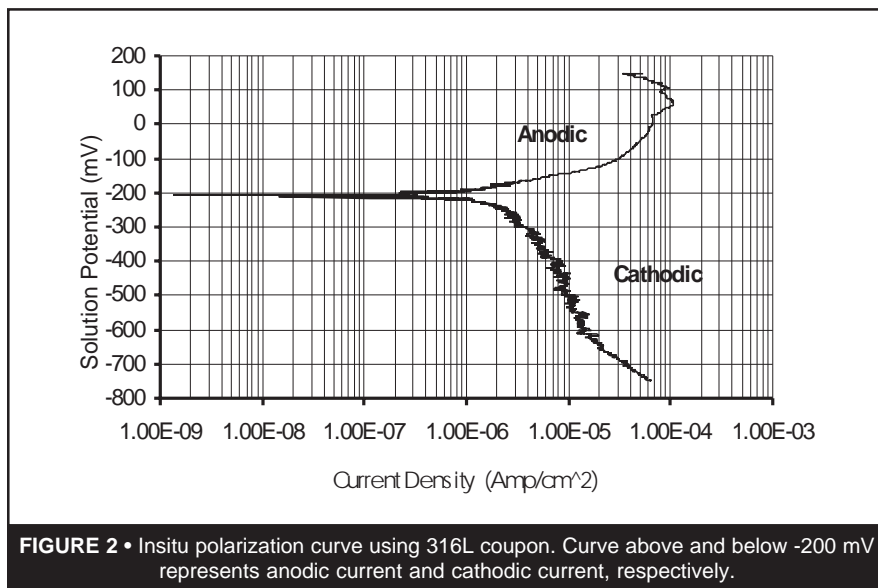
Design Considerations

Polarization curves were performed insitu to characterize the operating electrochemical conditions. A typical curve is shown in Figure 2. As previously discussed, application of a cathodic current to the reaction tank will shift the potential in the electronegative direction from the transpassive to the passive region. The curve shown

Chloride	5000-7000 ppm
pH	6
Temperature	140°F
Conductivity	47.2 X 10 ⁻⁶ Siemens

(Note: The tank operates under slight positive pressure.)

TABLE 2 • Normal Operating Condition of Reaction Tank Protected by Electrochemical Protection



is a composite of the anodic and cathodic polarization curves. The anodic portion of the curve represents metal oxidation. The oxidation reaction may be represented by the dissolution of iron (steel) as:



The cathodic portion of the curve represents the reduction reaction which is dependent on potential and electrolyte conditions. A possible cathodic reaction would be the reduction of dissolved oxygen (O₂) to hydroxyl (OH⁻) ion.

In addition to the polarization curve and potential measurements, the electrochemical protection design requires: magnitude of current density; current distribution calculations; voltage calculations, choice of suitable reference electrode and anode materials, and anode life calculations. The following is a brief description of these factors.

Current density is the amount of current per unit area that is required to protect the structure. A minimum current density is required to shift the potential by the amount required for protection.

To design for even current distribution in the reaction tank, structural geometry must be considered. The anodes must be placed strategically to balance current reaching all areas protected. A computer simulation was performed to determine the exact anode placement.

The voltage requirement is a function of the DC current output, number of anodes, length of anodes, length of DC cables, and conductivity of slurry in the tank.

The choice of reference electrode must be based on the electrode's potential stability and life. The anode material is chosen based on compatibility with the environment and maximum DC voltage applied. Anode life depends on chemical and physical characteristics of the anode material and the electrolyte.

EQUIPMENT

The DC current source was chosen based on the above design considerations. The selected unit requires a three phase 480 VAC input. It was supplied in a NEMA 4X enclosure. To

minimize DC cable lengths and keep the unit in a low traffic area, it was mounted on the reaction tank roof (Figure 3).

Anodes and reference electrodes were inserted from the tank roof in a symmetrical design. The vertical anode configuration provides more uniform current distribution to the vessel walls (Figures 3 to 6).

The positive output of the current source is connected to the anodes while the negative output is connected to the tank. One of the reference electrodes supplies a feedback potential to the current source. The current source operates in potential controlled mode. When the target potential is reached, the current source will automatically reduce current output to maintain the target potential in the passive zone of the metal. The additional reference electrodes are used as a cross-check and backup to the feedback probe.

To ensure the system operates with minimal down time, two monitoring methods were employed: i) by the operator, and ii) by a computer-modem based Remote Monitoring Unit

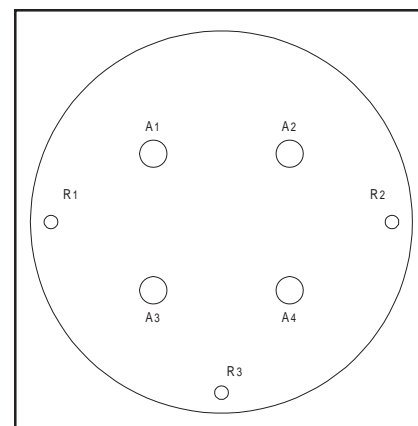


FIGURE 3 • Plan view of EP system anode and reference electrode arrangement on tank roof. This particular system depicts four anodes, A1 to A4, and three reference electrodes, R1 to R3.

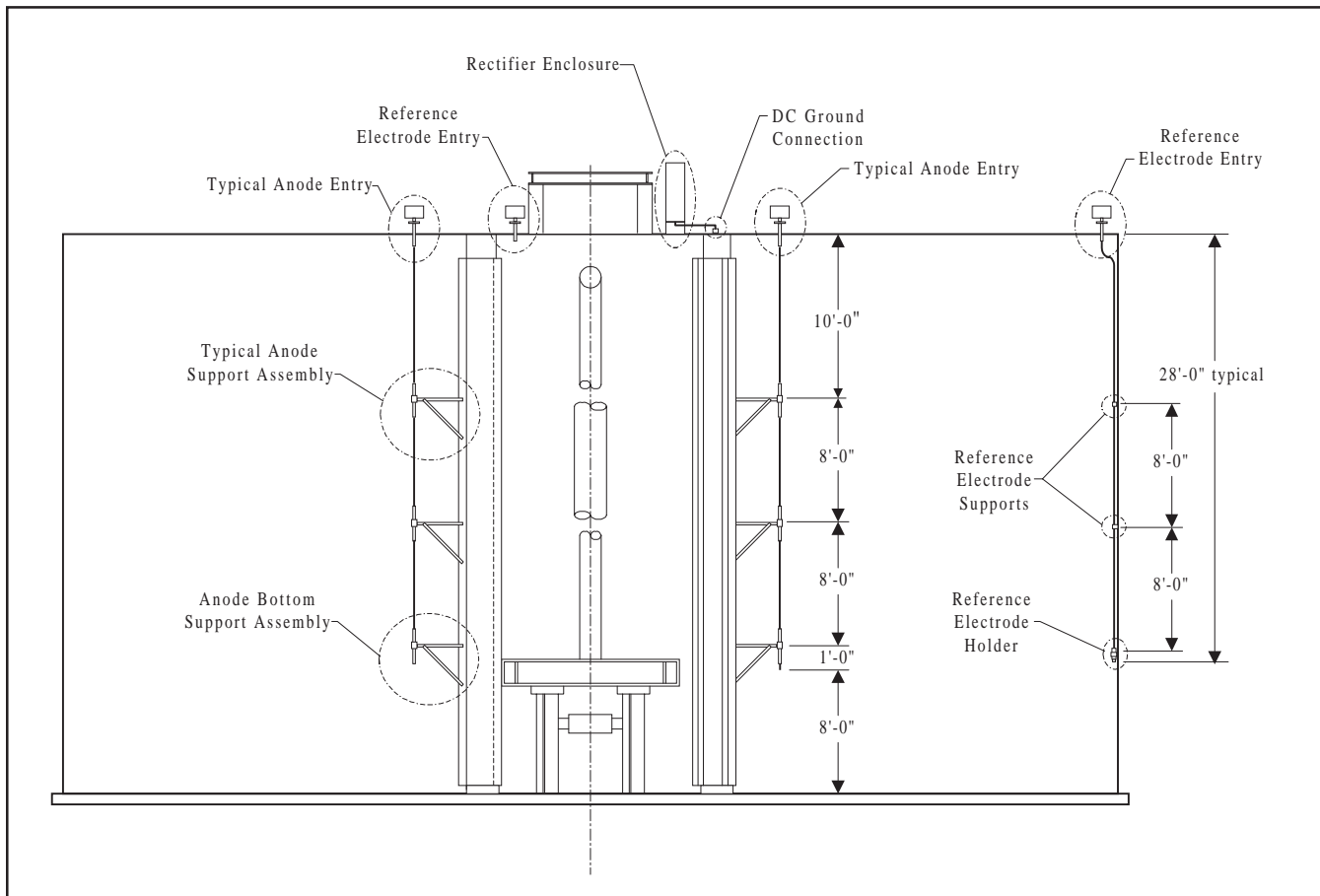


FIGURE 4 • General (EP) System Anode and Reference Electrode Arrangement in Reaction Tank

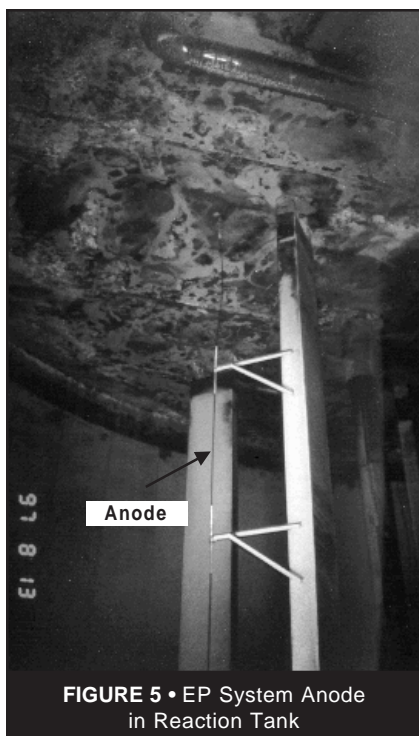


FIGURE 5 • EP System Anode in Reaction Tank

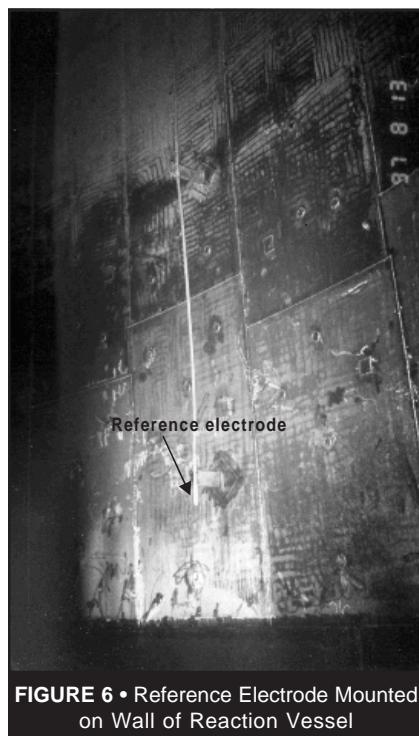


FIGURE 6 • Reference Electrode Mounted on Wall of Reaction Vessel

(RMU2). A warning signal is sent to the control room in the event of malfunction. To avoid nuisance alarms, a five minute delay was incorporated into the system design.

The RMU2 is housed inside the same cabinet as the current source and is supplied with state-of-the-art customized firmware that is programmed to the individual client's needs. Via a standard telephone line connected to the RMU2, the supplier monitors critical operating parameters of the system and immediately notifies the customer in the event of malfunction. Information from the RMU2 may also be accessed by customers using a PC operating Microsoft Windows®, a modem, and a custom software package. Figure 7 depicts a typical monitoring report.

Equipment Maintenance

The routine maintenance of the system is minimal. The anodes and reference electrodes are the only consumable items. The anodes are designed to have over 10 years of service life.

The replacement of anodes and reference electrodes requires scheduled down time, however, with coordination, the replacement can be scheduled during the normal maintenance shut-down.

RESULTS AND DISCUSSION

The potential measurement obtained using a reference electrode while the current source is operating has an “IR drop” component. This component always errs in the direction of readings that are more favorable than the true values. One established technique that has been used in the cathodic protection industry is to check for “off” (“rectifier off”) potential. The set potential must be adjusted to account for this IR error.

The protection system was energized in early April, 1996 and the target potential was achieved in less than 10 minutes. The set potential was set at about 75 mV more electronegative than the expected critical pitting potential.⁴

Coupon Results

A coupon set, consisting of two 316L coupons, was installed into the reaction tank. One coupon was connected to the tank and was therefore protected by the system, while the other coupon was left isolated as a *control*. At the end of a predetermined exposure period, the coupons were retrieved, cleaned, and checked for corrosion.

The first set of coupons was exposed from April, 1996 to August, 1996. No

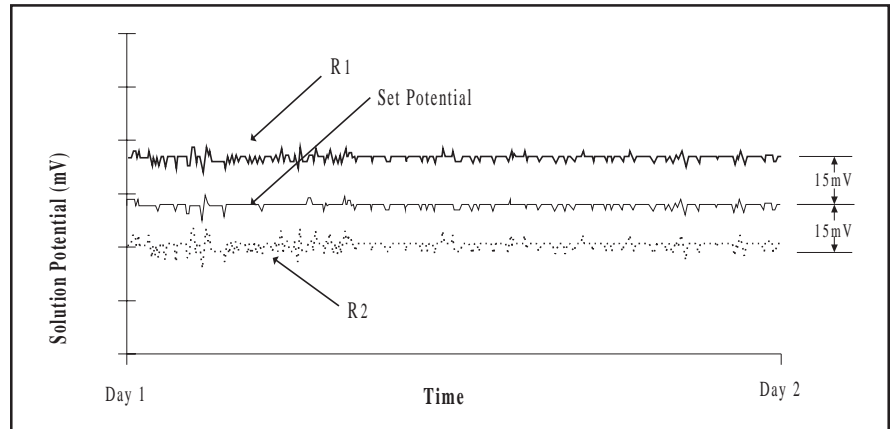


FIGURE 7 • Remote Monitoring Output Trending EP System Current and Voltage Over a Two Day Period



FIGURE 8 • Isolated 316L coupon (control) shows signs of crevice corrosion at the edge where a non-metallic washer was located. The crevice corrosion resulted in a ring above the stamped number “1” as indicated by uppermost arrow. Scattered pitting is shown by the two lower arrows.



FIGURE 9 • 316L coupon protected by EP system shows no signs of pitting corrosion after exposure in scrubber neutralization tank from January to July, 1997. Small amount of crevice corrosion was visible at the location where isolation washer was situated.

significant difference in corrosion rates between the two coupons was observed. It was suspected that the coupon holder was defective and the *control* coupon was inadvertently energized to the same potential as the protected coupon.

Another coupon set with a new holder was installed in January, 1997. In April, 1997 the coupons were retrieved and the customer reported that a black film was visible on the protected coupon. After cleaning off the black film, no sign of pitting was visible at 30 X magnification. A small amount of crevice corrosion was detected on the protected coupon. The isolated coupon showed severe crevice corrosion under the isolation

washer and scattered pitting on the surface. The coupons were reinstalled and retrieved again in July, 1997. No noticeable difference was apparent from the exposure from April to July, 1997 (Figures 8 and 9.)

INTERNAL TANK INSPECTION

A “tell-tale” system is used by the operators to detect leaks in the lining. Pipes are installed through the carbon steel wall and terminated at the carbon/stainless interface. The liquid emanating from these pipes is analyzed on a routine basis. A high chloride content in the liquid indicates that the stainless steel wallpaper has perforated.

As no high chloride containing liquid was detected, the internal thin metallic wallpaper was known to be intact. The tank was shutdown for inspection during August, 1997. Information received from the plant personnel indicated that very little repair was required, however, there were some areas on the stainless steel lining with reddish non-metallic deposits. Shallow pits were found beneath these deposits (Figure 10.)

Although the amount of red deposits, and resulting pitting, was relatively small, it was still a concern. Plant personnel assumed the source of red deposits to be steel filings from steel balls used to crush the limestone. The steel filings and the limestone are screened to -350 mesh and fed into the reaction tank. The suspension is mixed with the acidic scrubber effluent and neutralized in the tank. During this mixing with the agitator, the surface of the stainless steel wallpaper operates under very abrasive conditions. This abrasion also enhances pitting because it destroys the passive layer on the stainless steel and allows pitting to proceed.

A literature search^{7,8} indicated the possibility of thiosulfate ($S_2O_3^{2-}$) interaction causing pitting of stainless steel. The source of the thiosulfate may be a number of reactions of the sulfur compounds present. The general consensus from the literature is that by moving the potential another 150 mV in the electronegative direction, the pitting will be eliminated. The success of this change should be known sometime in 1998.



FIGURE 10 • Macrophotograph Showing Small Pits on the 316L Wallpaper Cladding Under Red Non-metallic Deposits

CONCLUSIONS

1. Electrochemical Protection has been used successfully in over 100 pulp mill bleach plant installations. The technology is applicable to FGD scrubbers and associated equipment.
2. Previous installations in FGD scrubbers were successful in mitigation corrosion.
3. After one year of operation, the tank inspection and coupon results showed that electrochemical protection system is providing corrosion protection to the reaction tank.
4. The present installation in the scrubber effluent reaction tank should prolong equipment life by at least 3 to 5 times.
5. Lowering the set potential should eliminate the small amount the pitting in the reaction tank, assuming that the attack is caused by thiosulfate.

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