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Electrochemical Corrosion Control of AL-6XN® Super-Austenitic Stainless Steel Flue Gas Desulfurization Scrubbers

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Abstract: *Flue Gas Desulfurization (FGD) scrubbers made of AL-6XN® super-austenitic stainless steel experienced premature through wall corrosion failure after 18 months of operation. Multiple remedial methods were evaluated. A PAP™ electrochemical corrosion prevention system supplied by Corrosion Service Company Limited was chosen and installed in the Spring of 2009. After 18 months of operation, internal scrubber inspection measurements showed corrosion was essentially halted.*

Introduction: Coal-fire generating stations that burn fuel with mid to high sulfur contents must use scrubbers to remove the SO_2 and SO_3 from the flue gas to meet EPA regulations. At Santee Cooper's Winyah Generating Station located in Georgetown, South Carolina, two Wheelabrator* scrubbers, Unit #1 and Unit #2, constructed of AL-6XN® were commissioned in 2007. AL-6XN® (UNS N08367) is a super-austenitic stainless steel, developed by Allegheny Ludlum Corporation, USA with the following composition[1]:

Table 1: AL6XN® Composition in Weight Percent (%wt)

Designation	UNS No.	C	Mn	Si	Cr	Ni	P	S	Mo	N
AL6XN®	N08367	.03	2.0	1.0	20.0-22.0	23.5-25.5	.04	.03	6.0-7.0	0.18-0.25

* Now Siemens Energy Inc., USA
PAP™ and Potential Adjustment Protection™ are registered trademarks of Corrosion Service Company Limited and the technology is patent pending.

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The high alloying content of AL-6XN®, especially the 6% molybdenum (Mo), gives the stainless steel its superior pitting and crevice corrosion resistance with superior resistance to chloride stress corrosion cracking as compared to the 300 series of austenitic stainless steels.

Unit #1 and Unit #2 are dimensionally identical scrubbers with a diameter of 52 feet and an overall height of 126 feet. The normal operating liquid height is 56 feet. The scrubbers utilize limestone slurry as the reagent and are designed to remove 97% of the SO_2 from the flue gas at a maximum inlet sulfur loading of 11,739 Lb/Hr. The design fuel is Eastern Bituminous with medium sulfur ranges of 1.0 – 2.5% (wt%) and chlorine ranges from 0 – 0.15% (wt%). Fluorine content was not specified in the technical specifications. Normal pH levels for the scrubbers are maintained between 5.5 – 5.6, however, they can range between 5.2 – 5.9 during upset conditions.

Observations: Within 18 months of putting the new scrubbers into operation, a through-wall penetration occurred in Unit #2 (Figure 1). The breach was close to the weld seam between the 1st and 2nd course from ground elevation and resulted in slurry leakage. Subsequent investigation pointed to pitting corrosion damage as being the cause. With an original 0.5625 inch wall thickness at that location, the corrosion rate is equivalent to 375 mils per year (mpy).

Figure 1: Through-wall corrosion damage after 18 months of putting a new scrubber into operation. Note brown staining below the damage.

Subsequent internal vessel inspection of both units showed extensive pitting damage below the liquid level. Pitting above the liquid level was either not observed or very minimal. The pitting appeared to concentrate at the Heat Affected Zone (HAZ) but base metal corrosion was also observed (See Figures 2 and 3). These findings were unexpected given that the super-austenitic stainless steel was tested to be immune to corrosion damage within the operating specifications of the scrubbers.

No corrosion damage was apparent in the weld crowns. The characteristic "scallops" on the welds were visible. The welding electrode used to join the AL-6XN® was ER NiCrMo-3 wire (Alloy 625).

Figure 2: Pitting damage on the side of a vertical weld seam after 18 months operation. Base metal pitting also visible at upper right area of photo.

Figure 3: Closer view of pitting corrosion at Heat Affected Zone (HAZ) of weld.

Scaling was extensive in the scrubbers. In general, the scales were either brown or black. When the scales were water blasted off, pitting was found to have occurred below both the brown scale and the black scale. The pitting damage morphologies were multifaceted. Some pitting was shallow and appeared to coalesce from multiple initiation points. Some pitting was of a “wormhole” nature where the loss of metal created a tunneling network that ran parallel to the plane of the wall. The extent of this “wormhole” damage was difficult to evaluate visually.

Initial forensic investigation eliminated the possibility that the pitting was caused by construction errors such as erroneous or out-of-specification alloy or inappropriate welding electrodes. The scrubbers were confirmed to be constructed as per design materials. Operational records showed little or no deviation from design specifications which eliminated the possibility that damage was caused by operation.

The concentrations of typical chemical species in the scrubber system are summarized in Table 2 and the operational characteristics are summarized in Table 3.

Table 2: Typical Chloride and Fluoride Concentrations in Winyah Scrubber

Chemical Species	Concentration
Chlorides	Up to 10,000 ppm
Fluorides	Up to 600 ppm

Table 3: Operational Characteristics of Winyah Scrubbers

Operational / Design	Specifications
Coal burned in boiler	Eastern Bituminous
pH	5.5
Temperature	129ºF (54ºC)
Oxidation	Forced air through horizontal headers in tanks
Wall thickness @ 0 to 16 foot elevation	0.5625 inch
Wall thickness @ 16 to 46 foot elevation	0.50 inch

Since the cause of damage could not specifically be linked to construction or operational issues but perhaps a combination of both, the logical solution was to incorporate a corrosion prevention system to prevent further damage. Following as exhaustive investigation, the management at Santee Cooper elected to use an electrochemical corrosion prevention system called PAP™ (also known as Potential Adjustment Protection™), supplied by Corrosion Service Company Limited (CSCL).

At the time Winyah station was considering the use of a PAP™ system, the technology had already been installed on 14 FGD scrubbers and 2 stainless steel brine concentrators in the United States dating back to 1979. All systems are still in operation today.

PAP™ is an electrochemical corrosion prevention system designed to protect stainless steels in acid chloride environments. Using a direct current source (See Figure 4) and anodes inserted into the scrubber, the electrochemical potential is moved in the negative direction into the "passive" zone.[2,3] The naturally occurring potential in the scrubber is very oxidizing and manifests itself as a very positive pitting potential in the polarization curve. The PAP™ technique differs from conventional cathodic protection systems where the structure potential is moved from active corrosion to metal immunity.

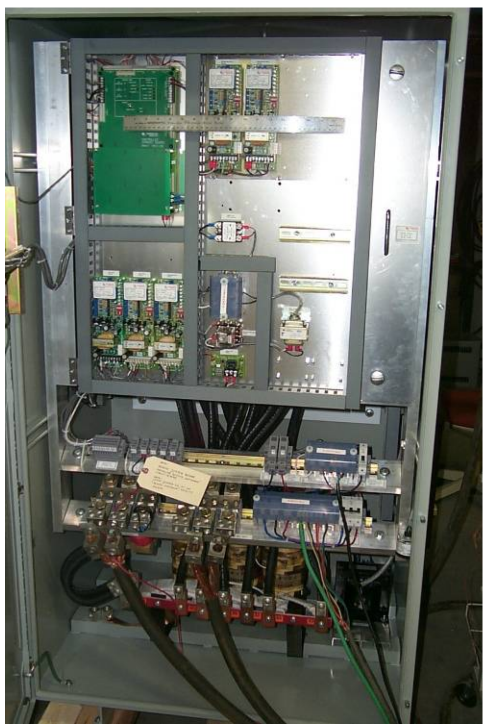

Figure 4: Internal of Custom Current Source

During the scheduled plant outage in the Spring of 2009, PAP™ systems were installed in both scrubber Unit #1 and Unit #2. The design used six anodes in each scrubber. The anodes were supported by the existing air sparger headers which minimized the mechanical work required to support the anode assemblies. PAP™ current output was controlled by feedback potential from multiple reference electrodes in the scrubber. A PAP™ system schematic is shown in Figure 5. Prior to system installation, some wall and floor repairs were completed in the scrubbers to address the very severe pitting damage, however, no repairs were carried out on shallow pitting.

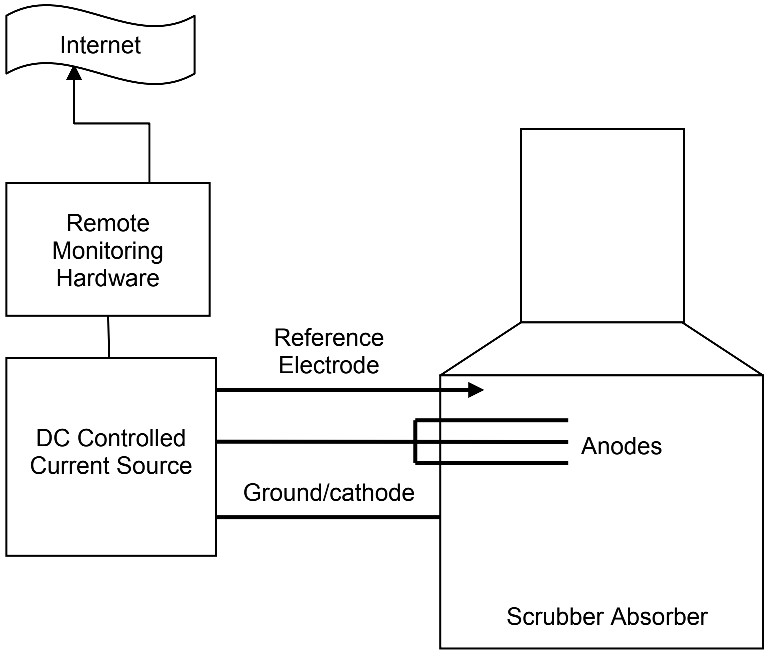

Figure 5: Schematic of PAP System Hardware with Remote Monitoring Equipment

Online retractable coupons were installed in the scrubber so that the effectiveness of the PAP™ system could be monitored without an outage. A set of two coupons made of the same metal as the scrubber (ie. AL-6XN®) were employed. One coupon was electrically connected to the scrubber and hence received the benefit of corrosion protection; the second coupon, used as a *control*, was installed in the same location as the first but electrically isolated from the scrubber. Crevice condition was pre-formed on the coupons by using non-metallic slotted disk washers. The electrochemical potential and other PAP™ operating parameters were monitored by a CSCL Remote Monitoring System (RMS). RMS is an extremely cost-effective way of having operating data reviewed regularly by experienced specialists. The front panel of a CSCL RMS unit is shown in Figure 6.

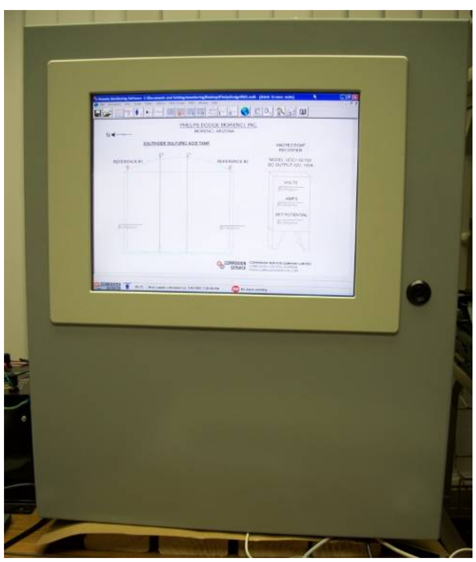

Figure 6: Typical Touch Screen Remote Monitoring Equipment

Over an 18 month period (from initial installation in the Spring of 2009 until the first outage in the Fall of 2010), the corrosion coupons were removed from the scrubbers via retractable probes every 15-60 days. Coupon monitoring allowed the effectiveness of the PAP™ system to be assessed prior to vessel entry. All coupons used at Winyah station were the slotted-disk type, with the non-metallic slots simulating crevices. Each set of coupons removed from the scrubber after a predetermined exposure duration was then replaced with a new set of coupons for another monitoring cycle. Upon removal, the exposed coupons routinely displayed black/brown scaling which was carefully cleaned to reveal the underlying condition. A typical coupon probe with the coupon head inside the scrubber is shown in Figure 7.

Figure 7: AL-6XN Coupons with Slotted Disk Installed to Gauge System Effectiveness during On-line Operation

Figures 8a & 8b show the first set of coupons that were exposed for 15 days following installation of the corrosion prevention system. The coupons clearly indicated the benefits of PAP™. The unprotected (i.e. *control*) coupon showed deep pitting, while the protected coupon was pristine. The corrosion rate of the pit on the unprotected coupon, shown in Figure 8c, was approximately 240 mpy (i.e. 9.8 mils in 15 days). At this rate, the 0.5 inch thick scrubber wall would be penetrated in about 2 years, which is consistent with observations in Unit #2 which suffered penetration after 18 months.

Figure 8a: Protected AL-6XN coupon after 15 days exposure. No signs of corrosion. Brown lines are stains on coupon. Coupon dimensions: 1 ¼ inch dia.; 1/8 inch thick

Figure 8b: Unprotected AL-6XN coupon after 15 days exposure. Three visible pits, with a maximum depth of 0.25 mm (250 mpy corrosion rate). Pit circled in yellow is magnified in Figure 8c.

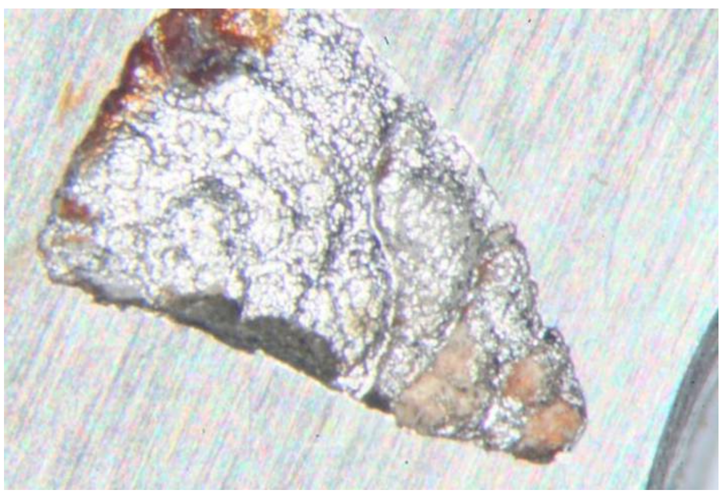

Figure 8c: Magnification of Pitting Damage encircled in Figure 8b.

The coupons shown in Figures 9a, 9b and 9c were subjected to a 43-day exposure. These coupons, and multiple sets of other coupons utilized prior to the outage in 2010, exhibited similar results and led to the conclusion that the PAP™ system was indeed effectively protecting the scrubber as designed. Coupon monitoring is a very accurate and flexible method of determining the "protected" and "unprotected" corrosion rates of a vessel, in that exposure durations can be altered and an accurate corrosion rate still ascertained.

Figure 9a: Protected AL-6XN coupon after cleaning. Slight discoloration where staining and deposits were present; no crevices. 43 day exposure. Coupon dimensions: 1 ¼ inch dia.; 1/8 inch thick

Figure 9b: Unprotected AL-6XN coupon cleaning. Stains largely eliminated, pits still visible. Pit circled in yellow is magnified in Figure 9c.

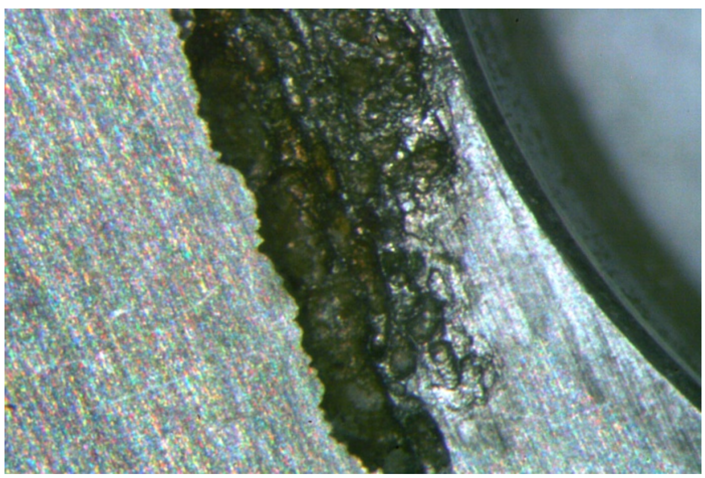

Figure 9c: Magnification of Pitting Damage encircled in Figure 9b.

Figure 10 depicts the layout of the anodes below the air sparger support. The reference electrode tip is shown in Figure 11.

Figure 10: Anodes Installed beneath Air Sparger Support Steel.

Figure 11: Reference Electrode Installation

During the Fall 2010 Winyah Station planned outage, the two scrubbers were available for personnel entry. Inspection measurements confirmed that the pitting corrosion was essentially halted by the PAP^{TM} system in both vessels.

Conclusions:

1) Following 18 months of the corrosion prevention system operation, inspection measurements showed that the accelerated 375 mpy corrosion rate of the Santee Cooper AL-6XN® scrubbers had essentially been halted.

2) The use of corrosion coupons is a very accurate and flexible method of checking corrosion rates without requiring a scrubber outage.

3) A remote monitoring system (RMS) is an extremely cost-effective way to have experienced corrosion specialists review system operating data on a regular basis.

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