Epoxy Vinyl Ester Polymer Lining for Flue Gas Desulfurization Absorber Modules

Heather M. Ramsey, *Sauereisen, Pittsburgh, Pennsylvania*
Don H. Kelley and Thom L. Johnson, *Ashland, Inc., Dublin, Ohio*

To meet more stringent EPA guidelines, coal-fired power plant owners must now build or retrofit their facilities with flue gas desulfurization (FGD) systems. A critical part of these systems is the FGD absorber. Common building materials for absorbers have been duplex UNS S32205/S31803 and UNS S32550 alloys. UNS S32205/S31803 alloy is showing signs of premature corrosion. A repair regimen is sorely needed. This article discusses UNS S32205/S31803 alloy corrosion and methods to rehabilitate and protect old and new absorbers with epoxy vinyl ester polymer lining.

Flue gas desulfurization (FGD) has been around for more than 100 years. More recently, the concept of cleaning the exhaust flue gas has become widespread globally. Initially started in England, removing the sulfur dioxide (SO_2) from exhaust flue gas is practiced in the United States, much of Europe, China, Japan, and a host of other countries. Wet FGD units are able to remove 95% or more of the SO_2 from flue gas and are therefore extremely attractive for the neighboring communities and the environment as a whole. Duplex UNS S32205/S31803 alloy has been extensively used in FGD absorbers. This alloy is generally known to be corrosion resistant, but the industry has seen widespread occurrence of chemical attack on FGD absorbers constructed from this material. This article discusses UNS S32205/S31803 alloy corrosion and ways to rehabilitate old absorbers and protect new ones with corrosion-resistant epoxy vinyl ester polymer linings. Proper cleaning, surface preparation, application, and polymer lining choice are covered.

FGD Process, Construction, and Absorber Attack

There are several different FGD systems available for a power plant to select, each with its own pros and cons. Most FGD systems employ two stages to clean the flue gas: 1) removal of fly ash and 2) removal of SO_2. In wet FGD systems (Figure 1), the flue gas first goes through fly ash removal. This process is typically conducted with either an electrostatic precipitator or a wet scrubber. The flue gas then passes into the second stage, the carbon dioxide (CO_2) absorber. These absorbers, often constructed with duplex UNS S32205/S31803 alloy, are subjected to the highly corrosive environment of the FGD scrubbing process.

In the wet scrubber process, the acidic flue gas passes into the absorber module and is quenched with an alkaline sorbent of either limestone ($CaCO_3$), lime [$Ca(OH)_2$], or magnesium hydroxide [$Mg(OH)_2$]. The sorbent reacts with the SO_2 and yields a precipitate along with CO_2 gas or water (H_2O) byproducts. In some facilities, the FGD installation cost can be partially offset when the calcium sulfite ($CaSO_3$) precipitate is further oxidized into gypsum ($CaSO_4 \cdot 2H_2O$) and then sold to wallboard manufacturers (Equations [1] through [4]).

$$CaCO_3\text{ (solid)} + SO_2\text{ (gas)} \rightarrow CaSO_3\text{ (solid)} + CO_2\text{ (gas)} \quad (1)$$

$$Ca(OH)_2\text{ (solid)} + SO_2\text{ (gas)} \rightarrow CaSO_3\text{ (solid)} + H_2O\text{ (liquid)} \quad (2)$$

$$Mg(OH)_2\text{ (solid)} + SO_2\text{ (gas)} \rightarrow MgSO_3\text{ (solid)} + H_2O\text{ (liquid)} \quad (3)$$

$$CaSO_3\text{ (solid)} + H_2O\text{ (liquid)} + \tfrac{1}{2}O_2\text{ (gas)} \rightarrow CaSO_4\text{ (solid)} + H_2O \quad (4)$$

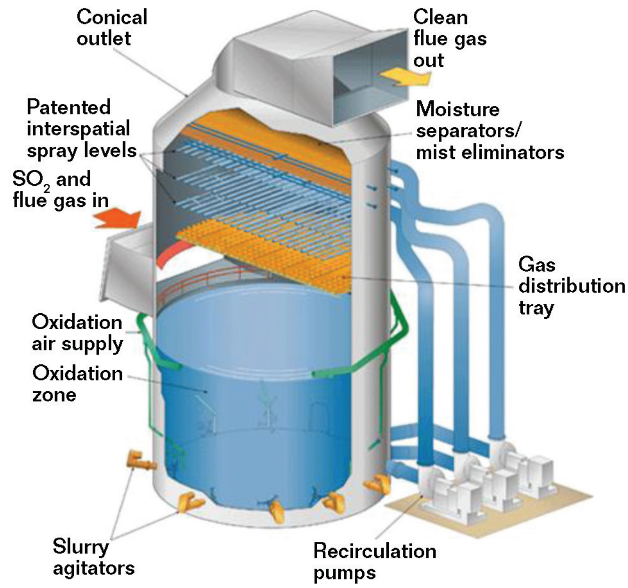

FIGURE 1 Wet flue gas desulfurization system. © 2012, The Babcock & Wilcox Co.

Because of cost, many utilities opt for a simple spray tower absorber rather than more complicated and expensive designs. These spray towers can be horizontal or vertical with the flue gases flowing cocurrently, counter-currently, or cross-currently with respect to the sorbent liquid. Whatever the design of the absorber, duplex UNS S32205/S31803 alloy is a typical construction material.

UNS S32205/S31803 alloy is called a duplex because it contains nearly equal portions of ferrite and austenite. It was first employed in Sweden for the sulfite paper industry, where the alloy was designed to resist corrosion from chloride-bearing cooling waters and other aggressive chemicals. The alloy composition (22% chromium, 3% molybdenum, and 5 to 6% nickel) enables it to be manufactured and sold at a significantly lower price than other stainless steels (SS). This has rapidly made it a workhorse SS product. The composition also helps to make this alloy's general, localized, and stress corrosion resistance relatively robust. Laboratory and early field studies demonstrated excellent resistance to scrubber environments with up to 10,000 ppm chloride, pH down to 5.5, and temperature reaching 130 °F (54 °C). Unfortunately, however, even with all these promising early data, the aggressive chemical environment found in FGD absorbers soon crippled the UNS S32205/S31803 alloy material.[1-2]

The U.S. utility industry has discovered aggressive corrosion in an alarming number of new and slightly older wet FGD units. The new facilities can range in age from three years to only three months. The corrosion is so severe in some FGD units that through-wall vessel leaks have been observed in less than one year of service. Though the root cause of the corrosion is still under debate, it is believed to largely be caused by acid condensates forming during the FGD process, which accelerate pitting and crevice corrosion. This acceleration is especially true in scrubbers with high sulfate and chloride solution concentrations. Early investigations have shown that the corroded systems seem to be forced-oxidation systems designed with UNS S32205/S31803 alloy.

The Electric Power Research Institute (EPRI) has indicated that of the roughly 365 FGD systems in the United States, at least 20% utilize UNS S32205/S31803 alloy and in major components of the FGD system.[3] The chemical environment, and therefore the corrosion, varies from one system to another because of factors such as dew point, acidity, high temperature, chloride and fluoride concentrations, wet-dry cycles, and gas velocity, even if the FGD systems are similarly designed from a materials standpoint. Epoxy vinyl ester polymer protective linings are able to combat a range of different chemical and abrasive environments and thus are ideal for use in FGD systems to protect materials such as the UNS S32205/S31803 alloy.[4-6]

Epoxy Vinyl Ester Polymer Lining

Epoxy vinyl ester resins have been used for wet FGD processes in absorber vessels, slurry piping, ductwork, and stack liners dating back to the early 1970s. The most prominent applications are limestone slurry piping followed by stack liners. FRP pipe based on epoxy vinyl ester resin has been successful in more than 150 plants dating back to 1977. In fact, during the period from 2004 to 2010, epoxy vinyl ester-based FRP was used in more than 70 stack liners, 75 limestone slurry piping systems, and over 25 FGD scrubbers. All of these systems are still in service today.[6]

FIGURE 2 Conventional spray application of epoxy vinyl ester polymer lining.

The same epoxy vinyl ester resin technology is employed in flake glass lining systems. Epoxy vinyl ester systems are specially designed to withstand the low pH, aqueous chloride environment commonly found in FGD absorbers. In fact, these polymers are frequently employed for corrosion control in much more aggressive chlorine environments such as sodium hypochlorite (NaClO) (bleach) and hydrochloric acid (HCl). It would be rare to find SS in the same environments.[6]

Selection, Surface Preperation, and Application

Selection

There are a variety of epoxy vinyl ester resin chemistries available because no one polymer can handle all chemical environments. Every job's environment must be analyzed to determine the most suitable epoxy vinyl ester polymer lining. The recommendation and selection of the epoxy vinyl ester resin must not only take into account the chemical environment, but also the physical environment such as high temperatures, temperature cycling, and abrasive material flow. Furthermore, field service case histories, laboratory and field tests, and the knowledge of trained scientists all go into making the proper selection of an epoxy vinyl ester resin. The proper resin for the specific job is needed, not a resin that can do every job.

Often epoxy vinyl ester resins are mistaken for or interchangeably referred to as polyester resins. The two resins, however, are significantly different in chemical makeup. Epoxy vinyl ester resins have improved mechanical properties such as better thermal shock and impact resistance. Within the family of epoxy vinyl ester resin systems, there are both bisphenol A and novolac modified epoxy vinyl ester resins. The novolac modified epoxy vinyl ester resin has a different chemical structure from the bisphenol A epoxy vinyl ester resin, which enables it to withstand higher temperatures as well as a more severe chemical environment.

Surface Preparation

Proper and complete surface preparation is absolutely necessary for a successful and lasting protective lining application. For the UNS S32205/S31803 alloy FGD absorber, a typical surface preparation program begins with abrasive blasting to a white metal surface (NACE No. 2/SSPC-SP 10[7]). An aggressive profile of nominally 3 to 4 mils (76 to 102 μm) is recommended. After abrasive blasting is complete, the surface must be checked for chlorides or other contaminants. If any contaminants are found, they must be removed by application of a contaminant removal solution per the manufacturer's instructions. Once all contaminants are gone, the surface of new UNS S32205/S31803 is ready to be coated. Absorbers that are being rehabilitated might have pitted surfaces so severe that they need to be filled and patched with a material compatible with the protective epoxy vinyl ester lining.

Application

At one time, the traditional application method was a hand-laid, trowel-applied lining. More contemporary application methods utilize airless spray equipment. All resin system components are mixed together per the manufacturer's directions and applied using atomizing spray technology (Figure 2). This method allows for a faster and more accurate application of material. The application man-hours are greatly reduced as are the overages generally associated with trowel-applied linings.

Catalyst-injected plural-component spray application is yet another method that can keep application times to a minimum and deliver material in a precise manner. With the catalyst-injected plural component application, the epoxy vinyl ester resin is first promoted and then a catalyst is injected into the spray stream at the nozzle. One factor for selecting the coating system is knowing which type of application process the contractor is using. Some epoxy vinyl ester resin systems are not designed for plural-component spray rigs.

Conclusions

The absorbers of wet FGD systems fabricated with duplex UNS S32205/S31803 alloy SS are showing significant premature corrosion. One way to combat the corrosion is to rehabilitate the corroded absorber unit with an epoxy vinyl ester polymer lining after proper surface preparation. The selection of epoxy vinyl ester resin must be specific to the chemical and physical environment present in the absorber and can be applied in a variety of methods per the epoxy vinyl ester manufacturer's recommendation. Newly constructed UNS S32205/S31803 absorbers should also be lined with an epoxy vinyl ester polymer lining to minimize future corrosion. Protecting FGD absorbers constructed of duplex UNS S32205/S31803 alloy is instrumental to both maintaining an efficient power plant as well as delivering better air quality to the surrounding communities.

References

1 I. Alvarez-Armas, "Duplex Stainless Steels: Brief History and Some Recent Alloys," *Recent Patents on Mechanical Engineering* 1 (2008): pp. 51-57.

2 M. Moskal, "EPRI Corrosion of Wet Flue Gas Desulfurization Systems," *The Conduit* 11, 1 (2011): pp. 1-2.

3 "Corrosion in Wet Flue Gas Desulfurization (FGD) Systems: Technical Root Cause Analysis of Internal Corrosion on Wet FGD Alloy Absorbers," Product ID: 1024920, April 30, 2012.

4 KKC Corrosion Control, "Advanced Coatings Protect Plant FGD Systems," *POWER,* September 1, 2011, http://www.powermag.com/Advanced-Coatings-Protect-Plant-FGD-Systems/ (Sept. 3, 2012).

5 J. Shingledecker, C. Dene, B. Tossey, "Accelerated Corrosion in FGD Systems," *Energy-Tech,* November 2011, http://www.energy-tech.com/article.cfm?id=31783 (Sept. 3, 2012).

6 T. Johnson, D. Kelley, M. Stevens, "The Rapid Growth of Fiberglass Reinforced Plastic (FRP) in FGD Systems," Second International EPRI Conference on Welding and Fabrication Technology for New Power Plants and Components held June 21-24, 2011 (Palo Alto, CA: EPRI, 2011).

7 NACE No. 2/SSPC-SP 10, "Near-White Metal Blast Cleaning" (Houston, TX: NACE International, 2007).

This article is based on CORROSION 2013 paper no. 2105, presented in Orlando, Florida.

HEATHER M. RAMSEY

DON H. KELLEY

THOM L. JOHNSON is the corrosion industry manager at Ashland Performance Materials, 5200 Blazer Pkwy., Dublin, OH 43017, e-mail: tljohnson@ashland.com. He began his career at Dow Chemical as a research chemist 35 years ago and has held his current position at Ashland for the last nine years. He has worked in the areas of research, product development, commercial development, and business management at both companies. He is extensively involved in the corrosion fields of water treatment, industrial coatings, and most recently, fiber-reinforced composites. He has a B.S. degree in chemistry from Central Michigan University, an M.S. degree in business from DePaul University, and is a member of NACE International. MP