Epoxy Vinyl Ester Polymer Lining for Duplex UNS S32205/S31803 Alloy FGD Absorber Modules

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ABSTRACT

In order to meet more stringent EPA guidelines, the coal-fired power industry must now build or retrofit their facilities with flue gas desulfurization (FGD) systems. A critical part of these systems is the FGD absorber. A common building material for the absorbers has been duplex UNS S32205/S31803 and UNS S32550 alloys; however, the UNS S32205/S31803 alloy is showing signs of premature corrosion throughout the industry. The root cause of this corrosion is still under investigation, but with some absorbers lasting less than 18 months, a repair regimen is sorely needed. This paper will discuss the issues surrounding UNS S32205/S31803 alloy corrosion as well as methods to rehabilitate and protect both old and new absorbers with epoxy vinyl ester polymer lining. The paper will also review the proper cleaning, surface preparation, application process, and choice of epoxy vinyl ester polymer lining to protect UNS S32205/S31803 alloy and prevent its premature breakdown in this environment.

Key words: Flue gas desulfurization, FGD, flue gas, desulfurization, absorbers, duplex UNS S32205/S31803 alloy, epoxy vinyl ester polymer lining, vinyl ester

INTRODUCTION

Though the idea and implementation of flue gas desulfurization (FGD) systems has been around for over 100 years, it wasn't until more recently that the concept of cleaning the exhaust flue gas of fossil-fuel power plants became more widespread globally. Initially started in England, today systems that remove the SO_2 from exhaust flue gas are found in the United States, much of Europe, China, Japan, and a host of other countries. Wet FGD units are able to remove 95 percent or more of the SO_2 from flue gas and are therefore extremely attractive for the neighboring communities and the environment as a whole. One particular stainless steel, duplex UNS S32205/S31803 alloy, has been extensively used in the construction of FGD absorbers. This alloy is generally known to be corrosion resistant, however, the industry has seen widespread occurrence of chemical attack on FGD absorbers constructed from UNS S32205/S31803. This paper will discuss the issues surrounding UNS S32205/S31803 alloy corrosion as well as ways to rehabilitate old absorbers and protect new ones through the use of corrosion resistant epoxy vinyl ester polymer linings. Proper cleaning, surface preparation, application, and polymer lining choice will also be discussed.

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, the flue gas first goes through a fly ash removal stage. This process is typically conducted with either an electrostatic precipitator or a wet scrubber. The flue gas then passes into the second stage, which is the SO_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 carbon dioxide (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 into wallboard manufacture (1-4).

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

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

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

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

Due to 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, countercurrently, or crosscurrently with respect to the sorbent liquid. Whatever the design of the absorber – horizontal or vertical – duplex UNS S32205/S31803 alloy is a typical construction material.

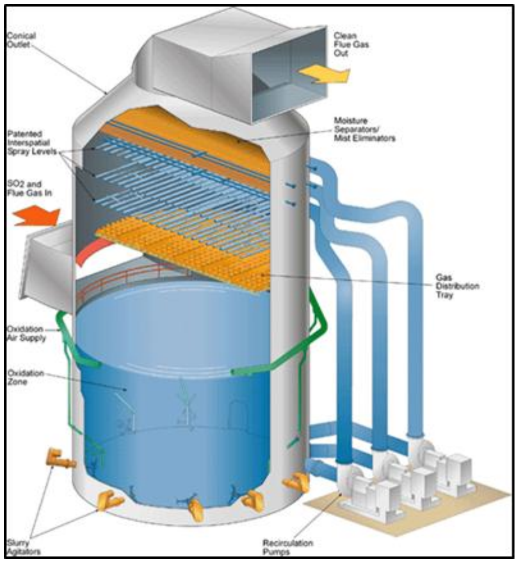

Figure 1: Wet flue gas desulfurization system.[1]

The UNS S32205/S31803 alloy is called a duplex due to the fact that 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 5-6% nickel) enables UNS S32205/S31803 to be manufactured and sold at a significantly lower price than other stainless steels. This has rapidly made UNS S32205/S31803 the workhorse product in the stainless steel alloy portfolio. This composition also helps to make UNS S32205/S31803 alloy's general, localized, and stress corrosion resistance relatively robust. Laboratory and early field studies demonstrated excellent resistance to scrubber environments up to 10,000 ppm chloride, pHs down to 5.5, and temperatures reaching 130°F (54°C). Unfortunately, however, even with all this promising early data, the aggressive chemical environment found in FGD absorbers soon crippled the UNS S32205/S31803 alloy material.[2, 3]

The U.S. utility industry has discovered aggressive corrosion in an alarming number of new and semi-new 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 actual 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-oxidations systems designed with UNS S32205/S31803 alloy.

Electric Power Research Institute (EPRI)[(1)] has indicated that of the roughly 360-370 FGD systems in the US, at least 20 percent utilize UNS S32205/S31803 alloy and the related UNS S32205/S31803 alloy in major components of the FGD system. Unfortunately, the chemical environment, and therefore the corrosion, varies from one system to another due to factors such as dew point, acidity, high temperature, chloride and fluoride concentrations, wet-dry

[(1)] Electric Power Research Institute (EPRI), 3420 Hillview Avenue, Palo Alto, California 94304.

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 inferior materials such as the UNS S32205/S31803 alloy.[4, 5, 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]

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 (bleach) and hydrochloric acid. It would be rare to find stainless steel in the same environments.[6]

SELECTION, SURFACE PREPERATION, AND APPLICATION

Selection

There are a variety of epoxy vinyl ester resin chemistries available on the market because no one polymer can handle all chemical environments. 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, case history of field service, 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 times epoxy vinyl ester resins are mistaken for or interchangeably referred to as polyester resins; however, they are significantly different in chemical makeup. Epoxy vinyl ester resins are indeed different due to their 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 than the bisphenol A epoxy vinyl ester resin which enables it to withstand higher temperatures as well as a more severe chemical environment. Every job's environment must be analyzed to determine the most suitable epoxy vinyl ester polymer lining.

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 blast (SSPC[(2)]-SP10).[7] An aggressive profile of nominally 3-4 mils 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 compatible material to the protective epoxy vinyl ester lining.

Application

At one time, the traditional application method was a hand-laid trowel applied lining; however, 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 as seen in 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.

Figure 2: Conventional spray application of epoxy vinyl ester polymer lining.

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 catalyst is injected into the spray stream at the nozzle. Knowing which type of application process the contractor is using is one factor in selecting the coating system as 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 stainless steel are showing significant premature corrosion. The best 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

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(2) Society for Protective Coatings (SSPC), 40 24th St 6th Fl, Pittsburgh, PA 15222.

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. The protection of the duplex UNS S32205/S31803 alloy constructed FGD absorbers is instrumental to both maintaining an efficient power plant as well as delivering better air quality to the surrounding communities.

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