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# Desulfurized flue gas corrosion coupled with deposits in a heating boiler

Peiyuan Pan, Heng Chen, Zhiyuan Liang, Qinxin Zhao\*

MOE Key Laboratory of Thermo-Fluid Science and Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China

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## ABSTRACT

In-plant corrosion tests of five steels were conducted in a heating boiler in China to study the desulfurized flue gas corrosion coupled with deposits after the FGD (flue gas desulfurization) unit. The surface temperature of the steel was the key factor in the deposition and corrosion process. As the surface temperature increased, the corrosion of the steels was first exacerbated due to the increase in the  $\text{Cl}^-$  concentration in the deposits and then mitigated due to the lack of the electrolyte. The stainless steels in this work showed much better performance than did the low alloy steel.

## 1. Introduction

$\text{SO}_2$  is one of the major pollutants from the combustion of fossil fuels, and its emissions need to be strictly controlled. An FGD unit is an important part of the flue gas cleaning system in coal-fired boilers, including utility, industrial and heating boilers. In China, the wet limestone-gypsum process is the most widely adopted FGD method due to its high efficiency and low cost [1,2]. A limestone slurry is used as the absorbent to remove  $\text{SO}_2$  in the flue gas and produce gypsum. The desulfurized flue gas leaves the FGD saturated with water vapour and entrains a large number of droplets. The temperature of which is usually only approximately  $50^\circ\text{C}$  or lower. If such a low-temperature flue gas enters the stack directly, the plume height will be quite low, and the concentration of pollutants around the plant will be relatively high [3–5]. Reheating is occasionally used to increase the exhaust flue gas temperature to  $75 \sim 90^\circ\text{C}$ , thereby accelerating the diffusion of the emissions. In China, tube-type heat exchangers, known as flue gas reheaters are used to heat the desulfurized flue gas from FGD and have gradually become a requirement in the flue gas cleaning systems of many newly constructed boilers. These devices use a high-temperature fluid, usually hot water, flowing in tubes to heat the low-temperature flue gas by running it over the tubes.

Although in China, most of the heating boilers used currently are not as well equipped as the utility ones, it should be noted that the heating boilers are more in need of flue gas reheaters because most of these heating boilers are located in downtown areas, with thousands of residents nearby. These boilers emit large amounts of pollutants in the low-temperature exhaust flue gas, and their stack heights are usually limited. The lack of plume buoyancy can result in health-threatening levels of local air pollution in urban areas and contribute to serious

environmental issues. Heavy smog, for example, had enveloped many cities of China over the past several heating seasons.

Over the past several decades, investigations into low-temperature corrosion in the back-end of coal-fired boilers have been a priority, and there are many studies on corrosion in FGD. Many field and laboratory tests have been conducted [6–18], and different materials, ranging from carbon steels to nickel-based alloys, have been evaluated. Shoemaker et al. [13,15] concluded that the condensation of acids normally accounted for most of the corrosion and that the presence of halides (chlorides and fluorides) could greatly increase the corrosive nature of the environment, especially its tendency to induce localized corrosion. Shoemaker et al. [15] also believed that tightly adhering deposits or films on the surface of metals could induce crevice corrosion. However, Phull et al. [11] indicated that thick, hard, adherent gypsum scales might protect the underlying metal surface. Cui et al. [17] reported that corrosive cathodic reactions were enhanced with the temperature in simulated desulfurized flue gas condensates.

The conditions within the various sections of an FGD vary greatly. Generally, nickel-based alloys were quite reliable [6–8,10]. Duplex stainless steels exhibit good corrosion resistance in some sections, but experienced severe corrosion in others. Austenitic stainless steel performed worse [11,13,15]. Shoemaker et al. [13] and Pettersson et al. [18] concluded that although the desulfurized flue gas at the outlet of FGD was not the most aggressive, it could lead to failures of duplex stainless steels in some cases. This is because at the outlet of an FGD, the flue gas is saturated of water vapour, which entrains numerous corrosive droplets that are composed mainly of the desulfurization scrubbing slurry and condensates of the acid vapours in the flue gas. The components of the droplets include diluted hydrochloric and sulfuric acids, chlorides and sulfates [2,19].

\* Corresponding author.

E-mail addresses: [ppy917@163.com](mailto:ppy917@163.com) (P. Pan), [zhaoqx@xjtu.edu.cn](mailto:zhaoqx@xjtu.edu.cn) (Q. Zhao).

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**Table 1**  
Chemical compositions of the tested steels used in this work (in wt%).

Steel	C	Si	Mn	P	S	Ni	Cr	Cu	Mo	N	Sb	Fe
09CrCuSb	0.078	0.26	0.48	0.012	0.010	–	0.90	0.37	–	–	0.060	Bal.
S30403	0.019	0.36	1.28	0.029	0.004	8.15	18.14	0.09	–	–	–	Bal.
S31603	0.020	0.40	1.45	0.018	0.002	10.73	16.97	0.12	2.47	–	–	Bal.
S32205	0.016	0.37	1.12	0.026	0.001	5.74	22.06	0.24	3.13	0.17	–	Bal.
S32750	0.018	0.25	0.77	0.015	0.001	7.08	25.18	0.21	3.89	0.27	–	Bal.

When the desulfurized flue gas is heated in the flue gas reheater after FGD, phase changes occur in the droplets. As the moisture evaporates, the concentrations of the free ions increase, and precipitates may deposit on the heat exchange surfaces. Kim et al. [20] reported corrosion and scaling failures in a rotatory gas–gas heater for FGD in a power plant in Korea. In China, frequent and critical failures of flue gas reheaters are also frequently encountered. Compared to the utility boilers in large-scale power plants, the condition of heating boilers seems to be more complex. Due to the simple flue gas cleaning system and low-efficiency demisters available for small heating boilers, the pollutant concentrations in the desulfurized flue gas are much higher, and the droplets are more numerous and larger. For some heating boilers, the mass concentration of droplets in the flue gas from the outlet of the FGD may reach 200 mg/m<sup>3</sup> (this value can be lower than 20 mg/m<sup>3</sup> for some utility boilers). Thus, the deposits left on heat exchange surfaces may be considerable and make a difference in terms of the corrosion processes.

The deposits are mainly composed of chlorides and sulfates, and the chlorides are usually far more aggressive than the sulfates [21,22]. Chloride can initiate pitting and crevice corrosion in steels and can break down passive films [23–26]. According to Ma et al. [27] and Nishimura [28], Cl<sup>−</sup> in deposits influence the corrosion rate and corrosion products. High amounts of Cl<sup>−</sup> lead to the formation of β-FeOOH, whereas low amounts of Cl<sup>−</sup> are conducive to the transformation of γ-FeOOH into α-FeOOH. Yamashita [29] found that α-FeOOH is the preferential form in the presence of SO<sub>4</sub><sup>2−</sup> and that the formation of β-FeOOH resulted from the coexistence of Cl<sup>−</sup>. Works by Asami et al. [30], Rémazeilles et al. [31] and Li et al. [32] indicated that β-FeOOH forms in the inner part of the corrosion layer and, to some extent, independently of oxygen flow. Prošek et al. [33] reported that the corrosivity of chloride deposits increased with temperature and decreased with relative humidity and that CaCl<sub>2</sub> is more aggressive than MgCl<sub>2</sub> and NaCl. According to Corvo et al. [34], Cl<sup>−</sup> is very significant in determining the corrosion rate in the presence of a deposition layer. However, for an incomplete layer, the influence of moisture is the controlling factor.

In a flue gas reheater, desulfurized flue gas corrosion coupled with deposits occurs on heat exchange surfaces. Research on corrosion in such conditions is limited, due to the short application history of flue gas reheaters, especially for heating boilers. However, corrosion issues in the low-temperature heat recovery devices before FGDs, which are similar to the structure of flue gas reheaters, have attracted attention for years. In this case, the dew point corrosion of sulfuric acid is the major cause [35–40]. The coupling mechanism of dew point corrosion and ash deposits is explored. According to Wang et al. [41] and Chen et al. [42], as the steel surface temperature increases, the corrosion and ash deposition rates decrease dramatically. For the flue gas reheater, the temperature of the heat exchange surface also appears to play a role.

Therefore, the materials, especially steels, which are likely to be used for manufacturing heat exchanger elements, in flue gas reheaters should be carefully reassessed. Additionally, the corrosion mechanism needs to be characterized.

In this work, field corrosion tests were conducted in a coal-fired heating boiler in China. Five different steels grades, i.e., 09CrCuSb, UNS

S31603, S30403, S32205 and S32507, were evaluated. The surface temperature of the steels was controlled as a key factor. After the tests, samples of these steels were analysed by XRD (X-ray diffraction), XRF (X-ray fluorescence), SEM (scanning electron microscope) and EDS (energy dispersive spectroscopy). The mechanism of desulfurized flue gas corrosion coupled with deposits was discussed, and the influence of surface temperature was investigated.

## 2. Materials and methods

### 2.1. Materials

Five kinds of corrosion-resistant steels that are frequently used to manufacture heat exchange elements such as finned tubes for flue gas heat exchangers were tested in this paper. The range of these steels spans from the low alloy steel 09CrCuSb to the austenitic stainless steels UNS S30403 and S31603, duplex stainless steel S32205, and super duplex S32750. 09CrCuSb has been widely used in China to address dew point corrosion. All the raw material was procured in tube form and machined to tube specifications of 38 mm in diameter and 4 mm in thickness. The outside surfaces of the steel tubes were ground using SiC paper up to 1200 grit before the tests. The chemical compositions of the steels are listed in Table 1.

### 2.2. Apparatus and procedure

The heat exchanger elements in the flue gas reheater are steel tubes, and the exposed surface temperature is determined primarily by the temperature of the liquid in the tubes. The testing apparatus used in this work is specialized for corrosion studies on heat exchange tubes.

Fig. 1(a) shows the schematic diagram of the testing apparatus, which consisted of a corrosion probe, a pump and a heater with automatic temperature control. Water hoses with thermal insulation were used to link the components. The corrosion probe was made up of a flange and two coaxial tubes of different diameters. Five steel tubes fabricated from the different tested steels were joined in series using single TIG (tungsten inert gas) welding with E2594 filler wire to construct the outside tube. The sequence was S31603, S32205, S32750, S30403 and 09CrCuSb. The length of each steel tube was no less than 150 mm to ensure that the middle section part was free of the galvanic corrosion and stress effects from the weld joints. The ends of the outside tube were sealed. The corrosion probe was inserted into the flue through a small round hole in the flue wall and maintained perpendicular to the direction of flue gas flow. In this way, the outside surfaces of the tested steels could be exposed to the flue gas during testing.

Circulating water driven by the pump flowed into the corrosion probe through the inside tube and out through the annular gap between the inside and outside tubes (see the blue arrows in Fig. 1(a)). The heater was used to maintain the temperature of circulating water. The error between the actual surface temperature of the outside tube and the design value was no more than ± 1.3 °C, with a standard deviation of no more than 0.4 (in this work). The error was mainly due to the heater, variations in the flue gas temperature and heat losses. In this way, the surface temperature of tested steels could be controlled, and the corrosion behaviour of the tested steels at different surface

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