Investigation on the Corrosion of the Elbows in the Flue Gas Cooler of a 600 MW Coal-Fired Power Plant

Peiyan Pan, Weijian Zhou, Heng Chen, and Naiqiang Zhang*

ABSTRACT: Sulfuric acid condensation has long been considered as the major cause of the corrosion issues at the cold-end of coal-fired boilers. However, in a flue gas cooler, where flue gas is cooled to around 90 °C for heat recovery, the influence of chlorides might be underestimated. In this article, some elbows of the heat transfer tubes in the flue gas cooler of a coal-fired power plant were found to be badly corroded, after a 5-year operation. The corroded elbows, coupled with the corrosion products and deposits on the tube wall, were sampled and analyzed by scanning electron microscopy, energy dispersive spectrometry, X-ray diffraction, X-ray fluorescence spectroscopy, and ion chromatography. The results indicated that chlorides, unexpectedly, formed in flue gas before the dew point for hydrochloric acid was met. The corrosion layer on the steel surface was mainly composed of Fe₂O₃, Fe₃O₄, and FeO(OH), while showing an oxidation gradient in depth. The sulfates in the corrosion products were rather limited. Instead, Cl⁻ from the deposits gradually accumulated deep inside the corrosion layer, resulting in a considerable generation of Cl⁻-containing compounds. The enrichment of Cl⁻ induced cracking and spalling of the corrosion products, and greatly accelerated the failure of the tube wall.

1. INTRODUCTION

Coal plays an important role in global electricity generation, heat generation, and other industries such as iron and steel. Up to 2019, China was the world’s biggest producer and consumer of coal, and coal-fired power plants supplied about 64% of electricity generation in China in 2018 and 2019. Efficiency is always a significant problem for coal-fired plants. In particular, the heat taken away by the exhaust gas usually accounts for more than 80% of the overall heat loss. Hence, a flue gas cooler, or a low-temperature economizer, is widely applied at the cold-end of the coal-fired power plants, to extract heat from flue gas of lower than 200 °C. The flue gas cooler is a kind of tubular heat exchanger, which cools flue gas out of the heat transfer tubes while transferring the heat into the flowing water inside the tubes.

However, the heat transfer surface exposed to low-temperature flue gas suffers a high risk of corrosion, and leakage failures of the tube bundles in the flue gas cooler frequently occurred. In the past, sulfuric acid (H₂SO₄) condensation on the metal surface was widely believed to be the major cause for corrosion issues in the flue gas cooler and other flue gas cooling processes because in flue gas from the combustion of fossil fuels, i.e., coal, oil, and natural gas, the concentration of sulfur oxides is far higher than other acidic gases, such as HCl, HF, and NO₂. As the flue gas temperature decreases, SO₂ reacts with water vapor and further forms H₂SO₄ vapor. Despite some controversy on the accurate value, the dew point temperature for sulfuric acid in flue gas is commonly recognized to be in the range of 110–150 °C, much higher than the dew point for hydrochloric acid, hydrofluoric acid, and nitric acid. According to some previous studies on the corrosion failures at the cold-end of fossil fuel boilers, the condensation of H₂SO₄ might lead to a highly acidic environment, and SO₄²⁻-containing compounds, such as FeSO₄ and Fe(OH)₂SO₄, were identified in the corrosion products.

Therefore, the sulfuric acid dew point is regarded as a critical threshold in heat exchanger design, and the degree of heat recovery and flue gas cooling should be strictly controlled to avoid the condensation of H₂SO₄ vapor on the metal parts. The involvement of other acidic gases is neglected since their dew point temperatures are not expected to be reached.

But in recent years, some investigations conducted on coal-fired boilers suggested that the flue gas temperature could be lowered beyond the sulfuric acid dew point. Flue gas generated by coal combustion contains a considerable amount...
of fly ash, and the alkaline components in the ash, such as CaO, reacted with SO\textsubscript{3} and H\textsubscript{2}SO\textsubscript{4} from flue gas and form sulfates, thus neutralizing the acidity of the condensate and preventing dew point corrosion.\textsuperscript{19–22} The experiments performed by Sun et al.\textsuperscript{23} and Yang et al.\textsuperscript{24} indicated that the optimal temperature for SO\textsubscript{3} absorption might be 20 °C or more below the sulfuric acid dew point. Wang et al.\textsuperscript{25} found that H\textsubscript{2}SO\textsubscript{4} vapor condensed on the deposit layer rather than directly on the low-temperature tube wall, so the metal substrate could be protected. Li et al.\textsuperscript{26} and Chen et al.\textsuperscript{27} conducted in-plant experiments to study the influence of the surface temperature on the corrosion and deposition characteristics on the tube wall. The 12 h tests by Li et al.\textsuperscript{26} indicated that the corrosion caused by acid condensation was insignificant until the surface temperature decreased to around 70 °C. Similar results were obtained in the 72 h tests by Chen et al.,\textsuperscript{27} but elements Cl and F were also detected in the corrosion products at 70 °C, despite the dew point of hydrochloric acid and hydrofluoric acid at about 50 °C.

Nowadays, in the coal-fired power plants and heating plants in China, flue gas is commonly cooled to about 90 °C in the well-designed flue gas cooler, to recover heat as much as possible. Furthermore, low-alloy steels specialized for resisting sulfuric acid dew point corrosion in flue gas were developed and widely applied.\textsuperscript{28–30} On the whole, most flue gas coolers have been working in good condition for several years. But local corrosion failures still had taken place.

In a recent routine inspection of the flue gas cooler of a 660 MW supercritical coal-fired power plant, extensive corrosion attacks were observed on the elbows of the heat transfer tubes, after a 5-year operation. In this article, the badly corroded elbows were studied by visual inspection, microscopic observation, and composition analysis, and the mechanism and real cause of the corrosion process were thus inferred.

2. SAMPLING INFORMATION

2.1. Flue Gas Cooler. Low-temperature corrosion and ash deposition had attacked the elbows of the heat transfer tubes in the flue gas cooler of a 660 MW supercritical coal-fired power plant. Proximate analysis results of the burned pulverized coal are shown in Table 1, and Table 2 lists X-ray fluorescence (XRF) elemental analysis results of the coal ash, expressed in the form of oxides.

| moisture | ash | C     | H     | O     | N     | S     | F     | Cl     |
|----------|-----|-------|-------|-------|-------|-------|-------|--------|
| 14.56    | 11.03 | 60.66 | 3.39  | 9.13  | 0.80  | 0.39  | 0.0123 | 0.021  |

Table 1. Proximate Analysis Results of the Pulverized Coal Used in the Boiler (in wt %, as-Received Basis)

| SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | TiO\textsubscript{2} | Fe\textsubscript{2}O\textsubscript{3} | CaO | MgO | Na\textsubscript{2}O | K\textsubscript{2}O | SO\textsubscript{3} |
|----------------------|-----------------|---------------------|-----------------|-----|-----|-----------------|-----------------|---------------|
| 48.44                | 21.28           | 1.02                | 6.64            | 10.00 | 1.30 | 1.10            | 1.54            | 4.71          |

Table 2. Elemental Analysis Results of the Coal Ash in the Form of Oxides (in wt %)

The flue gas cooler is placed after the DeNO\textsubscript{x} and air preheater and ahead of the electrostatic precipitator and wet desulfurization. The concentrations of SO\textsubscript{x}, NO\textsubscript{x}, O\textsubscript{2}, moisture, and fly ash in flue gas were monitored at the inlet of the flue gas cooler. Table 3 lists average values of the online measured results over a 2-week operation compared with calculated concentrations based on the chemical composition of the coal in Table 1 (assuming the air for combustion was dry and the extra air coefficient was 0.35). NO\textsubscript{x} concentration was difficult to calculate due to the complex formation of NO\textsubscript{x} in the combustion process and the transformation of NO\textsubscript{x} by selective noncatalytic reduction (SNCR).

| components | units | measured concentrations | calculated concentrations |
|------------|-------|-------------------------|----------------------------|
| SO\textsubscript{3} | mg/m\textsuperscript{3} | 858.66 | 891.32 (as SO\textsubscript{2}) |
| NO\textsubscript{x} | mg/m\textsuperscript{3} | 25.62 | - |
| O\textsubscript{2} | vol % | 6.84 | 6.55 |
| HCl | mg/m\textsuperscript{3} | - | 18.42 |
| moisture | vol % | 7.06 | 6.41 |
| fly ash | g/m\textsuperscript{3} | 12.47 | 12.60 |

Table 3. Online Measured and Calculated Concentrations of the Components in Flue Gas at the Inlet of the Flue Gas Cooler over a 2-Week Operation\textsuperscript{a}

\textsuperscript{a} No data.

Figure 1 shows schematic diagrams of the flue gas cooler and the tube bundles. The flue gas cooler consists of 4 × 6 bundles of spiral finned tubes for heat exchange. Flue gas flows vertically down in the flue, while the cooling water flows in the tubes from the bottom of the flue gas cooler to the top. The finned tubes are fixed on supporting plates and connected by elbows (highlighted by red in Figure 1b), which are also exposed to the flowing flue gas. The tubes and elbows are...
made of low-alloy steel 09CrCuSb, which was developed for the sake of sulfuric acid resistance, containing a small amount of Cr (∼0.9%) and other alloy elements including Mn, Cu, Si, and Sb. The outside diameter of the base tube was 38 mm and the thickness of the tube wall was 4 mm. Soot blowers were installed between the tube bundles, working for 10 min every 6 h to remove the deposited ash on the tube wall by steam.

The flue gas cooler was put into service in 2015. Five years later, in an inspection in 2020, some elbows of the heat transfer tubes were found to be seriously corroded (Figure 2a), in comparison to the finned tubes in a relatively good condition (Figure 2b). Moreover, perforations were also observed on the tube wall of the elbows (Figure 2c).

2.2. Sampling and Analysis. During operation, the fly ash in flue gas continually accumulated onto the surface of heat transfer tubes and formed deposits, most of which could be removed by the soot blowers in time. However, the elbows between the supporting plate and the flue wall seemed to be a blind side for the blowers, and some large lumps of caked deposits were observed on the flue wall and collected.

To study the deposition and corrosion behavior on the metal surface, as shown in Figure 3, two elbows (named A and B), of different corrosion levels were taken off from the heat transfer tubes of a bundle located in the third row of the bundle array (highlighted by orange in Figure 1a). Elbow A was installed during maintenance in 2019 and was in operation for about 13 months. Elbow B was in the flue gas cooler from the beginning and was in operation for 5 years. As shown in Figure 4, the macroscopic morphology of the elbows was visually inspected first, and then some deposits and corrosion products were carefully collected from the corroded area using a brush and a scraper.

Subsequently, the collected samples of deposits and corrosion products were ground into fine powders, respectively, which were analyzed by an electron microscope (SEM) Hitachi SU8020 for microstructure and analyzed by an energy dispersive spectrometer (EDS) Horiba EMAX for elementary composition. An X-ray diffraction (XRD) Bruker D8 ADVANCE was also applied for compound analysis. In addition, to trace and quantify some elements of an extremely low content in the deposits, X-ray fluorescence (XRF) spectroscopy was conducted on the deposit sample with a Thermo Fisher Scientific ARL ADVANT’X IntelliPower 3600, and 0.1126 g of the deposit sample was dissolved in 100 mL of pure water, and certain ions in the obtained clear leachate, including Cl\(^-\), PO\(_4\)\(^{3-}\), SO\(_4\)\(^{2-}\), SO\(_3\)\(^{2-}\), and NH\(_4\)^+, were accurately measured by an ion chromatography Thermo Dionex ICS-1100.

Furthermore, as illustrated in Figure 4, small arcuate coupons of the tube wall were cut off from the elbows and embedded by epoxy resin. After being polished, the cross section of the coupons was analyzed by a thermal field emission SEM Zeiss GeminiSEM 300 and an EDS Oxford Symmetry.

To obtain the corrosion rate on the tube wall during the 5-year operation, elbow B was further cut into 16 annular coupons. After removing the scaling on the outer surface, the remaining thickness of the tube wall was measured by observing the cross sections on an optical microscope.

3. RESULTS AND DISCUSSION

3.1. Visual Inspection. Figure 5 shows a large lump of the caked deposits, which was formed on the flue wall close to the corroded elbows A and B, while in other parts of the flue gas cooler, caking of the deposits was rather mild. A rise in the local moisture content could be inferred, which was the most important motivating factor in the agglomeration of the originally free ash particles.\(^{33,34}\) The deposit lump was dry, irregular in shape, and showed a homogeneous color of light gray. For analysis, some small pieces of the caked deposits were sampled from the large lump and named sample 1.

The surface of the heat transfer tubes in the flue gas cooler was originally painted in red. Figure 6 shows two different parts of elbow A, which had suffered from ash deposition coupled with corrosion over the 13-month operation. At the bending part in Figure 6a, although the red paint remained mostly intact on the tube wall, caked deposits were observed sticking to the metal surface, and some areas not covered by the deposits revealed damage of the substrate. Two small pieces of the caked deposits were collected and named sample 2. In comparison, the straight part of elbow A, shown in Figure 6b, seemed to be in a worse condition, and the deposits were greatly stained with rust. Some deposits and corrosion products that had accumulated on the metal surface were removed by the soot blowers in time. However, the elbows between the supporting plate and the flue wall seemed to be a blind side for the blowers, and some large lumps of caked deposits were observed on the flue wall and collected.

To study the deposition and corrosion behavior on the metal surface, as shown in Figure 3, two elbows (named A and B), of different corrosion levels were taken off from the heat transfer tubes of a bundle located in the third row of the bundle array (highlighted by orange in Figure 1a). Elbow A was installed during maintenance in 2019 and was in operation for about 13 months. Elbow B was in the flue gas cooler from the beginning and was in operation for 5 years.
had obviously fallen off from the tube wall so that the dark corrosion products beneath were exposed to flue gas.

The appearance of elbow B is shown in Figure 7. After a 5-year operation, elbow B exhibited apparently more extensive corrosion than elbow A, and the tube wall was completely covered by the rusty substance. In Figure 7b, some cracks and crevices were observed in the deposits and corrosion products on the metal surface, and spalling had also taken place.

Artificially, as shown in Figure 7c, along the cracks, flakes of the deposits and corrosion products could be easily taken off.
from the substrate and separated into the outer layer and the inner layer, named sample 3 and sample 4, respectively. Sample 4 was in a darker brown color than sample 3. There was probably a significant change in the composition from sample 3 to 4, resulting in a difference in their microstructure and thermal expansivity, and finally inducing spalling of the deposits and the corrosion products. Additionally, the steel substrate under the corrosion layer also presented some rust.

Figure 8 shows the corrosion rate on the tube wall of elbow B over the 5-year operation. The outer surface could be divided into six sections and 10 measuring points at intervals were selected in each section. Based on the thinning level of the tube wall, the average corrosion rate of each section was figured out. Apparently, the windward tube surface directly facing the flowing flue gas had suffered the most severe attack and thinned by about 0.26 mm per year. The corrosion of other areas on the straight parts of the elbow was also considerable, showing corrosion rates of higher than 0.10 mm/yr. The lateral surface of the bending part had the lowest corrosion rate, which benefited from the low level of ash deposition.

3.2. Analysis Results of the Deposits and Corrosion Products. SEM micrographs (×500) of the powders ground from samples 1 to 4 are shown in Figure 9, and EDS elementary analysis results of the samples are listed in Table 5. On the whole, the four samples mainly consisted of two types of particles: spheres and irregular particles. Sample 1 showed a high content of Si, Al, and Ca, suggesting that compounds containing these three elements were the main components in the deposits. The spheres might be SiO₂ particles, and the irregular particles could be formed by other oxides, salts, and metals. From samples 2 to 4, the mass fraction of Si, Al, and Ca decreased, while the fraction of Fe increased sharply. It is clear that sample 4 had a higher proportion of corrosion products than samples 1 and 2 and irregular particles were dominant on the micrograph. Besides, a little amount of S and Cl was also detected in the samples.

XRD patterns of samples 1 to 4 are shown in Figure 10. Based on the patterns, up to eight kinds of compounds, including SiO₂, CaCO₃, Al₄.64Si₁.36O₉.68, Fe₂O₃, Fe₃O₄, FeO-(OH), CaSO₄, and Fe₈O₈(OH)₈Cl₁.₃₅, were identified, and the semiquantitative analysis results for the mass fraction of these compounds in the samples are listed in Table 6. The peaks of
SiO₂ are quite considerable on the patterns for samples 1 and 2, but significantly weakened on the patterns for samples 3 and 4, where the peaks of Fe₃O₄ became the strongest.

Sample 1, the caked deposits from the flue wall around the elbows, mainly consisted of SiO₂, CaCO₃, and mullite (Al₄±0.6Si₁.36O₉.68), which were representative products generated by coal combustion. So, sample 1 resulted directly from fly ash deposition.

The iron oxides, mainly Fe₂O₃, Fe₃O₄ and FeO(OH), dominated in the corrosion products, and more or less existed in all of the four collected samples. FeO(OH) included goethite (α-FeO(OH)) and Cl-containing akaganeite (β-FeO(OH)). Hence, the damage of the tube wall was mainly caused by the reaction of the metal with O₂ and H₂O in flue gas and the formation of iron oxides, but influenced by Cl⁻.

Sample 2 was from the low-temperature surface of elbow A, where the sulfate oxides in flue gas might have reacted with CaO in the fly ash to form a small amount of CaSO₄ and Fe₂O₃, seemed to be the most abundant corrosion product.

On the badly corroded elbow B, the outer layer (sample 3) and the inner layer (sample 4) of the substance on the metal surface were noteworthy different in composition. Sample 3, which was exposed to flue gas directly, contained a higher proportion of deposits, and the corrosion products in sample 3 had undergone stronger oxidation. By contrast, in sample 4, which was close to the metal substrate, the suboxide Fe₂O₃ was dominant. Furthermore, there was a small amount of element Cl detected in samples 3 and 4, probably existing as Fe₈O₇(OH)₂Cl₁.₃₅, a common formula for β-FeO(OH), that is, Cl⁻ was involved in the corrosion of steel.

XRF results of sample 1, shown in Table 7, verified the existence of elements S and Cl in the caked deposits. Ion chromatographic results for the leachate of sample 1 are shown in Table 8, and equivalent mass fractions of the measured ions in the solid-state sample were calculated. SO₄²⁻ and Cl⁻ seemed to be the major anions in the deposits, which might dissolve on the tube wall and induce corrosion of the metal substrate. It should be noted that no ammonium salts were identified by XRD analysis, and no NH₄⁺ was detected in the leachate. So, hardly any NH₄HSO₄, (NH₄)₂SO₄, or other ammonium salts were formed in the fly ash or in the deposits. Although in many cases, ammonium salts in flue gas triggered moisture absorption and low-temperature corrosion on the surface of the metal parts, it could not be the major cause for the corrosion issue of the elbows in this article.

### 3.3. Analysis Results of the Cross Section of the Tube Wall

SEM micrographs of the cross section of the arcuate coupons from the tube wall of elbow B are shown in Figure 11. The light gray parts on the right side of the graphs are the metal substrate, while the substances in a darker color on the left are the corrosion products or deposits. On the whole, the boundary separating the substrate and the corrosion layer was smooth, and the average thickness of the corrosion layer in the observed sections was up to 2 mm, which must have resulted in a considerable thinning of the tube wall. However, there was also some local pitting on the corrosion frontier, from which the uniform corrosion probably evolved.

The corrosion products in Figure 11b generally remained intact, while quite a lot of crevices, including tangential ones and radial ones, were observed in the cases of Figure 11c,d.

Table 5. EDS Results of Samples 1–4 (wt %)ᵃ

| elements | O  | Si  | Al  | Ca  | Fe  | K  | Mg  | Ti  | S  | Cl  |
|----------|----|-----|-----|-----|-----|----|-----|-----|----|-----|
| sample 1 | 52.92 | 17.89 | 6.45 | 15.86 | 4.28 | 1.30 | -   | 0.52 | 0.78 | -   |
| sample 2 | 48.81 | 17.39 | 6.53 | 9.02 | 15.72 | 0.86 | -   | -   | 1.67 | -   |
| sample 3 | 44.24 | 14.64 | 6.47 | 1.95 | 29.81 | 0.51 | 0.52 | 0.58 | 0.73 | 0.55 |
| sample 4 | 31.98 | 3.69  | 2.49 | 0.53 | 59.91 | -   | -   | -   | -   | 1.40 |

ᵃ Undetected.
products in areas 1 and 2. However, this increasing trend was not constant, and Cl content in area 5, around the boundary of the corrosion layer and the metal substrate, was also limited.

Figure 12 shows EDS maps of elements Fe, O, S, and Cl for Figure 11 b−d. For the analyzed cross sections of the corrosion layers, the distribution of Fe and O was quite even, while the existence of S was almost negligible. By contrast, Cl had a low mass fraction in most areas but exhibited a significant enrichment in the corrosion products at depths of around 1200–1600 μm in the corrosion layer. Such Cl-enriched areas were quite close to the metal substrate but did not exactly reach the corrosion frontier. In Figure 12b,c, the corrosion products cracked right along the Cl-enriched strip, thus forming a wide crevice.

Table 6. Semiquantitative Analysis Results for the Identified Compounds in Samples 1−4 (wt %)\(^a\)

| compounds         | SiO\(_2\) | CaCO\(_3\) | Al\(_{16}\)Si\(_{33}\)O\(_{99}\).68 | Fe\(_2\)O\(_3\) | Fe\(_3\)O\(_4\) | FeO(OH) | CaSO\(_4\) | Fe\(_8\)O\(_8\)(OH)\(_8\)Cl\(_{13}\).5 | Cl\(_2\) |
|-------------------|-----------|------------|---------------------------------|----------------|----------------|----------|-----------|------------------------------------|--------|
| main source       | deposition| deposition | deposition                     | corrosion       | corrosion       | corrosion | deposition | corrosion                           |        |
| sample 1          | 58.4      | 16.6       | 15.1                           | 5.7             | 4.2             | -        | -         | -                                  |        |
| sample 2          | 42.3      | 7.1        | 11.6                           | 4.5             | 25.9            | 7.4      | -         | 1.2                                |        |
| sample 3          | 13.8      | -          | 16.5                           | 10.2            | 31.8            | 27.7     | -         | -                                  |        |
| sample 4          | 2.6       | -          | -                              | 3.9             | 77              | 13.9     | -         | 2.6                                |        |

\(^a\) Undetected.

Table 7. XRF Results of Sample 1 (wt %)

| elements | Si | Al | Ca | Fe | K | Na | Mg | Ti | Mn | S | P | Cl | Zn | O   |
|----------|----|----|----|----|---|----|----|----|----|---|---|----|----|-----|
| mass fraction | 23.84 | 9.63 | 12.26 | 5.02 | 1.70 | 0.849 | 0.668 | 0.52 | 0.147 | 0.371 | 0.0353 | 0.0305 | 0.0201 | bal. |

Table 8. Concentration of the Measured Ions in the Leachate of Sample 1 and the Equivalent Mass Fraction in Sample 1\(^a\)

| ions                | Cl\(^-\) | PO\(_4\)\(^{3-}\) | SO\(_2\)\(^{2-}\) | SO\(_3\)\(^{2-}\) | NH\(_4\)\(^+\) |
|---------------------|---------|-----------------|-----------------|-----------------|-------------|
| concentration in the leachate (mg/L) | 0.44248 | - | 1.77730 | - | - |
| mass fraction in the sample (wt %) | 0.039 | 0.158 | - | - | - |

\(^a\) Undetected.

of the corrosion layer and the metal substrate, was also limited.

Figure 12 shows EDS maps of elements Fe, O, S, and Cl for Figure 11b−d. For the analyzed cross sections of the corrosion layers, the distribution of Fe and O was quite even, while the existence of S was almost negligible. By contrast, Cl had a low mass fraction in most areas but exhibited a significant enrichment in the corrosion products at depths of around 1200–1600 μm in the corrosion layer. Such Cl-enriched areas were quite close to the metal substrate but did not exactly reach the corrosion frontier. In Figure 12b,c, the corrosion products cracked right along the Cl-enriched strip, thus forming a wide crevice.
3.4. Corrosion Mechanism of the Elbows in the Flue Gas Cooler.

Based on the analysis results of the corroded elbows from the flue gas cooler, the mechanism of the corrosion process could be inferred. As shown in Figure 13a, the fly ash generated by coal combustion consisted of various components, mainly including SiO₂, CaCO₃, and mullite, which led to severe ash deposition on the outer wall of the heat transfer tubes. Besides, gaseous SO₃, SO₂, and HCl were important components of coal flue gas. On being cooled by the heat transfer tubes in the flue gas cooler, these acid vapors, coupled with the water vapor in flue gas, might condense on the surface of the fine particles or directly on the low-temperature tube walls, forming solutions of H₂SO₄ and HCl. These acidic solutions rapidly reacted with alkaline compounds in the fly ash, such as CaO and K₂O, and generated sulfates and chlorides.

Over the past 5 years, in the flue gas cooler, the corroded elbows were located close to the flue wall. Compared to the normal heat transfer tubes in the inner zone of the flue, the elbows were exposed to a flue gas condition of a relatively low temperature, a high relative humidity, and a low flow rate, and thus suffered from stronger vapor condensation and ash deposition. In the flue gas cooler, the flue gas temperature was cooled to lower than the sulfuric acid dew point, and thus, SO₃ had condensed and formed sulfates in flue gas. However, the condensation of SO₂ and HCl was doubtful, because the overall temperature in the flue gas cooler seemed to be still higher than the dew point of hydrochloric acid. Some studies suggested that the acid gases in flue gas could directly react with solid and gaseous alkaline substances to form salts, even before the conditions for condensation were met. In this article, CaSO₄, CaCO₃, and CaCl₂ were all verified products of the neutralization. In the case of the condensation of SO₃ and HCl, the condensation in the flue gas cooler seemed to be still higher than the dew point of hydrochloric acid.

As shown in Figure 13b, in the deposits on the metal surface, fine particles of insoluble substances were dominant. Based on the data in Table 3 and 4, the highest relative humidity on the tube wall can be up to around 25%, which was adequate for water adsorption of some highly hygroscopic salts such as CaCl₂ and MgCl₂.41,42 The steam sprayed by the soot blowers could temporarily increase the moisture content in the flue gas and promote the salt solution formation. Downtime of the boiler was another problem. There was a significant increase in the relative humidity in the flue gas cooler, and the dry hygroscopic salts formed during the operation would absorb moisture, forming aggressive solutions on the metal surface. The moisture-containing fine gas might maintain a salt solution on the particle surface in the metal surface of the boiler. Therefore, additional measures are needed to prevent the formation of aggressive solutions.

Table 9. EDS Results of the Marked Areas in Figure 11b-d

| Area | O | F | Cr | Cu | Ni | Al | Si | S | Cl |
|------|---|---|----|----|----|----|----|---|----|
| 1    | 36.9 | 43.2 | 0.2 | - | - | 9.0 | 10.3 | 0.3 | 0.1 |
| 2    | 28.9 | 67.0 | 1.8 | 0.7 | 0.4 | 0.3 | 0.8 | - | 0.1 |
| 3    | 33.2 | 62.2 | 0.9 | 1.1 | 0.4 | 0.1 | 0.3 | 0.1 | 1.7 |
| 4    | 34.6 | 59.1 | 2.5 | 0.2 | 0.3 | 0.1 | 0.5 | 0.2 | 2.5 |
| 5    | 64.4 | 31.6 | 2.0 | 0.9 | 0.3 | - | 0.6 | - | 0.2 |
| 6    | 33.3 | 55.6 | - | 0.4 | 0.2 | 4.7 | 5.4 | - | 0.4 |
| 7    | 29.8 | 68.9 | 0.4 | 0.4 | 0.2 | - | 0.2 | - | 0.1 |
| 8    | 30.2 | 66.8 | 1.1 | 0.1 | 0.1 | 0.1 | 0.3 | 0.3 | 1.0 |
| 9    | 31.4 | 66.7 | 0.1 | - | 0.5 | 0.1 | 0.1 | - | 1.1 |
| 10   | 28.1 | 69.9 | 0.7 | 0.5 | - | 0.3 | 0.3 | - | - |
| 11   | 27.5 | 70.7 | 0.5 | 0.3 | - | 0.2 | 0.3 | - | - |
| 12   | 31.8 | 65.4 | 1.1 | 0.3 | 0.3 | - | 0.3 | - | 0.8 |

- Undetected.
Compared to the solids, the amount of the formed solution was limited and the deposits were basically dry. However, over the long period of operation, the deposits were inevitably permeated by some solutions containing free ions, which triggered corrosion of the steel substrate. Different from the conventional cases for dew point corrosion of sulfuric acid, the corrosion layer on the tube wall of the elbow part was mainly made up of iron oxides, rather than sulfates, bisulfates, or sulfides. Actually, EDS maps of the cross section indicated that the involvement of sulfuric acid or sulfates seemed to be

Figure 12. EDS maps of elements Fe, O, S, and Cl: (a) for Figure 11b, (b) for Figure 11c, and (c) for Figure 11d. There was a prominent Cl-enriched strip at depth in the corrosion layer, along which the corrosion products cracked.
insignificant in the corrosion process. Instead, Cl− played a more important role than SO4^{2−} did, in spite of an extremely low concentration in the deposits.

Under the accumulated deposits, dissolution of the metal substrate occurred. In neutral or slightly acidic conditions, with the supply of O2 from flue gas and H2O from the deposits, the steel started to oxidize and dissolve, according to the following reactions (taking Fe as the example)

\[
4 \text{Fe} + 3 \text{O}_2 + 12 \text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 6 \text{H}_2\text{O} \quad (1)
\]

\[
2 \text{Fe} + \text{O}_2 + 4 \text{H}^+ \rightarrow 2 \text{Fe}^{2+} + 2 \text{H}_2\text{O} \quad (2)
\]

Similar reactions might also occur for other metallic elements in the steel including Cr, Cu, and Ni. Subsequently, the metal ions hydrolyzed in the solution and formed hydroxides, which were not stable and soon dehydrated into insoluble oxides

\[
\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 3 \text{H}^+ \quad (3)
\]

\[
\text{Fe}^{2+} + 2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2 \text{H}^+ \quad (4)
\]

\[
\text{Fe(OH)}_3 \rightarrow \text{FeOOH} + \text{H}_2\text{O} \quad (5)
\]

\[
2\text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (6)
\]

\[
\text{Fe(OH)}_2 + 2\text{Fe(OH)}_3 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad (7)
\]

\[
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (8)
\]

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \quad (9)
\]

Fe3O4, FeOOH, and Fe2O3 were the major components of the corrosion products detected on the elbows. As shown in Figure 14a, at the beginning of the corrosion process, Fe(III)

Figure 13. Deposition characteristics on the steel surface in the flue gas cooler: (a) ash particles deposited on the metal surface and acidic gases condensed on or reacted with the particles and (b) free ions permeated the deposits on the metal substrate.

Figure 14. Corrosion evolution on the metal substrate: (a) initiation, (b) oxidation difference in the corrosion products, and (c) Cl enrichment deep inside the corrosion layer, inducing crevice formation.
ions and compounds were formed in the area exposed to flue gas \((\text{reactions } 1, 3, 5, \text{ and } 6)\), while in the area covered by the caked deposits, Fe(II) ions and compounds were more likely to form due to the lack of \(\text{O}_2\) \((\text{reactions } 2 \text{ and } 4)\), and then oxidized by \(\text{Fe(OH)}_3\) to generate \(\text{Fe}_2\text{O}_3\) \((\text{reaction } 7)\). Over time, the deposits and corrosion products on the steel surface kept increasing, and the shortage of \(\text{O}_2\) was exacerbated deep inside the thickening deposit and corrosion layer. As a result, as shown in Figure 14b, \(\text{Fe}_2\text{O}_3\) was the most abundant in the first formed corrosion products.

The concentration of \(\text{Cl}^-\) in the deposits was far less than \(\text{SO}_4^{2-}\). However, as shown in Figure 14c, \(\text{Cl}^-\) showed high mobility and steadily penetrated the deposits and corrosion products. Consequently, \(\text{Cl}^-\) was enriched deep inside the corrosion layer, giving rise to a high \(\text{Cl}\) content in the corrosion products. Akaganeite \((\beta-\text{FeOOH})\) is a representative \(\text{Cl}\)-containing corrosion product formed in the environment containing a high concentration of both \(\text{Cl}^-\) and Fe(II) species. The general formula for \(\beta-\text{FeOOH}\) is known as \(\beta-\text{Fe}_{x-1}(-\text{OH})_x\text{Cl}_x\) which results from the oxidation of Fe(II) hydrochloride \(\beta-\text{Fe}_2(\text{OH})\text{Cl}\)

\[
2\text{Fe}^{2+} + 3\text{H}_2\text{O} + \text{Cl}^- \rightarrow \beta - \text{Fe}_2(\text{OH})_3\text{Cl} + 3\text{H}^+ \quad (10)
\]

\[
4\text{Fe}^{2+} + 6\text{H}_2\text{O} + 4x\text{Cl}^- + \text{O}_2 \rightarrow 4\beta - \text{Fe}_{x-1}(-\text{OH})_x\text{Cl}_x + (8 - 4x)\text{H}^+ \quad (11)
\]

According to the SEM results, the generation of \(\beta-\text{FeOOH}\) was unfavorable for the durability of the corrosion layer. Crevices tended to appear alongside the \(\text{Cl}\)-enriched strip and caused spalling of the deposits and corrosion products. As shown in Figure 15a, upon the widening of the crevice, the outer corrosion products and deposits fell off from the metal substrate, thus losing their barrier effect for the metal substrate. Consequently, the less oxidized corrosion products were exposed to flue gas and gradually formed Fe(III) compounds \((\text{reactions } 8 \text{ and } 9)\). Meanwhile, as shown in Figure 15b, the ash deposition and corrosion continued, and the corrosion frontier would continually invade the metal substrate, until the next spalling took place. Over time, as shown in Figure 15c, the deposits could hardly stay on the substrate. Consequently, the less oxidized corrosion products might temporarily cause thickening of the tube wall. But the adherence of the deposits and corrosion products on the metal substrate could not be permanently maintained. Repeated spalling would result in a significant thinning of the tube wall and finally, the failure of the heat transfer tube.

Based on the analysis results and discussions above, some suggestions could be proposed for corrosion prevention of the tube elbows close to the flue wall. Stainless steels, such as type \(304 \text{ and } 316\) austenitic stainless steels, and coating methods, such as enamel coatings and amorphous metallic coatings, can be used for the elbow parts to improve their resistance against \(\text{Cl}^-\) attack. Furthermore, because some of the elbows are beyond the scope of the existing soot blowers, ash removal methods specialized for the zone adjacent to the flue wall are necessary. Compressed air blowing and other methods not generating water vapor should be given priority than steam blowing, to mitigate water absorption by the hygroscopic species in the deposits.

4. CONCLUSIONS

At present, coal is still the most widely used fuel in China and some other Asian countries. In the coal-fired plants, the exhaust flue gas was greatly cooled to around 90 °C for heat recovery. Much attention had been devoted to sulfurous acid condensation, which was considered as the major cause for low-temperature corrosion in the flue gas cooler. The deposits accumulated on the metal surface could act as a barrier against flue gas and the condensed acids. However, these might not be entirely accurate. The unexpected chlorides in the deposits might play an important role in corrosion failures of the heat transfer tubes in the flue gas cooler.

In an inspection of the flue gas cooler of a coal-fired power plant, some elbows of the heat transfer tubes were found to be badly corroded over the 5-year operation. In this article, the corroded elbows and some deposits were collected and analyzed, and the following conclusions can be made:

1. The windward tube surface of the elbow suffered the highest corrosion rate of around 0.26 mm/yr on average in the 5-year operation. The formed corrosion products on the steel substrate were layered and dominated by iron oxides. The outer layer was mainly made up of Fe(III) compounds including \(\text{Fe}_2\text{O}_3\) and \(\text{FeOOH}\), while the inner layer contained abundant \(\text{Fe}_2\text{O}_3\).
2. Upon flue gas cooling, aggressive chlorides might form at a temperature level much higher than the expected
dew point of hydrochloric acid. The elbows by the flue wall suffered a higher risk of chloride interaction due to a lower local temperature.

3. Despite a very limited concentration in the deposits, Cl\textsuperscript{-} could continually permeate the corrosion products and accumulate in the area near the interface of the corrosion products and the substrate, which was favorable for further corrosion of the steel. Furthermore, the Cl-enriched corrosion products tended to crack, leading to the spalling of the corrosion layer and exposure of the inner corrosion products.

4. In the flue gas cooler, the existence of chlorides could greatly exacerbate the corrosion problem on the steel surface and accelerate the failure of the tube wall. By contrast, the involvement of SO\textsubscript{4}\textsuperscript{2-} in corrosion was relatively insignificant.

# AUTHOR INFORMATION

Corresponding Author
Naiqiang Zhang — National Thermal Power Engineering & Technology Research Center, North China Electric Power University, Beijing 102206, China; Email: zhngq@ncepu.edu.cn

Authors
Peiyuan Pan — National Thermal Power Engineering & Technology Research Center, North China Electric Power University, Beijing 102206, China; orcid.org/0000-0001-7150-1732

Weijian Zhou — National Thermal Power Engineering & Technology Research Center, North China Electric Power University, Beijing 102206, China

Heng Chen — National Thermal Power Engineering & Technology Research Center, North China Electric Power University, Beijing 102206, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04838

Notes
The authors declare no competing financial interest.

# ACKNOWLEDGMENTS

This work was supported by the China Postdoctoral Science Foundation [grant number 2020M670248] and the National Natural Science Foundation of China [grant number 51806062].

# REFERENCES

(1) IEA. Coal Information: Overview. https://www.iea.org/reports/coal-information-overview/ (accessed Sept 24, 2020).
(2) China Electricity Council. China Power 2020; China Building Materials Press: Beijing (in Chinese), 2020.
(3) Ember. Global Electricity Review 2020. https://ember-climate.org/project/global-power-2020/ (accessed Sept 24, 2020).
(4) Xu, G.; Xu, C.; Yang, Y.; Fang, Y.; Li, Y.; Song, X. A novel flue gas waste heat recovery system for coal-fired ultra-supercritical power plants. Appl. Therm. Eng. 2014, 67, 240–249.
(5) Wang, C.; He, B.; Sun, S.; Wu, Y.; Yan, N.; Yan, L.; Pei, X. Application of a low pressure economizer for waste heat recovery from the exhaust flue gas in a 600 MW power plant. Energy 2012, 48, 196–202.
(6) Malik, A. U.; Al-Fozan, S. A.; Mobin, M.; Al-Hajri, M. Studies on the Failure of Economizer Tubes Involving Acid Dew-Point Corrosion in High Pressure Boilers. Int. J. Sci. Eng. Res. 2013, 4, 1726–1736.
(7) Holmes, D. R. Dewpoint Corrosion; John Wiley & Sons: New York, 1985.
(8) Huijbregts, W. M. M.; Leferink, R. G. I. Latest advances in the understanding of acid dewpoint corrosion: corrosion and stress corrosion cracking in combustion gas condensates. Anti-Corros. Methods Mater. 2004, 51, 173–188.
(9) Li, Y.; Zhu, Q.; Yi, Q.; Zuo, W.; Feng, Y.; Chen, S.; Dong, Y. Experimental method for observing the fate of SO3/H2SO4 in a temperature-decreasing flue gas flow: Creation of state diagram. Fuel 2019, 249, 449–456.
(10) Zheng, C.; Wang, Y.; Liu, Y.; Yang, Z.; Qu, R.; Ye, D.; Liang, C.; Liu, S.; Gao, X. Formation, transformation, measurement, and control of SO3 in coal-fired power plants. Fuel 2019, 241, 327–346.
(11) Jeong, K.; Levy, E. K. Theoretical prediction of sulfuric acid condensation rates in boiler flue gas. Int. J. Heat Mass Transfer 2012, 55, 8010–8019.
(12) Bahadori, A. Estimation of combustion flue gas acid dew point during heat recovery and efficiency gain. Appl. Therm. Eng. 2011, 31, 1457–1462.
(13) Zuo, W.; Zhang, X.; Li, Y. Review of flue gas acid dew-point and related low temperature corrosion. J. Energy Inst. 2020, 93, 1666–1677.
(14) Chandra, K.; Kain, V.; Dey, G. K. Accelerated Corrosion of a Boiler Chimney: Causes and Preventive Steps. J. Failure Anal. Prev. 2011, 11, 466–472.
(15) Ebara, R.; Tanaka, F.; Kawasaki, M. Sulfuric acid dew point corrosion in waste heat boiler tube for copper smelting furnace. Eng. Failure Anal. 2013, 33, 29–36.
(16) Moakhar, R. S.; Mehdiopour, M.; Ghobani, M.; Mohabeli, M.; Koohbor, B. Investigations of the Failure in Boilers Economizer Tubes Used in Power Plants. J. Mater. Eng. Perform. 2013, 22, 2691–2697.
(17) Shayan, M. R.; Ranjbar, K.; Hajidavalloo, E.; Heidari Kydan, A. On the failure analysis of an air preheater in a steam power plant. J. Failure Anal. Prev. 2015, 15, 941–951.
(18) Liang, Z.; Zhao, Q. Failure analysis of spiral finned tube on the economizer. Eng. Failure Anal. 2013, 28, 208–214.
(19) Liu, L.; Deng, Q.; Zheng, C.; Wang, S.; Wang, J.; Gao, X. An insight into electrostatic field effects on SO\textsubscript{3} adsorption by CaO with CO\textsubscript{2}, SO\textsubscript{2}, and H\textsubscript{2}O: a DFT approach. Aerosol Air Qual. Res. 2019, 19, 2320–2330.
(20) Chen, H.; Pan, P.; Chen, X.; Wang, Y.; Zhao, Q. Fouling of the flue gas cooler in a large-scale coal-fired power plant. Appl. Therm. Eng. 2017, 117, 698–707.
(21) Chen, H.; Pan, P.; Shao, H.; Wang, Y.; Zhao, Q. Corrosion and viscous ash deposition of a rotary air preheater in a coal-fired power plant. Appl. Therm. Eng. 2017, 113, 373–385.
(22) Chen, X.; Liang, Z.; Yang, W.; Zhao, Q. Investigation into the ash deposits in a coal-fired traveling grate boiler with the ammonia present in the flue gas. Energy Fuels 2018, 32, 11328–11334.
(23) Sun, K.; Yan, Y.; Jiang, J.; Deng, L.; Che, D. SO\textsubscript{3} removal efficiency and ash particle flowability of low-low-temperature flue gas systems (LLTSs). Appl. Therm. Eng. 2020, 171, No. 115132.
(24) Yang, Z.; Ji, P.; Li, Q.; Jiang, Y.; Zheng, C.; Wang, Y.; Gao, X.; Lin, R. Comprehensive understanding of SO\textsubscript{3} effects on synergies among air pollution control devices in ultra-low emission power plants burning high-sulfur coal. J. Cleaner Prod. 2019, 239, No. 118096.
(25) Wang, Y.; Zhao, Q.; Zhang, Z.; Zhang, Z.; Tao, W. Mechanism research on coupling effect between dew point corrosion and ash deposition. Appl. Therm. Eng. 2013, 54, 102–110.
(26) Li, Z.; Sun, F.; Shi, Y.; Li, F.; Ma, L. Experimental study and mechanism analysis on low temperature corrosion of coal fired boiler heating surface. Appl. Therm. Eng. 2015, 80, 355–361.
(27) Chen, H.; Pan, P.; Wang, Y.; Zhao, Q. Field study on the corrosion and ash deposition of low-temperature heating surface in a large-scale coal-fired power plant. Fuel 2017, 208, 149–159.
(28) Wenlong Z, R. W. Y. Y. The Performances of ND Steel Resistant to Dew Point Corrosion of Sulfuric Acid and Application. Petrochem. Corros. Prot. 1997, No. 271.
(29) Okamoto, J.; Soeno, A.; Ishitsuka, T. New S-TENTM 1 Steel Tubes-Renewal of Sulfuric-Acid-Resistant Steel, S-TENTM 1; Steel Research Laboratories, 2004; pp 98–103.
(30) Jun, W. Development of sulfuric acid dew point corrosion-resistant JNS steel plate. Shandong Metall. 2007, 29, 31–33. (in Chinese).
(31) Tang, Y.; He, X.; Cheng, A.; Li, W.; Deng, X.; Wei, Q.; Li, L. Occurrence and sedimentary control of sulfur in coals of China. J. China Coal Soc. 2015, 40, 1977–1988. (In Chinese).
(32) Dai, S.; Ren, D.; Chou, C.; Finkelman, R. B.; Seredin, V. V.; Zhou, Y. Geochemistry of trace elements in Chinese coals: A review of abundances, genetic types, impacts on human health, and industrial utilization. Int. J. Coal Geol. 2012, 94, 5–21.
(33) Dufier, D.; Palzer, S.; Heinrich, S.; Fries, L.; Antonyuk, S.; Haider, C.; Salman, A. D. Adhesion mechanisms between water soluble particles. Powder Technol. 2013, 238, 35–49.
(34) Chen, M.; Zhang, D.; Dong, W.; Luo, Z.; Kang, C.; Li, H.; Wang, G.; Gong, J. Amorphous and humidity caking: A review. Chin. J. Chem. Eng. 2019, 27, 1429–1438.
(35) Guffre, J. Eliminating air heater plugging and corrosion caused by SCR/SNCR systems for NOx control on coal-fired boilers. Power Eng. 2007, 111, 84–87.
(36) Wang, Y.; Tan, H.; Dong, K.; Liu, H.; Xiao, J.; Zhang, J. Study of ash fouling on the blade of induced fan in a 330 MW coal-fired power plant with ultra-low pollutant emission. Appl. Therm. Eng. 2017, 118, 283–291.
(37) Vassilev, S. V.; Vassileva, C. G.; Vassilev, V. S. Advantages and disadvantages of composition and properties of biomass in comparison with coal: An overview. Fuel 2015, 158, 330–350.
(38) Chen, X.; Zhao, Q.; Liang, Z. Investigations on the Ash Deposit Formation of Tubular Air Preheater in a Coal-Fired Traveling Grate Boiler. Energy Fuels 2017, 31, 13215–13220.
(39) Herzog, T.; Müller, W.; Spiegel, W.; Brell, J.; Molitor, D.; Schneider, D. Corrosion Caused by Dew Point and Deliquescent Salts in the Boiler and Flue Gas Cleaning. In VGL: KG Thome-Kozmiensky og M. Beckmann: Energie aus Abfall; CheMin, 2012; Vol. 9, pp 429–460.
(40) Niu, Y.; Tan, H.; Hui, S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. Prog. Energy Combust. Sci. 2016, 52, 1–61.
(41) Vainio, E.; Kinnunen, H.; Lauren, T.; Brink, A.; Yrjas, P.; DeMartini, N.; Hupa, M. Low-temperature corrosion in co-combustion of biomass and solid recovered fuels. Fuel 2016, 184, 957–965.
(42) Vainio, E.; DeMartini, N.; Hupa, L.; Åmand, L.; Richards, T.; Hupa, M. Hygroscopic properties of calcium chloride and its role on cold-end corrosion in biomass combustion. Energy Fuels 2019, 33, 11913–11922.