THE EFFECT OF SO\textsubscript{2}/HCl RATIO ON SUPERHEATER HIGH TEMPERATURE CORROSION

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ABSTRACT

High temperature superheater corrosion is a major operating problem in waste-to-energy plants since it is responsible for plant shutdowns and low energy recovery. This has been largely attributed to the chloride content in municipal solid wastes and the subsequent reactions that occur with generated chlorine gas. While several methods have been developed to reduce corrosion, one which has received more interest is increasing the concentration of sulfur dioxide, SO\textsubscript{2}, in the boiler. The addition of SO\textsubscript{2} to WTE post combustion gas streams has been shown at times to have a favorable impact on corrosion and is said to be an effective method of suppressing dioxin formation by reacting with molecular chlorine, Cl\textsubscript{2}.

The following paper is part of an ongoing work to understand the effect of the SO\textsubscript{2}/HCl ratio on the corrosion of alloys exposed to superheater temperatures and flue gas compositions. A commercial low carbon steel alloy, SA178A, was exposed under various flue gas compositions at 500°C, while varying the SO\textsubscript{2}/HCl ratio as well as the water concentration. For tests operated at 5% H\textsubscript{2}O, corrosion was reduced by more than 40% as the SO\textsubscript{2}/HCl ratio was increased from 1/8 to 5/8. These results were obtained in the absence of chloride salts, suggesting that SO\textsubscript{2} can decrease chlorine corrosion by interacting with HCl. Tests conducted at 15% H\textsubscript{2}O however demonstrated a constant corrosion rate, with magnitudes comparable to 5% H\textsubscript{2}O at 1/8 SO\textsubscript{2}/HCl. Further work is needed to relate the SO\textsubscript{2}/HCl relationship to water and to elucidate the mechanism associated with mitigating corrosion.

INTRODUCTION

Superheater corrosion is a major operating problem for WTE boilers as it causes downtime and periodic shutdowns and accounts for a significant portion of a facility’s total operating cost [1]. Additionally, superheater corrosion impacts electricity production by limiting the boiler’s maximum achievable temperature, above which the corrosion rate becomes impractically high [2].

The corrosion problems experienced in boilers fueled by municipal solid wastes (MSW) are different from those observed in fossil fuels in that comparatively higher amounts of chlorine present in waste are the primary corrosion agent. The average chlorine content of MSW in the United States is close to 0.7 wt.%, and the chlorine content of MSW combusted in WTE plants is about 0.5 wt.%. Coal utilized in the U.S. only contains about 0.05 wt% chlorine [1].

More than half of chlorine contained in MSW is found in organics, such as polyvinylchloride (PVC). This will produce HCl in the combustion process. The other half of the chlorine is from inorganics such as alkali chlorides like sodium chloride and potassium chloride (NaCl and KCl). Whereas inorganic chlorides are vaporized in the flame and can ultimately condense in the boiler to cause the formation of low melting eutectics [3], the HCl produced in the flue gas presents an even more aggressive attack.

The corrosion associated with HCl in an oxidizing environment is commonly referred to as high temperature corrosion. Despite numerous studies on the oxidation-chlorination of alloys and pure metals, the mechanism is still under debate [4]. The current understanding is a so-called “chlorine cycle” in which HCl is oxidized to form molecular chlorine which diffuses through unprotective oxide scales to form metal chlorides. These gases are then oxidized, yielding metal oxides which deposit above the metal surface and
regenerating molecular chlorine. A schematic of the chlorine cycle is shown in Figure 1.

Many primary and secondary corrosion prevention methods have been suggested to manage high temperature corrosion. Primary methods refer to process modifications while secondary methods concern material choice. One primary approach which has received more interest as of late for WTE superheater corrosion is the addition or recirculation of sulfur into the flue gas [2]. Previous literature has demonstrated that addition of elemental sulfur into MSW can decrease boiler corrosion [5]. More recently, Andersson et al. investigated the recirculation of SO\textsubscript{2} in full scale testing. By increasing the SO\textsubscript{2}/HCl ratio from about 1/3 to 5/8, significant corrosion reduction was observed for 16Mo3 and Inconel 625, and Sanicro28 [2]. In practice however, the SO\textsubscript{2}/HCl ratio alone does not decrease superheater corrosion. A WTE plant survey conducted by WTERT in 2005 had varying results on superheater base tubing wastage rate versus reported SO\textsubscript{2} concentration and the HCl/SO\textsubscript{2} ratio [1]. It can be suggested therefore that other factors may dominate the effect obtained by increasing SO\textsubscript{2}.

The following discussion is part of ongoing experimental work aimed at understanding the influence of the SO\textsubscript{2}/HCl ratio on WTE superheater corrosion. Since the moisture content of MSW can vary significantly, this study considered how varying the water concentration can impact the process.

**EXPERIMENTAL PROCEDURE**

A laboratory-scale flow through reactor consisting of a Lindberg horizontal electrical furnace with a 12” heated zone and a 1” ID quartz tube was utilized for isothermal testing. This design was used partly to compare with previous experiments at Columbia Combustion and Catalysis Laboratory which maintained a thermal gradient by controlling both the gas and metal temperatures. The apparatus in current use is pictured in Figure 2.

SA178A, a commercial low carbon steel alloy, cited as a waterwall material in boilers [1], was investigated. This particular alloy was expected to demonstrate poor corrosion resistance at tested superheater temperatures (> 450 °C) under average flue gas concentrations. The chemical composition is summarized in table 1. Coupons were cut into dimensions of 0.5” x 1.0” x 0.078” by a water cooled device. Pre-test sample cleaning followed the standard procedures of ASTM G1-90 [6] which includes degreasing in an organic solvent, grinding with SiC paper, ultrasonic cleaning, and drying at 100 °C for 1 hour. An image of a typical coupon before testing is shown in figure 3a.

The composition of synthetic flue gas consisted of 8% O\textsubscript{2}, 12% CO\textsubscript{2}, and 800 ppmv HCl, while varying SO\textsubscript{2} (100-500 ppmv). Water was also varied (0-15%) to determine the influence of the system on its concentration. Nitrogen was included to maintain a balance of 500 cm\textsuperscript{3}/min for each test. A summary of the test conditions is included in table 2. Gases were heated to 325°C with heat tape before entering the reactor. Furnace temperatures were controlled either by a variable autotransformer (temperature accuracy ± 2%) or a PID temperature controller with temperature monitored using a K-type thermocouple for 50 hours experiments.

![Figure 2. Configuration of the apparatus](image)

The amount of corrosion was determined by the mass loss after multiple cleaning cycles which combined light brushing, ultrasonic cleaning and chemical cleaning until corrosion products were removed and constant weight was obtained.

![Figure 1. A schematic of the chlorine cycle](image)

![Table 1. Composition of tested alloy](image)

<table>
<thead>
<tr>
<th>Composition of SA-178A (wt%)</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Nb+Ta</th>
<th>Others*</th>
<th>Fe</th>
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<tbody>
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<td></td>
<td>0.07</td>
<td>0.06</td>
<td>0.47</td>
<td>0.054</td>
<td>0.016</td>
<td>0.01</td>
<td>0.119</td>
<td>0.002</td>
<td>0.128</td>
<td>bal.</td>
</tr>
</tbody>
</table>

*Others include S, Al, Ti, V, Co, N

Post test corrosion evaluation and cleaning also followed ASTM G1-90. Analysis of the surface morphology and surface elementary composition has been conducted with scanning electron microscopy (JEOL JSM-5600). Scales recovered from light scraping have been also analyzed with x-ray diffraction (INEL XRG 3000).

The amount of corrosion was determined by the mass loss after multiple cleaning cycles which combined light brushing, ultrasonic cleaning and chemical cleaning until corrosion products were removed and constant weight was obtained.
Average corrosion rates were calculated from the mass loss according to the equation listed below. The density of SA178A was assumed to be 7.85g/cm$^3$ based on table XI in ASTM G 1-90. The constant, K, was also provided in the method to report units in mils per year, mpy (1 mil = 0.001 in.).

Calculation of average corrosion rate (mils per year, mpy):

$$\text{mpy} = \frac{K \cdot W}{A \cdot t \cdot D}$$

K: constant, 3.45 E+06 (for mpy) W: mass loss, g A: area, cm$^2$ t: time, hrs D: density (7.95 g/cm$^3$)

RESULTS AND DISCUSSION

Three SO$_2$/HCl ratios were investigated at 500 °C: 1/8, 3/8, and 5/8 respectively, corresponding to 100, 300, 500 ppmv of SO$_2$ in the flue gas stream. 100 ppmv was identified as an initial SO$_2$ concentration, based on the average amount present in the combustion of US municipal solid wastes [7].

A typical surface morphology of SA178A before and after experiments at 500°C is shown in figure 3. Coupons exhibited some spalling after 50 hours, prior to cooling in the furnace. Scales recovered from coupons without water vapor exhibited a black and gray colored scale, as shown in figure 3b. Tests with water vapor (5% and 10%) also exhibited a red colored scale at air-scale interface, followed by black colored scale and dark gray. Preliminary XRD analysis of the scales confirmed the presence of Fe$_2$O$_3$ and Fe$_3$O$_4$ in analysis of water vapor experiments, which was expected based on appearance and oxidation literature [7, 8].

At 5% H$_2$O, as shown in Figure 4, an increase in sulfur dioxide had a significant impact on the corrosion rate, decreasing the average corrosion rate by 43% under an SO$_2$/HCl ratio of 5/8. The corrosion rate yielded at 5/8 is comparable to high wastage rates that are typically experienced in waste facilities at (157 mpy = ~4 mm/y) [8].

Previous work on the impact of sulfur on superheater corrosion attributed the decrease in corrosion to the conversion of metal chlorides (M = Na, K, etc.) present to sulfates [2,8] as shown in reaction 1:

$$2\text{MCl} + \text{SO}_2 + \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{M}_2\text{SO}_4 + 2\text{HCl} \quad (1)$$

At superheater conditions, the formation of sulfates is not considered harmful and the HCl formed is transported away, presumably downstream. In the case of the experiments discussed here, no chloride salt mixtures or ash were introduced.

One other possible explanation for the behavior observed at 5% H$_2$O, is the formation of SO$_3$, as shown in reaction 2 below:

$$\text{Cl}_2 + \text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{SO}_3 + 2\text{HCl} \quad (2)$$

This reaction has been previously proposed to explain the effect of sulfur on the concentration of hazardous chlorinated organics, such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in WTE flue gas streams [9]. Since HCl is much less likely to undergo reactions that yield PCDDS or PCDFS, Cl$_2$ is considered the more likely precursor. Therefore, the conversion of Cl$_2$ to HCl is desirable, just as in corrosion-assuming the mechanism of the chlorine cycle (shown in figure 1). As SO$_2$ is increased, less Cl$_2$ is available to diffuse in the mixed oxide layer and thus reduces corrosion.

At 15% H$_2$O there was no increase or decrease in corrosion at the previously tested SO$_2$/HCl ratios but remained steadily at 240 ±19 mpy, as shown in Figure 5. It should be noted that

![Figure 3](image-url)  
(a) Photo of surface SA178A prior to experiment. (b) Photo of SA-178A after 50 hr (1/8 SO$_2$/HCl).

![Figure 4](image-url)  
Figure 4. Effect of SO$_2$/HCl ratio on average corrosion rate on SA178A at 500°C (5% H$_2$O, 12% CO$_2$, 8% O$_2$, N$_2$ balance, Flowrate = 500 cm$^3$/min)
varying the concentration of water from 5% to 15% had no effect on the corrosion at SO\textsubscript{2}/HCl = 1/8.

One possible explanation for this behavior is that the increase of water and SO\textsubscript{2} will increase the concentration of HCl as shown in reaction 2. If the concentration of HCl is increased, in the presence of sufficient oxygen, more chlorine can be generated and increase the corrosion rate. Previous literature regarding the SO\textsubscript{2}/HCl ratio has recommended ratios of 3-4 for effective corrosion prevention [10]. This may indicate that more HCl/Cl\textsubscript{2} is liberated at higher water concentrations and excess SO\textsubscript{2} is needed to react with Cl\textsubscript{2}-and yield the behavior observed in this study at 5% H\textsubscript{2}O.

Future work will include quantifying the effluent HCl, SO\textsubscript{2}, Cl\textsubscript{2} and SO\textsubscript{3} concentrations in order to get a better understanding of a possible mechanism. Additional tests will include higher SO\textsubscript{2}/HCl ratios, intermediate water concentrations between 5-15% and different metal temperatures.

CONCLUSION

SA178A was exposed to a corrosive environment at 500 °C under various SO\textsubscript{2}/HCl ratios. Water concentration was also varied to determine its effect on the corrosion behavior. At 5% H\textsubscript{2}O, the average corrosion was reduced substantially by increasing the SO\textsubscript{2}/HCl ratio from 1/8 to 5/8. At 15% H\textsubscript{2}O however, the average corrosion rate remained constant at the same ratios. This demonstrates that the concentration of water in the flue gas stream significantly impacts the behavior of HCl and SO\textsubscript{2}.

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REFERENCES
