Corrosion and carburization of superheater materials in oxyfuel combustion

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Abstract

The energy sector is globally the largest CO₂ emitter. Carbon capture and storage (CCS) is a concept to reduce greenhouse gas emissions resulting from the use of fossil fuels in power generation, and integrated oxyfuel combustion concepts, combustion in oxygen-enriched environment to make post-combustion extraction easier, is studied one of the options for CCS. Oxyfuel combustion can be expected to differ from combustion in air by e.g. modified distribution of fireside temperatures, much reduced NOx but increased levels of fireside CO₂, SO₂ and water levels due to extensive flue gas recirculation. Increased flue gas recirculation may increase the concentration of a number of contaminants in the deposited ash and promote fouling and corrosion. In addition to development of low CO₂ emitting energy generation technologies, improved energy efficiency is essential in order to reach emission reduction targets. Increasing process efficiency requires high in-service temperatures for superheaters and reheaters.

In this paper the corrosion performance of two superheater austenitic steels (TP347HFG and Sanicro 25) has been studied in laboratory tests under simulated oxyfuel conditions with and without a synthetic deposits (85 CaCO₃ - 15 wt% CaSO₄, CaSO₄-0.55 wt% KCl) at 650 and 720°C up to 1000 hours.

1. Introduction

CO₂ emissions are gaining a significant attention in the policy reducing air pollutant emissions. The most cost effective and readily available option is to mitigate CO₂ emissions by increasing the plant efficiency. At the same time new technologies to CO₂ emissions reduction such as carbon capture and sequestration (CCS) processes have been developed. In these processes, CO₂ is captured from the cleaned products of combustion or gasification. It has been estimated that CCS for base load power generation is likely to become commercially available at around 2025. Oxyfuel combustion is one of the CCS technologies under research focus to CO₂ capture from flue gases. Compared to conventional air-fired combustion, the oxyfuel process will use a combination of oxygen, with a purity of more than 95 vol %, and recycled flue gas to combust the fuel producing a gas consisting of mainly CO₂ and water vapour, which is after purification and compression ready for storage [1,2]. The risk of enrichment of corrosive species, such as SO₂ and Cl, in the flue gas environment increases due to recycling of flue gas in oxy-fired combustion compared to air
firing. The changes in the combustion gas chemistry will also affect the chemistry and formation of deposits, with potentially increasing corrosion and internal attack of the boiler components that are in contact with the combustion and flue gas environment [3-5].

The corrosion mechanisms and limiting factors in air-fired combustion have been extensively studied over the past years. However, there is still relatively little experimental information available about the effects of oxyfuel combustion on the boiler material performance. The first demonstrations of the oxy-fuel concept are carried out currently used high temperature materials. Typically the presence of sulphur strongly increases the corrosion rate, but the influence of sulphur on corrosion can be complicated, as in the form of SO$_2$ it can also slow down corrosion. The phenomenon is dependent on time, fireside environment, gas partial pressures and alloying elements [6-11]. In oxyfuel combustion the likelihood of the presence of sticky deposits is increased [12-13]. Sulphation and carbonation of ash particles under oxyfuel combustion is higher due to high SO$_2$ and CO$_2$ potential. There are indications that oxide scales developing in O$_2$/CO$_2$/H$_2$O atmospheres are not that protective and internal carburisation may occur [8,14-15]. Limestone (CaCO$_3$) can be used in oxyfuel circulating fluidized bed (CFB) boilers as absorbent for capture of SO$_2$. In oxyfuel combustion the CaO-CaCO$_3$ equilibrium comes close to the normal operating temperature and the capture mechanisms may change from normal sulphation (CaCO$_3$-CaO-CaSO$_4$) to direct sulphation path (CaCO$_3$-CaSO$_4$) due to high CO$_2$ concentration. Hard deposits may occur during the simultaneous occurrence of calcination, sulphation and recarbonation. Such a deposit may cause operational problems like plugging of gas channels and/or corrosion of superheaters [16].

2. Experimental

Two superheater austenitic steels (TP347HFG and Sanicro 25) have been studied in laboratory tests under simulated oxyfuel conditions (2%O$_2$-29%H$_2$O-44%CO$_2$-0.6%SO$_2$-0.2HCl-N$_2$) with and without synthetic deposits (85 wt% CaCO$_3$ – 15 CaSO$_4$, CaSO$_4$-0.55 wt% KCl) at 650 and 720°C up to 1000 hours. Table 1 shows the chemical composition of used materials. Rectangle shape specimens with dimensions of 15 x 15 x 3 mm were machined from thick walled tubes. The samples were bright polished with SiC paper (P1200), washed with deionized water and ultrasonically degreased in ethanol. Exposure testing was carried out in horizontal Al$_2$O$_3$ tube furnace. The test environments were prepared from premixed and/or pure gases that were mixed based on flow rates and controlled using calibrated mass-flow controllers. The flow rate of gases was 10 l/h. The carrier gas was passed through a humidifying unit containing deionized water before the furnace, to add moisture to the gas mixture. In tests with synthetic deposit, deposit covered the half of sample, Figure 1.

After testing the samples were moulded in plastic after which the prepared and polished sample cross-sections were studied with optical and scanning electron microscope (SEM). The composition of oxide layers was determined with energy dispersive X-ray spectroscopy (EDX).

Corrosion behaviour of the materials was based on the estimation of the oxide layer thickness and depth of material degradation. The oxide thickness was determined by optical microscopy. There was some spallation of the oxide layers and thus the measurement results are taken as indicative only. In addition to oxide thickness measurement, weight change measurements were carried out for the specimens exposed without deposit.

Table 1. Chemical composition of test materials [wt%]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Nb</th>
<th>Fe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP347HFG</td>
<td>18.3</td>
<td>11.7</td>
<td>0.23</td>
<td>0.92</td>
<td>bal.</td>
<td>1.64 Mn, 0.33 Cu, 0.4 Si, 0.07 C</td>
</tr>
<tr>
<td>Sanicro 25</td>
<td>22.3</td>
<td>24.9</td>
<td>0.5</td>
<td>bal.</td>
<td>3.4 W, 1.5 Co, 2.9 Cu, 0.2 Si, 0.3 Mn, 0.24 N, 0.06 C</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. Sample set-up during exposure with deposit, the half of sample covered with deposit.

### 3. Results

Table 2 summarises the observed oxide thickness values and depth of possible internal degradation after 1000 h of exposure at 650 and 720°C under 2%O$_2$–29%H$_2$O–44%CO$_2$–0.6%SO$_2$–0.2%HCl–N$_2$ gas. After 1000 h exposure without deposit at 650°C TP347HFG showed more extensive oxidation than Sanicro 25. Uneven oxides with a two-layer nodule structure formed on the TP347HFG surface although locally a continuous scale was found in some parts of the sample. With short exposure times (168 and 500 h), only very thin or no oxide scale formed on alloy TP347HFG. EDX analyses showed an iron rich outer oxide layer and a mixed oxide inner layer mainly containing iron, chromium and nickel. At 720°C only a very thin oxide (~1 µm) formed on the TP347HFG surface and the weight change was negative. The oxidation rate of Sanicro 25 was almost negligible at 650°C. A negative weight change was observed at 720°C and a very thin Cr rich oxide scale was found on the surfaces. Figure 2 shows the weight change results of the exposure without deposit at 650 and 720°C.

Table 2. Summary of the observed oxide thickness and depth of internal degradation on the tested materials after 1000 h of exposure at 650 and 720°C. *outer layer detached

<table>
<thead>
<tr>
<th>Material</th>
<th>Environment</th>
<th>650°C Oxide</th>
<th>650°C Internal</th>
<th>720°C Oxide</th>
<th>720°C Internal</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP347HFG</td>
<td>Gas exposure</td>
<td>~20 µm</td>
<td>~1 µm</td>
<td>~80 µm</td>
<td>~50 µm</td>
<td>~150 µm*</td>
</tr>
<tr>
<td></td>
<td>with CaCO$_3$ – 15 wt% CaSO$_4$</td>
<td>~80 µm</td>
<td>~50 µm</td>
<td>~150 µm*</td>
<td>~80 µm</td>
<td>Internal carburization. S at GB’s at 720°C</td>
</tr>
<tr>
<td></td>
<td>with CaSO$_4$ – 0.55 wt% KCl</td>
<td>~100 µm</td>
<td>~50 µm</td>
<td>~100 µm*</td>
<td>~100 µm</td>
<td>S penetration through GB’s</td>
</tr>
<tr>
<td>San 25</td>
<td>Gas exposure</td>
<td>0.5…1 µm</td>
<td>~1 µm</td>
<td>10 µm</td>
<td>~20 µm</td>
<td>very badly corroded</td>
</tr>
<tr>
<td></td>
<td>with CaCO$_3$ – 15 wt% CaSO$_4$</td>
<td>~10 µm</td>
<td>~20 µm</td>
<td>~100 µm</td>
<td>~100 µm</td>
<td>very badly corroded</td>
</tr>
<tr>
<td></td>
<td>with CaSO$_4$ – 0.55 wt% KCl</td>
<td>200-500 µm</td>
<td>20-50 µm</td>
<td>&lt;300 µm*</td>
<td>300-500 µm</td>
<td>S, Cl traces at GB’s at 720°C</td>
</tr>
</tbody>
</table>

Corrosion was observed under deposits on both test materials. The oxide scale on TP347HFG was continuous around the sample both under deposit layer and above it (deposit covered only the half of the sample). Under the deposit layer the formed oxide was thicker. At 650°C a two layer oxide scale was observed, and at 720°C the outer layer of the oxide was detached, Figure 3. Sulphur was detected inside the oxide scale, and also at grain boundaries under the oxide. No chlorine was observed in the corrosion
products. In addition to oxidation, carburisation of TP347HFG was observed at both exposure temperatures with the CaCO$_3$-CaSO$_4$ deposit, Figure 4. Carburisation occurred both in the gaseous environment (in the part of sample above the deposit) and under the deposit.

**Figure 2.** Weight change results at 650 and 720°C under 2%O$_2$-29%H$_2$O-44%CO$_2$-0.6%SO$_2$-0.2HCl-N$_2$ gas without deposit

**Figure 3.** EDX analyses of oxides formed on TP347HFG steel after 1000 h exposure, a) at 650°C with CaSO$_4$-0.55 wt% KCl and b) at 720°C with CaCO$_3$ – 15 wt% CaSO$_4$. Note scales
The deposits accelerated corrosion of Sanicro 25 samples under the deposit. A thin oxide layer and some deeper pits through grain boundaries were detected in the gaseous environment (above the deposit), Figure 5. The deposit containing KCl accelerated corrosion of Sanicro 25 at 650°C. With the CaCO$_3$-15 wt% CaSO$_4$ deposit a relatively thin oxide formed on the Sanicro 25 surface and composed mostly of Cr$_2$O$_3$. With the CaSO$_4$-0.55 wt% KCl deposit a thick layered oxide was formed structure with an outer Fe rich oxide and an inner Cr rich scale, Figure 6. When the exposure temperature was increased to 720°C, corrosion was accelerated remarkably, especially with CaCO$_3$-15 wt% CaSO$_4$ deposit and the part of specimen covered with deposit was almost completely destroyed, Figure 7. Sulphur was detected in the oxide structures, and traces of Cl were found in the oxide and at the grain boundaries under the oxide scale with the CaSO$_4$-0.55 wt% KCl deposit.
Figure 6. Main components of the oxides formed on Sanicro 25 after 1000 h exposure at 650°C a) with CaSO₄-0.55 wt% KCl and b) CaCO₃ – 15 wt% CaSO₄. Note different scales.
a) Figure 7. EDX analyses of the oxides on Sanicro 25 after exposure at 720°C a) with CaSO₄-0.55 wt% KCl and b) CaCO₃ – 15 wt% CaSO₄. Note different scales

4. Discussion

The results imply that without deposit, the oxidation rate under simulated oxyfuel conditions (2%O₂-29%H₂O-44%CO₂-0.6%SO₂-0.2%HCl-N₂) is very reasonable at 650°C after 1000 h for both tested materials. At 720°C the formed oxide scale thickness was small, however negative weight change was observed due to chromium evaporation, no spallation of formed scales was seen. There is a general agreement that water vapour tends to accelerate the oxidation of chromia formers, especially at temperatures above 700°C [e.g. 17]. The scatter in results (no linear weight loss) was probably due to the depletion of surface chromium causing at least temporary diminishing of evaporation until new chromium is diffused to the surface area.

Corrosion of both test materials was found to occur under deposits. Some sulphur penetration was observed through grain boundaries in chromium depletion area under the oxide scale. At the 650°C exposure with deposits the oxide formed on TP347HFG had a two-layer structure, which had started by nodule formation at weak points such as grain boundaries. This nodular growth would have continued until the nod-
ules grow together to form a continuous oxide covering the whole surface. At 720°C the oxidation rate was higher and the part of the oxide scale, probably outer Fe-rich layer, had peeled off. In particular, exposure with the carbonate deposit resulted in corrosion and carburisation by formation of grain boundary carbides in TP347HFG steel. Earlier results [16] suggest that the critical limits of Cr and Ni content for carburisation are around 20% under the applied gas and deposit environments. The limits may be affected by the Cr/Ni ratio, extended time of exposure, and changes in the chemical and thermodynamic equilibria of the surfaces due to gradual modification in alloys, its oxides and deposits.

At 650°C the KCl containing deposit accelerated the corrosion of Sanicro 25 compared to exposure with CaCO$_3$ – CaSO$_4$ deposit. At 720°C this carbonate base deposit was more aggressive and the part of the specimen covered with deposit was almost completely destroyed.

5. Summary

Two boiler tube steels (TP347HFG and Sanicro 25) have been subjected to oxidation/corrosion testing at 650 and 720°C under simulated oxyfuel conditions with and without CaSO$_4$ based deposits.

A protective chromia was formed on Sanicro 25 during gas exposure without deposits at 650°C. On the surface of TP347HFG a two layer oxide structure with iron based oxides was formed. At 720°C both materials suffered from chromium evaporation. The materials exposed with deposits retained an oxide without notable spalling at 650°C, but at 720°C the spallation of outer oxide layer occurred. Also internal material degradation was observed and some sulphur penetration at grain boundaries below oxide scale was detected. The increase of test temperature to 720°C was detrimental and corrosion rate accelerated remarkably, especially in the case of Sanicro 25 under the CaCO$_3$ – CaSO$_4$ deposit.

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