Impact of oxy-fuel combustion on fly ash transformations and resulting corrosive behavior of alloys 310 and 617

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Abstract

Within fireside corrosion tests performed at University of Stuttgart, two alloys dedicated for ultra-supercritical boilers were chosen for a series of tests under oxy-fuel conditions at a metal temperature of 650°C and 750°C. Three real fly ash deposits and three minerals well-known from coal combustion were considered. The fireside corrosion was studied having in focus interactions between flue gas atmosphere, deposits and alloys during oxy-fuel firing with 0,5% SO₂ and exposure time of 350 h.

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1. Introduction

Oxy-fuel combustion process with recirculated flue gas was proposed in the early eighties on one side to produce CO₂ for Enhanced Oil Recovery by Abraham et al. [1] and on the other side to reduce significantly CO₂ emissions resulting from combustion of fossil fuels for the energy generation purposes, as proposed by Horn and Steinberg [2]. In the nineties, due to the re-emerging discussions about how to prevent global warming, oxy-fuel combustion received renewed interest [3] and it is seen as one of the most promising technologies for carbon capture and storage (CCS) [4] being economically and technically feasible for power station retrofitting [4][5].

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Within the last years one of the significant topics in the energy generation from fossil fuels have been ultra-supercritical and advanced ultra-supercritical power plants. The idea here is to raise the steam parameters in order to increase the net power plant efficiency while simultaneously reducing the emitted amount of CO₂/kWh. Henceforth operation of an oxy-fuel power plant under ultra-supercritical parameters would help to compensate the efficiency penalties resulting from the air separation and CO₂-compression processes. In this regard, development of superalloys to be applied as heat exchanger materials inside the boiler is necessary. From the fireside, apart from increased thermo-mechanical stresses, the boiler materials need to be resistant as well to fouling, slagging and the gas atmosphere itself. In case of oxy-fuel both fouling and slagging might be affected not only by the increased metal surface temperature but also by a different gas composition from conventional air-firing and longer gas residence time.

Pulverized coal-fired boilers, widely used in power plants, apply air for the combustion process. Air contains approximately 79%-vol. of nitrogen, which dilutes CO₂ content in the flue gas [6]. During oxy-fuel combustion, a blend of oxygen (> 95%) and recycled flue gas is applied for the combustion [5][7] thus significantly higher concentrations of species such as CO₂, SO₂, H₂O and HCl are present compared to the conventional combustion of coal with air as an oxidizer, assuming there is neither a deSOₓ-system nor a dry recirculation incorporated [5][7].

Higher SOₓ concentrations are of notable interest due to their role in corrosion process as well as sulphur retention in fly ash [6][8]. This risk is higher for most planned processes that apply recycle of flue gas without previous sulphur removal due to elevated partial pressures of SO₂ and SO₃ together with higher residence time comparing oxy-fuel to conventional air combustion. Accordingly, studies by Spörl et al. [9] revealed that the SO₃ concentrations in oxy-fuel are higher than in air-firing. This higher SO₃ formation is induced by higher partial pressure of oxygen and higher water level in the atmosphere [10][11]. Maier et al. [8] identified that the higher concentration of SO₃ promotes the sulphur retention in the ash at the convective section of the furnace (sulphur retention is negligible in radiative section, above 1150°C). This increased sulphur retention can intensify corrosion process from molten and solid ash in boiler deposits [5]. However, in terms of positive or negative impact on corrosion process, type of salts and their stability are the key factors. Studies by Maier et al. [8] and Tan et al. [3] have shown that sulphur retention is very dependent on both, the content of alkaline and alkaline earth metals, which result in sulphate salts and how these elements are bound in the ash [8].

In oxy-fuel combustion, the formation temperatures of CaCO₃ and CaSO₄ from CaO increase compared to air-case according to equilibrium calculations [5]. In the study of Stanger and Wall [5] the transition temperature of CaSO₄ is reported to increase due to higher concentrations of SO₂ and respectively the formation temperature of CaCO₃ is strongly related to CO₂ concentration [5]. The “temperature window” between CaSO₄ and CaCO₃ transition temperatures decreases and direct sulphation during decomposition of CaCO₃ can occur [5]. According to Mönckert et al. [10] and Buhre et al. [12], not only sulphation but also carburization occurs at deposit surfaces under oxy-fuel conditions, since the decomposition temperature of carbonates increases with high partial pressures of CO₂. Here the temperature range is significant. As Wigley et al. [13] state, the higher partial pressures of CO₂ in oxy-fuel combustion might affect transformations of carbonate minerals. This is the case of siderite (FeCO₃) and calcite (CaCO₃), important sources of iron (Fe) and calcium (Ca) which decrease the viscosity of aluminosilicate liquids, altering the stickiness of ash particles and the rate of sintering of deposits [13]. The temperature of calcite dissociation (CaCO₃ → CaO + CO₂) may increase in oxy-fuel combustion according to Wigley [13] what was later confirmed by Stanger and Wall [5]. Studies by Kull et al. [14] suggest that due to significant increase of local partial pressure of CO₂ resulting from calcite dissociation, carburization process might be increased at the metal surface. Tuurna et al. [15] found some carbon enrichment near the interface oxide/alloy after an exposure time of 1000 h at 650°C under oxy-fuel
atmosphere (60% CO₂, 30% H₂O, 3.6% O₂, 6.4% Ar), however carburization was not detected on any alloy (HR3C, Sanicro 25, A263 and A617) [15]. Under CaCO₃ deposit, carburization of X20CrMoV11-1 and TP347HFG was clear [15]; under CaSO₄ deposit, carburization was not observed on any alloy (X20, TP347HFG, HR3C, Sanicro 25, A263 and A617), nevertheless blends of CaCO₃/CaSO₄ deposits (85%-wt CaCO₃ + 15%-wt CaSO₄) change this behavior after an exposure time of 168 h [15]. Moreover the above case confirms that carburization is not only environment (atmosphere and deposit) but also alloy-dependent.

Concerning oxidation, carburization and sulphur induced corrosion in oxy-fuel combustion conditions, different observations have been made worldwide ([14] - [18] are only some of them). Generally, it can be concluded that a crucial role on these corrosion processes is played by the exact exposure conditions such as gas atmosphere, deposit, temperature, pressure and the alloy itself.

In the here described study influence on fireside corrosion of two austenitic superalloys under three real fly ash deposits and three minerals, well-known from coal combustion, is discussed. The fireside corrosion was studied having in focus interactions between flue gas atmosphere, deposits and alloys during oxy-fuel firing with 0.5% SO₂ at 650°C and at 750°C and exposure time of 350 h.

### Nomenclature

| CCS | Carbon Capture and Storage |
| El Cer | Colombian S-lean bituminous coal of alumino-silicatic character |
| EMPA | Electron Micro-Probe-Analysis |
| ICP-OES | Inductively Coupled Plasma Optical Emission Spectrometer |
| IFK | Institute of Combustion and Power Plant Technology, University of Stuttgart |
| KSVA | KohlenStaubVerbrennungsAnlage, 500 kWₜₜ test rig of IFK |
| LaTBK | Dry Lausatian S-lean lignite of basic character |
| LaTBK-S | Dry Lausatian S-rich lignite of silicatic character |
| S | Sulphur |
| XRD | X-Ray Diffraction |

### 2. Experimental part

The experiments were conducted in the corrosion test set-up at the Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart. The set-up consists of two electrically heated furnaces supplied with a gas blend which can be composed of water vapor, CO₂, O₂, SO₂ and N₂ and adjusted easily according to the needs of the given experiment [19]. The dedicated temperatures were set at 650°C and 750°C in order to simulate the conditions for an (advanced) ultra-supercritical power plant in superheater and reheater section of a boiler. The fireside corrosion was studied having in focus the synergetic effect of combustion gas atmosphere, deposit and the alloy itself.
The selected gas atmosphere corresponds to oxy-fuel combustion of a sulphur rich coal and comprises 77.0%-vol. CO₂, 4.5%-vol. O₂, 18.0%-vol. H₂O and 0.5%-vol. SO₂. The exposure time encompasses 350 h.

2.2. Tested alloys

Two well-known austenitic steels with a different base (Fe or Ni) were selected for the tests. These are TP310HCbN tested at 650°C and DMV 617 tested at 750°C (see Table 1).

Table 1. Composition of the tested austenitic alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Unit</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP310HCbN</td>
<td>%-wt</td>
<td>25</td>
<td>21</td>
<td>Bal. (51,9)</td>
<td>C, Si, Mn, P, S, N, Nb</td>
</tr>
<tr>
<td>DMV 617</td>
<td>%-wt</td>
<td>22</td>
<td></td>
<td>Bal. (54,8)</td>
<td>Co (11 %-wt), Mo (9 %-wt), Al, Ti,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C, Si, Mn, Cu,N, B, P, S, As, Pb</td>
</tr>
</tbody>
</table>

2.3. Deposits

The real fly ashes used in the exposure tests in the laboratory corrosion test set-up were collected during three measuring campaigns at 500 kWh solid fuel combustion test rig KSVA, at the University of Stuttgart [20]. Three different coal qualities were considered: a Colombian S-lean bituminous coal of alumino-silicatic character (El Cer), a dry Lausatian S-lean lignite of basic character (LaTBK) as well as a dry Lausatian S-rich lignite of silicatic character (LaTBK-S) (see Fig. 2 bar "before exposure"). Due to its high alkaline earth metals content, LaTBK ashes are found to contain the most sulphur even though the coal itself contains ca. 4 times less sulphur than S-rich lignite used in the combustion tests. On the contrary the El Cerrejón ashes are characterized by the lowest sulphur amount, what confirms predictions based on fuel analysis (the lowest alkaline earth metals content among tested fuels) (see Fig. 2 bar "before exposure").

The mono-mineral deposits applied in the tests (pyrite, calcite and anhydrite) are some typical minerals found in coal and/or in fly ashes resulting from conventional coal combustion. They were applied in order to determine what effect these significant coal/fly ash constituents might impose on the corrosion process of heat exchanger materials in a combustor under oxy-fuel conditions. Moreover, pyrite was selected additionally after observing its corrosive behavior during measurements performed at a superheater section in a power plant combusting hard coal.

2.4. Samples preparation

For the purpose of this study the tubes of the selected alloys were cut into rings and then into arcs, which were positioned in ceramic crucibles (see Fig. 1). Subsequently outer surface of each alloy specimen was covered with the deposit of real fly ashes collected during the combustion tests at the test rig (see Fig. 1) and reagent grade minerals typically found during conventional coal combustion (pyrite, anhydrite, calcite). Both corners of the alloy specimen were manually covered with the deposit, thus
approximately half of the alloy surface was deposit-free in order to analyze both interactions, gas phase -
deposit - metal surface as well as gas phase - metal surface [18], [19]. Finally each sample (alloy
specimen + deposit + ceramic crucible) was weighted before and after exposure.

Fig. 1. Preparation of samples for exposure tests [21].

2.5. Analytics

After the exposure tests were completed, the samples were cooled down in an inert atmosphere to
avoid condensation of sulphuric acid and water vapor. Subsequently, the samples were carefully
embedded in a resin. Following grinding and polishing of the samples surfaces, the analyses were
performed. Standard reflected light microscopy techniques were applied for the first characterization. For
more detailed metallographic micro-analyses, electron microscopy techniques were applied with an
electron micro-probe-analyzer CAMECA SX 100 [18], [19]. In addition, the chemical composition of
selected points was determined with the micro-analyzer. Part of the deposit was removed before
embedding without affecting the metal surface and further ICP-OES and XRD analyses were performed.

3. Results and discussion

3.1. Deposit transformation

3.1.1. Real fly ash deposits

After the exposure time of 350 h at both temperatures, all three fly ash deposits were significantly
enriched with sulphur (see Fig. 2). Moreover, the highest SO$_3$ content is shown by the LaTBK fly ash
deposit. As it was already indicated in Chapter 2.3, LaTBK fly ash is characterized by a significantly
higher alkaline earth metals content compared to the other two fly ashes, what influences strongly its
capture capacity of sulphur.

The sulphur enrichment factor of fly ash deposits$^\dagger$ after the exposure was similar at both temperatures
over the time of 350 h and was varying from ca. 3 for lignite ashes to more than 4 for the bituminous coal
ashes. This can be explained by the smaller size of fly ash particles from the combustion of the
bituminous coal, what results in an increase of the active surface of these fly ashes. Another significant
issue is the form in which sulphur is bound.

$^\dagger$ ratio of [SO$_3$] in deposit after exposure to [SO$_3$] in deposit before exposure using ICP-OES analysis data
XRD analyses were performed on fly ashes before and after the exposures. A peak series not seen before exposures was detected in all the fly ashes after the tests at 650°C as well as at 750°C. The diffraction pattern belongs to calcium-magnesium-sulphate. Moreover an increase in anhydrite and hematite is accompanied by a decrease in periclase, calcium ferrite and magnetite, which are transformed into sulphates and hematite. Differences between the diffraction patterns of the same fly ash exposed to both temperatures are negligible. It can be concluded that under the test conditions all three fly ashes, although varying in character, act as a “sulphur sink” due to their Ca- and Mg-content as well as due to the type of compounds that these elements belong in the fly ash.

Fig. 2. Main elements of real fly ash deposits before and after exposures at 650°C and 750°C at 77,0%-vol. CO₂, 4,5%-vol. O₂, 18,0%-vol. H₂O and 0,5%-vol. SO₂

3.1.2. Mono-mineral deposits

At both temperatures, 650°C and 750°C under studied conditions, calcite is transformed to anhydrite whereas anhydrite stays stable under tested oxy-fuel combustion atmosphere. Pyrite is oxidized to hematite. Based on these results, only calcite acts as a “sulphur sink” in the current conditions whereas anhydrite stays inert. Pyrite, due to its oxidation route, forms pyrrhotite before being completely oxidized to hematite and releases gaseous SO₂ [23]; both reactants can increase the sulphur induced corrosion potential, the latter given a rise in the local partial pressure of SO₂.

3.2. Fireside corrosion

None of the alloys developed a continuous protective oxide scale within 350 h at tested conditions. TP310HCbN alloy shows oxide reach isles characterized by outer iron rich and inner chromium rich layers. There is almost no chromium depletion zone. The alloy DMV 617 is characterized, additionally, by some irregular intergranular aluminium oxides. Sulphur induced corrosion on TP310HCbN alloy was not detected under real fly ash deposits after 350 h, however after 1000 h, after the fly ash cannot adsorb any more sulphur and corrosion process becomes gas-governed, chromium sulphides are found in alloy matrix [18]. EMPA results are consistent with XRD analyses; EMPA element maps of sulphur and
calcium overlap very well. The above findings indicate that fly ashes create a sort of protection layer in terms of sulphur induced corrosion under studied conditions.

The results obtained under the studied oxy-fuel conditions were compared against results from corresponding exposures under air combustion atmosphere [20]. Under oxy-fuel conditions the alloy TP310HCbN developed a thicker oxide scale than under air conditions. Montgomery et al. [16], Stein et al. [22] and Piron-Abellán et al. [17] have indicated that under oxy-fuel combustion, faster oxidation rates result from the presence of water content. Moreover studies by Montgomery et al. [16] have found that high content of carbon dioxide (CO$_2$) and water (H$_2$O) result in larger oxide thickness, compared with high oxygen (O$_2$) content. The alloy TP310HCbN did not develop a continuous and homogenous protective oxide scale under any of both conditions, neither air nor oxy-fuel. Moreover, no sulphur induced corrosion was detected under any of these atmospheres and real fly ashes after 350 h. In case of corrosion tests performed at longer exposures, after the fly ash deposit gets saturated with sulphur, the corrosion process is governed by gas reactions since no hot corrosion type II has been confirmed and clear sulphur induced corrosion is noticed [18].

Under calcite deposit there are no signs of sulphur induced corrosion due to the fact that calcite is being completely sulphated to anhydrite. Due to direct sulphation reaction (CaCO$_3$ + SO$_2$ + 1/2O$_2$ → CaSO$_4$ + CO$_2$ [24]) calcite captures sulphur at the considered conditions and thus protects metal surface against sulphur attack. On the contrary, TP310HCbN specimen exposed under anhydrite deposit shows occasionally presence of sulphur in the not evenly distributed oxide scale. This is believed to occur due to null-capacity of the deposit to adsorb sulphur, since anhydrite is stable at 650°C under studied conditions. Therefore, there is lack of filtration barrier towards SO$_2$/SO$_3$ coming from the gas atmosphere. At the tested conditions, a certain transformation of SO$_2$ to more reactive SO$_3$ is expected and confirmed qualitatively.

A catastrophic corrosion is observed at both TP310HCbN and DMV 617 specimens covered with pyrite. Due to oxidation of pyrite to hematite (see 3.1.2) pyrrhotite is formed and higher local partial pressure of SO$_2$ is produced, thus the increased sulphur activity enables formation of sulphides. Performed EMPA analyses confirm presence of nickel and molybdenum sulphides as well as very thick oxide layers (see Fig. 3). Ni$_2$S$_2$ and Mo$_2$S$_3$ eutectics have melting points at 635°C [25] and 664°C [26] respectively, which are within the tested conditions and thus could explain the observed corrosion rate.

Fig. 3. Samples after exposure under pyrite deposit. On the left TP310HCbN on the right DMV 617.

4. Conclusions

The fireside corrosion was studied having in focus interactions between the flue gas atmosphere, deposits and heat exchanger materials during oxy-fuel firing with 0.5% SO$_2$. After 350 h of exposure time
at 650°C and 750°C under studied conditions TP310HCbN, iron base superalloy containing 25% Cr, does not develop a constant homogenous protective oxide scale. Only oxide-rich isles are noticed. Moreover, no sulphur induced corrosion is detected on the alloy specimens exposed under real fly ashes- and CaCO₃-deposits. These deposits act to a certain extent as a protective barrier for the metal while being a "sulphur sink" to gaseous SO₂/SO₃, what has been confirmed by the comparison of chemical and mineral composition of the deposits before and after the exposures. For all the three real fly ash deposits analyzed with XRD before and after exposures, anhydrite increases and calcium-magnesium-sulphate is detected only after exposure indicating Ca- and Mg- rich particles are a significant “sulphur sink” in the performed study, what is consistent with the literature. Moreover, due to the sulphur enrichment factor of the bituminous coal ashes is higher than those of lignite ashes after exposures, it is confirmed that the sulphur retention capacity of a fly ash depends not only on the content of sulphate forming elements such as alkaline earth metals but also on how these elements are bound in the fly ash, what is consistent with the literature [8]. Very detrimental sulphur induced corrosion is observed in case of alloy specimens exposed to pyrite, a sulphur-rich mineral well-known from conventional air combustion. Since the mineral is undergoing a rapid oxidation at the tested conditions, high amounts of pyrrhotite and higher local partial pressure of SO₂/SO₃ are produced, what increases sulphur activity enabling sulphides formation at the tested samples.

At the metal sample exposed under a deposit already saturated with sulphur before the exposure (CaSO₄), little sulphur presence has been witnessed after the tests. Due to its stability at the tested conditions and due to lack of the adsorption capacity towards the gaseous SO₂/SO₃, the deposit stayed inert and thus did not act as a protective barrier against sulphur species present in the test atmosphere.

After an exposure time of 350 h the corrosion process is much more related to interactions gas atmosphere-deposit, which involves the adsorption capacity towards SO₂/SO₃ as well as the stability of the deposit, than to interactions with the alloy itself. In case of corrosion tests performed over longer time, after the fly ash deposit gets saturated with sulphur, the corrosion process is governed by gas reactions since no hot corrosion type II has been confirmed at studied conditions.

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References


