Experimental investigations on deposit formation by recarbonation on external heat exchanger surfaces in oxyfuel CFB boilers

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Abstract

Applying the oxyfuel process to the circulating fluidized bed technology, one of the major process concerns is the possible deposit formation on the immersed surfaces of the external heat exchangers caused by the recarbonation of unused calcined desulphurization sorbent (CaO). This paper presents first results from experiments carried out under air- and oxyfuel atmospheres in a lab-scale BFB of calcined limestone with an in-bed cooled deposition probe. It was found, that under oxyfuel conditions, the strong recarbonation of calcined particles on the cool surface lead to hard and stable carbonate depositions.

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1. Introduction

The oxyfuel process is a promising option for CO\textsubscript{2} capture in coal fired power plants. Here the fuel is burned in a mixture of pure oxygen and recirculated flue gas. The CO\textsubscript{2} rich flue gas stream can then be processed and stored. The application of this process in a circulating fluidized bed (CFB) boiler can combine potential advantages regarding the CO\textsubscript{2} capture efficiency with well-known CFB benefits such as fuel flexibility and in-situ desulphurization [1].

In comparison to the pulverized coal oxyfuel process, external heat exchangers (EHE) in CFB systems allows direct heat removal from the solid inventory to control the temperature in the combustion chamber. External heat exchangers in CFB systems are operated as bubbling fluidized beds. Heat exchanger surfaces are immersed into the bed to ensure optimal heat transfer from the bed particles. In air fired
boilers, the EHE is fluidized with air. In the oxyfuel case, one option is to establish the fluidization by a stream of recirculated flue gas. This prevents nitrogen ingress, and a separate convective heat recovery area for the EHE fluidization gas is not necessary. In Table 1, flue gas compositions from oxyfuel pilot plant tests described in the literature are listed. Unfortunately, there are only very limited information published about the temperature range EHEs are operated in: The upper temperature limit is set by the temperature in the combustion chamber, hence a maximum temperature of 850-900°C is realistic. The lower limit is set by possible quenching effects in the combustion chamber caused by too cold solid recirculation.

Table 1 Flue gas composition from oxyfuel fluidized bed pilot tests [2,3,4]

<table>
<thead>
<tr>
<th>Flue gas component</th>
<th>vol.-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>60-90</td>
</tr>
<tr>
<td>H₂O</td>
<td>5-30</td>
</tr>
<tr>
<td>N₂</td>
<td>2-5</td>
</tr>
<tr>
<td>O₂</td>
<td>3-5</td>
</tr>
</tbody>
</table>

Taking into account the lower amount of flue gas to be recirculated due to the cooling of the solids, and thereby the smaller combustion chamber volume; the fraction of heat transferred in external heat exchangers can rise up to 70% in the oxyfuel case [5,6]. Hence, a reduction of the heat transfer capacity in this component due to depositions will strongly effect the overall process efficiency. The deposition mechanism investigated in this work is caused by the recarbonation reaction of excess lime (CaO), not reacted during desulphurization.

In coal fired CFB boilers, limestone can be continuously injected into the combustion chamber to capture the sulphur dioxide formed from sulphur components of the coal. In typical air-fired CFBs with operating temperatures of around 800-850°C, the inserted limestone is first calcined (Eq. 1) and then sulphated to CaSO₄ (Eq. 2)[7].

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaO} + \text{SO}_2 + 1/2\text{O}_2 & \rightarrow \text{CaSO}_4
\end{align*}
\]

(1) \hspace{1cm} (2)

The equilibrium of the calcination reaction (Eq. 1) is depending on the temperature and the partial pressure of the carbon dioxide in the fluidization gas. Equation 4 represents this behavior [8]. \( E \) is the activation energy of 159,000 kJ/kmol and \( R \) is the universal gas constant.

The function is shown in Figure 2.

\[
P_e = 1.2 \times 10^7 \times \exp(-E/RT)
\]

(4)

Under oxyfuel condition (Table 1), the high partial pressure of CO₂ will inhibit the calcination of the limestone below temperatures of 870°C [9]. In this case the direct sulphation of the limestone particles will take place (Eq. 3 [10]).
CaCO₃ + SO₂ + 1/2O₂ → CaSO₄ + CO₂       (3)

Due to the conditions during oxyfuel CFB combustion and to reach efficient desulphurization, temperatures above 870°C in the boiler are reported to be beneficial [4,11]. Taking into account the calcining conditions and the excess sorbent not being sulphated [12], a considerable amount of active CaO (30-45 wt.-%) will circulate in the CFB system [13].

A portion of the active CaO leaves the reactor as fly ash and is cooled down in the convective section of the boiler. The other part of bigger calcined particles is separated from the gas in the cyclone and then recirculated via the loop-seal and external heat exchanger back into the combustion chamber. In both cases, in the flue gas path and in the EHE, CaO is cooled down in contact with oxyfuel flue gas, containing up to 90 vol.-% CO₂. Here recarbonation of the calcined material will occur by taking up CO₂ from the flue gas (Eq.5).

CaO + CO₂ → CaCO₃       (5)

Furthermore, oxyfuel flue gas can contain high amounts of water vapor, up to 30 vol.-%. It has been described in the literature [14], that the H₂O catalyzes the carbonation reaction (see eq. 6 and 7).

CaO + H₂O → Ca(OH)₂       (6)

Ca(OH)₂ + CO₂ → CaCO₃ + H₂O       (7)

The recarbonation effect of fly ash and its consequences in the convective section is not within the focus of this work, the reader is referred elsewhere [13].

In oxyfuel EHEs, carbonate depositions may form on cool heat exchanger surfaces immersed into the fluidized bed where the particle temperature drops below the calcination temperature. These carbonate formations are to be very resistant to the possible erosion in bubbling fluidized beds. A build-up of deposits caused by the carbonation of the continuous stream of active CaO particles into the EHE will decrease its heat transfer capacity. As mentioned above, due to the larger heat fraction transferred here under oxyfuel conditions, this will significantly influence the overall boiler performance more than in air-fired CFB systems.

So far the recarbonation issue has been investigated concerning fly ash depositions in the convection path of oxyfuel CFB boilers [13]. Concerning EHE, a possible defluidization due to CO₂ uptake from the fluidizing agent has been mentioned [15]. But potential deposit formation because of recarbonation of bed ash material has not yet been described in the literature.
2. Experimental

A new lab-scale bubbling fluidized bed reactor has been designed, built and successfully commissioned for deposition experiments of immersed heat exchanger surfaces in fluidized beds. The reactor has an inner diameter of 70mm and a height of 1000mm. To be able to adjust and maintain representative bed temperatures for EHEs, the reactor is equipped with electric heating along its height. Together with the gas preheater a total electric heating power of 11kW has been installed.

In Figure 2 a sketch of the general facility configuration is presented: The fluidization gas can be mixed from air, nitrogen, carbon dioxide and steam. This enables comparative studies between air and oxyfuel modes. The gas mixture is then fed through a gas preheater where the gas temperature is increased up to 500°C. The preheated gas enters the reactor to fluidize the bed material. Fresh bed material can be fed continuously into the reactor. In the middle of the bed height, a steel sample tube is positioned. The temperature of the tube wall is controlled via the cooling air stream through the tube. During the commissioning of the facility, the operating ranges of all crucial parameters have been confirmed to reflect the conditions in external heat exchangers (see Table 2).

Table 2 operating range of test facility

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Operating range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed temperature</td>
<td>( T_{\text{Bed}} )</td>
</tr>
<tr>
<td>Probe tube wall temperature</td>
<td>( T_{\text{Wall}} )</td>
</tr>
<tr>
<td>Superficial velocity</td>
<td>( u_0 )</td>
</tr>
<tr>
<td>Fluidization gas</td>
<td>( \text{CO}_2 )</td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2\text{O} )</td>
</tr>
<tr>
<td></td>
<td>0.3-1 m/s</td>
</tr>
<tr>
<td></td>
<td>0-100 vol.-%</td>
</tr>
<tr>
<td></td>
<td>0-50 vol.-%</td>
</tr>
</tbody>
</table>
The aim of the experiments carried out in this work was to study the deposition behavior of the unused excess lime in air- and oxyfuel conditions. For these first fundamental experiments, calcined limestone was used as bed material (91.76 wt.-% CaO). This is to avoid the influence of coal ash components on any deposition mechanisms and to examine the deposition behavior only related to recarbonation.

Two depositions experiments were carried out: A reference case with air as fluidization gas, and one oxyfuel case with fluidization provided by a simulated oxyfuel flue gas consisting of CO₂, H₂O and N₂. Fresh calcined limestone was continuously fed into the reactor.

In both cases the bed temperature was set to 700°C. In Figure 2 it is shown that thereby strong carbonating conditions were established in the oxyfuel case; while in the air case, still calcining conditions occur. The sample tube wall temperature was set to 400°C to ensure a cool tube surface with strong carbonating conditions. A summary of the two cases and the conditions in the BFB reactor is given in Table 3.

After the experiments, the reactor was cooled down. The deposition sample tube was removed from the reactor and prepared for inspection and mineral analysis. The deposition patterns are visually inspected with an optical microscope and Raman spectroscopy was used to confirm of the mineral phase of the deposited material.

### Table 3  Conditions at the experimental points

<table>
<thead>
<tr>
<th>Case</th>
<th>Air</th>
<th>Oxyfuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{Bed}</td>
<td>700°C</td>
<td>700°C</td>
</tr>
<tr>
<td>T_{Wall}</td>
<td>400°C</td>
<td>400°C</td>
</tr>
<tr>
<td>Fluidization Gas</td>
<td>Air</td>
<td>CO₂: 60 Vol.-%</td>
</tr>
<tr>
<td>Composition</td>
<td>H₂O: 30 Vol.-%</td>
<td>N₂: 10 Vol.-%</td>
</tr>
<tr>
<td>Duration</td>
<td>30h</td>
<td>30h</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>Calcining</td>
<td>Carbonating</td>
</tr>
</tbody>
</table>

Figure 2  CaO-CaCO₃ equilibrium and experimental points

### 3. Results

In Figure 3, two different deposition patterns for each experiment are shown. The microscope photographs have been taken at tenfold magnification. Photographs (b) and (d) show deposits at the edge of the sample tube, near the reactor walls. This can represent dead zones in EHEs, which are not influenced by the fluidization gas. For both experiments - air and oxyfuel - this deposition was thicker and more homogeneous. Photographs (a) and (c) are taken from the middle of the sample tube, immersed into the center of the fluidized bed. The deposition surface appears sputtered by bed particles.

The depositions under oxyfuel conditions are seen in Photographs (a) and (b). Particularly conspicuous is the mechanical stability and hardness of the deposited material. The microscopy examination revealed
an amorphous mineral structure formed on the metal surface. A thin primary coating grew directly on the surface, formed by small dust-like particle. In Photo (b) the transition from the dead zone with a thick deposit to the area affected by the fluidization with the primary deposit layer is visible. In the center of the reactor (Photo (a)), bigger particles were able to impact on and coalesce with this primary layer. In order to check the mineral composition of both layers, Raman spectroscopy analysis has been carried out: All measurements delivered a specific spectrum. It was clearly identified as pure calcite (CaCO₃). Based on the boundary conditions of the experiment, the sintering effect on the sample tube surface has to be caused by the recarbonation reaction. It is expected, that calcined particles first impact on the cool surface followed by their carbonation. The carbonation reaction on the surface leads to the observed hard and stable mineral coalescence.

In the air case (see photos (c) and (d)), more material deposited on the tube. But the deposition has a low mechanical stability. Flakes of deposited material are easily removed from the sample tube by hand. It is expected, that this fragile depositions are not able to withstand erosion forces appearing in a BFB of real bed ash, especially regarding hard minerals like silica compounds. The microscopy photos do not show the sintered mineral structure found under oxyfuel conditions. A smooth layer of calcined material formed a ground layer around the cooled tube. Bigger particle then impact and stick to this surface. However they did not merge or sinter with it. The surface remains rough and fragile, because due to the reaction conditions, no recarbonation can take place.

Figure 3 Microscopy photos of deposition samples: oxyfuel (a,b) and air (c,d)
4. Conclusions

Experiments in a lab-scale BFB with calcined limestone as bed material were conducted to study the depositions caused by recarbonation of active CaO around immersed heat exchanger surfaces. The results showed that strong carbonating conditions, as they appear in EHE fluidized by oxyfuel flue gas, can lead to hard and stable carbonate deposits on cool surfaces. The properties and structure of the mineral formations are rooted to mineral coalescence of particles during their recarbonation on the surface. This did not occur with air fluidization. Depending on the combustion chamber operation, this specific deposition mechanism will influence the performance of external heat exchangers in oxyfuel CFBs fluidized with recirculated flue gas. Therefore, the application of presented deposition mechanism have to be proved with a realistic coal ash bed material and the influence of operating parameters like the bed temperature have to be investigated.

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References


