Study of Recarbonation in Circulating Fluidized Bed Combustion

Marko Palonen
*Metso Power Oy*

Irina Hyyatiäinen
*Tampere University of Technology*

Anna Mahlamäki
*Tampere University of Technology*

Mikko Varonen
*Tampere University of Technology*

Follow this and additional works at: [http://dc.engconfintl.org/cfb10](http://dc.engconfintl.org/cfb10)

Part of the [Chemical Engineering Commons](http://dc.engconfintl.org/cfb10)

Recommended Citation


This Conference Proceeding is brought to you for free and open access by the Refereed Proceedings at ECI Digital Archives. It has been accepted for inclusion in 10th International Conference on Circulating Fluidized Beds and Fluidization Technology - CFB-10 by an authorized administrator of ECI Digital Archives. For more information, please contact franco@bepress.com.
ABSTRACT

Oxy-fuel circulating fluidized bed combustion (CFBC) can use calcium based sorbents, primarily limestone, for the in-situ capture of much of the sulfur dioxide in the fuel. Under oxy-fuel CFBC conditions, the CO₂ content is usually high, and at high combustor temperatures sulfur capture can occur in two steps, calcination and then sulfation. The typical Ca utilization ratio in oxy-fuel CFBCs is less than half. When temperature is below the calcination temperature while remaining exposed to a high CO₂ environment, recarbonation of unused CaO may occur. This reaction between calcium oxide and carbon dioxide has the potential to create serious operational problems and boiler maintenance issues. The main purposes of this study were to design a test method to study recarbonation of limestone under oxy-firing fluidized bed conditions using a test reactor and to carry out test runs using this method. The test runs were carried out in a test reactor at Metso Power Research and Development Center in Tampere, Finland.

The results show that the recarbonation and calcination reactions are limited by thermodynamic equilibrium, while the partial pressure of CO₂ and the temperature also play important roles. The effects of N₂ and O₂ are not significant during the fast reaction period, but become more pronounced during the slow, diffusion-controlled reaction stage. Repeatability of the test method was good.

INTRODUCTION

Carbon-dioxide capture and storage (CCS) offers the potential for major reduction in carbon dioxide emissions from fossil fuel based power generation. Oxygen enriched combustion has been identified as one of the main CCS technology options. The main design parameter in oxy-firing is to burn fossil fuel in a mixture of oxygen instead of air and recycled flue gas, which contain mostly CO₂. (Eriksson et al. (1), Zhao et al. (2))

Oxy-fuel circulating fluidized bed combustion (CFBC) can use solid sorbents, primarily limestone, for in-situ capture of much of the sulfur dioxide in the fuel. Under oxy-fuel CFB combustion conditions, the CO₂ content is higher than 70%, and at high combustor temperatures sulfur capture can occur in two steps. First, the limestone is expected to decompose to CaO, and calcination (I) and subsequent reaction between CaO and SO₂ will lead to the formation of solid CaSO₄, sulfation (II).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination</td>
<td>CaCO₃(s) + heat → CaO(s) + CO₂(g)</td>
</tr>
<tr>
<td>Sulfation</td>
<td>CaO(s) + SO₂(g) + 1/2O₂(g) → CaSO₄(s) + heat</td>
</tr>
<tr>
<td>Recarbonation</td>
<td>CaO(s) + CO₂(g) → CaCO₃(s) + heat</td>
</tr>
</tbody>
</table>
Calcination will proceed only if the partial pressure of the \( \text{CO}_2 \) in the gas above the limestone is less than the equilibrium partial pressure of carbon dioxide, at the calcination temperature. For each partial pressure of \( \text{CO}_2 \) there is a corresponding temperature, known as the equilibrium calcination temperature. Figure 1 plots five of the expressions for dissociation pressures and corresponding equilibrium calcination temperatures listed in the literature.

![Figure 1. Dissociation pressures and corresponding equilibrium calcination temperatures. (Basu et al. (3), Baker (4), FACT-database (5), CRC Handbook (6), Nskala et al.(7))](image)

The typical Ca utilization ratio during sulfation in CFBCs is about 30–45%. Therefore, the CaO content in CFBC fly ash and bed ash is generally high. When CFBC ash cools while remaining exposed to a high \( \text{CO}_2 \) environment, recarbonation (III) of unused CaO deposited on cool surfaces may occur. (Wang et al. (8)) Recarbonation is the reverse reaction to calcination, and it occurs below calcination temperatures. This phenomenon has the potential to create serious operational problems and boiler maintenance issues.

There are relatively few findings on oxy-fuel fluidized bed combustion published in the open literature, especially studies on recarbonation. However, there are a few studies in which the recarbonation was carried out mainly in TGA. The main purposes of this study were to design a test method to study recarbonation of limestone under oxy-firing fluidized bed conditions using a test reactor and to carry out test runs using this method.

**EXPERIMENTAL SET-UP AND PROCEDURE**

The experimental tests were carried out in a vertical tube reactor with an internal diameter of 4.9 cm. The test reactor simulates a fluidized bed furnace where a limestone sample is fluidized in a sand bed using inlet gas. In this experimental study, the reactor was supplied with \( \text{CO}_2 \) and \( \text{O}_2 \) in an \( \text{N}_2 \) balance. The pure gases are mixed before entering the reactor inlet. The gases flow through a perforated grid at the bottom of the reactor up to the top of the reactor. The fine particles in the flue gas are separated and captured by a cyclone. The sand and limestone can be fed in batches from the top of the reactor. The hot bed material can be removed by an ejector from above the tube reactor. Also the cyclone can be emptied. The flue gas flows through gas analyzers to the stack. The test equipment used in this study is illustrated in Figure 2.
The test reactor is fully automated and computer-controlled. Its temperature is controlled by electric heaters with a combined heat input of 10.4kW. Electrical heaters encircle the reactor. The heaters can maintain the bed region at a maximum temperature of 850°C. The temperature at many different points along the tube reactor (at different heights from the grid) can be measured with thermocouples. The walls of the reactor are insulated with thermo wool to avoid heat loss. The pressure differences can be controlled by pressure control valves, and pressure differences in the reactor tube and at the grid plate are measured. The pressure difference between the reactor tube and atmospheric pressure is also measured. Mass flow meters are utilized to obtain the desired inlet volume flow rates (l/min). The concentrations of CO\(_2\) and O\(_2\) in the gas leaving the bed were measured continuously, using gas analyzers. The evolution of gas concentrations in the outlet gas and the temperature and pressure differences were continuously monitored and recorded at intervals of one second.

**Table 1. Chemical compositions of Piney Creek limestone.**

<table>
<thead>
<tr>
<th>Element</th>
<th>wt-%</th>
<th>Element</th>
<th>wt-%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>51.6</td>
<td>K(_2)O</td>
<td>0.13</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>3.1</td>
<td>Na(_2)O</td>
<td>0.02</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.04</td>
<td>MnO</td>
<td>0.053</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>0.69</td>
<td>P(_2)O(_5)</td>
<td>0.067</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>1.4</td>
<td>S-Eltra</td>
<td>0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.55</td>
<td>H.h. 950°C</td>
<td>41.7</td>
</tr>
</tbody>
</table>

**Table 2. Experimental conditions.**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>X(_{CO_2}) (vol-%)</th>
<th>X(_{O_2}) (vol-%)</th>
<th>X(_{N_2}) (vol-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650, 750, 850</td>
<td>10,40,60,90</td>
<td>4, 10</td>
<td>0.6,36,56,86</td>
</tr>
</tbody>
</table>
The limestone used in this study was Piney Creek (PC) limestone from the USA; its chemical composition is shown in Table 1. The limestone samples were prepared before the experiments. All experiments followed the same procedure. First, the limestone was sieved to a size fraction of 500–710µm, which was considered to be appropriate for the fluidized-bed system. Another reason for sieving was to remove all the small particles and to obtain a coarse enough batch, because if the particles are too small they may escape with the flue gas. After sieving, 20 g of limestone was calcined in a furnace at 900°C (30 minutes) under air. The tube reactor was operated in oxy-fuel combustion mode under atmospheric conditions. In each run, 130 g of sand at a size of 0.1–0.5mm was loaded from the top of the reactor to form a fluidized bed. A constant fluidization velocity of 0.3m/s was maintained throughout the tests. Each test run was initiated by loading a calcined and weighed batch of limestone onto the hot sand bed, which had been heated to the required temperature and was simultaneously fluidized by a gas mixture containing the desired content of CO₂ and O₂ in an N₂ balance. The CaO conversion was calculated according to the amount of CO₂ which had reacted during the test run. The calcination was studied by using 20 g of fresh and unprepared Piney Creek limestone as the sample instead of the calcined sample. Table 2 shows the experimental conditions during the series of experiments.

RESULTS AND DISCUSSION

To estimate the composition of the samples (calcined limestones) it is necessary to determine the free lime (CaO) contents. After calcination and before each recarbonation test, the calcined sample was weighed to measure mass loss during the calcination process, and thereby the extent of the calcination. The total weight loss of the sample after calcination should be due to the weight of the CO₂ lost through the CaCO₃ decomposition. The total molar content of CaO in the calcined sample was calculated from this weight loss. Respectively, the conversion of CaO to CaCO₃ during the recarbonation test in the tube reactor was calculated according to the amount of CO₂ reacted during the test run, while conversion of calcium oxide was calculated on a molar basis.

The first 320 seconds of reaction were taken into consideration, as this period was ascertained to be sufficient to achieve the maximum reaction rate and therefore bring the reaction into the slower (diffusion-limited) reaction regime.

Effect of CO₂ content

Conversions of CaO vs. time for different CO₂ contents at three different temperatures are presented in Figures 3 (a)–(c). There were four different CO₂ contents and 4% of O₂ in N₂ atmosphere. As can be seen in Figure 3 (a), high CO₂ plays a particularly important role in the recarbonation of CaO. The figure shows that the conversions of CaO are close to each other except for conversion in high (90%) CO₂ content. The higher content of CO₂ corresponds to the increased conversion of CaO. CO₂ and CaO are both reactants and the higher content of CO₂ leads to the adding shift of the reaction toward the product side (CaCO₃), which compensates for the imposed change in the conditions.
Figure 3 (b) shows that in the recarbonation results obtained at a temperature of 750°C, the conversion at 90% CO$_2$ is highest while the difference in the CaO conversion between 60% CO$_2$ and 40% CO$_2$ is not significant. Several observations can be made for conversion at 10% CO$_2$. First, the low concentration of CO$_2$ leads to the low conversion of CaO. Second, as can be seen in Figure 1, this test point overlaps the equilibrium curve, and such a test point position causes a drop in the conversion of CaO.

The recarbonation of CaO at 850°C is shown in Figure 3 (c). The conversion of CaO at 90% CO$_2$ is over 1. This is impossible and must represent a measuring error. The conversion of CaO at 40% CO$_2$ is close to zero, because at this point the pressure of CO$_2$ is close to the dissociation pressure. At 10% CO$_2$, conversion of CaO is negative because the partial pressure of CO$_2$ is below the dissociation pressure at this point. Under these conditions, the reverse reaction to recarbonation, i.e. calcination, takes place.

**Effect of temperature**

Figures 4 (a)–(d) show the recarbonation results obtained for a CO$_2$ content of 10–90%, 4% O$_2$ in an N$_2$ balance. The effect of temperature on recarbonation was studied and was found to have a strong effect on the conversion of CaO. Recarbonation is exothermic, which means that the forward reaction is favored by lower temperatures. Nevertheless, experiments show that higher temperatures lead to higher conversions of CaO.
The conversion of CaO decreases rapidly as the temperature approaches the equilibrium temperature, as shown in Figure 4 (b) at 850°C, (c) at 850°C and (d) at 750°C. When the temperature is above the equilibrium temperature, the conversion of CaO is negative, as shown in Figure 4 (c) at 850°C.

Effect of N\textsubscript{2} and O\textsubscript{2}

The effect of temperature on the reaction between CaO and CO\textsubscript{2} in a mixture of 90% CO\textsubscript{2} and 10% O\textsubscript{2} without N\textsubscript{2} is shown in Figure 5, curves (b), (d), and (f). It seems that the higher temperature corresponds to the increased conversion of CaO. This is the same observation as that made for the tests at 90% CO\textsubscript{2}, 4% O\textsubscript{2} in an N\textsubscript{2} balance, and three different temperatures, as presented in Figure 4 (a).
Figure 5 presents in parallel the curves of CaO conversion with and without N\textsubscript{2} and with different O\textsubscript{2} content. Figure 5, curves (c) and (d) at 750°C and curves (e) and (f) at 650°C show that the conversions of CaO at the same temperature (650°C and 750°C) with and without N\textsubscript{2} (with 4% and 10% O\textsubscript{2}) during the fast reaction period are similar. The slight differences between the runs become more prominent during the slow, diffusion-controlled reaction stage, when conversion of CaO at 90% CO\textsubscript{2}, 4% of O\textsubscript{2} in an N\textsubscript{2} balance becomes greater than the conversion of CaO at 90% CO\textsubscript{2} and 10% O\textsubscript{2}. As can be seen in Figure 5, curves (a) and (b) at 850°C, there is difference between the conversions of CaO, probably due to an error in measurement of curve (a).

**Repeatability**

To verify the oxy-fuel firing results, repeat tests were conducted with calcined samples. Repeatability is assessed through the variation in measurements taken under the same conditions. The test conditions were identical in both tests, but they were carried out on different days. It seems that the consumption rates of CaO were close to each other for the tests and repeat tests. In summary, it can be said that the repeatability of this test method is good.

**CaCO\textsubscript{3} feeding – calcination**

The conversion of CaCO\textsubscript{3} at 850°C is presented in Figure 6. Here, the conversion of CaCO\textsubscript{3} is the molar ratio of the reacted CaCO\textsubscript{3} in relation to the initial content of CaCO\textsubscript{3} in the sample.

![Figure 6. Conversion of CaCO\textsubscript{3} at temperature of 850°C. 10–90% CO\textsubscript{2}, 4% O\textsubscript{2} in an N\textsubscript{2} balance.](image)

As can be seen in Figure 6, the highest conversion of CaCO\textsubscript{3} is at 10% CO\textsubscript{2}. The conversion of CaCO\textsubscript{3} at 40% CO\textsubscript{2} is low, and at 60% CO\textsubscript{2} near to zero. This is because the partial pressures of CO\textsubscript{2} at these test points are close to the dissociation pressure of CO\textsubscript{2}. The conversion of CaCO\textsubscript{3} at 90% CO\textsubscript{2} is negative, because the partial pressure of CO\textsubscript{2} at this point is above the dissociation pressure of CO\textsubscript{2}. This means that the recarbonation takes place at these conditions and the equilibrium is on the reactant (CaCO\textsubscript{3}) side.

**CONCLUSIONS**

The experimental tests on recarbonation were carried out in a test reactor, which simulates oxy-firing fluidized bed conditions. The extent of recarbonation was determined using the differences in the concentrations of CO\textsubscript{2} in the flue gas during the tests.
The conversion of CaO showed that recarbonation occurred easily at conditions, where the values for the CO$_2$ concentration was noticeably higher than the equilibrium CO$_2$ concentration at the reference bed temperature under certain conditions. Observations during the experiments show that the conversion of CaO is also sensitive to temperature, the conversion of CaO being significantly higher at high temperatures than at low temperatures, when the temperature is above the equilibrium temperature. The experiments show that the conversion of CaO decreases rapidly as the temperature approaches the equilibrium temperature. When the temperature is below the equilibrium temperature, the conversion of CaO is negative, and under these conditions the reverse reaction to recarbonation (calcination) takes place. Calcination was examined by using fresh limestone as the sample instead of the calcined sample. The highest conversion of CaCO$_3$ was when the CO$_2$ content was low, whereas when the CO$_2$ content was high, recarbonation took place instead of calcination. The conversions of CaO with and without N$_2$ (with 4% and 10% O$_2$) during the fast reaction period are similar. The small differences between the runs are pronounced during the slow, diffusion-controlled reaction stage. The experimental data show that repeatability for this test method is good.

The study of recarbonation will continue in a 4 MW oxy-fuel CFB pilot-scale unit during several weeks in the fall of 2010. The bigger test equipment makes it possible to study the effects of many important parameters, e.g. moisture, temperature and Ca/S ratio, on recarbonation.

REFERENCES

5. FACT-database. Bale, C.W., Pelton, A.D., Thompson, W.T. CRCT École Polytechnique de Montréal, Quebec, Canada.