Pressurised calcination–atmospheric carbonation of limestone for cyclic CO₂ capture from flue gases

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A B S T R A C T
A study was carried out to investigate the CO₂ capture performance of limestone under atmospheric carbonations following pressurised calcination. A series of tests was carried out to study the role of pressurised calcination using a fluidised bed reactor. In this investigation, calcination of limestone particles was carried out at three levels of pressure: 0.1 MPa, 0.5 MPa, and 1.0 MPa. After calcination, the capture performance of the calcined sorbent was tested at atmospheric pressure. As expected, the results indicate that the carbonation conversion of calcined sorbent decreases as the pressure is increased during calcination. Pressurised calcination requires higher temperatures and causes an increase in sorbent sintering, albeit that it would have the advantage of reducing equipment size as well as the compression energy necessary for CO₂ transport and storage, and an analysis has been provided to give an assessment of the potential benefits associated with such an option using process software. Crown Copyright © 2015 Published by Elsevier B.V. on behalf of The Institution of Chemical Engineers. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Current technologies for capturing CO₂ are based on absorption by means of liquid solvents, which are expensive and have serious drawbacks in terms of the energy requirements vs. solvent regeneration percentage (Feron and Hendriks, 2005). Solid sorbents offer considerable potential, especially if the sorbents are inexpensive and remain effective over many sorption/regeneration cycles. Using limestone in a Ca-looping cycle appears to be a promising approach based on the reversible calcination/carbonation reaction: CaCO₃ ↔ CaO + CO₂, for CO₂ capture.

During the cyclic capture of CO₂ by circulating solid sorbents transferred between the carbonation reactor (carbonator, combustor, gasifier, or steam reformer) and the calcination reactor, sorbents experience a loss in their ability to capture CO₂. The sorbent performance over many cycles is influenced by a number of factors including the total pressure, CO₂ partial pressure, temperature, sorbent composition, carbonation period, calcination conditions, and the presence or absence of other gases such as steam and SO₂ (Anthony, 2008; Sun et al., 2007a; Kavosh et al., 2014). The performance of a Ca looping system could potentially be improved by means of a pressurised system operating at 850–900 °C, which is typical of fluidised bed combustion conditions, and so far this has only been explored using a pressurised thermogravimetric analyser (PTGA) (Chen et al., 2010). Such a route might also make sense for enhanced H₂ production in a pressurised gasifier for clean energy production for instance.

However, the situation concerning pressurised calcination is less clear, and the most likely reason for carrying this out would be to reduce compression costs associated with carbon capture, since the solid sorbents carrying the CO₂ are themselves not subject to losses associated with pressure changes.

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To explore the potential of this approach an experimental study was carried out on the performance of limestone in a cycle which included pressurised calcination. This was supplemented by a UniSim process simulation to evaluate the change in required compression energy with the calciner operating at different pressures. The simulation looks at all critical elements of the plant and also includes an estimate of the air separation unit (ASU) energy consumption given the oxygen flowrate and delivery pressure required for the calciner using a correlation from literature (Fu and Gundersen, 2012) and the same pressures used for the test regime, namely 0.1, 0.5 and 1.0 MPa.

2. Experimental equipment and methodology

A small bubbling fluidised bed was designed, capable of operating at temperatures up to 1200 °C. A schematic of the system is presented in Fig. 1. The major components consist of a quartz tube, an outer tube and an electrical heater. This is followed by a hot gas filter for the flue stream, a gas dryer, a water pump, and an ADC 7000 gas-analysing unit to measure CO2 concentration. The outer tube has a height of 1180 mm and internal diameter of 37 mm. The distributor consists of a sintered plate, with a preheater section at the base to achieve the desired reaction temperature.

Reactors temperatures were measured by a K-type thermocouple, and they and the differential pressure across the bed were recorded by a data acquisition system. Reactant gases, CO2, O2, and N2, were fed to the system via a bottom flange of the outer tube, and passed through the pre-heater zone prior to entering the reactor. The flow rates of gases were controlled using highly accurate Mass Flow Controllers (MFC), (Bronkhorst; EL-FLOW Series).

Fig. 1 – Bubbling bed test facility.
Table 1 – Experimental conditions in tests run with pressurised calcination and atmospheric carbonation.

<table>
<thead>
<tr>
<th>Test run (pressure during calcination)</th>
<th>CO₂ partial pressure in calciner (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Press 1 (0.1 MPa)</td>
<td>0.015</td>
</tr>
<tr>
<td>Press 2 (0.5 MPa)</td>
<td>0.075</td>
</tr>
<tr>
<td>Press 3 (1.0 MPa)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* All mixtures in calciner and carbonator are 15% CO₂ + 4% O₂ + N₂ balance.

For this work the limestone used was Longcliffe (Longcal SP52), which has a minimum 98.25% CaCO₃ content, and specific gravity 2.65 g/cm³. The limestone particles were ground and sieved to 125–250 µm for the experiments presented in this article. The chemical composition of the limestone used has been presented elsewhere (Kavosh et al., 2014). The multi-cycle split calcination and carbonation experiments with elevated pressure during the sorbent decomposition stages were carried out in a bubbling fluidised bed reactor. The tests were run in batch mode.

The steel reactor was loaded with 10 g of limestone and then heated for the calcination. In order to reduce the reaction period and to prevent subsequent changes in the steel reactor (such as sintering of particles and corrosion of the reactor), the pressurised test at 1.0 MPa was carried out using 5 g of sample. The temperature of the fluidised bed reactor was raised to the rate of 25 °C/min to the target value of 950 °C. The reactor bed was fluidised with a sweep gas at flow rates of 1.2, 6.0, and 12.0 NL/min to provide a bubbling regime during the gas–solid reaction under elevated pressures. The calcination step was carried out until CO₂ levels had dropped to a negligible level. After the calcination the reactor was cooled to 650 °C at the rate of 10 °C/min, and the pressure was reduced to atmospheric level.

Once the temperature reached 650 °C, the produced lime was exposed to carbonating gas mixtures containing a certain percentage of CO₂ (15%) at a flow of 1.6 NL/min. The carbonation step was continued until the reaction was completed, which corresponded to CO₂ vol. % reaching a constant level in the exit gas stream effectively equal to the feed level. The capture step lasted about 30 min. After complete carbonation, the bed temperature was increased again to 950 °C to regenerate the lime. These sequential processes were repeated for 8–10 cycles for each set of operating pressures and the experimental conditions for both calcination and carbonation are given in Table 1. Typically, the unit was run at a U/Uₐ₀ ratio of about 3 to 4.

The changes in sorbent morphology and microstructure of calcined particles after the first and final cycles were investigated using scanning electron microscopy (SEM). The specific surface area, pore volume, porosity, and pore size distribution of the CaO particles were also determined. More details of the instruments and methods used for morphological measurements of particles are presented elsewhere (Kavosh et al., 2014). Finally, it is recognised that the heating rates achieved in this system are far slower than particles would experience in a real system, and if sintering is excessive under these conditions, then it is anticipated that it would be much worse in a real system, in which case high-pressure calcination is likely to be problematic if the results are negative in this type of system (German, 1996).

3. Results and discussions

Carbonation conversions of the calcined particles were calculated by integrating the CO₂ concentration over the reaction time using the following equation (Kavosh et al., 2014):

\[
X_{\text{Carbon}}(t) = \frac{Q \frac{m_\text{CaCO}_3}{\text{mol}_{\text{CO}_2}(t)}}{m_\text{CaCO}_3} \int_0^t \frac{C_{\text{CO}_2, \text{in}} - C_{\text{CO}_2, \text{out}}(t)}{1 - C_{\text{CO}_2, \text{out}}(t)} \, dt
\]

where \(X_{\text{Carbon}}(t)\) is the carbonation conversion at any given time, \(Q\) denotes gas flow rates [L/min], \(C\) shows volume fractions of gas species, \(V_{\text{mCO}_2}(t, p)\) is the molar volume of \(\text{CO}_2\) at a given temperature and pressure [L/mol], \(m_\text{CaCO}_3\) denotes the initial sample mass [g] and \(M_{\text{CaCO}_3}\) is the relative molar mass of limestone [g/mol].

The carbonation conversion curves obtained are shown in Fig. 2. As can be seen, the carbonation conversion of calcined sorbent decreases as the pressure is increased during calcination. The average conversion for the CaO produced at atmospheric pressure adopted the rather high value of 0.40; however, it declined significantly to 0.15 and 0.11 for the sorbents calcined under 0.5 MPa and 1.0 MPa, respectively. What is noticeable is a dramatic difference between 0.1 MPa and 0.5 MPa, and relatively small change between 0.5 and 1.0 MPa.

Fig. 3 shows that the decomposition began at 790 °C, 870 °C and 940 °C at elevated pressures of 0.1 MPa, 0.5 MPa, and 1.0 MPa, respectively.

The time required for calcination increased significantly with increasing pressure. The calcination periods were 13 min, 40 min, and 110 min for calcination at 0.1 MPa, 0.5 MPa, and 1.0 MPa pressure, respectively, as expected (Sun et al., 2007b; Hughes et al., 2009; Stanmore and Gilot, 2005; Abanades et al., 2005). These results were supported by the SEM images of sorbents after the first and the last cycle of calcination at elevated pressure. Fig. 4. The number of cycles and the calcination pressures are given on each SEM image. Fig. 4a shows the porous structure of particles calcined at 0.1 MPa, with a desirable sorbent texture consisting mainly of small pores. Existence of small pores increases the surface area and enables sorbents to achieve a higher CO₂ capture. The series of images shown in Fig. 4a to f illustrates the trend of surface texture of sorbents with increasing calcination pressure and number of cycles. The images reveal the development of necks between the
grains and increasing pore size (associated with sintering).

The specific surface area and pore volume of particles are given in Table 2. Pore volumes show the volumes of small pores and medium-size pores (~60–300 nm). The values are calculated as the difference between cumulative volume of pores with diameters of 1.7–300 nm, and the pore volume measured for smaller pores. Table 2 gives the BET specific surface areas that were measured at 18 m²/g for the initial calcined sorbent at 0.1 MPa pressure, and that value decreased to 2.5 and 1.1 m²/g for calcined particles produced at pressures of 0.5 and 1.0 MPa, respectively. The corresponding volumes of small pores were 0.022, 0.004, and 0.001 cm³/g for particles calcined at three levels of the calcination pressures.

Pore size distributions, plotted in Fig. 5, reveal that the number of small pores is higher in CaO particles, which were calcined at 0.1 MPa and that increasing pressure dramatically decreases the number of those pores even by the first cycle. It is also clear that even by the 10th cycle calcined particles have more pores in the range of 10 to 100 nm than do ones calcined at elevated pressure by the first cycle (Fig. 5).

Specific surface areas and meso-pore volumes for CaO particles calcined in the 10th or 8th cycle are given in Table 2. The surface areas and pore volumes of calcined sorbent decreased after pressurised calcination. Calcined sorbent produced under 0.1 MPa (in the 10th cycle) contains a surface area of 5.7 m²/g, and pore volume of 0.01 cm³/g. However, the corresponding values for CaO calcined under 0.5 MPa and 1.0 MPa (in the 8th cycle) have decreased to 1.2 and 0.25 m²/g with surface area, and 0.002 and 0.0006 cm³/g of pore volume, respectively. There also seems little doubt that sorbent deterioration would have been worse if the calcination gases had been nearly pure CO₂. Given the significant fall in sorbent carrying capacity, it seems likely that such a system would also require some reactivation strategy, such as for instance by hydration (Manovic and Anthony, 2007) using a separate reactor, or by using high CO₂ concentrations to reactivate the sorbent after calcination, as suggested by CanmetENERGY and the Spanish Research Council, and now being developed by the Spanish Research Council (Elena Diego et al., 2014; Salvador et al., 2003). Although such options increase complexity and cost, they may well be necessary in the future if Ca looping technology is to be considered fully competitive with amine scrubbing in situations where there is not a major demand for the spent sorbent such as the cement industry. However, a detailed analysis of the use of reactivation strategies is outside the scope of this paper.

4. Simulation of pressurised calcination

The steady-state simulation is based on a typical retrofit case where a calcium looping system is integrated into an existing plant. In this case, a 250 MWₑₑ air-fired coal boiler is the CO₂ source of interest. The key assumptions for this simulation are that the carbonator is operated at atmospheric pressure and 650 °C as would be expected if the Ca looping plant were added to an existing plant. The calciner is operated at 0.1, 0.5 and 1.0 MPa in different cases to determine the impact of calciner operating pressure on the required energy to produce a 15.0 MPa pipeline-ready CO₂ stream. For the purposes of the simulation we assumed that the fuel used in the base plant and calciner was Daw Mills coal (see Table 3), and we have ignored sulphur removal assuming that inherent capture of SO₂ is essentially 100% (Arias et al., 2013). A simplified process flow diagram of the simulated process is shown in Fig. 6. The significant assumptions on which the simulation is based are presented in Table 4 and the composition of the inlet stream to both the calciner and carbonator reactors are presented in Table 5. The temperature of the calciner was selected based on the partial pressure of CO₂ present and the equilibrium relationship presented by García-Labiano et al. (2002) The calciner temperature must increase as the absolute pressure increases due to the inherent increase in the partial pressure of CO₂. In addition to those assumptions, it should be noted that no heat integration has been performed. All heating and cooling are done with heater or cooler units. These units will only

Table 2 – Porous structural properties of calcined particles at elevated pressure after the initial and multiple cycles (see Table 1 for details of reaction conditions).

<table>
<thead>
<tr>
<th>Calcinated sample, pressure and cycle number</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Calcinated sample, pressure and cycle number</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt; (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 MPa, 1st cycle</td>
<td>18</td>
<td>0.022</td>
<td>0.1 MPa, 10th cycle</td>
<td>5.7</td>
<td>0.010</td>
</tr>
<tr>
<td>0.5 MPa, 1st cycle</td>
<td>2.5</td>
<td>0.004</td>
<td>0.5 MPa, 8th cycle</td>
<td>1.2</td>
<td>0.002</td>
</tr>
<tr>
<td>1.0 MPa, 1st cycle</td>
<td>1.1</td>
<td>0.001</td>
<td>1.0 MPa, 8th cycle</td>
<td>0.25</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

Table 3 – Daw Mill coal properties.

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Daw Mill coal</th>
<th>Ar</th>
<th>Dry</th>
<th>Daf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (wt%)</td>
<td>3.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ash (wt%)</td>
<td>12.39</td>
<td>12.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile matter (wt%)</td>
<td>27.59</td>
<td>28.5</td>
<td>32.68</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon (wt%)</td>
<td>56.82</td>
<td>58.7</td>
<td>67.32</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis</th>
<th>Daw Mill coal</th>
<th>Ar</th>
<th>Dry</th>
<th>Daf</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (wt%)</td>
<td>67.08</td>
<td>69.3</td>
<td>79.47</td>
<td></td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>4.16</td>
<td>4.3</td>
<td>4.93</td>
<td></td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>1.16</td>
<td>1.2</td>
<td>1.38</td>
<td></td>
</tr>
<tr>
<td>Sulphur (wt%)</td>
<td>1.43</td>
<td>1.48</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Oxygen (wt%)</td>
<td>10.32</td>
<td>10.66</td>
<td>12.22</td>
<td></td>
</tr>
<tr>
<td>Gross CV (MJ/kg)</td>
<td>26.29</td>
<td>27.16</td>
<td>31.14</td>
<td></td>
</tr>
<tr>
<td>Net CV (MJ/kg)</td>
<td>25.3</td>
<td>26.22</td>
<td>30.07</td>
<td></td>
</tr>
</tbody>
</table>
calculate the amount of energy required to heat or cool the stream, not utility requirements.

Several important trends came out of the process simulation. The number of compression stages and compressor power required for each stage is summarised for three calciner operating pressures in Fig. 7. The energy required for the first compression stage is similar for all three calciner pressures. However, as the number of stages increases, there is a clear increase in required compressor power with decreasing calciner pressure. Additionally, the number of stages required for each calciner pressure shows a clear increase with increasing calciner pressure.
Fig. 6 – Simplified process flow diagram of UniSim simulation.

Table 4 – Key assumptions made in the development of the UniSim process simulation.

<table>
<thead>
<tr>
<th>Calciner</th>
<th>Carbonator</th>
<th>CO₂ compression</th>
<th>Base boiler (CO₂ source)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operated at 897 °C, 987 °C and 1040 °C 0.1, 0.5 and 1.0 MPa absolute pressures Oxy-fuel combustion with flue gas recycle Complete combustion of coal Equilibrium reactor used for calcination Solids enter from carbonator at 650 °C Flue gas cooled to 130 °C</td>
<td>Operated at 650 °C Atmospheric pressure Solids from calciner enter at 750 °C 20% carbonation conversion 90% capture efficiency Exhaust cooled to 150 °C</td>
<td>Pipeline pressure of 15.0 MPa Maximum compression ratio of 2.5 Cooled to 35 °C between stages 75% polytropic efficiency for compressors</td>
<td>250 MW&lt;sub&gt;th&lt;/sub&gt; air-fired boiler Flue gas cooled to 200 °C before carbonator</td>
</tr>
</tbody>
</table>

Table 5 – Composition of inlet gas to the calciner and carbonator reactor from UniSim process simulation.

<table>
<thead>
<tr>
<th>Component (mol%)</th>
<th>Calciner gas inlet</th>
<th>Carbonator gas inlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.68</td>
<td>0.13</td>
</tr>
<tr>
<td>O₂</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>N₂</td>
<td>0.04</td>
<td>0.75</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.26</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Small increases in calciner operating pressure. Although there are benefits to running at elevated pressure on the product compression side, there is a cost on the reactant side. Operating an air separation unit at the higher pressures required for pressurised calcination comes at an energy cost. ASU energy consumption was estimated using the pressure and flowrate from the simulation and a correlation from Fu and Gundersen (2012). The energy requirements for compression, intercooling and the ASU are summarised in Table 6. The increase in ASU energy consumption is greater than the reduction in required compression energy due to the increased oxygen demand driven by the higher calcination temperatures required with high CO₂ partial pressures. Comparing the 0.1 and 1 MPa cases, there is a net increase of 6.95 MW considering...
Table 6 – Total compression, intercooling and air separation unit duties for process simulation cases with the calciner operating at 0.1, 0.5 and 1.0 MPa.

<table>
<thead>
<tr>
<th>Calciner operating pressure (MPa)</th>
<th>Calciner temperature (°C)</th>
<th>CO₂ partial pressure in Calciner (MPa)</th>
<th>Total compression duty (MW)</th>
<th>Total intercooling duty (MW)</th>
<th>Air separation unit duty (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>897</td>
<td>0.07</td>
<td>18.97</td>
<td>44.17</td>
<td>15.00</td>
</tr>
<tr>
<td>0.5</td>
<td>987</td>
<td>0.36</td>
<td>15.68</td>
<td>46.77</td>
<td>21.87</td>
</tr>
<tr>
<td>1.0</td>
<td>1040</td>
<td>0.71</td>
<td>13.56</td>
<td>46.50</td>
<td>25.02</td>
</tr>
</tbody>
</table>

only compression, intercooling and ASU duties. The reduction in compression energy demand is approximately half of the increase in ASU demand. This indicates there could be a net increase in energy usage in a calcium looping plant operating with a pressurised calciner.

There are additional potential drawbacks to operating a calcium looping plant with a pressurised calciner and atmospheric carbonator. Pressure-swing equipment, such as lock hoppers, is generally not designed to function at temperatures as high as 950 °C. There would likely be a need to cool the solids after exiting the calciner or carbonator before the pressure-swing equipment. This could result in a significant energy penalty as the sorbent carries a large amount of heat between the two fluid beds. This loss of heat would have to be well integrated into the system to mitigate this, but this is likely to be the case for any pressure-swing system that can be considered.

5. Conclusions

A study was carried out on the CO₂ capture performance of limestone following pressurised calcinations and has led to the following conclusions:

Carbonation conversion of calcined sorbent decreases as the system pressure is increased during calcination. As demanded by thermodynamics the incipient temperature of calcination increases with increasing CO₂ partial pressure, but there is dramatic reduction in carbon capture for calcination with increasing CO₂ levels in the calciner, for absolute pressures between 0.1 MPa and 0.5 MPa, and a relatively small change between 0.5 and 1 MPa. In addition, as expected pressurised calcination requires higher temperatures and longer calcination times, and causes an increase in sorbent sintering, as is shown by the fact that SEM images reveal the development of necks between the grains and increasing pore size with increasing pressure during calcination. This is also reflected in the fact that the BET specific surface areas were measured for the initial calcined particles and showed a decrease for particles calcined at 0.5 and 1.0 MPa. The corresponding pore volumes experienced an extreme drop with increasing calcination pressure. While there appears to be significant plant flowsheet simplification (capital savings), a simulation performed on this system showed there is no saving in energy if a pressurised calciner is used.

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