AN INVESTIGATION INTO PARTIAL CAPTURE OF CO\textsubscript{2} RELEASED FROM A LARGE COAL/PETCOKE FIRED CIRCULATING FLUIDIZED BED BOILER WITH LIMESTONE INJECTION USING ITS FLY AND BOTTOM ASH

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Abstract -Circulating Fluidized Bed (CFB) power plants have been gaining popularity globally due to its ability to utilize less expensive solid fuels, in-situ capture of SO\textsubscript{x}, low NO\textsubscript{x} emission and flexible operating characteristics. Higher CO\textsubscript{2} emission from sulfur capturing CFB plants is, however, a major shortcoming of this technology. Additionally, fly ash generated from such CFB power plants is not much suitable for many commercial applications. An investigation was conducted to examine if fly ash produced in a CFB power plants with limestone feed can capture a part of the CO\textsubscript{2} released from it. It examined the factors affecting the utilization of such CFB ash in carbonation reaction to capture CO\textsubscript{2}. Two sets of experiments were carried out for dry and hydrated fly ash at 500-750 °C and 30-80 °C respectively. It showed that CaO conversion increased with temperature up to 700 °C for the dry case and 50 °C for hydrated case thereafter it started to reduce. Effect of partial pressure of CO\textsubscript{2} (17 kPa to 31 kPa) on the total carbonation reaction was minor, but, the duration of initial rapid CO\textsubscript{2} capture stage was inversely proportional to the CO\textsubscript{2} partial pressure. The capture characteristics of lime were compared with that of CFB ash at the same conditions. In most cases carbonation reaction in lime followed a similar pattern as in fly ash. The capture characteristics were also similar for bottom ash (particle size, 116 μm to 275 μm). However, the amount of CO\textsubscript{2} captured by the coarser bottom ash was significantly lower than that by dry fly ash at the same condition. This study, thus showed the potential of using fly ash from sulfur capturing CFB power plants in reducing the CO\textsubscript{2} emission from the very plant and thereby achieve better disposal of the fly ash.

Keywords: CFB Fly Ash, CO\textsubscript{2} capture, Carbonation, Ash Utilization

1. INTRODUCTION

Circulating fluidized bed (CFB) combustion has gained much popularity due to its ability to utilize low-grade fuel or mixtures of fuels (such as coal and petroleum coke), fuel flexibility, in-situ capture of SO\textsubscript{x} and low NO\textsubscript{x} emission. However, the emission intensity (for GHG gases CO\textsubscript{2} and N\textsubscript{2}O) of a CFB power plant is higher than that of a pulverised-fuel (PF) fired power plant especially when limestone is added in such boilers to capture SO\textsubscript{x} released during combustion. Additional CO\textsubscript{2} is released here due to calcination of limestone in its furnace (Basu, 2015). A major challenge in post-combustion CO\textsubscript{2} capture from a typical coal or petcoke fired power plant is the low concentration of CO\textsubscript{2} in the flue gas from a CFB boiler, which makes its direct compression, transportation and storage difficult. Thus, it is necessary to explore new cost effective and less energy-intensive practical methods for carbon capture.

Interestingly, the ash produced from a CFB power plant firing high sulphur fuels do not find much use in building industries due to its large volumetric expansion when cured at normal temperature (Zhang et al., 2012). Fly ash and bottom ash from typical CFB power plants contain significant amounts of free CaO, as only 35-40% of the lime feed is utilized in SO\textsubscript{x} capture (Wang et al., 2008). So, disposal of fly ash from such CFB plants is difficult. This work therefore examines if the unutilized CaO in CFB ash can be utilized through carbonation reaction for partial capture CO\textsubscript{2} from flue gas for CFB boiler.

Carbonation of alkaline solid wastes such as coal ash containing lime can proceed through two routes: dry (gas-solid) carbonation and wet (aqueous) carbonation (Pan et al., 2012). In gas-solid carbonation, carbon dioxide reacts with available CaO in the ash to produce CaCO\textsubscript{3} as below:

\[ \text{CaO} + \text{CO}_2 = \text{CaCO}_3 \] (1)

In aqueous carbonation, CO\textsubscript{2} gas reacts with water and produces carbonic acid and Ca\textsuperscript{2+} ions leached from Ca(OH)\textsubscript{2} reacts with CO\textsubscript{2}\textsuperscript{−} of carbonic acid (Reddy et al., 2011, Pan et al., 2012, Beruto and Botter, 2000 and Samari, 2014). The overall reaction can therefore be written as:
Ca(OH)$_2$ + CO$_2$ + H$_2$O $\leftrightarrow$ CaCO$_3$ + H$_2$O \hspace{1cm} (2)

In addition, there is also the formation of calcium bicarbonate, which gives enhanced CO$_2$ diffusion due to its higher solubility. Calcium bicarbonate reacts with calcium hydroxide and forms calcium carbonate as below (Samari, 2014).

Ca(HCO$_3$)$_2$ + Ca(OH)$_2$ $\rightarrow$ 2CaCO$_3$ + 2H$_2$O \hspace{1cm} (3)

A number of studies were conducted for CO$_2$ capture and CaO utilization in carbonation reaction of fly ash or limestone derived materials (Reddy et al., 2011; Wang et al., 2008; Grasa and Abanades, 2006; González et al., 2014). Reddy et al. (2011) conducted carbonation reaction in fly ash fluidized by flue gas in a pilot scale plant at ~30-45 °C achieving a reduction in CO$_2$ concentration from 13% to 9% within few minutes. Based on this they estimated the cost of mineralization of one tonne of CO$_2$ as $11 at mineralization capacity of 207 kg CO$_2$/tonne of fly ash for a 532 MW plant.

Only a limited number of studies are available on the carbonation reaction of CFB fly ash and presently there is no information on the carbonation reaction of CFB bottom ash of different particle sizes. Wang et al. (2008) investigated carbonation reactions in CFB fly ash in oxy-fuel condition (CO$_2$ concentration 80%), and observed that CaO utilization increased with increase in temperature and below a critical temperature (less than 400 °C) there was not any significant capture in dry carbonation experiments. Whereas, addition of steam enhanced the carbonation reaction even at low temperature (~250 °C). Although Wang et al. (2008) studied CO$_2$ capture by dry CFB fly ash in oxy-fired condition above 400 °C and in presence of water vapour above 250 °C, the reaction at low CO$_2$ partial pressure as expected in air fired CFB boiler, and, at low temperature for hydrated fly ash could differ considerably. González et al. (2014) investigated carbonation in aqueous condition at 100% CO$_2$ concentration, however, in typical air fired CFB boiler CO$_2$ accounts for less than 20% (Wang et al., 2008). Thus, it is necessary to evaluate the effect of partial pressure of carbon dioxide on the carbonation reaction of CFB fly ash. In this, paper we investigated carbonation reaction at CO$_2$ concentration between 16% and 36%.

The novelty of this work is, firstly, investigation of CO$_2$ capture by un-treated CFB fly ash at low CO$_2$ partial pressure and at different temperature in dry and hydrated conditions. Secondly, comparison of CO$_2$ capture with pure lime for the same experiments. Thirdly, study of carbonation reaction in CFB bottom ash of different particle size.

2. METHODOLOGY

Ash for the experiments was collected from the 197 MWe, CFB power plant in Point Aconi, NS, Canada. The CFB power plant uses a mixture of petroleum coke and coal as fuel in a ratio of 80:20. Limestone is added for in-situ capture of SO$_2$. Fly ash contains 37.25% unutilized CaO from the sulfation reaction in the furnace. The size distribution of the fly ash (Figure 1) shows that 95% of fly ash particle size falls under 120 μm. Table 1 gives full composition of the fly ash.

A schematic of the experimental setup is shown in Figure 2. Un-treated dry fly ash or quicklime samples were spread on quartz wool and placed in the reactor. Quartz wool served as a highly porous support for the sample, with free access to gas from all directions. For CO$_2$ capture comparison, high calcium quicklime (termed lime) contained more than 90% CaO, and was collected from Graymont Limited, Havelock, NB, Canada.

<table>
<thead>
<tr>
<th>Element</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>SiO$_2$</th>
<th>V$_2$O$_5$</th>
<th>P$_2$O$_5$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt(%)</td>
<td>1.70</td>
<td>37.25</td>
<td>0.87</td>
<td>0.32</td>
<td>0.45</td>
<td>0.11</td>
<td>15.88</td>
<td>0.22</td>
<td>0.22</td>
<td>0.05</td>
<td>11.08</td>
</tr>
</tbody>
</table>

Table 1: Fly ash analysis

Figure 1: Fly ash particle size distribution  
Figure 2: Schematic of experiment setup
2.1 Test conditions

Experiments were conducted at dry and hydrated conditions for ash and lime. As the reactor has a fixed volume and the dry and hydrated samples have different densities it was not possible to accommodate the same mass of hydrated lime sample in the reactor. Hydrated lime sample of smaller mass (i.e., 30 g) was selected. Table 2 gives sample preparation information, such as weight of ash/lime and amount of water added. Table 3 shows the test matrix prepared for this study. For all the experiments, nitrogen flow rate was maintained constant at 0.46 liters/min and the amount of water for hydration was kept constant at liquid to lime ratio of 0.65.

<table>
<thead>
<tr>
<th>Table 2: Sample details</th>
<th>Dry Fly Ash</th>
<th>Hydrated Fly Ash</th>
<th>Dry Lime</th>
<th>Hydrated Lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Weight (g)</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Water Added (g)</td>
<td>0</td>
<td>12</td>
<td>0</td>
<td>19.5</td>
</tr>
</tbody>
</table>

2.1.1 Effect of temperature in dry and hydrates samples:

Previous study noted that gas solid carbonation reaction in CFB fly ash below 500 °C is insignificant even at CO₂ concentration as high as 80% (Wang et al., 2008). Also, they noted that CO₂ capture increased with temperature. So, all experiments to investigate the effect of temperature for dry conditions were conducted at temperature range from 500 to 750 °C, at significantly lower CO₂ concentration (16-36%) than that investigated by Wang et al. (2008).

Carbonation of hydrated fly ash is conducted typically below water evaporation temperature to prevent steam from escaping, and thus avoiding an expensive pressurized carbonation vessel. This less energy intensive choice simplifies industrial processes and makes it cost-effective.

<table>
<thead>
<tr>
<th>Table 3: Test conditions</th>
<th>Temperature (°C)</th>
<th>Hydrated fly ash</th>
<th>Hydrated lime</th>
<th>Dry fly ash</th>
<th>Dry lime</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂ = 0.20 l/min (vol: 30%), N₂ = 0.46 l/min (vol: 70%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>✓</td>
<td>✓</td>
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</tr>
<tr>
<td></td>
<td>50</td>
<td>✓, *</td>
<td>✓, *</td>
<td>N/A</td>
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<td></td>
<td>60</td>
<td>✓</td>
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<td>80</td>
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<td>600</td>
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<tr>
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<td>700</td>
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<td>✓, *</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td></td>
<td>✓, *</td>
<td>✓, *</td>
<td>✓, *</td>
</tr>
</tbody>
</table>

*test conducted for CO₂ volume concentration: 16%, 22%, 30%, 36%

2.1.2 Experiments at different CO₂ partial pressure

To investigate the effect of CO₂ partial pressure on carbonation reaction, tests were conducted at four CO₂ partial pressures at temperature 50 °C for hydrated and 700 °C for dry case and by keeping all other parameter constant. The CO₂ partial pressures were 17, 22, 31 and 37 kPa (Volume: 16%, 22%, 30%, 36%) keeping N₂ flow at 0.46 l/min.

2.1.3 Experiments on effect of particle size

To investigate the effect of particle sizes on the CO₂ capture, bottom ash of average particle sizes 116 μm, 196μm and 275 μm were selected and the capture results were compared with the same particle sizes of dry lime experiments carried out at similar operating conditions. Operating condition for all the experiments was fixed at temperature 700 °C and CO₂ partial pressure at 31kPa.

3. RESULT AND DISCUSSION

All experiments in this study have shown an initial stage of rapid CO₂ conversion into CaCO₃ followed by a rather slow reaction stage, when the CO₂ capture level of all dry ash samples dropped to ~50%, and, after that, it reduced asymptotically. The similar observation has been noted by Bhatia and Perlmuter (1983), Dedman and A.J. Owen (1962), Silaban (1993). The initial rapid reaction is essentially a surface reaction of CO₂ with CaO, which was kinetically controlled due to the high gas-exterior surface mass transfer. The carbonation reaction produced a product layer of CaCO₃ on the exterior surface of available CaO in ash, which restricts further direct contact of CO₂ with available CaO beneath it (Sun et al., 2007). This mass transfer restriction slows down the reaction, and thus, the reaction was controlled by diffusion of
CO₂ gas into pores to react with CaO. The CO₂ diffusion was very slow in the second stage phase of carbonation of lime. The total CO₂ capture was found nearly independent of CO₂ partial pressures, as also noted in other studies (Grasa and Abanades, 2006; Silaban, 1993).

3.1 Effect of temperature
3.1.1 Dry test
It is apparent from Figure 3 that initial level of CO₂ capture increased with the increase in flue gas temperature up to 700 °C. However, after the initial stage of about 10 minute, the capture level reduced slowly below ~50% capture for all samples. At 750 °C there was a reduction in CO₂ capture in the rapid reaction regime because above 700 °C, the change in Gibbs free energy would be negligible at the modest partial pressure of CO₂ of the present experiments, and, hence, the carbonation reaction could not take place (Li et al., 2005).

Figure 4 shows similar experiments with high-calcium quicklime (lime) instead of fly ash. The dry fly ash samples here typically contained 37.25% CaO in comparison with lime sample which had more than 90% CaO. Except for tests at 500 °C the capture level at 10th minute for all tests varied between 100-76%. At 750 °C the drop to 50% capture level, occurred well after 160 minutes.

Figure 5 shows the amount of CO₂ captured per unit mass of the sample (including CaO and other components of the ash) in the kinetically controlled regime at different temperatures. For dry fly ash, the highest CO₂ captured was ~0.04 kg per kg sample at 700 °C, and the minimum was ~0.01 kg per unit sample at 750 °C. The highest value translates into 14% conversion of the CaO in ash. The CO₂ captured per unit mass of sorbent was higher for dry lime remaining constant at ~0.1 kg CO₂ at both 600 °C and 700 °C, then it dropped to the same level as dry fly ash at 750 °C. Interestingly this translate into lower (12.8%) conversion of the CaO in quicklime. One notes here lower level of CaO utilization in case of lime.

3.1.2 Hydrated Tests
Dry carbonation reaction at lower temperature (30-80 °C) being negligible, effort was made to conduct tests through hydration as a part of the available CaO in fly ash and lime could be converted to Ca(OH)₂ through hydration. However, it was not possible to verify the extent of Ca(OH)₂ conversion by measurement of mass change as significant amount of water was taken up in the reaction to form phases such as hydrated aluminosilicates (Gora et al., 2006). Hence, for hydrated fly ash experiments, both free CaO or Ca(OH)₂ may be expressed as CaO.
A reaction mechanism for Ca(OH)$_2$ and CO$_2$ in presence of water vapour (Samari, 2014) showed that CO$_2$ and Ca(OH)$_2$ dissolve in the nano-droplets of water formed on the surface of sorbent (Figure 6) precipitating CaCO$_3$ as product layer through carbonation reactions. The initial rapid reaction stage could be considered gas-liquid-solid process (Yang et al., 2003; Beruto and Botter, 2000). At the start of the reaction, CO$_2$ reacted with sorbent in presence of water droplets and formed a product layer of CaCO$_3$. This product layer on the surface of sorbent hindered further carbonation reaction resulting in a transition to a slow second stage reaction that was controlled by diffusion of CO$_2$ in the pores.

The change in CO$_2$ conversion or capture by hydrated fly ash with time in the lower temperature range of 30 °C to 80 °C is shown in Figure 7 and Figure 8. It is apparent that CO$_2$ capture level increased with increase in temperature but only up to 50 °C. Above 50 °C, the capture started to reduce again because the carbonation reaction of Ca(OH)$_2$ depends on the amount of water on the sorbent surface, relative humidity (RH) and temperature. The solubility of CO$_2$ in water reduces (carbonic acid) with rising temperature, but calcium leaching increases in the water layer (González et al., 2014, Ukwattage et al., 2015). So, the CO$_2$ dissolution reduced above 50 °C hindering the further carbonation reaction at 0.65 liquid to lime ratio in this study. It is supported by the observation of Ukwattage et al. (2015).

At the start all samples for hydrated tests had similar moisture/water content (liquid to lime ratio: 0.65); but increase in temperature reduced the RH in the reaction environment. Although increase in temperature had a positive effect on CO$_2$ capture, the reduction in RH depressed the amount of capture. For this reason, one notes dominant effect of RH causing the capture start to reduce. This observation is in agreement with those made by Shih et al. (1999) and Girard et al. (2008). The nano-droplets from the sorbent surface evaporated rapidly with temperatures above 50 °C, which reduced, the carbonation reaction significantly.

Figure 7 shows that with increase in temperature, CO$_2$ capture increased in rapid reaction stage but declined above 50 °C as the RH in reaction environment decreased with the thickness of water droplets. It can be observed for most experiments that transition from an initial rapid kinetically controlled stage to a slower diffusion stage took place rapidly, and the start of this quick transition was considered at when CO$_2$ capture reached ~95%. A comparison of CO$_2$ capture in the kinetically controlled regime for dry and hydrated fly ash at different temperature is shown in Figure 9. Except for one case, the amount of CO$_2$ capture was higher for hydrated samples at similar conditions.
3.2 Effect of partial pressure

3.2.1 Dry test

The decline in the amount of CO\textsubscript{2} capture after the initial period of rapid kinetic controlled reaction to asymptotically slower CO\textsubscript{2} diffusion regime occurred early for higher CO\textsubscript{2} partial pressure. Figure 11 shows that the time required to reach that stage controlled by diffusion of gas into the pores, was around 30 minutes at the lowest partial pressure (17 kPa) while at the highest partial pressure (37 kPa) it was 8 minutes. The slow reaction stage, being diffusion controlled, the effect of partial pressure of CO\textsubscript{2} on capture was negligible (Bhatia and Perlmutter, 1983; Sun et al., 2007).

At a given initial time period, a higher amount of CO\textsubscript{2} capture was noted for lime (Figure 12) compared to that for fly ash (Figure 11). Except for this, the general characteristics of capture in both samples at different partial pressure were similar.

The amount of CO\textsubscript{2} captured per unit mass of fly ash or lime sample increased with CO\textsubscript{2} partial pressure during the first reaction stage (Figure 13) because the speed of surface carbonation (kinetically controlled) was higher for high CO\textsubscript{2} partial pressure (Bhatia and Perlmutter, 1983 and Sun et al., 2007).

3.2.2 Hydrated Test

The effect of CO\textsubscript{2} partial pressures on CO\textsubscript{2} capture by hydrated fly ash and hydrated lime at 50 °C is shown in Figure 14 and Figure 15, respectively. This characteristic was similar to that noted in dry test cases (Figure 11 and Figure 12). Also, in the diffusion-controlled regime, no effect of CO\textsubscript{2} partial pressure was observed. The reasons for higher capture by hydrated samples in comparison with dry samples have been discussed earlier.
Hydrated lime showed a large increase in CO₂ capture when its partial pressure increased from 17 kPa to 22 kPa (Figure 16), but above 30 kPa there was reduction. This could be because of the carbonation of hydrated lime, being an exothermic reaction, released heat that increased reaction temperature and above a certain temperature, the capture started to reduce. This is evident from Figure 8, where increase in temperature above 60 °C, at 30% CO₂ concentration, showed significant reduction in capture in the rapid reaction stage.

It was noted that at CO₂ partial pressures 17 kPa and 37 kPa, the increase in temperature inside the reactor was around 5 °C and 15 °C respectively. The reduction in amount of CO₂ captured in rapid reaction stage above 30 kPa partial pressure (Figure 16) could be because of this sudden increase in localised temperature at the reaction environment.

3.3 Effect of Particle Size
The average size of fly ash is the range of 20-50 μm (Figure 1) while that of bed ash was about 300 μm in Point Aconi CFB ash. There was no notable difference in CO₂ capture by bottom ash of any particle size (Figure 17). Figure 18 for lime shows that at 19th minute (in the fast reaction stage), CO₂ captured by 116μm, 196μm and 275μm lime particles was 100%, 98% and 95% respectively apparently due to smaller particles’ higher pore surface area than larger particles. A relatively small amount of capture in the initial stage was observed for bed ash all sizes of particles, which carbonated under diffusion controlled regime soon after the start of the experiment. After 5 minutes, CO₂ captured by bottom ash reduced to around 50%, whereas dry fly ash captured nearly 98% of the CO₂ supplied for similar experiments (Figure 3).

4. CONCLUSION
This work investigated into the factors affecting carbonation of untreated CFB ash in dry and hydrated conditions to capture CO₂ from CFB power plants with limestone feed. Comparison of results with lime showed that carbonation reaction in CFB ash and lime follows the same pattern: initial rapid conversion of the sorbent, followed by a slow reaction. Effect of temperature showed that carbon dioxide capture in the fast-reaction regime increased with temperature, but above a certain temperature (700 °C for dry cases and 50 °C for hydrated cases) the capture reduced. Hydrated fly ash showed similar or even higher capture level...
than dry fly ash at significantly lower temperature (30-80 °C). The rapid initial CO$_2$ capture by fly ash was kinetically controlled and its duration varied inversely with partial pressure of CO$_2$. At partial pressures 37 kPa and 17 kPa, the time required by dry fly ash was 30 minutes and 8 minutes respectively at 700 °C. There was no significant effect of particle size for bottom ash in the size range of 116 μm to 196 μm. The capture level dropped below 60% in 1 minute of the start, while for dry fly ash it took 10 minutes to drop to this level.

Thus, this work concludes that a partial CO$_2$ sequestration by untreated hydrated fly ash could be an effective option for capture and sequestration CO$_2$ from CFB power plant with sorbent injection.

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