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The effect of steam addition to the calciner in a calcium looping pilot plant

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ABSTRACT

Calcium looping is a post-combustion carbon capture technology which uses natural limestone as a sorbent. The carrying capacity of the natural limestone, as a CO_2 sorbent, decays with each calcination/carbonation cycle. Steam has been shown to decrease the carrying capacity decay and can also be used to reactivate spent sorbent. A testing campaign with continuous CO_2 capture and various levels of steam in the oxy-fired calciner was completed in a 100 kW$_{th}$ dual-fluidized bed pilot plant. The calciner was operated with steam concentrations of 0 vol.%, 15 vol.% and 65 vol.% at the inlet of the windbox and at 850 °C and 910 °C at the highest steam concentration. The increase in steam in the calciner decreased the fresh sorbent make-up requirement; for instance a 78% reduction in the make-up was required with 65 vol.% steam in the calciner relative to the no-steam case. Reducing the temperature of calcination with 65 vol.% steam did not further reduce the make-up requirement. The decreased decay in sorbent carrying capacity was attributed to a stable pore structure resulting from the increase in steam concentration and the corresponding reduction of the CO_2 concentration in the calciner. The reduced CO_2-induced sintering resulted in an increased surface area and pore volume which was stable over many calcination/carbonation cycles.

1. Introduction

Coal and other fossil fuels continue to provide over 80% of global energy supply [1]. Carbon Capture and Storage (CCS) technologies will be instrumental in the coming years to curb greenhouse gas emissions while fossil fuels will remain a major resource for the continually increasing world-wide energy demand. Calcium looping is an emerging carbon capture technology which utilizes mature fluidized bed technology and has applications in both pre- and post-combustion capture of CO_2. The calcium looping process can utilize natural limestone, which is abundant and inexpensive, to capture CO_2 from flue or fuel gas. The reversible carbonation/calcination reaction shown below is the basis for the process.

$$CaO_s + CO_{2g} \leftrightarrow CaCO_{3s} + 178.2 \frac{kJ}{mol} \qquad (1)$$
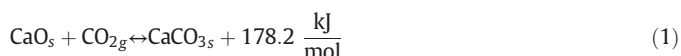
There are many proposed configurations for this process; [2–4] however the most common one for post-combustion CO_2 capture is a dual-circulating fluidized bed system. The process at atmospheric pressure is illustrated in Fig. 1. Carbon dioxide rich flue gas from a

fossil-fuel fired power plant is fed into a fluidized bed, the carbonator, where it reacts with lime (CaO) resulting in an exhaust composed primarily of N_2 and H_2O. The resulting $CaCO_3$ is circulated back to the other fluidized bed, the calciner, which regenerates the sorbent by releasing the captured CO_2. The calciner is an oxy-fired combustor which provides the energy necessary for calcination and produces a concentrated CO_2 exhaust which is suitable for compression and sequestration after removal of moisture and minor impurities.

Two key performance parameters for this process are the calcium looping ratio (F_{CaO}/F_{CO_2}) and the carbonation efficiency (E_{carb}). The calcium looping ratio relates the amount of calcined sorbent (F_{CaO}) to the amount of CO_2 in flue gas (F_{CO_2}) sent to the carbonator on a molar basis, with the ideal ratio being 1. A high calcium looping ratio indicates poor performance of the sorbent as more sorbent is being circulated than is stoichiometrically required which increases energy consumption. The carbonation efficiency represents the effectiveness of the process and is defined by Eq. (2).

$$E_{carb} = \frac{F_{CO_2} - F_{carb}}{F_{CO_2}} \qquad (2)$$

where F_{CO_2} is the molar flow rate of CO_2 entering the carbonator and F_{carb} is the molar flow rate of CO_2 leaving the carbonator. In addition to being able to effectively produce a purified CO_2 stream from a

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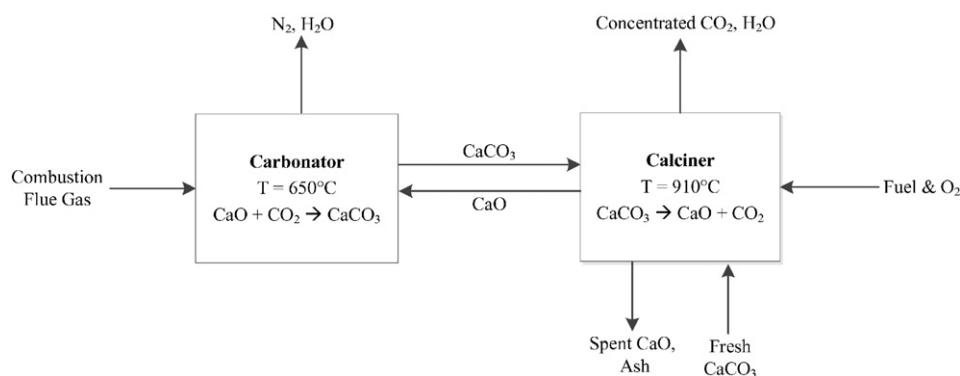 E-mail address: dennis.lu@nrcan.gc.ca (D.Y. Lu).

Fig. 1. Calcium looping process flow diagram.

comparably dilute flue gas, this process potentially has a 5 percentage point higher efficiency when compared to more developed, competing technologies such as amine scrubbing [5]. This is due to the additional electric power which can be produced from the high temperature processes required for both calcination (>900 °C) and carbonation (650 °C). However, calcium looping has several limitations which impact the techno-economic viability of the process.

One of the primary developmental hurdles is the decay in sorbent carrying capacity, defined as the amount of CO_2 captured per unit of sorbent, with increased numbers of carbonation/calcination cycles. The CO_2 carrying capacity of limestone sorbents decays due to various mechanisms such as thermal sintering, sintering due to gaseous atmosphere, sulphation and ash deposition [6]. A make-up flow of new sorbent is required to maintain an average activity in the carbonator which is adequate for the desired level of CO_2 removal. This make-up flow is expected to be a significant operating expense.

Research has focused on reducing the decay in carrying capacity of natural limestone by changing operating conditions, sorbent doping and manufacturing novel pelletized sorbents [7–9]. Sorbent modification and pelletization have the potential to be costly and to add additional, complex unit operations to the process. However, there are opportunities to optimize the operating conditions or procedures which could reduce the decay in sorbent carrying capacity and therefore reduce sorbent make-up and operating costs [10].

It has been shown in literature that steam addition in the carbonator or calciner can result in increased sorbent carrying capacity. Manovic and Anthony [11] and Symonds et al. [12] have shown in a Thermogravimetric Analyzer (TGA) and at the pilot scale that steam injected into the carbonator results in an increase in sorbent carrying capacity. Donat et al. [13] have reported that steam injection in a fluidized bed during calcination and carbonation both result in increased sorbent carrying capacity. The authors attributed the increased carrying capacity to a shift in pore volume to larger diameter pores enhanced by the steam which results in a pore structure advantageous for carbonation. Champagne et al. [14] investigated the impact of steam during calcination in a TGA. The authors stated that steam injection during calcination results in a greater extent of carbonation without affecting the rate of reaction. It was also noted that steam must be present from the first calcination onward for the effect to be observed. To date, the effect of steam injection during calcination has been clearly defined at the bench scale. However, it has been shown that a TGA does not adequately emulate all aspects of larger scale operation, such as gas–solid contacting and heating rate [15]. Therefore, any benefits from steam addition to the calciner must be demonstrated at the pilot-scale before any economic or operational benefits can be assessed.

This study presents results from continuous operation of the CanmetENERGY dual-fluidized bed pilot plant with various levels of steam injection in the oxy-fired calciner. The goal of this work is thus to determine if the observed advantages of steam injection during calcination at the TGA scale will result in meaningful operational improvements at the pilot scale. Additionally, the sorbent samples will be characterized to better relate sorbent characteristics with pilot plant performance. The calcium looping process has been demonstrated at various pilot facilities varying in scale from 10 kW_{th} to 1.7 MW_{th} [16–18]. The pilot studies in literature have focused on the viability of the process, identifying operational challenges and getting data crucial for scale up such as sorbent circulation rate, sorbent make-up rates, bed inventories, carbonation efficiency and fuel consumption. No pilot studies have been completed with moisture levels in the calciner in excess of that resulting from combustion.

2. Experimental

2.1. Dual-fluidized bed pilot plant

The dual-fluidized bed pilot plant used for this work is shown schematically in Fig. 2.

The calciner was operated as a circulating fluidized bed (CFB) and the carbonator as a bubbling bed (BFB). Both reactors were lined with electric heaters. Physical dimensions and other specifications for the reactors are in Table 1. Energy for calcination is supplied by the combustion of solid fuels; for this work hardwood pellets were used as they have a low sulfur (<0.05 wt.%) and ash content (0.68 wt.%) which reduces the impact of sulphation and ash deposition on sorbent performance, thus reducing uncertainty in determining the cause of performance changes. The proximate and ultimate analyses of the hardwood pellets are presented in Table 2. The calciner contains a bed of inert material (olivine sand) to help absorb and distribute heat which remained in the bed and was not circulated with the sorbent. The sand average particle size (D_p = 613 μm) was selected to ensure it would not be entrained at the superficial velocities of interest. Oxygen was supplied to the calciner from a bulk tank and the flue gas was recirculated via a blower after passing through a baghouse to remove fine particles and condenser to remove moisture. Steam was supplied to the calciner by an electric boiler and was superheated to 190 °C before being mixed with other gases at the windbox. Gas analyzers continually monitored O_2 (paramagnetic), CO_2 (IR), CO (IR), and SO_2 (IR) concentrations in the calciner exhaust and O_2 (paramagnetic), CO_2 (IR), and CO (IR) in the carbonator exhaust.

The flue gas supplied to the carbonator was generated using a natural gas burner. The flow of air and natural gas were controlled with needle valves and measured by rotameters. The flue gas was sent to the carbonator via a heated diaphragm pump and entered the windbox at 175 °C. The CO_2 and moisture levels in the flue gas were continuously monitored and recorded.

2.2. Operating conditions & procedures

The primary objective of this work is to evaluate the impact of injecting various levels of steam into the calciner; thus three levels of