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Sulphation and carbonation properties of hydrated sorbents from a fluidized bed CO_2 looping cycle reactor

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ABSTRACT

Sulphation and carbonation have been performed on hydrated spent residues from a 75 kW_{th} dual fluidized bed combustion (FBC) pilot plant operating as a CO_2 looping cycle unit. The sulphation and carbonation tests were done in an atmospheric pressure thermogravimetric analyzer (TGA), with the sulphation performed using synthetic flue gas (0.45% SO_2, 3% O_2, 15% CO_2 and N_2 balance). Additional tests were carried out in a tube furnace (TF) with a higher SO_2 concentration (1%) and conversions were determined by quantitative X-ray diffraction (QXRD) analyses. The morphology of the sulphated samples from the TF was examined by scanning electron microscopy (SEM). Sulphation tests were performed at 850 °C for 150 min and carbonation tests at 750 °C, 10 cycles for 15 min (7.5 min calcination + 7.5 min carbonation). Sulphation conversions obtained for the hydrated samples depended on sample type: in the TGA, they were ~75–85% (higher values were obtained for samples from the carbonator); and in the TF, values around 90% and 70% for sample from carbonator and calciner, respectively, were achieved, in comparison to the 40% conversion seen with the original sample. The SEM analyses showed significant residual porosity that can increase total conversion with longer sulphation time. The carbonation tests showed a smaller influence of the sample type and typical conversions after 10 cycles were 50% – about 10% higher than that for the original sample. The influence of hydration duration, in the range of 15–60 min, is not apparent, indicating that samples are ready for use for either SO_2 retention, or further CO_2 capture after at most 15 min using saturated steam. The present results show that, upon hydration, spent residues from FBC CO_2 capture cycles are good sorbents for both SO_2 retention and additional CO_2 capture.

1. Introduction

An important limitation for CaO-based sorbents used for *in situ* SO_2 retention in fluidized bed combustion (FBC) systems is their relatively low utilization (~30–40%) [1], demanding the use of extra sorbent above that required by reaction stoichiometry. The extra sorbent is in effect ballast, which reduces the economic advantages of FBC combustion technology [1,2]. It also increases overall costs through its production and transport, and storage of the spent residues. This extra material also results in a loss of process efficiency because decomposition of limestone is endothermic. The spent residue contains high levels of unreacted calcium oxide, which cause highly exothermic side reactions when coming in contact with water, creating a possible safety hazard. The presence of $CaSO_4$ and high alkalinity (due to this free CaO and water) are associated with ettringite formation and expansion in the landfill, leading to cracking and increased permeability, facilitating leaching and increasing the amount of leachate to be treated. Another potential disadvantage of this use of extra limestone is that it can cause an effective increase of several percent in CO_2 production when firing a high-sulphur fuel such as petroleum coke.

Research [3–8] on the possible use of CaO-based sorbent in a looping cycle for *in situ* CO_2 capture in FBC systems has shown loss of sorbent reactivity due to sintering, which produces significant amounts of spent residue. Moreover, the presence of SO_2 accelerates this loss of reactivity because the sorbent is irreversibly bound as $CaSO_4$ [9–13]. Overall, this use of extra sorbent can be expected to diminish the environmental and economic benefits of the proposed process for scrubbing CO_2 [14,15] in a similar manner to that of SO_2 retention in FBC.

Hence, similar solutions of the problems related to the use of extra sorbent and production of spent residues need to be explored. The most thoroughly investigated method for reducing limestone use for sulphur capture is reactivation of spent sorbent [16] and the best method appears to be hydration by steam [17–20] or liquid water [21–22]. Grinding [23] and sonication [24] can also enhance processes using liquid water. Initial research on hydration by steam [13,25] and by moist air [26] showed that hydration is also a promising method for reactivation of spent sorbent from CO_2 looping cycles. Better results were obtained than those with spent sorbent for SO_2 retention and the most likely

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explanation is the reversibility of carbonation (reaction for CO_2 capture), *i.e.*, the possibility of reactivation of sorbent with an eliminated or reduced $CaCO_3$ product layer. This is supported by the fact that "maximally" carbonated sorbents were not successfully reactivated by hydration [13,27].

Reactivated sorbents have very good properties for additional CO_2 capture cycles [13,25,26] and SO_2 retention [12,13]. The enhanced surface area of reactivated sorbents provides an explanation for their improved CO_2 capture. The influence of sorbent surface area on conversions, as cycles proceed, *via* critical product layer thickness, has been explained in the literature [28]. Apart from surface area, sulphation (reaction for SO_2 retention) is enhanced by higher pore volume because it enables "storage" of the "voluminous" product layer of $CaSO_4$. Moreover, $Ca(OH)_2$ obtained after hydration during calcination produces CaO with the plate-like pore geometry that is favorable for sulphation [29]. More discussion on these issues can be seen elsewhere [13,30].

Past investigations on sulphation and cyclic carbonation of reactivated spent sorbent from CO_2 capture cycles were performed on samples cycled in systems such as the tube furnace (TF) and thermogravimetric analyzer (TGA), produced under idealized conditions and without influence of fuel ash. Unfortunately, the literature suggests that such experiments are not always relevant to real systems [16] and a similar limitation may be expected for reactivation of sorbent from CO_2 cycles. Hence, in our previous study [30] we have hydrated sorbent obtained from a pilot plant FBC functioning as a continuous CO_2 looping cycle reactor [31]. This work showed that the sorbent samples produced have favorable properties for SO_2 retention and CO_2 capture, and suggested an investigation of their sulphation and cyclic carbonation properties as presented here.

2. Experimental

Spent sorbent samples reactivated by steam were used in this investigation. The spent samples were obtained from a 75 kW_{th} pilot-scale atmospheric dual FBC system with *in situ* CO_2 capture [30,31], where Havelock limestone (eastern Canada) was used as sorbent. Carbonation temperature in the FBC reactor was typically ~650–700 °C and the calcination temperature was typically ~900 °C. The carbonator was fluidized by a mixture of air and 15% CO_2 to simulate flue gas. The carbonator was heated by electrical heaters; the calciner was heated by electrical heaters (only), with biomass burning in air, or with coal or biomass combustion in oxy-fuel mode. More details concerning the experimental pilot-scale reactor, operating conditions and procedures, and fuel and sorbent characteristics are given elsewhere [31]. Samples obtained under different conditions from different reactor locations (calciner/carbonator, bed/cyclone) using different types of carbonator heating were collected during and at the end of CO_2 capture tests.

Samples of spent sorbent obtained from the dual pilot-scale FBC reactor were hydrated by steam in a 2-dm^3 Parr 4522M pressure reactor under atmospheric pressure and at 100 °C for different durations: 15, 30 and 60 min. After hydration, samples were dried in a vacuum oven and characterized by swelling measurements, TGA (hydration and carbonation levels), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), quantitative X-ray diffraction (QXRD), nitrogen adsorption/desorption (BET and BJH) and He pycnometry (skeletal densities). More details on the sample hydration and characterization are presented elsewhere [30]. The same sample designation is maintained in this paper.

The samples of spent and reactivated (for different durations) sorbent, as well as original sample for comparisons, were sulphated and calcined/carbonated for 10 CO_2 looping cycles in a TGA. A Perkin Elmer TGA-7 thermogravimetric analyzer was used for these experiments. The samples were suspended in a quartz tube (i.d. 20 mm) on a platinum pan (diam. 5 mm). The gas flow rate, controlled by a flowmeter, was 0.04 dm^3/min. The temperature and gas used were controlled by Pyris software.

Sulphation was performed at 850 °C for 150 min. The gas mixture used was synthetic flue gas (0.45% SO_2, 3% O_2, 15% CO_2, and N_2 balance). The sorbent (fresh, spent and reactivated) mass was chosen such that the amount of CaO in all samples was approximately the same, ~10 mg, yielding an approximately uniform S/Ca molar ratio increase during experiments of 2.7h. The sulphation degree was calculated on the basis of mass increase due to formation of $CaSO_4$.

Cyclic carbonation was carried out at 750 °C, for 15 min each cycle (7.5 min calcination + 7.5 min carbonation). Ten cycles were performed with all sorbent samples. The sorbent mass was chosen such that the amount of CaO in runs with different sorbent samples was the same, ~10 mg. The gas used for calcination was 100% N_2 and that for carbonation was 50% CO_2 (N_2 balance). The degree of carbonation was calculated on the basis of mass increase due to formation of $CaCO_3$.

The sulphated samples used for XRD and SEM characterization were obtained in a TF at 850 °C for 150 min under higher (1%) concentration of SO_2 in synthetic flue gas (1 dm^3/min). Two typical hydrated samples (carbonator #4 and calciner #4) and original sample for comparison were sulphated in the TF (0.5 g sample was used for sulphation). XRD data were collected on a Bruker D500TT diffractometer over the angular range 10–70° (2θ) in 0.02° steps and 20 s per step. The phases were identified and quantitative analyses of the samples were done using alpha-alumina (Al_2O_3), as an internal spiking standard. It should be noted that samples were exposed to air during the XRD process but they are not considered reactive to atmospheric moisture and CO_2 because of their high level of sulphation. A Hitachi S3400 SEM with 20 kV of accelerating voltage was used for examination of sulphated particle surface area morphologies.

3. Results and discussion

In this study reactivated samples from a dual FBC CO_2 looping cycle reactor were examined in terms of their sulphation and cyclic carbonation characteristics. This paper focuses on sulphation and cyclic carbonation of the reactivated samples; however, some data presented previously [30] are used where they elucidate aspects of the carbonation or sulphation of these residues.

The characteristic values obtained from TGA runs are presented in Table 1 and the discussion here is mainly based on TGA curves. The TGA sulphation curves for samples from the carbonator are shown in Fig. 1. Interesting differences between the original samples and those of spent sorbent can be seen. At the beginning, sulphation of the original sample is faster than that of the spent samples; however, the reaction rate for the original sample falls faster than those for samples that have undergone the CO_2 looping cycle process. This phenomenon is more pronounced for samples that have experienced more cycles (#4) and appears to be directly related to the pore changes during CO_2 cycles. It is known that during CO_2 cycles, CaO sinters and the effective surface shrinks, while small pores are transformed into larger ones. The original sample has a greater surface area and thus sulphation is faster in the outer shell normally leading to the formation of an unreacted CaO core or other unreacted areas (network pattern, [32]). However, with a smaller surface area and larger pores (and cracks formed during CO_2 cycles), reaction of the spent samples becomes less limited by diffusion than is the case with the original sample. Hence, the chance for formation of an unreacted core/shell pattern is lower