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Engineering Scale-Up Challenges, and effects of SO_2 on the Calcium Looping Cycle for Post Combustion CO_2 Capture

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Abstract

Engineering scale-up challenges, and potential effects of SO_2 on the calcium looping cycle for post combustion CO_2 capture have been investigated in Cranfield University's pilot scale reactor (25 kW_{th}). Following reactor and process modifications, close to 80% capture was achieved. SO_2 was found to have a detrimental effect on the calcium looping cycle in both batch and continuous cyclic tests, although the presence of steam from natural gas-fired burners was found to have a positive effect on maintaining capture capacity of the sorbent.

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Keywords: CO_2 Capture; Calcium looping; Scale-up; SO_2; Post combustion

1. Introduction

Calcium looping cycle technology has been identified as a promising carbon capture technology, in particular from coal-derived flue gas, since first being proposed by Shimuzu et al. [1]. The process has been researched extensively at bench scale, but it is widely acknowledged that further work is required prior to industrial implementation. The pilot scale calcium looping facility at Cranfield is the largest of its kind in the UK (as part of

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the Pilot Advanced Capture Technologies; www.PACT.ac.uk), and is considered capable of achieving beyond 80 % capture with improved components in place. This is considered important in order to show the capability of the technology and in turn build a demand for it, as the UK moves towards a low carbon energy scenario incorporating CO_2 capture. This study shares the lessons learnt and improvements made in operating and developing the Ca looping cycle at the pilot-scale.

Figure 1 outlines the calcium looping process, which comprises calcination of limestone in a calciner reactor to produce CaO sorbent, which is then transferred to a second reactor, where CaO reacts with flue-gas derived CO_2 to form $CaCO_3$ via the carbonation process. The $CaCO_3$ is then transferred back to calciner for where it is thermally decomposed, releasing CO_2 for compression, transport and storage, and reproducing CaO for repeated cycles of CO_2 capture. The process encompasses gas-solid fluidised bed technology.

Sulphur is naturally present in coal, primarily forming SO_2 on combustion, which in turn during the sulphation reaction, reacts with CaO to form $CaSO_4$ and CaS, the production ratio of which is temperature dependent [2]. Sulphation causes blocking of larger CaO pores formed during cyclic carbonation-calcination, which could otherwise react with CO_2 to form $CaCO_3$. Research at the bench scale [3] [4] [5] has shown that SO_2 and the resulting $CaSO_4$ formation contribute to the deactivation of CaO. Effects of SO_2 on the calcium looping cycle have therefore been investigated as part of this work.

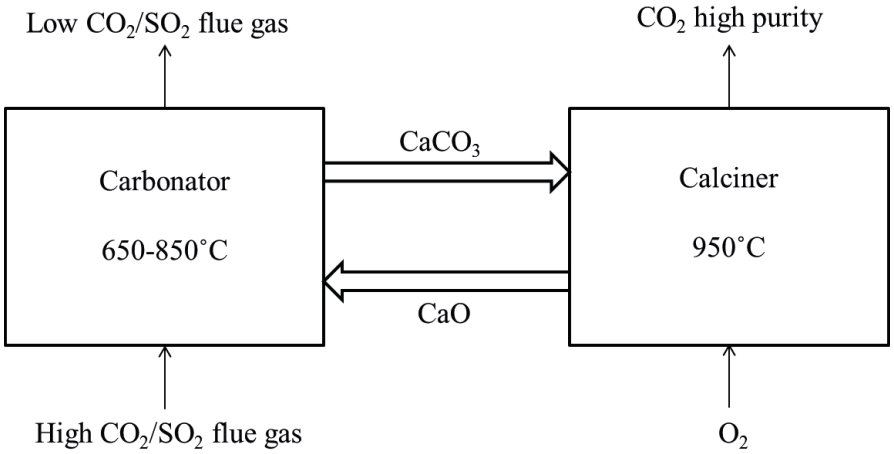

Figure 1 Calcium looping cycle, comprising calcination of $CaCO_3$ in the calciner to produce a high-purity CO_2 stream for transport and storage, after which CaO is transferred to the carbonator for CO_2 capture, producing $CaCO_3$ which is then cycled back to the calciner.

2. Methodology

Experiments were undertaken in a 25kW_{th} pilot-scale CO_2 capture rig comprising an entrained flow bed carbonator reactor, and a bubbling fluidised bed calciner reactor. The carbonator is of 0.1 m diameter, and 4.3 m length, and the fluidising gases are provided by a natural gas-fuelled air burner, the fuel gas in which provides the fluidised bed. The calciner is of 0.165m diameter, and of 1.2m length, and is a natural gas oxy-fuel combustor. Both reactors and associated fittings are made of 310 stainless steel.

A view port is located at the top of the calciner from where the reactor is filled with solids prior to testing, and the calciner also has a drain to allow sampling of solids during and after testing. Two cyclones are present in series at the carbonator exhaust to ensure efficient particulate removal from the flue gases, and therefore prevent particulate

emissions to the environment. The carbonator and calciner are connected by two loop seals, comprising an upper loop seal (ULS) and a lower loop seal (LLS), allowing controlled solids transfer, and thus regulating the solids flux from the calciner to the carbonator, and vice versa. Following entrainment of solids in the carbonator, solids are separated from the gas stream by the first cyclone, allowing exhaust gases to exit the system, and solids to continue in a looping mode. The ULS is present downstream of the cyclone exit standpipe, to allow controlled transfer of solids to the calciner. The LLS is located towards the bottom of the calciner, allowing controlled transfer of solids from the calciner to the carbonator. Both loop seals must be fluidised in order for the solids to be transferred. Therefore, each loop seal has two gas distributor nozzles in the 'entry' half of the loop seal, and two distributor nozzles in the 'exit' side of the loop seal.

Trace heating is present the length of the carbonator and calciner and is required to ensure the desired temperature for the initial start-up of the system, to maintain the required operating temperatures, and also to reduce condensation effects. The carbonator has a total of eight trace heating elements whilst the calciner has a total of four heating elements along its length. Each heating element is of 1 kW capacity and can be independently controlled, thus allowing different temperatures to be set to meet the required thermal conditions and to maintain a constant temperature along each reactor length. Typically, each carbonator heating element was set to approximately 600˚C, whilst each calciner heated element was set to approximately 900˚C.

In order to observe any morphological changes which may have occurred to the limestone sorbent as a result of the calcium-looping process, a number of chemical analytical techniques have been used. Energy Dispersive X-Ray Spectroscopy (EDS) was to confirm the elemental composition of each sample. Particle Size Distribution (PSD) analysis was carried out prior to and after testing using a Malvern Mastersizer 2000. Brunauer-Emmett-Teller (BET) surface area analysis and Barrett-Joyner-Halenda (BJH) (Tristar 3000) pore size and volume analysis were also carried out to determine any changes in sorbent morphology as a result of testing

3. Results and Discussion

Close to 80 % CO_2 capture has been achieved in the pilot scale reactor (Figure 2) through experimental development.

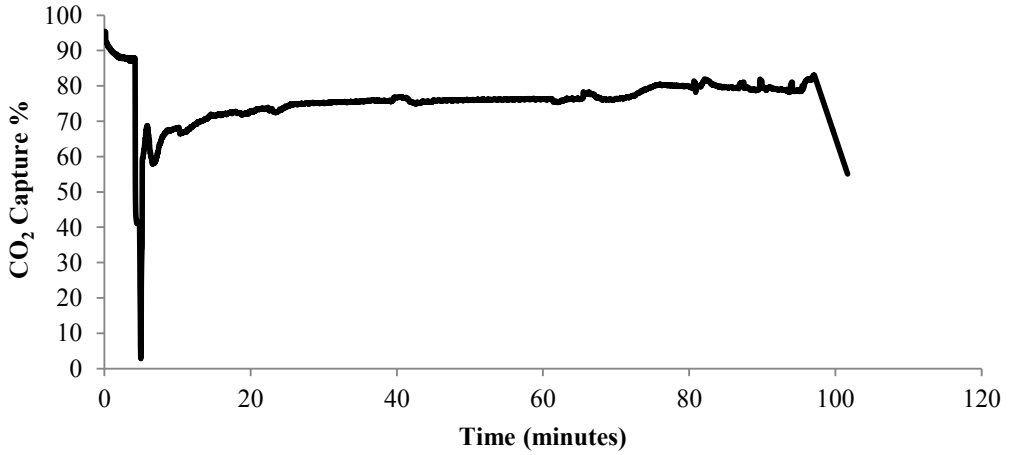

Figure 2. CO_2 capture achieved following reactor and process modifications

This development has comprised a number of process and reactor modifications, including, but not limited to, optimisation of reactor temperatures, enhanced heating of the 'loop seal' non-mechanical transfer valves through the

addition of heated elements, and also addition of pneumatic vibration components on loop seals to encourage solids transfer .

Lower carbonator temperatures of ~600-650 °C have previously been identified as being beneficial at the pilot scale due to the presence of temperature gradient across a fluidised bed [6], and this has been confirmed in this study. Decreasing the carbonation temperature by approximately 50˚C had a positive effect on increasing % capture in the reactor, from an optimum capture of ~ 60 % for a carbonator temperature of 650-700˚C, to ~ 70 % capture for a carbonator temperature of 600-650˚C. This is primarily due to the effect of partial pressure of CO_2 on the carbonation reaction. By reducing the temperature in the carbonator, the partial pressure required for carbonation was also reduced, thereby driving forward the formation of $CaCO_3$ from CaO and CO_2.

The importance of sufficiently high temperatures above 420°C [7] in transfer lines between the reactors, including loop seals and associated standpipes, has been proven in this study as a mitigation measure against $Ca(OH)_2$ formation, to minimise its associate negative attributes on the Ca looping cycle, to thereby improve the capture %.

With particular regard to pilot scale testing, the use of efficient gas distributors (bubble caps in this case) is considered to hold potential benefits over conventional distributors such as those used in this study. It is considered that the use of bubble caps may reduce weeping of solids from the reactor the plenum, particularly when a pressure drop is experienced in the system, and also to prevent blockage of gas distributors which can lead to reduced gas flows and in turn reduced fluidization and CO_2 capture.

3.1. Effects of SO_2 – Batch tests

The effect of SO_2 has been investigated at the pilot scale, and Figure 3 shows results from single column batch experiments. Increasing SO_2 concentrations appears to decrease % CO_2 capture, which is likely to be caused by the well-documented detrimental effect of SO_2 on CO_2 capture, due to the formation of $CaSO_4$. $CaSO_4$ has a molar volume of 46 cm^3/mol, compared to a molar volume of 37 cm^3/mol for $CaCO_3$ [8], and therefore acts to block pores and impede CO_2 capture. This is supported by Figure 4, which shows the average pore diameter of sorbent sampled from the reactor after each test for 0, 1000 and 2000 ppm SO_2, and identifies that increasing SO_2 concentration reduces the average pore diameter, from 55 nm to 28 to 10 nm for 0, 1000 and 2000 ppm respectively. In general, reactions are limited by pore size, as well as by pore surface area and pore distribution. Pore surface area can be considered the area where reactions can take place, while pore volume is the space in which products can grow. Pore diameter can be defined as the space limitation in a single pore [8].

For 0 ppm SO_2, the % CO_2 capture remained close to 100 % for the longest period of time before beginning to decrease. However, for 1000 ppm SO_2, this remained at a high level (above approximately 90 %) for the longest period of time before beginning to decrease. Further, the % capture at the end of the test was approximately 36 %, 2 % and 9 % for 0, 1000, and 2000 ppm SO_2 respectively. The fact that the 1000 ppm SO_2 test had a lower final capture % than the 2000 ppm SO_2 test is unexpected, as given the well-documented detrimental effects of SO_2 on carbonation, it would be expected that the 2000 ppm test had the lowest final % capture. A reason for this outcome however could be the positive effect that SO_2 may have in decreasing effects of attrition [3]. This is supported by Figure 5 which shows that sorbent from the 0 ppm test experienced the greatest decrease in particle diameter, whilst the sorbent tested with 1000 ppm SO_2 had the largest mean particle diameter and volume when compared with sorbent tested in 0 and 2000 ppm SO_2, suggesting that 1000 ppm SO_2 represents a compromise between pore blockage and attrition. Jia *et al.* [9] too found that ‘light’ sulphation of limestone in SO_2 concentration of 1800 ppm resulted in reduced material loss as a result of attrition.

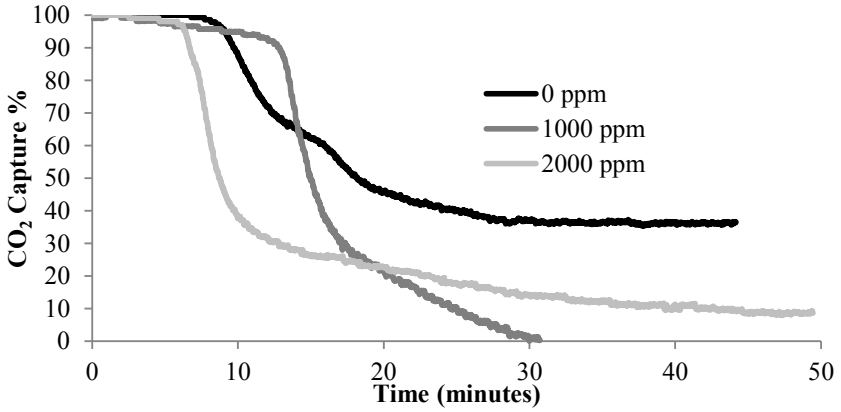

Figure 3 Effect of increasing SO_2 concentration on % CO_2 capture.

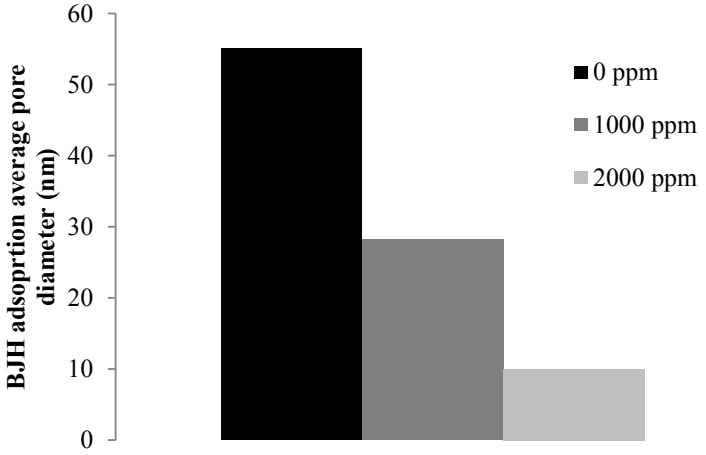

Figure 4 BJH analysis showing average pore diameter of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO_2.

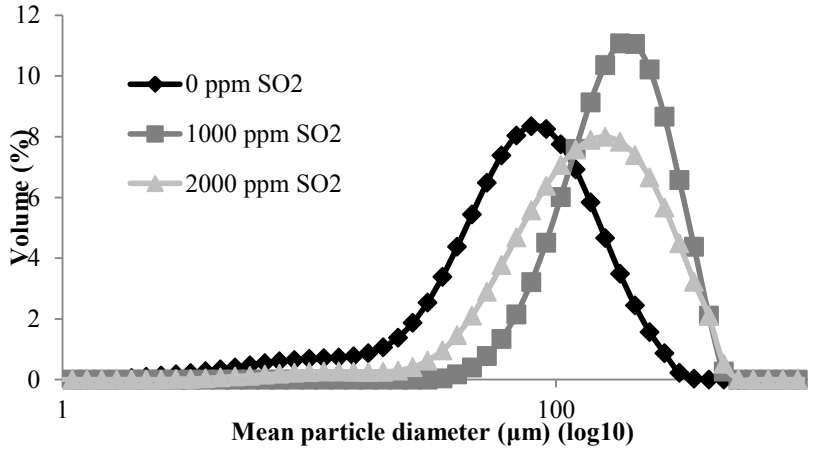

Figure 5 PSD analysis of sorbent sampled from the reactor after each tests, for 0, 1000 and 2000 ppm SO_2.

EDS analysis (Figure 6) of sorbent after each test suggests reduced carbonation with increasing SO_2 concentration, implied by decreasing weight % of C and O, and increasing weight % of S. However, the weight % of Ca does not increase linearly, as would be expected for reduced carbonation, and instead decreases from 40.5 % at 0 ppm, to 36.7 % 1000 ppm, before then rising to 41 % for 2000 ppm SO_2. This again could be indicative of 1000 ppm producing some form of compromise between pore blockage and reduced attrition effects, or may be attributed to an anomalous reading obtained from the EDS analysis.

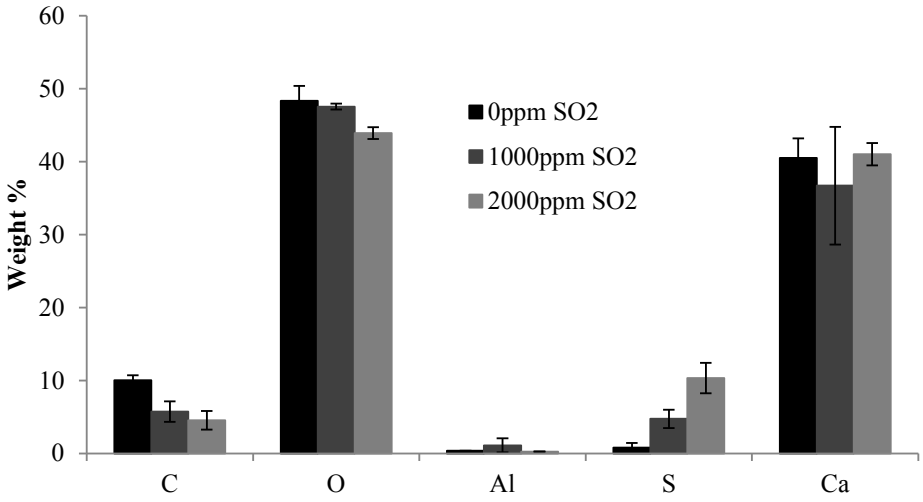

Figure 6 EDS analysis of sorbent exposed to increasing SO_2 concentrations in single column experiments.

3.2. Effects of SO_2 –Continuous Cycling tests

The effect of increasing SO_2 concentration on the CO_2 capture efficiency of the calcium-looping cycle was also investigated in continuous cycling tests, which identified that increasing SO_2 concentration appears to decrease the % capture efficiency (Figure 7). This is likely due to pore blockage as a result of $CaSO_4$ formation. This is in

accordance with the majority of work available in the literature [5] [10]. However, it is apparent that the % capture for each test shown does not appear to decrease over time with increasing carbonation/calcination cycles, as would be expected from typical CO_2 capture curves. The reason for this may be due to the quantities of steam produced by the carbonator's air-fired burner, and the calciner's oxy-fired burner, at 87 l/min and 108 l/min H_2O in the carbonator and calciner respectively. The effects of additional steam on % CO_2 capture in the calcium-looping cycle have been investigated, and it is apparent from this work and research available in the literature that addition of steam during carbonation/ calcination improves % CO_2 capture due to the acceleration and enhancement of the fast-diffusion process in carbonation.

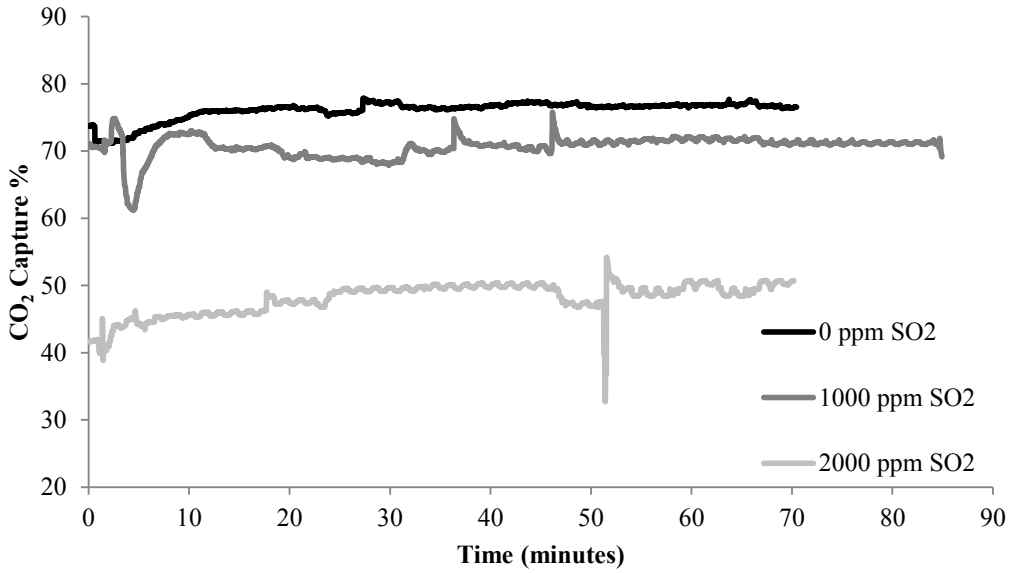

Figure 7 Effect of SO_2 concentration on % CO_2 capture during pilot scale calcium-looping.

With further regard to the reduction in CO_2 % capture proposed due to pore blockage, Figure 8 shows the results of BET analysis for sorbent sampled from the reactor after each test. It identifies that the sorbent tested in 2000 ppm and 1000 ppm SO_2 has a smaller pore volume than that tested without, implying pore blockage had occurred. The pore diameter for sorbents from all three test scenarios was very similar, with sorbent from 0 and 1000 ppm SO_2 addition tests showing slightly smaller diameters, the smallest of which was approximately 2 nm and can be considered small pores (<6 nm), compared to a close value of 7nm for the 2000 ppm SO_2 test. The pronounced peak in pore volume at a diameter of ~3nm for the 0 ppm test and also to a lesser extent for the 1000 ppm test is interesting. It suggests that the small pores that contribute to pore volume and thus important for CO_2 capture, are filled with increasing SO_2 concentration, and thus in this case it is both the small and large pores that are active in reducing CO_2 capture capacity. This is in contrast to thermogravimetric analysis (TGA) work carried out by Chen *et al.* [8] who suggested that decay in activity is largely due to changes in large pores, and also Gullet and Bruce [11] (from Sun *et al.* [5]) who suggested sulphation fills pores of 10-60 nm or larger. In the carbonator, where CaO particles are transferred in order to be carbonated, sulphation (i.e. sulphation of CaO) is more likely to occur than direct sulphation (sulphation of $CaCO_3$) because of the larger surface area of CaO. The reason for this filling of small pores may be due to diffusion of CO_2 through the $CaSO_4$ layer, due to its smaller molecular volume when compared to SO_2, thereby filling smaller pores, which in the absence of SO_2 is not 'necessary' for it to do. This may be more pronounced at pilot scale than bench scale because of the larger area available over which reactions can take place in a fluidised bed, compared to a fixed bed in a TGA.

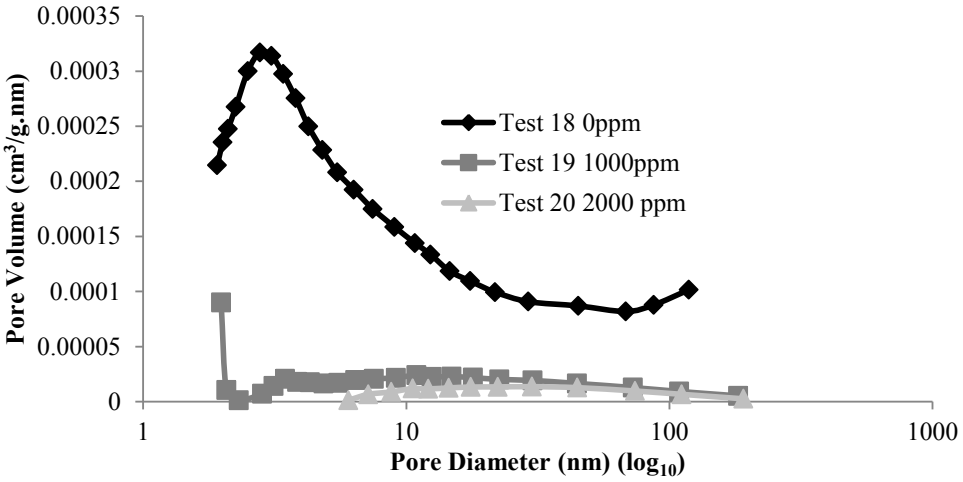

Figure 8 BET analysis of sorbent taken from reactor after testing with increasing SO_2 concentrations.

With regards to attrition, Figure 9 shows the results of sorbent PSD analysis after testing, showing very similar PSD for all 3 tests. In this case the sorbent from the 2000 ppm SO_2 test shows a slightly higher extent of attrition than the 1000 ppm, and in turn the 0 ppm test. This is in contrast to single column tests with SO2 which showed slight a decrease in attrition with SO_2 present. The difference may be due to the looping cycle process, during which particles are subjected to other forces, including gravitational, drag, buoyancy and pressure forces [12], which in single column tests they would not experience, including the abrasive bed, and the reactor walls. This in turn may result in a weaker $CaSO_4$ surface layer, and / or removal of said layer. Similar results whereby increasing SO_2 caused a slight increase in attrition were found by Coppola *et al.* [10] in bench scale, batch tests with 1800 ppm SO_2.

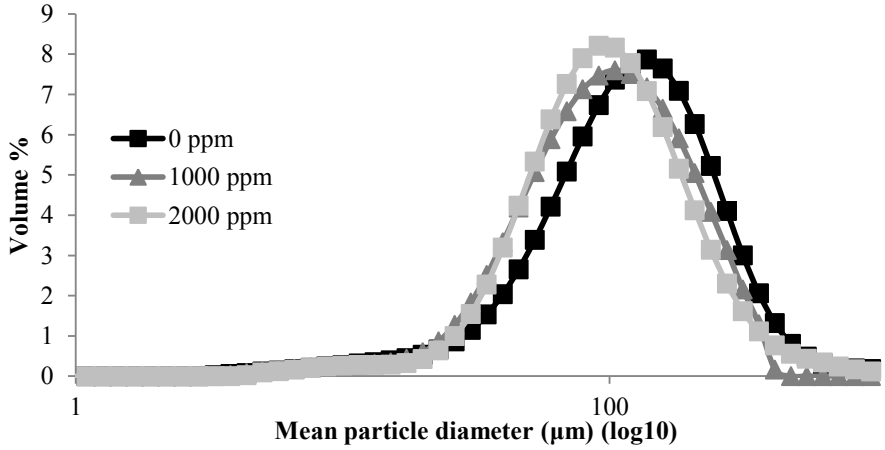

Figure 9 PSD analysis of sorbent sampled from reactor after testing with increasing concentrations of SO_2.

4. Conclusions

CO_2 capture tests have been carried out in a pilot scale reactor employing the calcium looping cycle in continuous mode. A maximum CO_2 capture % of close to 80% has been achieved in this reactor, following a number of process and reactor modifications. It is considered that a higher % capture could be achieved with further modifications to

improve the solids inventory, solids circulation rate and residence time of solids in the reactor, as well as improvements to the burner reliability. The effects of SO_2 have been investigated at the pilot scale in both batch and continuous experiments, and it was found, in accordance with work available in the literature, that SO_2 has a detrimental effect on CO_2 capture. This is supported by PSD, BET, and EDS analysis of sorbent samples subsequent to testing. The large water content present in the reactor from the use of an air and oxy-fired burner seems to have a positive effect in maintaining the CO_2 capture % achieved by the sorbent.

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