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Spray Water Reactivation/Pelletization of Spent CaO-based Sorbent from Calcium Looping Cycles

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ABSTRACT: This paper presents a novel method for reactivation of spent CaO-based sorbents from calcium looping (CaL) cycles for CO_2 capture. A spent Cadomin limestone-derived sorbent sample from a pilot-scale fluidized bed (FBC) CaL reactor is used for reactivation. The calcined sorbent is sprayed by water in a pelletization vessel. This reactivation method produces pellets ready to be used in FBC reactors. Moreover, this procedure enables the addition of calcium aluminate cement to further enhance sorbent strength. The characterization of reactivated material by nitrogen physisorption (BET, BJH) and scanning electron microscopy (SEM) confirmed the enhanced morphology of sorbent particles for reaction with CO_2. This improved CO_2 carrying capacity was demonstrated in calcination/carbonation tests performed in a thermogravimetric analyzer (TGA). Finally, the resulting pellets displayed a high resistance to attrition during fluidization in a bubbling bed.
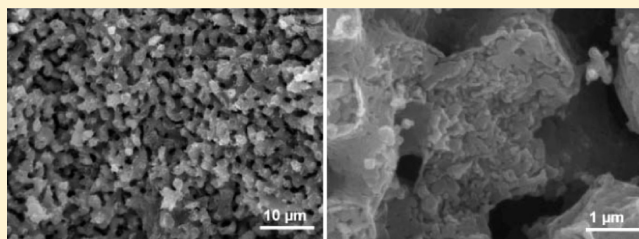
INTRODUCTION

Calcium looping (CaL) cycles has been intensively investigated in order to produce a concentrated CO_2 stream from the utilization of fossil fuels and biomass, to allow the sequestration of CO_2 from large stationary thermal power sources such as fossil-fuel-fired power plants[1] to mitigate anthropogenic climate change.[2,3]

CaL processes are based on a reversible carbonation reaction:

$$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)} \Delta H_r^0 = -178 \text{kJ/mol} \qquad (1)$$
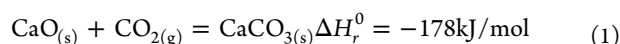
The forward reaction, carbonation, captures CO_2 from gases during precombustion processes such as sorption-enhanced reforming[4] or from flue gases produced during combustion in a postcombustion CO_2 capture scenario.[1]

The reverse reaction, calcination, enables sorbent regeneration and produces a concentrated CO_2 stream. However, calcination must take place at higher temperatures, typically >900 °C, which in the presence of an almost pure CO_2 atmosphere enhances sintering,[5] which significantly reduces sorbent CO_2 capture activity during subsequent cycles.[6] Natural CaO-based sorbent maintain a residual reactivity even over a very long series of carbonation/calcination cycles,[7] but the deactivation phenomenon is exacerbated by the presence of SO_2.[8,9] Here the sorbent is irreversibly sulphated, but more importantly, the $CaSO_4$ product covers pore surfaces preventing further reaction between CaO and CO_2. This means that sorbent becomes deactivated (spent sorbent), and an increased make up of fresh sorbent is needed to maintain desired CO_2 capture efficiency. Unfortunately, this increases the cost of CO_2 capture,[10,11] and may prevent the use of the spent material in cement manufacture.[12,13]

Numerous methods to retain sorbent carrying capacity have been tested including sorbent pretreatments by initial heating at high temperature or by the use of chemical agents, or sorbent reactivation, carried out by means of hydration.[14] Hydration is the most well investigated methods for CaL spent sorbent reactivation. Unfortunately, the use of liquid water is probably not practical because it creates additional energy penalties for drying of the wet hydrated lime. Therefore, steam hydration is proposed as an optimal sorbent treatment,[15,16] especially given that spent sorbent has been shown to be very reactive toward steam, and even ambient moisture is able to regenerate sorbents at room temperature.[17]

Past hydration studies have demonstrated successful reactivation for sorbent cycled and sintered under different conditions and in variously sized equipment such as the thermogravimetric analyzer (TGA), and fixed or fluidized bed facilities.[15−18] However, these studies have also shown that large cracks were formed in the particles, resulting in poor mechanical strength, leading to powdering of the material during handling. This means that reactivated material cannot be used directly in fluidized bed combustion (FBC) reactors, which are currently the preferred technology for CaL cycle processes. One possible method of mitigating such shortcomings could be calcination of hydrated sorbent in an atmosphere of CO_2.[19,20] This produces reactivated sorbent calcined at temperatures which are much higher than the decomposition temperature for $Ca(OH)_2$ and the resulting material appears to be mechanically stronger than if the sorbent is simply calcined at a temperature sufficient to decompose $Ca(OH)_2$.

In addition to a decay of sorbent activity, loss of CaO-based sorbents from FBC CaL cycle reactors due to attrition and elutriation also increases demand for fresh sorbent makeup.[21,22] Recent studies on pelletization of CaO-based sorbents showed that the mechanical strength of such materials can be enhanced by the addition of binders.[23,24] In particular, it has been shown that pelletization can be employed for both reactivated spent sorbent and elutriated material. Therefore, pelletization can be considered as a process which decreases demand for fresh sorbent makeup, which is additionally valuable when the binder contributes to enhanced sorbent CO_2 capture activity such as is the case with calcium aluminate cements.[23,24]

Our recent studies showed that granulation of both hydrated lime and quick lime powder by a mechanical pelletizer is a suitable method for preparation of CaO-based pellets.[25] During this process a water spray is used to promote granulation of the hydrated powder sorbent. The goal of this study was to develop a new process for spent sorbent reactivation using a water spray with simultaneous pelletization of reactivated material.

MATERIALS AND METHODS

Materials. Spent Cadomin limestone sample obtained after four calcination/carbonation cycles in a pilot-plant dual fluidized bed reactor was used in this study. The FBC facility is described in detail elsewhere.[26] The calcination occurred at 905−915 °C under oxy-fuel combustion conditions in the presence of 2000 ppm SO_2 and 15% steam, while the carbonation process took place at 650 °C in 8% CO_2 and 15% steam (balance was air). The residue obtained after the fourth carbonation was collected and used for reactivation/pelletization tests reported here. The X-ray fluorescence (XRF) elemental analysis of original limestone and that of the sorbent after four calcination/carbonation cycles is presented in Table 1. A commercial calcium aluminate cement, CA-14, (71% Al_2O_3

Table 1. Elemental Composition of Cadomin Limestone and Ca Looping Cycle Residue after the Fourth Carbonation

component (wt%)	original limestone	spent sorbent
SiO_2	1.03	1.40
Al_2O_3	0.33	0.34
Fe_2O_3	0.09	0.33
P_2O_5	<0.03	<0.03
CaO	54.91	70.65
MgO	0.20	1.21
SO_3	<0.10	13.71
K_2O	0.06	0.15
Na_2O	<0.20	<0.20
loss on fusion	43.09	12.10
sum	99.93	99.96

and 28% CaO), produced by Almatis Inc., was used as a binder for pelletization and was supplied as a very fine powder with >80% of the particles <45 μm.

Reactivation/Pelletization. The reactivation tests with simultaneous pelletization were done with a mechanical pelletizer (Glatt GmbH) operated in batch mode. The calcined spent sorbent and calcium aluminate cement (total 300 g) were mixed in the reactivation/pelletization vessel (1 dm^3). The schematic representation of the reactivation/pelletization vessel is presented in Figure 1. A certain amount of water was sprayed intermittently during hydration and pelletization with a nozzle, which can produce the micrometer-sized water droplets (<300
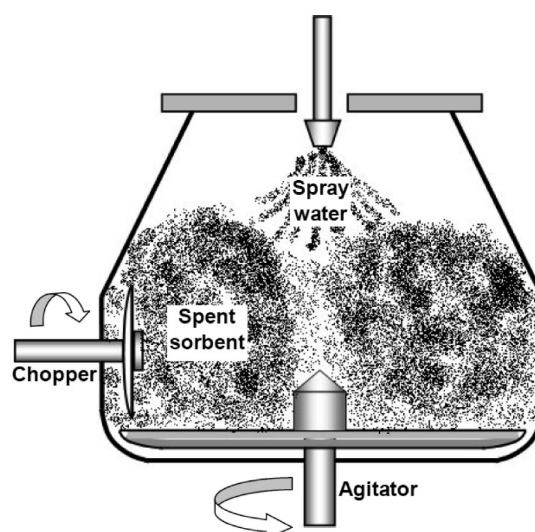

Figure 1. Scheme of reactivation/pelletization vessel.

μm) required for the reactivation/pelletization process. Moreover, when hydration started some water evaporated due to the high temperature produced, and a fog like atmosphere was formed from the spray water. The amount of spray water varied depending on the starting material used, but the water droplet size and the total amount of water required appeared to be the most important factors affecting the pellet size. The pellet size was also controlled by the speed of a pair of rotor blades attached to the vessel, that is, one agitator (operated at 500 rpm) located on the bottom and one chopper (operated at 2500 rpm) on the side. Typically one batch of pellets can be produced in 20−30 min.

The pellets were also prepared with no addition of cement. Also, pellets with a core-in-shell structure were prepared in a two-step process. For this process, spent sorbent was first hydrated and granulated and the pellets obtained were then sieved, and particles with a size fraction 0.425−1.0 mm were returned to the pelletization vessel together with cement addition only. It is assumed that a cement-containing layer would be formed externally to the original pellets, that is, around the reactivated sorbent core. To avoid damage to the already formed "core" particles the rotation speed of the chopper was reduced to 300 rpm (agitator speed reduced to 100−200 rpm) during the coating step.

After pelletization, the pellets were again sieved and dried in the open air for several days before storage. It should be noted that for the preparation of the core-in-shell pellets, the cores obtained after the first stage were not dried, which we believe results in stronger adhesion between the core and shell. After each run the smaller (<0.425 mm) and larger (>1.4 mm) particles were collected and returned to the pelletization vessel to be remade and pelletized with the new batch of spent sorbent during the next run. It was noticed here that CaO from calcined spent sorbent adsorbs water from particles made in the previous run and releases heat during hydration, which caused powdering of particles from previous runs. This effect is also enhanced by the high speed of the chopper. The fact that the sorbent particles during hydration become fragile and easily powdered is employed here in two ways. First, spent sorbent is easily powdered during reactivation which means that grinding is not required before pelletization. Second, excessively large particles, which are unavoidable during real pelletization
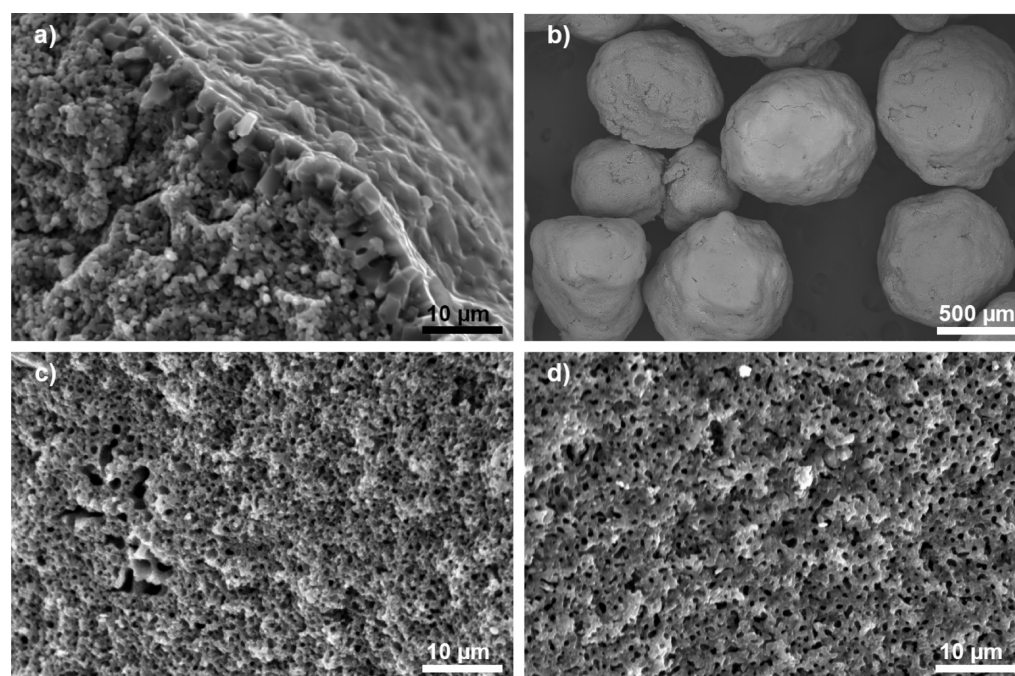
Figure 2. SEM images of tested CaO-based sorbents: (a) sectioned spent sorbent particle, (b) reactivated/pelletized sorbent pellets, (c) morphology of reactivated and calcined sorbent with 10% cement, and (d) morphology of reactivated sorbent (10% cement) after 30 carbonation/calcination cycles.

operations, can be powdered during the next run to produce particles in the desirable size range so that we have no oversized particles wasted. The use of particles from previous runs, therefore, reduces the amount of waste material and effectively the process becomes semicontinuous.

Sorbent Characterization. CO_2 carrying capacities of pellets were determined by a Perkin-Elmer TGA-7 apparatus using ~30 mg samples suspended in a quartz tube (i.d. 20 mm) on a platinum pan (i.d. 5 mm). The gas flow rate was 0.04 dm^3/min and the temperature and gas used were controlled by Pyris software. Data on sample mass during the experiments were monitored and conversions were calculated on the basis of mass change, assuming that mass change occurs only due to formation/decomposition of $CaCO_3$. The experiments were done isothermally at 800 °C, with carbonation in 50% CO_2 (N_2 balance) for 30 min, and calcination in 100% N_2 for 10 min.

The attrition tests were performed in a bubbling fluidized bed (BFB), with an internal diameter of 50 mm (which is described in detail elsewhere [25]). The pellets (0.425−1.4 mm) were precalcined in a muffle furnace in air for 2 h at 850 °C and their particle size distribution was determined by sieving before the attrition tests. The precalcined sample was weighed (~80−100 g in calcined form) before loading into the reactor. The minimum fluidization velocity, U_{mf}, was determined experimentally for each batch of sample by pressure drop ($\triangle P$) vs. superficial gas velocity (U) correlations. The sample was heated in 100% N_2 from room temperature to 850 °C at a heating rate of 30 °C/min prior to each experiment. Minimum fluidization velocities at 850 °C of precalcined pellet samples were found to be in the range of $U_{mf} = 0.16−0.17$ m/s. Three carbonation/calcination cycles were conducted by alternating temperature and gas composition: 15% CO_2 (N_2 balance) at 700 °C for 30 min at a superficial gas velocity of 1.0 m/s for carbonation; and 100% N_2 at 850 °C for 15 min at a superficial gas velocity of 0.35 m/s during calcination. When the attrition test was

completed, the bed inventory was carefully removed from the bed by vacuum with a 10 mm internal diameter stainless steel tube. The collected bed material was then weighed and the particle size distribution was determined again. While only three attrition cycles were performed, previous studies have shown that initial cycles produce the largest degree of attrition, although some degree of attrition will occur with every cycle.[21,22]

The original limestone, spent sorbent and reactivated pellets were all subjected to N_2 adsorption/desorption analyses for pore surface area. Pore surface areas (BET) and pore size and volume distributions (BJH) were determined using a Micromeritics TriStar II 3020 V1.02 N_2 sorption analyzer. The sample morphologies were observed with a Hitachi S3400 scanning electron microscope (SEM) with 20 kV of accelerating voltage under high vacuum. The samples were coated with gold/palladium before SEM examination and images obtained by secondary electrons are presented here.

RESULTS AND DISCUSSION

The sorbent used in this work was obtained under realistic CaL cycle conditions including the presence of steam and SO_2 during cycles, which resulted in 13.6% sulphation conversion (Table 1). Moreover, it can be seen in Figure 2a that a sulfate shell is formed at the sorbent particle surface which together with sorbent sintering hinders carbonation and since SO_2 will be present both in the carbonator and the calciner, these results are likely to be more realistic than for systems in which SO_2 is excluded. Under these conditions $CaSO_4$ formation is irreversible under both calcination and carbonation conditions. Therefore, to prolong sorbent cycle life a reactivation step is required, and a hydration technique appears as the most appropriate method. However, as noted above, the hydration typically causes particle swelling resulting in large cracks which lead to destruction of the particles on further handling,

something which would be especially pronounced in a FBC system.[15−17] This is considered as an "Achilles heel" of any hydration/reactivation technique; however, with the pelletization approach employed in this work such resulting sorbent fragility becomes a benefit and any remaining need to reduce the particle size is achieved by means of the mechanical work of two blades in the hydration/pelletization vessel (Figure 1). Furthermore, the hydration process and consequent release of heat cause evaporation which means that hydration readily occurs in a mixture of spray water and steam. During reactivation sorbent particles quickly become a very fine powder which easily achieves complete hydration, and any further addition of water results in granulation of the powder into relatively spherical pellet particles (presented in Figure 2b). Therefore, the proposed technique practically involves three processes in the same reactor: powdering, hydration/reactivation, and pelletization of CaO-based sorbent.

However, the purpose and main goal of the proposed technique is reactivation of spent sorbent from CaL cycles. The morphology of the reactivated pellets after calcination is shown in Figure 2c. It can be seen that the morphology in terms of porosity is significantly enhanced when compared with that of the original spent sorbent presented in Figure 2a. In this case the sulfate shell is destroyed during reactivation and smaller grains and a more developed porous structure are formed. Due to the presence of calcium aluminates (from the added cement) the sorbent texture remains relatively stable during carbonation/calcination cycles conducted in the TGA (Figure 2d).

The results of nitrogen physisorption tests presented in Table 2 show that the BET pore surface area of the spent

Table 2. BET Pore Surface Area and BJH Cumulative Pore Volume of Calcined Limestone, Spent Sorbent, And Reactivated Pellets

sorbent	BET pore surface area [m²/g]	BJH cumulative pore volume [cm³/g]
original lime	4.19	0.015
spent sorbent	0.73	0.004
reactivated pellets with no cement	3.96	0.011
reactivated pellets with 10% cement	4.16	0.012
reactivated core-in-shell pellets with 10% cement	4.23	0.013

sorbent was only 0.73 m²/g. However, after reactivation pore surface area is significantly higher (3.96−4.23 m²/g) and in the range of that for fresh limestone after calcination (4.19 m²/g). Previous studies on hydration[15] showed that the BET surface area of reactivated sorbent can be even higher than that of the original sorbent. However, in this case the sorbent prior to hydration was already significantly sulphated (13.6%), which also resulted in the lower pore surface area of reactivated sorbent. The addition of calcium aluminate cement slightly increased the pore surface area due to the presence of aluminum compounds.

The pore surface area distribution presented in Figure 3a shows that the spent sorbent is deficient in small pores which are mainly responsible for "maximum" carbonation conversion. It is interesting that the spent sorbent after reactivation showed similar pore surface area distribution to that of the original limestone. In both cases the peak for pore surface area distribution occurs at ∼5 nm pore diameter. These results are
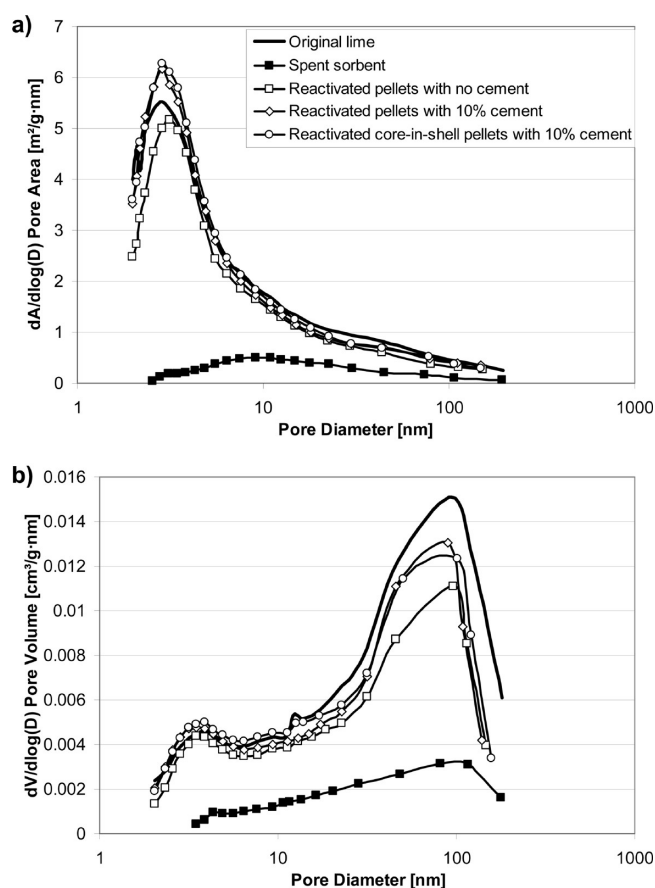

Figure 3. Pore surface area distribution (a), and pore volume distribution (b) of tested lime-based sorbents.

in agreement with that from the data for pore volume distribution. Two peaks are present in this case. The first peak corresponds to ∼5 nm pores and the second one is slightly below 100 nm. The observed enhancement of pore surface area and pore volume of pores smaller than 150 nm is crucial for carbonation conversion. Thus, Fennell et al.[27] found a correlation between CO_2 capture capacity and available volume for accommodation of formed product ($CaCO_3$) in pores of size 150 nm. Similarly, Alvarez and Abanades[28] explained their maximum carbonation conversions during CO_2 capture cycles by the formation of a critical product layer (49 nm), which again implies that the enhancement of sorbent texture seen here should benefit in a higher CO_2 capture activity.

The CO_2 capture activity of spent sorbent and that seen after reactivation, as well as conversion of the original limestone in a series of 30 calcination/carbonation cycles in the TGA are presented in Figure 4a. As can be seen, the activity of spent sorbent is poor; with only about 11 g of CO_2 captured by 100 g of sorbent, which corresponds to only 20% conversion of available CaO (as CaO from $CaSO_4$ is unavailable for carbonation). However, the initial CO_2 uptake is almost three times as high after reactivation (∼30 g/100 g), which clearly demonstrates the beneficial effect of reactivation and still 30% higher at 30 cycles. While it should be noted that CO_2 uptake is still lower than that for the original sorbent, this can be explained by the fact that spent/reactivated sorbent is partially sulphated. Finally, a small beneficial effect of cement addition on conversion after 30 cycles can be seen, which is attributed
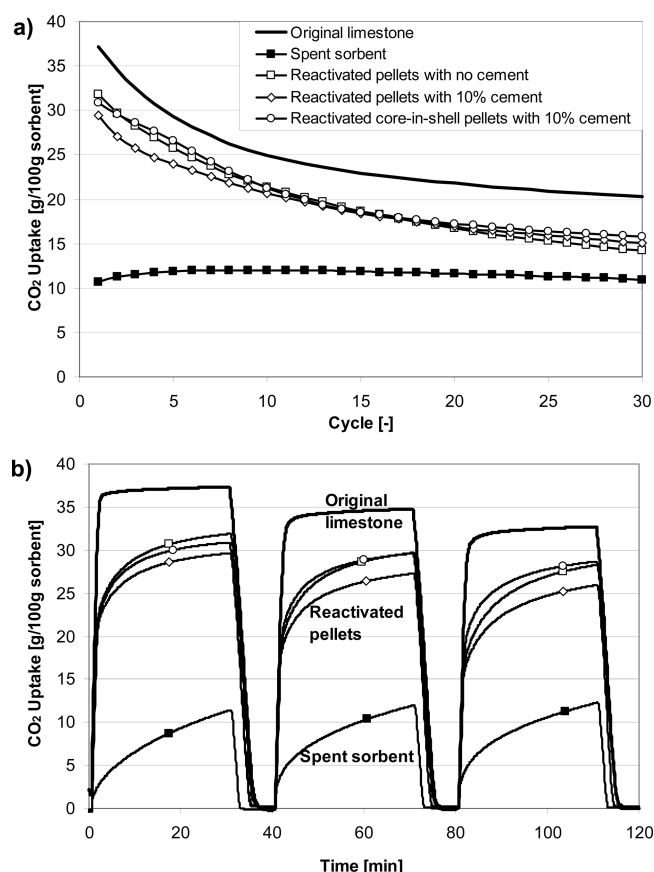
a)

b)

Figure 4. CO_2 capture performance of tested sorbents: (a) CO_2 capture capacity during 30 cycles, and (b) conversion profiles during the first three cycles. Conditions: carbonation in 50% CO_2 (N_2 balance) for 30 min, calcination in 100% N_2 for 10 min, isothermally at 800 °C.

here to mayenite ($Ca_{12}Al_{14}O_{33}$) formation, which was also noted and discussed in our earlier studies on calcium aluminate pellets.[23,24] However, the effect of cement addition is less pronounced in this study due to sulphates present in the sorbent.

Figure 4b shows that the beneficial effect of reactivation can be even more important when sorbents are used under more realistic conditions in FBC reactors. Namely, the conversion profiles show that only a few percent of CO_2 capture is achieved for spent sorbent during the first few minutes, which is an expected residence time of sorbent particles in CaL FBC systems. In this case, for all practical purposes there is no fast initial reaction stage, that is, the conversion progresses slowly from the beginning and after a relatively long reaction time (30 min) the CO_2 uptake is only 11 g/100 g. By contrast, a fast initial reaction stage is clearly present after reactivation. However, reactivated sorbent also shows different conversion profiles when compared with that of the original sorbent. The shift between the kinetically- and diffusion-controlled stages is not sharp here as it is in the case of natural limestone. It can be seen that carbonation of reactivated pellets continues noticeably even during the diffusion-controlled stage. These differences should also be taken into account when simulating the CO_2 capture activity of a modified sorbent, since these "modified" sorbents can be considered synthetic sorbents, given that they have experienced realistic calcination/carbonation cycles in an atmosphere containing steam and SO_2. This means that

semiempirical formulas/models which correlate "maximum" conversions during capture cycles,[29,30] developed for natural sorbent cycled under atmospheres containing only N_2 and CO_2, are almost certainly not appropriate for use with modified sorbents or sorbents cycled under more realistic conditions.

It is also well established that the first calcination and a few first calcination/carbonation cycles in FBC reactors are associated with the most significant attrition,[21,22] which may result in loss of 40% of the sorbent due to elutriation from FBC reactors. The causes for attrition are related to mechanical and thermal stresses, and attrition extent greatly depends on sorbent type and sphericity of the particles. The pelletization procedure applied here results in highly spherical particles (Figure 2b) which naturally resist attrition. Moreover, given that such "agglomerated particles" already experience some "attrition" during circulation in the pelletization vessel, any material or structure which is less mechanically strong is reshaped during pelletization. The superior resistance to attrition of the pellets obtained by this method is also confirmed by tests in the BFB, as shown in Figure 5. After
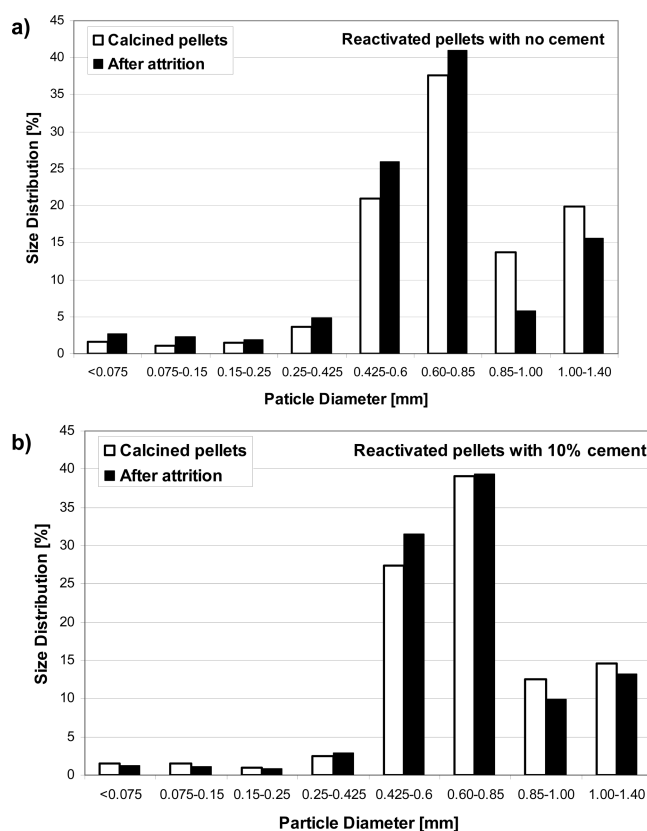
a)

b)

Figure 5. Results of attrition tests in bubbling bed reactor: (a) reactivated sorbent with no cement, and (b) reactivated sorbent with 10% calcium aluminate cement.

three carbonation/calcination cycles were performed, only a few percent of small particle size fractions are formed. Moreover, as expected, the sorbent with cement addition performed better. It can be concluded that reactivation/pelletization can be achieved even without cement addition especially if the resulting material was used in processes which require shorter residence time in an FBC reactor. That could be the case if reactivated sorbent is used in a guard bed to remove SO_2 before CaL cycles.[31] Otherwise, if reactivated material is to

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be used in longer series of CO_2 capture cycles, the addition of cement is desirable due both to improved mechanical strength and reduced sintering. It should also be noted for multiple reactivations during a series of CaL cycles the addition of cement is required only for the first reactivation/pelletization, and after that such pellets can be reactivated and reshaped with no additional cement added, which is an important advantage.[32]

Results presented here show that the proposed method for simultaneous reactivation and pelletization is extremely promising. Deactivated or extremely unreactive sorbents can be reactivated, and pellets suitable for FBC applications can be obtained. The reactivated material can be used for additional CO_2 capture cycles with reasonable activity even if it had been partially sulphated before reactivation. The attrition resistance and CO_2 capture activity are improved with cement addition. It can be concluded that the proposed method encompasses several advantages when compared with previously proposed steam reactivation methods. Namely, in this case spray water is used, which is less energy intensive than supplying steam. Moreover, the obtained pellets are ready to be used directly in the FBC reactor, which is not case with steam hydrated materials, which require further processing before their utilization in FBC reactors.

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Notes
The authors declare no competing financial interest.

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