# Post-combustion calcium looping process with a high stable sorbent activity by recarbonation

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# ABSTRACT

This paper presents a novel sorbent regeneration technique for post-combustion calcium looping CO<sub>2</sub> capture systems. The advantage of this technique is that it can drastically reduce the consumption of limestone in the plant without affecting its efficiency and without the need for additional reagents. The method is based on the recarbonation of carbonated particles circulating from the carbonator using pure CO<sub>2</sub> obtained from the gas stream generated in the calciner. The aim is to maintain the CO<sub>2</sub> carrying capacity of the sorbent close to optimum values for CaL post-combustion systems (around 0.2). This is achieved by placing a small regeneration reactor between the carbonator and the calciner. This reactor increases slightly the conversion of CaO to carbonate so that it exceeds the so-called maximum CO<sub>2</sub> carrying capacity of the sorbent. This increase compensates for the loss of CO<sub>2</sub> carrying capacity that the solids undergo in the next calcination-carbonation cycle. Two series of experiments carried out in a thermogravimetric analyzer over 100 cycles of carbonation-recarbonationcalcination show that the inclusion of this recarbonation step is responsible for an increase in the residual CO<sub>2</sub> carrying capacity from 0.07 to 0.16. A conceptual design of the resulting capture system shows that a limestone make-up flow designed specifically for a CO<sub>2</sub> capture system can approach zero, when the solid sorbents purged from the CaL system are re-used to desulfurize the flue gas in the existing power plant.

# INTRODUCTION

Any serious attempt to combat climate change has to seek a viable solution for the huge emissions of  $CO_2$  expected from coal combustion in the next few decades. Exploitable coal reserves account for 846 Gt.<sup>1</sup> The combustion of these reserves would entail the emission of more than 2000 Gt of  $CO_2$  into the atmosphere. These coal reserves will almost certainly to be burned because coal is still a very low cost source of energy, and the expensive infrastructure needed to burn it is already available or is being built today (i.e. China power sector). No realistic policies or alternative competitive energy systems to prevent the owners from exploiting these vast coal reserves have yet been proposed. Therefore, decoupling the use of coal from its  $CO_2$  emissions is one of the most urgent options for mitigating climate change. Furthermore, the deployment of  $CO_2$  capture and storage technologies, CCS, may substantially reduce the overall cost of mitigation.<sup>2</sup>

The current level of understanding of mature CO<sub>2</sub> capture technologies<sup>3</sup> is already sufficient to enable us to proceed to large scale demonstration, at least in Europe.<sup>4</sup> The cost of avoiding CO<sub>2</sub> in optimized plants with existing capture technologies is expected to be around 30-40  $\notin$ /t CO<sub>2</sub> while increments in the levelized cost of electricity will be around 0.025  $\notin$ /kWhe.<sup>4</sup> This is fully consistent with earlier assessments of CCS.<sup>2</sup> Furthermore, it is generally acknowledged that these costs can be reduced by adopting a *learning by doing* approach and by developing a small emerging group of second generation CO<sub>2</sub> capture technologies that will further reduce energy consumption and costs.

The post-combustion calcium looping process, CaL, is one of the most promising new CO<sub>2</sub> capture processes. It has rapidly developed from small scale pilot testing facility<sup>5,6,7,8,9,10,11</sup> to a large pilot plant of up to 1.7 MW<sub>t</sub> as part of the CaOling project<sup>12</sup> and a second pilot plant of 1 MW<sub>t</sub> is already reporting positive results.<sup>13</sup> These post-combustion processes are based on the carbonation/calcination equilibrium of CaO and CO<sub>2</sub>. Although several combustion-based processes are being developed with different types of reactor and calcination reaction systems,<sup>14</sup> the most mature CaL process is that proposed by Shimizu et al. <sup>15</sup> and depicted in Figure 1. In its generally preferred configuration, it incorporates a CaO-based CO<sub>2</sub> absorption process that uses a circulating fluidized bed (CFB) carbonator. CaCO<sub>3</sub> is regenerated by passing an O<sub>2</sub>/CO<sub>2</sub> mixture through a fluidized bed. Shimizu et al. <sup>15</sup> have already noted the very large amount of heat required to conduct this calcination (comparable to the heat input of the existing power plant). However the additional energy required for the capture system

can be effectively recovered during the actual process of capture since carbonation takes place at high temperatures (650-700°C), which allows energy to be recovered from the very high temperature gas and solid streams that form part the process.<sup>16,17,18,19,20,21</sup> As a result, the efficiency penalties are as low as 6-7 net points taking into account the requirements of the air separation unit and CO<sub>2</sub> compression. Indeed, post combustion Ca-looping, CaL, is the only CO<sub>2</sub> capture system that repowers the existing power plant, because the sorbent regenerator (calciner) is itself an oxy-fired fluidized bed power plant (see Figure 1).



Figure 1. Scheme of the proposed  $CO_2$  capture process based on a carbonation/calcination loop.

One of the key problems associated with all practical CaL systems  $^{15,22}$  is the rapid decay in the CO<sub>2</sub> absorption capacity of the sorbent as it cycles between carbonation and calcination conditions. This has been the subject of much research in recent years.<sup>23,24</sup> Abanades et al.  $^{25,26}$  maintain that this decay can be compensated for at a reasonable cost by using a sufficiently large make-up flow of limestone (a very low-cost material compared to all other sorbents) which will serve not only to capture CO<sub>2</sub> but also to purge the system of ashes, CaSO<sub>4</sub>, and deactivated CaO. Furthermore, it has recently been demonstrated through a thermal integration exercise  $^{27}$  that the optimum CO<sub>2</sub> carrying capacity for minimizing the heat requirements of the calciner<sup>28</sup> is around 0.2 (Ca molar conversion) for post-combustion applications with limestone as the make-up flow. However, to attain this average carrying capacity (considering the typical deactivation curves of CaO) a large amount of sorbent make up is required (of the order of 50-100 t of fresh limestone/hr for a 1000 MW<sub>t</sub> coal-fired power plant, according to the calculation methodology described in<sup>25</sup>). In such large make-up flow conditions, the

overall cost of the CaL capture system would be very sensitive to the cost of limestone.<sup>29</sup> Furthermore applying the CaL system may depend the existence of a strong synergy with the cement industry,<sup>30</sup> which may not always be the case. It is therefore important for the large scale deployment of CaL technologies that they be able to operate with a minimum sorbent requirement and a maximum sorbent stability. In recent years, scientific literature and patent databases have reported intensive R&D work on the reactivation of CaO materials and the development of routes to obtain more stable CaO-based CO<sub>2</sub> sorbents. A brief overview of the main options and their limitations is provided below (more details can be found in recent reviews <sup>23,24</sup>):

-Hydration of CaO. This is a reactivation reaction that is known to be effective,  $^{31,32,33,34,35}$  because the formation of Ca(OH)<sub>2</sub> and its subsequent calcination tends to generate highly active CaO for CO<sub>2</sub> capture. However, doubts surround the very poor mechanical stability of the sorbent when hydration is applied to natural low cost materials. In addition, intense hydration consumes high quantities of steam and/or the solids need to be brought down to very low temperatures, which seriously undermines the energy efficiency of the CO<sub>2</sub> capture system.<sup>36</sup>

-Preactivation. This involves the controlled pre-calcination of the material to obtain a more stable pore texture. Several authors<sup>24</sup> claim this to be a promising technique for some limestones. However, most available results have been obtained under conditions that are not suitable for post-combustion applications.

-Self-reactivation effect. Manovic et at <sup>37</sup> have demonstrated that the activity of pretreated sorbent can increase with the number of cycles, maintaining a residual activity which is higher than it was at the beginning. However, new tests conducted under controlled conditions at lab scale<sup>38</sup> have revealed that this process may be effective for some CaL processes, but cannot work under the low particle reaction times per cycle that are typical of post-combustion CaL systems.

-Sorbent doping. The results of some previous works have indicated that the activity of CaO could be increased by doping.<sup>24</sup> However many of the dopants considered in the literature (K, Na..) may not be compatible with the safe running of power plants.

-Synthetic sorbents. A variety of supports and binders have been proposed.<sup>24</sup> Their high cost and lack of long term stability in flue gases where  $SO_2$  is present are obstacles to the application of these synthetic materials.<sup>26</sup> They may be attractive for cleaning applications in CaL systems (e.g. sorption enhanced reforming<sup>39</sup>) but this topic is beyond the scope of the present study. A promising compromise between cost and

performance has been proposed by Manovic et al. <sup>40</sup>, in which low-cost binders (alumina cements) are used with low-cost CaO precursors.

The present study proposes a post-combustion CaL process scheme that incorporates a new sorbent reactivation method able to operate in continuous mode and attempts to maintain the average  $CO_2$  carrying capacity of the CaO particles between 0.15-0.2, with negligible energy penalties, using only the materials available in the process scheme of Figure 1. If successful, this process could represent an important step towards reinforcing the viability of CaL for post-combustion technologies. The process could also be applied to other CaL concepts.

# **PROCESS DESCRIPTION**

The process proposed in this paper involves a novel method of maintaining the activity of CaO particles by introducing an additional re-carbonation step in which partially carbonated particles circulating between the carbonator and calciner are forced to increase their conversion so that it slightly exceeds the "maximum" CO<sub>2</sub> carrying capacity of the solids in the carbonator. This is achieved by bringing a small flow of highly concentrated  $CO_2$  (generated in the calciner) into contact with the highly carbonated solids coming from the carbonator. In these conditions, even under the so called "slow carbonation regime" it is possible to produce a slight, additional recarbonation of the solids in each cycle, thus compensating for the decay in carrying capacity that the solids will experience the next time they pass through the calciner and carbonator. In theory, this should be sufficient to cause the recarbonation of a very small fraction of CaO that is inactive, thereby ensuring a higher level of residual activity.<sup>41</sup>



The fundamentals of the proposed process are rooted in an early piece of research on the reversibility of the carbonation reaction of  $CO_2$  with CaO. As far back as 1973, Barker<sup>42</sup> conducted multicycle carbonation/calcination test experiments in which he carbonated CaO for a period of 24 hours in pure  $CO_2$ .

He observed no significant decay in the CO<sub>2</sub> carrying capacity (approx. 0.82 after 10

Figure 2. Simplified scheme of the proposed CaL process proposed in this work, with a new reactor for sorbent regeneration (recarbonator) and the use of the resulting CaO cycles) of the sorbent during these long carbonation times. More recently, Lysikov et al.<sup>43</sup> and Sun et al.<sup>44</sup> have shown that when experiments are carried out over extended carbonation times (up to 30 minutes), the residual activity of the CaO can be kept substantially higher than one might expect from the experiments performed over short carbonation times such as those of Grasa et al.<sup>45</sup> A similar finding was reported by Dennis et al.<sup>46</sup> who increased the CO<sub>2</sub> partial pressure, during carbonation in the fluidized bed, the result being a substantial increase in the uptake of  $CO_2$  by the synthetic sorbent even after more than 40 cycles. These results have recently been interpreted using a carbonation model <sup>36,38</sup> that takes into account the cumulative contribution of the slow diffusion stage of CO<sub>2</sub> after each cycle. This can translate into sorbents with a higher CO<sub>2</sub> carrying capacity provided that the carbonation conditions allow a slight increase in the conversion of CaO to carbonate during the slow reaction regime. However, it is not possible to apply in standard post-combustion CaL systems the carbonation conditions used in these previous works, because the particle residence times in the carbonator reactors are usually much lower than 5 minutes<sup>10,11</sup> and the CO<sub>2</sub> partial pressures are below 0.15 atm.

Therefore, we propose<sup>47</sup> to carry out the re-carbonation step in a different type of reactor (referred to as "recarbonator") under conditions that favor the fastest possible carbonation rates in the slow carbonation regime. This entails carrying out the recarbonation with pure  $CO_2$  obtained by recycling the  $CO_2$  stream generated in the calciner, as illustrated in Figure 2. It is important to note that the amount of flow required for the recycle of concentrated  $CO_2$  will be a modest one because the  $CO_2$  will only be needed to slightly recarbonate particles which have already been carbonated in the carbonator and which are ideally close to their maximum  $CO_2$  carrying capacity.

The incorporation of a new reactor (recarbonator) to treat the bulk of the large solid flow circulating between the carbonator and calciner requires a re-evaluation and the adaptation of several key components of the CaL system. In principle, for compact recarbonation-schemes to be realistically feasible, the reaction times must be kept as low as possible. There is some evidence from kinetic studies on carbonation rates including the slow reaction regime<sup>48,49</sup> that using a pure atmosphere of CO<sub>2</sub> in the recarbonation step (where average partial pressures are about 20 times higher than in the carbonator) should facilitate additional carbonation conversions ( $\Delta X_{recarb}$ ) by a few net percentual points in a matter of minutes. These increments in carbonation conversion, in every cycle, should lead<sup>36</sup> to a residual activity in the sorbent after hundreds of carbonation-calcination cycles that is substantially higher than that achieved when only the completion of the fast carbonation regime is allowed in every cycle. This improvement in CO<sub>2</sub> carrying capacity may be sufficient to maintain an effective CaL process without the need for a limestone make-up flow (other than that required to compensate for the losses due to attrition and the purging of ashes and CaSO<sub>4</sub>).

#### **EXPERIMENTAL**

In order to confirm whether under the conditions and reaction times that might be expected of the system illustrated in Figure 2, there is a substantial gain in CO<sub>2</sub> carrying capacity by the sorbent, two sets of experiments of long duration were conducted using TG equipment. The thermobalance employed has been described in detail elsewhere.<sup>45</sup> A high purity limestone (main components of the calcined limestone: 95.42 %wt CaO, 2.64 %wt Fe<sub>2</sub>O<sub>3</sub>, 0.81 %wt MgO, 0.49 %wt K<sub>2</sub>O, 0.39 %wt TiO<sub>2</sub>, 0.17 %wt Al<sub>2</sub>O<sub>3</sub>, 0.07 %wt SiO<sub>2</sub>, 0.01%wt Na<sub>2</sub>O) of particle size 63-200 µm were subjected to 100 cycles of calcination/carbonation/recarbonation and 100 cycles of carbonation-calcination in identical conditions. The reacting gas mixture (CO<sub>2</sub>/air) was fed in through the bottom of a quartz tube reactor placed inside a furnace. The gas flow was regulated by mass flow controllers, the sample mass being less than 3 mg and the total gas flow of 120 mL/min. The temperature and weight of the sample were continuously recorded on a computer. The experimental routine consisted in calcining the sample under air at 900 °C for 5 min, then carbonating it in a mixture of gases (pCO<sub>2</sub> =10 kPa, air as balance) at 650 °C for 5 min and finally recarbonating it under pure CO<sub>2</sub> at 800 °C for 3 min.

Figure 3a shows the typical evolution of the carbonate content of the sorbent with time for 15 and 100 cycles. Two different stages can be observed. The first stage corresponds to the fast carbonation (60-70 seconds). This is followed by a transition to a slow carbonation stage lasting 300 s. The conversion achieved at end of the fast reaction period is the maximum or "useful" CO<sub>2</sub> carrying capacity of the sorbent ( $X_N$ ) for post-combustion CO<sub>2</sub> capture in a CFB carbonator. The second stage illustrated in Figure 3a corresponds to the recarbonation step that begins after 300s. As can be seen, when the reaction temperature and CO<sub>2</sub> partial pressure reach the recarbonation conditions (800°C and pure CO<sub>2</sub>), there is a rapid increase in the carbonate content ( $\Delta X_{recarb}$ ) to above the maximum CO<sub>2</sub> carrying capacity, which tends to stabilize after about 60 seconds of recarbonation reaction.



Figure 3. a) Example of the increase in  $CO_2$  carrying capacity experienced by two particles cycling through the system (black dots, after 15 carbonation calcination cycles and white dots after 100 cycles). b) Evolution of the  $CO_2$  carrying capacity of CaO with

the number of cycles (black dots with recarbonation and white dots without recarbonation).

Figure 3b compares the evolution of the maximum  $CO_2$  carrying capacity (X<sub>N</sub>) during cycling with and without the recarbonation step. As can be seen, the addition of a recarbonation step greatly improves the activity of the sorbent which is almost two times higher after 100 cycles. These experimental results were fitted using the equation proposed by Grasa et al.<sup>45</sup> to determine the residual activity of the sorbent (X<sub>r</sub>) under both sets of experimental conditions. The value obtained without a recarbonation step is 0.071, which is in agreement with the value obtained by Grasa et al.<sup>45</sup> for a wide range of sorbents (X<sub>r</sub>=0.075). On the other hand, when the recarbonation step is included, the residual activity of the sorbent increases to 0.16. This confirms that the inclusion of a short recarbonation step maintains the residual activity of the sorbent at a value more than 200% higher than that of the residual activity of the reference test where there is no recarbonation step.

## DISCUSSION

The experimental results presented above confirm that there are operating windows for designing a practical process following the scheme of Figure 2. Accordingly, mass and heat balances were performed on a reference case both with recarbonation and without recarbonation. It is assumed here that a suitable moving bed reactor (with a standpipe connected to the cyclone of the carbonator) and/or a fluidized bed reactor (feeding  $CO_2$  into the loop seal connected to the cyclone of the carbonator) will allow sufficient residence time for the solids to reach the desired recarbonator level. In order to minimize the size (and capital investment) of the new re-carbonator reactor, short average reaction times (of the order of 1 minute as shown in Figure 3a) for the full stream of circulating solids must be used. Alternatively, a small fraction of the solids circulating between the carbonator and calciner could be subjected to much longer recarbonation times. However, we have ruled out this second possibility because the mechanism of carbonation in the slow reaction regime is known to slow down with increasing conversions<sup>50</sup> and this would only lead to irrelevant gains in carrying capacity under realistic reaction times.

In order to minimize the consumption of  $CO_2$  in the recarbonator (and the cost associated with this new gas recycle) it is also important to ensure that most of the particles arrive at the recarbonator with a carbonate conversion as close as possible to their maximum  $CO_2$  carrying capacity. Most pilot data and model predictions available for CFB carbonators<sup>7,8,9,10,11</sup> suggest that it is possible to design carbonator reactors that achieve conversion of solids very close to the maximum carrying capacity of the material. However, there will need to be enough  $CO_2$  for the recarbonator to complete the fast carbonation stage of particles not completely converted in the carbonator.

We have conducted a preliminary conceptual design of the system to illustrate the potential benefits of the new reactivation process and highlight the need to minimize the reaction times and  $CO_2$  consumption in the recarbonator. Two different types of coals were considered for use in the power station and in the calciner (see Table 1).

Any coal can be burned in the existing power plant (which we will assume to be of the CFBC type), but we have chosen a good quality coal (i.e. low sulfur and ash content) to be used in the calciner, because this is known to reduce the energy demand of the CaL system.<sup>28</sup> We have assumed a thermal input to the power plant of 1 GWt. The plant can be of any type or design but the choice of a CFBC design makes it easier to assess the synergy of SO<sub>2</sub> capture with the CaL system with recarbonation. Two different scenarios (one with and one without recarbonation step) were assessed for their ability to capture 80 % of the CO<sub>2</sub> produced in the power plant. In both cases, the maximum CO<sub>2</sub> carrying capacity of the CaO in the bed of the carbonator was assumed to be 0.20 and the carbonate content of the solids leaving the calciner to be 0.19.

	Power	Oxy-fuel	
	plant	calciner	
Composition			
(%wt)			
С	58.0	74.0	
Н	4.0	4.0	
S	1.0	0.5	
Ο	8.0	8.0	

Table 1. Composition and LHV of the fuels fed into the combustors of the power plant and calciner of Figure 2

$H_2O$	8.0	8.0
Ν	0.5	0.5
Ash	20.0	5.0
LHV (MJ/kg)	25.0	30.0

The power plant feeds flue gases (390 kg/s) into a CFB carbonator (see Figure 2), that is continuously supplied with a stream of solids from the calciner (500 kg/s in the CFB carbonator riser). The stream of solids contains 91.0 %w of free CaO in the case of the CaL with no recarbonation step. The desired carrying capacity is achieved in the case of the CaL with no recarbonation step by feeding a make-up flow of limestone of 23.2 kg/s into the calciner. This flow is calculated from the mass balance that links the average carrying capacity of the sorbent in the CaL system with the solids circulation flow.<sup>25,51</sup> If similar mass balances incorporating the improvement in sorbent activity produced by the recarbonation step are applied (Figure 3b), after the CO<sub>2</sub> carrying capacity has been suitably fitted to the Grasa et al.<sup>45</sup> equation (as shown previously), the required make-up flow turns out to be much lower (5.0 kg of limestone/s). The reduction in make-up flow could even approach zero if it were not necessary to purge the ash and CaSO<sub>4</sub> in the CO<sub>2</sub> capture solids loop. For the sake of simplicity, no losses due attrition are considered in any of the processes discussed in this work. Attrition tends to occur mainly in the first calcination cycle 52,53,54,55 both in CaL systems and in large scale CFBC systems. Therefore, a lower attrition can be expected in processes that use reduced flows of fresh limestone.

In the new scenario which includes a recarbonation step, the energy demand in the calciner increases to 885 MW<sub>t</sub> (from 825 MW<sub>t</sub> without the recarbonation step). No additional energy penalty due to the sorbent reactivation step (other than that required by the auxiliary equipment to power the small CO<sub>2</sub> recycle) is to be expected because the reactivation is carried out at very high temperatures and all the additional energy needed to calcine the additional carbonated solids is released during the recarbonation reaction, thereby increasing the temperature of the solids entering the calciner. The reason for the increase in energy demand is mainly due to the larger amount of solids circulating between both reactors (700 kg/s in the carbonator) since the use of a lower make-up flow results in an increase in the mass fraction of ash and CaSO<sub>4</sub> (which reach values of 19 %w and 16%w, respectively) that acts as thermal ballast in the carbonation-calcination cycle. However, it should be noted that the energy used in the

calciner to heat up the stream of solids can be recovered to produce power, the only real penalty being the associated increase in O<sub>2</sub> consumption in the calciner.

Assuming a residence time for the solids of 60 s and a bulk density for the solids of 800 kg/m<sup>3</sup> in the recarbonator, the reactor volume needed is close to 60 m<sup>3</sup> which is very small compared with the size of the carbonator and calciner (with cross sections of around 200 m<sup>2</sup> and reactor heights of over 30 m. i.e., of a similar scale to those of CFBC's). The amount of CO<sub>2</sub> that needs to be fed into the recarbonator can be calculated by taking into account the results in the experimental section which show that an increase in the conversion of carbonate of 0.02 above the maximum CO<sub>2</sub> carrying capacity is enough to maintain the activity of the sorbent. From this value, a consumption rate of 10.6 kg CO<sub>2</sub>/s which is less than 3% of the CO<sub>2</sub> leaving the calciner is estimated.

The material purged from the calcium loop can also be used to capture  $SO_2$  from the flue gases generated in the CFBC boiler (see Figure 2). In the light of previously published reports for other CaL systems,<sup>56,57,58</sup> it can be expected that the purged material extracted from this modified CaL system will be very active in the capture of  $SO_2$  under carbonation conditions.<sup>59</sup> This is because particles that have been calcined and carbonated tens or hundreds of times according to the scheme of Figure 2 will display large pores less prone to plugging by the CaSO<sub>4</sub> formed during hot flue gas desulfurization conditions.

To assess the impact of using the purge from the CaL as SO<sub>2</sub> sorbent, we calculated the limestone requirements for capturing the SO<sub>2</sub> produced in the reference power plant. To ensure similar sulfur inputs ( $t_{Sulfur}/MJ$ ), we have assumed that a mixture of the coals in Table 1 is used in the reference power plant. Bearing in mind that the mass ratio for this mixture was calculated from the average value of the coals used in Case 1 and 2, Table 2 displays the different possible scenarios. The limestone requirement in the power plant (reference case) for capturing SO<sub>2</sub> is 2.74 kg/GJ (assuming a Ca/S molar ratio of 3) which yields a consumption rate of 0.07 kg of limestone per kg of coal fed in. In the case of the power plant equipped with the CO<sub>2</sub> capture system but without the recarbonation step, the consumption of limestone increases to 0.347 kg/kg of total coal fed in. In this case, a higher demand is placed on the limestone by the CaL in order to maintain the activity of the sorbent at 0.2 when the residual activity is only 0.071. From the point of view of the sulfur balance, there is now an excess of limestone in the system, as the Ca/S ratio has increased to 14. This high value shows that only a fraction of the purge produced in the CaL can be used in the power plant to capture SO<sub>2</sub>.

Finally, in the case of CaL with the recarbonation step, the consumption of limestone needed in the CaL to sustain the activity of the solids with a  $CO_2$  carrying capacity of 0.20 is only 0.07 kg limestone/kg coal. This value almost matches the amount needed to remove the  $SO_2$  in the reference case, where the limestone is used only as sorbent in the power plant. We have chosen the compositions of the coals for these scenarios in order to get a perfect match between the limestone requirements for the CaL and for use as a

	Ref. Case	Case 1	Case 2
Heat power plant/Heat total	1	0.55	0.53
Ratio Coal 1 to total coal fed	0.58	0.59	0.57
Sulfur fed (kg <sub>sulfur</sub> /GJ)	0.292	0.295	0.290
Ca/S	3.0	14.0	3.0
Total flow of limestone (kg/GJ)	2.74	12.84	2.68
kg limestone/kg coal total	0.074	0.347	0.073

 $SO_2$  sorbent. However, the final result is of a much wider value. If coals with a higher sulfur content are used in the process shown in Figure 2, a higher flow of limestone must be used to maintain the Ca/S=3 and to retain the sulfur that has been fed into the system. This will improve the performance of the CaL because the maximum carrying capacity of the solids in the CO<sub>2</sub> capture process will increase to above 0.20 and the solids circulation between the carbonator and calciner will be reduced since a higher amount of ashes and CaSO<sub>4</sub> can be expected to be purged.

Table 2. Limestone consumption and SO<sub>2</sub> sorbent requirements for the different cases

Ref. Case: power station

Case1: power station with CaL without recarbonation

Case2: power station with CaL with recarbonation

Therefore, a large saving of limestone in the make-up flow can be anticipated from the system proposed in Figure 2, which will reduce to virtually zero the additional limestone requirements for  $CO_2$  capture. This will make post-combustion CaL systems even more generally applicable and economically attractive for coal-fired power plants.

# CONCLUSIONS

This work presents a novel process that may have profound implications for the viability of all CaL CO<sub>2</sub> capture technologies under development in Europe and elsewhere, in which circulating fluidized bed technology for coal based-postcombustion  $CO_2$  capture is used. The process employs a new sorbent reactivation method that is able to operate in continuous mode. This is made possible by the incorporation of an additional reactor to recarbonate already carbonated particles of CaO. This allows the average  $CO_2$  carrying capacity of CaO particles to be maintained between 0.15-0.2, which is more than two times higher than the residual carrying capacity of the same particles without the recarbonation step.

In the new conditions, the net consumption of limestone in can be drastically reduced and may even approach zero since the residue from the Ca-loop (sintered CaO) may serve to capture  $SO_2$  in the existing power plant with desulfurization. In this case, the CaL process can be specially designed to produce a purge of solids large enough to satisfy the power plant's desulfurization requirements. It has been shown that the makeup flow of limestone can be as low as 0.07 kg limestone/kg coal. A significant reduction in energy consumption can therefore be expected due to the reduced amount of fresh limestone required by the system and the direct reduction of coal and oxygen consumption. In view of the low reaction times required for the recarbonation step (of the order of a few minutes), a feasible compact reactor could be designed and integrated into already existing process schemes for calcium looping systems.

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