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CO₂ Capture by Calcium Looping at Relevant Conditions for Cement Plants: Experimental Testing in a 30 kW_{th} Pilot Plant

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ABSTRACT: Calcium looping technology has a high potential for capturing CO_2 in cement plants as the CaO-rich purge from the calciner can be used to replace a sizable fraction of the CaCO₃ used as feedstock. Integrating the CaL process into the cement plant requires the carbonator reactor to operate under new conditions (i.e., a higher carbonator CO_2 load, a more active sorbent, smaller particle sizes). This work analyzes the impact of some of the new CaL operating conditions on the performance of the carbonator in a retrofitted 30 kW_{th} testing facility as there is little experimental information available nowadays. A wide range of sorbent activities has been tested, including those corresponding to very large makeup flows of limestone that would be characteristic of CaL applications in cement plants. The results have been interpreted using a basic reactor carbonator model that required little modification of previous versions developed for power plants.



INTRODUCTON

One of the largest sources of anthropogenic CO_2 is the cement industry which accounts for 5.7% of global CO₂ emissions.¹ Approximately 60% of CO_2 emissions are inherent to the cement production process, as they come from the decomposition of $CaCO_3$ to form CaO (used as precursor of clinker). It is generally agreed therefore that effective CO₂ emission reductions in the cement industry can only be achieved by using CO₂ capture and storage (CCS) systems. Of these, oxy-fuel combustion and postcombustion CO₂ capture technologies seem to be the most favored.^{2,3} As a hybrid technology between the two groups, calcium looping is recognized as the technology with a high potential for capturing CO_2 in cement plants.^{4–17} In this process, a flow of CaO particles is used to capture CO₂ from a flue gas stream in a carbonator operating at temperatures close to 650 °C to form $CaCO_3$. As a result, a flue gas with a low CO_2 content is released to the atmosphere after an effective heat recovery. The carbonated stream of solids leaving the carbonator is then sent to a second reactor, the calciner, where the CaCO₃ formed is decomposed to regenerate a CaO-rich sorbent. The heat demand in the calciner is fulfilled by burning a fuel under oxy-fuel conditions at temperatures slightly over 900 °C. Thus, the CO₂ captured from the flue gas as well as the CO₂ produced during fuel combustion are obtained in the form of a concentrated gas stream, ready to be cooled down, purified, and compressed for storing.

As in the case of other CCS technologies, the capture of CO_2 from power plants has been the main R&D focus of recent CaL developments. For this specific application, CaL has advanced rapidly over past decade to reach TRL 6-7, and it has been tested in several pilot plants up to MW_{th} scale.^{18–22}

To exploit the synergy between the CaL and the cement plant, several process schemes have been proposed that involve different degrees of integration between the cement plant and the CaL system. In principle, CaL could be used to capture CO₂ as a standalone postcombustion system retrofitted to the cement plant without any integration step other than that of a connecting pipe for the flue gases and some means of using the purge of solids material arriving from the CaL system in the clinker oven.^{4,10,12,15,16} For this purpose, a CaL configuration based on circulating fluidized bed reactors, similar to the one used for capturing CO_2 from power plants, may be adequate. The main difference between such a configuration and a standard CaL configuration in power plants is related with the high CO₂ load sent to the carbonator (due to the higher concentration of flue gas from the cement plant) and the use of sorbents with a higher activity as a consequence of the larger limestone makeup flows being used in the calciner. Two of key parameters affecting the CO₂ capture efficiency in the carbonator are the inventory of CaO in the reactor bed and the fraction of active CaO. Two of key parameters affecting the CO₂ capture efficiency in the carbonator are the inventory of CaO in the reactor bed and the fraction of active CaO. Previous studies have shown that is possible to achieve high CO₂ capture efficiencies in the carbonator when operating with solid with low CO₂ carrying capacities at the expenses of increasing the inventory of solids in this reactor.¹⁹ As a result, the residence time of the particles in the carbonator is increased and carbonation conversions close to the maximum CO₂ carrying capacity of the sorbent can be achieved. Also, operating with fine particles would facilitate the use of a CaO-rich purge in the cement plant.¹⁶ However, an inherent shortcoming of these low integration approaches is that the energy requirements for calcination of the CaCO₃ formed in the

Received:	November 28, 2016
Revised:	February 23, 2017
Accepted:	February 24, 2017
Published:	February 24, 2017

carbonator increase substantially because part of the $CaCO_3$ is formed by the reacted CO_2 that has evolved from the calcination of the raw meal rich in $CaCO_3$.

More integrated schemes have also been proposed in order to reduce the consumption of energy in the calciner of the CaL system. Some of these processes are aimed at replacing the existing precalciners in cement plants with the calcium looping system (as depicted in Figure 1), so that the raw materials fed to



Figure 1. Basic process scheme of a cement plant operating with a calcium looping system.

the plant leave the calcium loop completely calcined before entering the clinker oven.^{9,13,16} In these systems, the raw material is calcined in an oxy-fired calciner after being preheated, and only a fraction of the CaO-rich material is sent to the carbonator in order to capture the CO₂ from the rotary kiln flue gas. For these specific configurations, it may be beneficial to use an entrained flow reactor in order to handle the small particle size required in the raw mill (below 30 μ m), which would imply the development of advanced process schemes for the entire cement plant integrated with the calcium looping system to minimize energy needs.^{13,16}

Despite the increasing number of publications highlighting the theoretical advantages of CaL technology in cement plant environments, there is little experimental information on the performance of the main reactors operating under conditions close to those expected of CaL systems designed to capture CO₂ from a cement plant (i.e., a higher carbonator CO_2 load, a more active sorbent in the solids circulation loop because of the increased makeup flows of CaCO₃, and small particle sizes to facilitate clinker reactions in the rotary kiln, etc.). Accordingly, the aim of this work is to experimentally investigate the effect of some of these new CaL operating conditions on the performance of the carbonator reactor in the capture of CO_2 . For this purpose, several experimental campaigns were carried out in a small retrofitted 30 kW_{th} pilot plant made up of two interconnected circulating fluidized bed reactors. A basic reactor carbonator model was then applied to interpret the results obtained from the pilot in an attempt to establish a sounder better basis for the future scaling up of this technology.

EXPERIMENTAL SECTION

The results presented in this work were obtained in a 30 kW_{th} pilot plant at INCAR-CSIC. The main characteristics of this facility have been described in detail in a previous work²³ and are

briefly summarized here. The pilot was composed of two interconnected fluidized bed reactors acting as carbonator and calciner with an internal diameter of 0.1 m and a total height of 6.0 and 6.5 m, respectively. Each riser was equipped with a primary cyclone to separate the gas flow from the solid particles. The stream of solids leaving each riser circulated to the opposite reactor through a bubbling fluidized-bed loop seal that closes the pressure balance. A synthetic flue gas was fed to the carbonator by mixing air and CO₂ using mass flow controllers. Some experiments were carried out by adding water vapor to the air/CO₂ mixture in order to produce a more realistic flue gas. For this purpose, a small steam generator with a maximum rate of 2.0 kg H₂O/h was used to supply the continuous flow of water vapor needed.

The calciner was fed with coal and limestone from two hoppers using screw feeders. Two gas analysers were used to measure the composition of the flue gas leaving each reactor. There were several ports for measuring the pressure and temperature to facilitate the control of the pilot and the analysis of the experimental results. The inventory of solids in the carbonator and calciner was estimated by measuring the pressure drop in each riser. Ports for sampling the solids were located at different points in the pilot. These solids were routinely characterized to measure reactivity toward CO_2 and CO_2 carrying capacity as well as particle size distribution and CaSO₄ content as detailed described in previous work.²³ The solids circulation between reactors in this facility can be estimated continuously by performing an energy balance between the pipe connecting the loop seal and the riser of the carbonator using the temperature of the solids at the inlet and outlet as the heat losses were calibrated according to the wall temperature. The resulting value can be periodically checked by using a bypass located below the loop seals, which allowed the solids flow to be diverted to a dead volume for a certain period of time so that the circulation of solids can be experimentally measured.

The insulation of the reactors has been recently upgraded, and additional heating elements have been installed at the top of the reactors. This has made it possible to increase the thermal power available for calcination, which is essential for operating with high limestone makeup flows. New recycle loops have also been installed so as to maintain a particle size distribution of solids with finer particles within the calcium loop. These recycles consisted of a secondary cyclone that captured the particles, leaving the primary cyclone, and a return leg so that the particles can be reinjected into the standpipes of the carbonator and calciner, as depicted in Figure 2.

The initial tests were carried out by calcining a limestone of high purity (composition of the calcined limestone: $96.13\%_{wt}$ CaO, $1.19\%_{wt}$ MgO, $1.11\%_{wt}$ SiO₂, $0.21\%_{wt}$ Fe₂O₃, $0.10\%_{wt}$ Al_2O_3 , $0.05\%_{wt}$ K₂O, $0.01\%_{wt}$ Na₂O, < $0.05\%_{wt}$ TiO₂). A low ash and sulfur coal was also burned in the calciner (71.1%_{wt} C, 4.4%_{wt} H, 0.2%_{wt} S, 3.9%_{wt} ash). Figure 3 exemplifies a particle size distribution typical of the pilot test carried out in this work. As one would expect, the material circulating between the reactors in the primary loop is of a larger particle size $(dp_{50} = 76)$ μ m in this example). The moderate solids separation efficiency of the primary cyclones allows small particles to escape toward the recycle loop, where a large fraction of the solids is captured by the secondary cyclones. As a result, the particles circulating through the recycle loops are of a smaller particle size ($dp_{50} = 35 \ \mu m$). Only solids with a fine particle size (typically below a dp_{50} of 10 μ m) leave the system through the stack. These represent only a small fraction of the total inventory in the pilot and, as a result,



Figure 2. Schematic representation of the 30 $\rm kW_{th}$ test facility at INCAR-CSIC.



Figure 3. Particle size distributions in the 30 kW_{th} test facility retrofitted with recycle loops (d_{p50} : 76 μ m primary loop, 35 μ m recycle loop, 7 μ m stack).

the overall solids mass balance in each experiment can be closed with a total solids mass loss of less than 10%.

Ca-based materials with a particle size below 30 μ m are commonly handled in large-scale cement plants,²⁴ but this pilot was not able to operate with such fine materials. The circulation of solids between reactors was unstable due to frequent blockage of the standpipes (only 50 mm i.d. in this pilot) that prevented the steady-state capture of CO₂ under these experimental conditions. It was therefore decided to avoid operating with fine materials below 70 μ m in the primary loop. When operating under these conditions, the recycle loops were used to purge the system of the finest particles.

The main operating condition ranges tested in these experiments are summarized in Table 1. A wide range of sorbent activities was tested from moderate limestone makeup flows to freshly calcined limestones as those expected in CaL applications to cement plant. An inlet CO₂ concentration of up to 27% was used in experiments both with and without steam in order to simulate the flue gas composition of a cement plant. Despite the limitations to particle size (i.e., d_{p50} no less than 70 μ m), the experimental conditions tested can be considered as being representative of most of the CaL process schemes integrated

Table 1. Range of Operating	Conditions and	d Main	Variables
during the CO ₂ Capture Test	S		

carbonator temperature (°C)	$T_{\rm carb}$	620-725
carbonator inlet velocity (m/s)	<i>u</i> _{carb}	2.0 - 3.7
inlet CO ₂ volume fraction to the carbonator	$\nu_{ m CO2}$	0.10-0.27
inlet steam volume fraction to the carbonator	$ u_{ m H2O}$	0-0.12
inventory of solids in the carbonator $\left(kg/m^{2} ight)$	W _{carb}	15-590
maximum CO ₂ carrying capacity	$X_{ m ave}$	0.18-0.66
solids circulation flow rate (kg/m ² s)	$G_{\rm s}$	0.9-3.7
calciner temperature (°C)	$T_{\rm calc}$	800-920
calciner inlet velocity (m/s)	$u_{\rm calc}$	1.5-3.3
average particle size in the primary loop (μm)	d _{p50}	74-100
molar ratio of fresh makeup to the inlet $\rm CO_2$	$F_0/F_{\rm CO2}$	0-0.55
experimental CO ₂ capture efficiency (%)	$E_{\rm carb}$	30-95

with cement plants based on circulating fluidized bed reactors. The results presented in this work correspond to the results obtained during more than 85 h of CO_2 capture where a good closure of the overall carbon balances (see below) was achieved.

RESULTS AND DICUSSION

To analyze the effect of the different operating variables, the experiments were divided into relatively steady-state periods of at least 20 min, where the CO₂ inlet and outlet concentrations to the carbonator, temperature, bed inventory, and solids circulation rates can be considered constant and can be measured independently. CO2 mass balances were solved and closed at each of these points in order to validate the consistency of the experimental information and the stability of the facility. As an example, Figure 4 shows the results obtained during a particularly stable experimental period of 30 min. The average reactor temperature during this period was 655 and 860 °C in the carbonator and calciner, respectively. A flue gas flow with a CO₂ concentration of 12% was fed to the carbonator, operating at an inlet gas velocity of 2.0 m/s. In this case, a moderate makeup flow was fed to the calciner ($F_0/F_{CO2} = 0.23$), which yielded a sorbent with a maximum CO_2 carrying capacity (X_{ave}) of 0.32. The average CO_2 capture efficiency during this experiment was 0.8.

CO₂ captured from the gas phase is calculated continuously as the CO₂ fed to the carbonator (F_{CO2in}) is already known and the molar flow at the exit ($F_{\rm CO2out}$) can be determined by measuring the flow of flue gas, leaving the reactor and its composition. Similarly, the CO_2 produced by calcination in the calciner can be calculated by discounting the CO₂ produced by coal combustion. Figure 4b shows the calculated molar flow of CO₂ captured in the carbonator ($F_{CO2capt}$) and the molar flow of CO₂ calcined in the calciner ($F_{CO2calc}$). Ideally, under steady-state conditions and low makeup flows of limestone when there is no accumulation of CaCO₃ in the inventory of solids, the CO₂ captured should be the same as the CO₂ calcined. The difference observed in Figure 4b is due to the makeup flow of limestone fed into the calciner during this test period. The molar flow of CO₂ at the inlet and exit of the carbonator are used to calculate the capture efficiency which is defined as follows:

$$E_{\rm carb} = \frac{F_{\rm CO2in} - F_{\rm CO2out}}{F_{\rm CO2in}} \tag{1}$$

When interpreting the performance of the carbonator reactor, it is important to bear in mind that the maximum CO₂ capture efficiency ($E_{\text{carb eq}} = (F_{\text{CO2in}} - F_{\text{CO2out eq}})/F_{\text{CO2in}}$) is limited by the minimum CO₂ molar fraction permitted by the equilibrium.²⁵



Figure 4. Example of a steady state in the 30 kW_{th} experimental facility ($W_{carb} = 600 \text{ kg/m}^2$, $F_0/F_{CO2} = 0.23$, $X_{carb} = 0.27$, $X_{calc} = 0.08$, $X_{ave} = 0.32$, $dp_{50} = 97 \mu$ m).



Figure 5. Example of experimental results. (a) Test operating with high activity materials ($T_{carb} = 700 \degree C$, $u_{carb} = 2.8 \ m/s$, $\nu_{CO2} = 0.18$, $X_{ave} = 0.47$, $G_s = 2.7 \ kg/m^2s$, $dp_{50} = 75 \ \mu$ m). (b) Test operating with a CO₂ concentration of 27% ($T_{carb} = 704 \degree C$, $u_{carb} = 2.6 \ m/s$, $\nu_{CO2} = 0.26$, $X_{ave} = 0.34$, $W_{carb} = 117 \ kg/m^2$, $dp_{50} = 77 \ \mu$ m). (c) Test showing the effect of steam on CO₂ capture ($T_{carb} = 673 \degree C$, $u_{carb} = 2.5 \ m/s$, $\nu_{CO2} = 0.14$, $X_{ave} = 0.34$, $W_{carb} = 117 \ kg/m^2$, $dp_{50} = 77 \ \mu$ m). (d) Test operating with limited solids circulation between reactors ($T_{carb} = 674 \degree C$, $u_{carb} = 2.0 \ m/s$, $\nu_{CO2} = 0.18$, $X_{ave} = 0.32$, $W_{carb} = 540 \ kg/m^2$, $dp_{50} = 78 \ \mu$ m).

Another important mass balance that must be fulfilled is that which corresponds to the molar flow of $CaCO_3$ formed in the stream of solids circulating through the carbonator which should be the same as the molar CO_2 captured from the gas phase. The molar flow of CaCO₃ can be calculated for each steady state from the circulation of solids between the reactors and the carbonate content of the solids samples taken from the carbonator (X_{carb}) and calciner (X_{calc}). The calculated molar flow of CaCO₃ during

Article

the test presented in Figure 4 was 2.7 mol/m²s, which matches the CO_2 captured from the gas phase.

Another example of CaL operating with a high-activity sorbent typical of cement plant applications with a high makeup flow of limestone is shown in Figure 5a. The X_{ave} during this test was 0.47, and the average particle diameter (d_{p50}) was 75 μ m. These fine solids resulted in a low inventory in the circulating fluidized bed reactors (around 100 kg/m² in the carbonator and 75 kg/m² in the calciner). Almost the maximum capture efficiency allowed by the equilibrium (around 80% when the carbonator is operating at 700 °C) was achieved, even with a very modest inventory of solids in the carbonator. Figure 5b shows a representative example of a CaL integrated with a cement plant operating with a high CO_2 load to the carbonator. The inlet concentration during this test was 26%, and the CO₂ molar flow at the inlet was 9.6 mol/m²s. An average CO_2 capture efficiency of 0.78 was achieved by maintaining a solids circulation rate of 2.2 kg/m^2s between the reactors by using a sorbent with a CO_2 carrying capacity of 0.34.

As mentioned above, several tests were carried out by feeding steam into the flue gas. Figure 5c shows an experimental period of 40 min with an inlet CO₂ concentration of 14%_v. At 13:02, a steam flow of 2.0 kg/h was injected into the flue gas while the air flow was reduced in order to maintain the other operation conditions constant (i.e., ν_{CO2} , gas velocity in the carbonator, inventory of solids). As can be seen, the presence of steam increased the flow of CO₂ captured in the carbonator from 3.3 mol/m²s up to 3.8 mol/m²s. The positive effect of steam on CaO carbonation has been reported in the literature by other authors.^{26–29}

To validate the carbonator models, the operation conditions were tested using low CO₂ capture efficiencies. As an example, Figure 5d shows an experimental period where CO₂ capture efficiency is limited by the solids circulation between the reactors. The low circulation of solids $(0.9 \text{ kg/m}^2\text{s})$ and the high inventory of solids in the carbonator (540 kg/m²) led to a long particle residence time as a result of which the particles almost reached their maximum conversion ($X_{ave} = 0.32$).

To analyze the carbonator performance in a quantitative manner, a methodology similar to the one proposed in previous works for testing power plant configurations was applied in this work. The key assumption is that the carbonator behaves like a perfectly mixed reactor for the solids.^{23,30} In steady states, the amount of CO_2 reacting with the inventory of CaO particles is the same as that being removed from the gas phase.

As mentioned above, the molar flow of CO_2 entering and leaving the carbonator is continuously determined throughout the experiments. The molar flow of CO_2 reacting with the CaO particles in the carbonator bed is calculated as the product of the average reaction rate of the solids at carbonator conditions and the active inventory of sorbent ($n_{Ca, active}$) as follows:

$$F_{\rm CO2in}E_{\rm carb} = n_{\rm Ca,active} \left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_{\rm reactor} \tag{3}$$

To calculate the average reaction rate of the solids, a constant rate is assumed until the particles achieve their maximum CO_2 carrying capacity (X_{ave}) .³¹ From this point, the reaction rate drops to such a low point that it can be considered zero. Of

course, more accurate reaction rate models could be applied.³² However, this simple approach for the kinetics of carbonation is consistent with the experimental data available from the TG tests (see, for example, ref 33) and consistent with the level of detail and modest accuracy of the experimental information on the behavior of the solids in this pilot. The particle reaction rate can now be calculated as a function of the CO₂ carrying capacity of the sorbent (X_{ave}) and the average CO₂ concentration in the carbonator as follows:

$$\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right)_{\mathrm{reactor}} = k_{\mathrm{s}}\varphi X_{\mathrm{ave}}(\overline{v_{\mathrm{CO2}} - v_{\mathrm{CO2eq}}}) \tag{4}$$

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where $k_{\rm s}$ is the constant reaction rate of the limestone used and φ is the gas–solid contact factor as defined in previous works.²³ The active inventory of sorbent is composed of those particles that have not reached their maximum CO₂ carrying capacity $(X_{\rm ave})$. Assuming that the carbonator behaves like a perfectly mixed reactor, the fraction of active solids in the bed $(f_{\rm a})$ can be calculated as the fraction of particles with a residence time lower than that required to increase the carbonate content of the particles from $X_{\rm calc}$ to $X_{\rm ave}$ under carbonator conditions (t^*) :

$$f_{\rm a} = (1 - e^{-t*/n_{\rm Ca}/F_{\rm Ca}}) \tag{5}$$

where n_{Ca} is the total inventory of calcium in the carbonator and F_{Ca} is the molar flow of calcium between the reactors. The characteristic reaction time (t^*) can be estimated using the X_{calc} and X_{ave} values measured from the samples taken from the reactors and the reaction rate defined in eq 3.

$$t^* = \frac{X_{\text{ave}} - X_{\text{calc}}}{k_s \varphi X_{\text{ave}}(v_{\text{CO2}} - v_{\text{CO2eq}})}$$
(6)

By introducing eqs 4 and 5 into eq 3, all the CaL operation parameters become linked in the following expression:

$$F_{\rm CO2}E_{\rm Carb} = n_{\rm Ca}f_{\rm Ca}k_{\rm s}\varphi X_{\rm ave}(\overline{v_{\rm CO2} - v_{\rm CO2eq}})$$
(7)

The apparent constant reaction rate $(k_s\varphi)$ can be calculated as a fitting parameter by comparing both terms of eq 7. A value of $k_s\varphi$ = 0.36 s⁻¹ was calculated using the new set of experimental results obtained under experimental conditions similar to those expected of cement plants. This value is in agreement with that found in previous works, including those obtained in a 1.7 MW_{th} testing facility that captured CO₂ from a power plant flue gases.^{19,30} This result is not surprising as the reaction of CO₂ with cycled CaO particles follows a homogeneous model and particle size has reduced impact on sorbent activity.³²

Finally, to correlate the CO_2 capture efficiency with the main operation variables in the carbonator, eq 7 can be rearranged into the following expression:

$$E_{\text{Carb}} = \tau_{\text{active}} k_s \varphi(\overline{v_{\text{CO2}} - v_{\text{CO2eq}}})$$
(8)

where τ_{active} is the active space time $(n_{Ca}f_{Ca}X_{ave}/F_{CO2})$.³⁰ Figure 6 shows the equilibrium normalized CO₂ capture efficiency (E_{carb}/E_{carbeq}) against the active space time. The solid line corresponds to the values calculated from eq 8 and the average values of the parameters based on the experimental data obtained for each series of data. In this graph, the dotted line calculated with the model corresponding to an inlet molar fraction of 0.13 may be considered as a reference case for power plant applications. Despite the dispersion, there is reasonable agreement between the experimental results and those predicted by the model when the data are grouped around the three representative average



Figure 6. Normalized CO₂ capture efficiency as a function of the active space time (model lines: $T_{carb} = 655 \,^{\circ}C_{1} k_{s} \varphi = 0.36 \,^{-1}s^{-1}$, dotted line v_{CO2in} = 0.13 (typical CO₂ flue gas concentration in power plants), solid line $v_{\text{CO2in}} = 0.16$ dashed line $v_{\text{CO2in}} = 0.23$).

partial pressures of CO₂ used to estimate the model curves from eq 8. The dispersion of the data points in Figure 6 is due to the uncertainty in the experimental determination of $\tau_{\rm active}$, which is a combination of three experimental variables inherently difficult to measure with precision in this small pilot plant (in particular, the solids circulation rates and a representative value of X_{ave} for the entire solids inventory in the carbonator).

No attempt has been made to perform an exhaustive analysis of the effect of the steam on carbonator performance due to the limited number of experimental tests carried out. However, as can be seen in Figure 6, the experimental CO_2 capture efficiency achieved during the experiments where steam is introduced into the flue gas is systematically above the values predicted by the model (solid line). This confirms the positive effect of steam on carbonator performance observed in other pilot plants.^{34–36}

Tests under conditions similar to those of cement plants have yielded fundamental parameters very close to those developed for power plant configurations that have been tested at pilot level in a number of studies around the world. Thus, the results presented in this work lend support to the scalability of this technology for capturing CO₂ in cement plants by using the knowledge acquired in these large facilities.

CONCLUSIONS

Postcombustion CO₂ capture by calcium looping adapted to capture CO₂ from cement plants has been studied in this work. For this purpose, a 30 kW_{th} pilot was retrofitted to operate with a higher carbonator CO2 load, more active sorbent, and smaller particle sizes. The use of materials of low particle size resulted in a lower inventory of solids in the carbonator (as low as 75 kg/m^2) at typical gas velocities in the carbonator reactor of the pilot (around 2.5 m/s). Under these conditions, despite the high CO_2 load in the carbonator and low inventories, it is possible to achieve high capture efficiencies (close to the limit allowed by the equilibrium) when there is a high sorbent activity, which is characteristic of calcium looping in cement plants. The apparent carbonation constant rate calculated from all the experimental results in the pilot is 0.36 s^{-1} , which is consistent with the equivalent parameters of previous works aimed at capturing CO2 from power plants. In summary, the results of this work indicate that CaL technology can be retrofitted to cement plants on the basis of the knowledge acquired with CaL in the more developed systems of power plants.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 641185 (CEMCAP) and from the Spanish Ministry of Economy and Competitivity ENE2015-68885-C2-1-R. B. Arias also acknowledges the award of a Ramon y Cajal contract from the Spanish MINECO RYC-2012-10147.

NOTATION

 $E_{carb} = CO_2$ capture efficiency

 $E_{carb eq}$ =maximum CO_2 capture efficiency allowed by the equilibrium

 f_a =fraction of active particles in the carbonator bed

 F_{C_2} mol/m²s=Ca molar flow circulating between reactors $F_{CO2calc}$ mol/m²s=molar flow of CO₂ produced by calcination leaving the calciner

 F_{CO2in} mol/m²s=molar flow of CO₂ entering the carbonator F_{CO2out} mol/m²s=molar flow of CO₂ leaving the carbonator F_{Ω} mol/s=makeup flow of limestone

G_s kg/m²s=solids flow circulation rate from carbonator to calciner

 $k_{\rm c}$ s-1=constant reaction rate

 n_{ca} mol/m²=total inventory of Ca in the carbonator bed

t* s=time required to increase the carbonate content from X_{calc} to X_{ave}

 $T_{\text{calc}} \circ C$ =average calciner temperature $T_{\text{carb}} \circ C$ =average carbonator temperature

 u_{calc} m/s=calciner gas velocity

u_{carb} m/s=carbonator gas velocity

 W_{CC} kg/m²=total inventory of solids in the calciner

 W_{CB} kg/m²=total inventory of solids in the carbonator

 X_{ave} =maximum CO₂ carrying capacity

 X_{calc} =molar carbonate content of the solids in the calciner X_{carb} =molar carbonate content of the solids in the carbonator φ =gas-solids contact effectivity factor

REFERENCES

(1) Boden, T. A.; Marland, G.; Andres, R. J.Global, Regional, and National Fossil-Fuel CO2 Emissions; Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory: Oak Ridge, TN, 2016; http://cdiac.ornl.gov/CO2_Emission/timeseries/global, DOI 10.3334/CDIAC/00001 V2016 (accessed October 2016).

(2) Koring, K.; Hoenig, V.; Hoppe, H.; Horsh, J.; Suchak, C.; Llevenz, V.; Emberger, B., Deployment of CCS in the Cement Industry. IEA Report 2013/19 IEA: Paris, 2013.

(3) Carrasco-Maldonado, F.; Spörl, R.; Fleiger, K.; Hoenig, V.; Maier, J.; Scheffknecht, G. Oxy-fuel combustion technology for cement production - State of the art research and technology development. Int. J. Greenhouse Gas Control 2016, 45, 189-199.

(4) Trevino, V. L.; Martínez, E. R., Method for capturing CO₂ produced by cement plant by using the calcium cycle. Patent EP 2461892A1, 2009.

(5) Bosoaga, A.; Masek, O.; Oakey, J. E. CO2 Capture Technologies for Cement Industry. Energy Procedia 2009, 1, 133-140.

Industrial & Engineering Chemistry Research

(6) Dean, C. C.; Dugwell, D.; Fennell, P. S. Investigation into potential synergy between power generation, cement manufacture and CO2 abatement using the calcium looping cycle. *Energy Environ. Sci.* **2011**, *4*, 2050–2053.

(7) Naranjo, M.; Brownlow, D. T.; Garza, A. CO2 capture and sequestration in the cement industry. *Energy Procedia* **2011**, *4*, 2716–2723.

(8) Dean, C. C.; Blamey, J.; Florin, N. H.; Al-Jeboori, M. J.; Fennell, P. S. The calcium looping cycle for CO2 capture from power generation, cement manufacture and hydrogen production. *Chem. Eng. Res. Des.* **2011**, *89*, 836–855.

(9) Rodríguez, N.; Murillo, R.; Abanades, J. C. CO₂ Capture from Cement Plants Using Oxyfired Precalcination and/or Calcium Looping. *Environ. Sci. Technol.* **2012**, *46*, 2460–2466.

(10) Vatopoulos, K.; Tzimas, E. Assessment of CO2 capture technologies in cement manufacturing process. J. Cleaner Prod. 2012, 32, 251–261.

(11) Pathi, S. K.; Lin, W.; Illerup, J. B.; Dam-Johansen, K.; Hjuler, K. CO2 Capture by Cement Raw Meal. *Energy Fuels* **2013**, *27*, 5397–5406.

(12) Ozcan, D. C.; Ahn, H.; Brandani, S. Process integration of a Calooping carbon capture process in a cement plant. *Int. J. Greenhouse Gas Control* **2013**, *19*, 530–540.

(13) Romano, M. C.; Spinelli, M.; Campanari, S.; Consonni, S.; Cinti, G.; Marchi, M.; Borgarello, E. *The calcium looping process for low CO2 emission cement and power. Energy Procedia* **2013**, *37*, 7091–7099.

(14) Telesca, A.; Calabrese, D.; Marroccoli, M.; Tomasulo, M.; Valenti, G. L.; Duelli (Varela), G.; Montagnaro, F. Spent limestone sorbent from calcium looping cycle as a raw material for the cement industry. *Fuel* **2014**, *118*, 202–205.

(15) Atsonios, K.; Grammelis, P.; Antiohos, S. K.; Nikolopoulos, N.; Kakaras, E. Integration of calcium looping technology in existing cement plant for CO2 capture: Process modeling and technical considerations. *Fuel* **2015**, *153*, 210–223.

(16) Spinelli, M.; Martínez, I.; De Lena, E.; Cinti, G.; Hornberger, M.; Spörl, R.; Abanades, J. C.; Becker, S.; Mathai, R.; Fleiger, K.; Hoenig, V.; Gatti, M.; Scaccabarozzi, R.; Campanari, S.; Consonni, S.; Romano, M. C. Integration of Ca-looping systems for CO₂ capture in cement plants. *Energy Procedia* **2016**, In Press.

(17) Hills, T.; Leeson, D.; Florin, N.; Fennell, P. Carbon capture in the cement industry. Technologies, progress and retrofitting. *Environ. Sci. Technol.* **2016**, *50*, 368–377.

(18) Dieter, H.; Bidwe, A. R.; Varela-Duelli, G.; Charitos, A.; Hawthorne, C.; Scheffknecht, G. Development of the calcium looping CO2 capture technology from lab to pilot scale at IFK, University of Stuttgart. *Fuel* **2014**, *127*, 23–37.

(19) Arias, B.; Diego, M. E.; Abanades, J. C.; Lorenzo, M.; Diaz, L.; Martínez, D.; Alvarez, J.; Sánchez-Biezma, A. Demonstration of steady state CO2 capture in a 1.7MWth calcium looping pilot. *Int. J. Greenhouse Gas Control* **2013**, *18*, 237–245.

(20) Kremer, J.; Galloy, A.; Ströhle, J.; Epple, B. Continuous CO2 Capture in a 1-MWth Carbonate Looping Pilot Plant. *Chem. Eng. Technol.* **2013**, 36, 1518–1524.

(21) Chang, M. H.; Huang, C. M.; Liu, W. H.; Chen, W. C.; Cheng, J. Y.; Chen, W.; Wen, T. W.; Ouyang, S.; Shen, C. H.; Hsu, H. W. Design and Experimental Investigation of Calcium Looping Process for 3-kWth and 1.9-MWth Facilities. *Chem. Eng. Technol.* **2013**, *36*, 1525–1532.

(22) Alonso, M.; Diego, M. E.; Abanades, J. C.; Perez, C.; Chamberlain, J. Biomass combustion with in situ CO_2 capture by CaO in a 300 kW_{th} circulating fluidized bed test facility. *Int. J. Greenhouse Gas Control* **2014**, 29, 142–152.

(23) Rodriguez, N.; Alonso, M.; Abanades, J. C. Experimental Investigation of a Circulating Fluidized-Bed Reactor to Capture CO2 with CaO. *AIChE J.* **2011**, *57*, 1356–1366.

(24) Telschow, S.; Frandsen, F.; Theisen, K.; Dam-Johansen, K. Cement formation-A success story in a black box: High temperature phase formation of portland cement clinker. *Ind. Eng. Chem. Res.* **2012**, *51*, 10983–11004.

(25) Baker, E. H. The calcium oxide-calcium dioxide system in the pressure range 1–300 atm. *J. Chem. Soc.* **1962**, *0*, 464–470.

(26) Arias, B.; Grasa, G.; Abanades, J. C.; Manovic, V.; Anthony, E. J. The Effect of Steam on the Fast Carbonation Reaction Rates of CaO. *Ind. Eng. Chem. Res.* **2012**, *51*, 2478–2482.

(27) Manovic, V.; Fennell, P. S.; Al-Jeboori, M. J.; Anthony, E. J. Steamenhanced calcium looping cycles with calcium aluminate pellets doped with bromides. *Ind. Eng. Chem. Res.* **2013**, *52*, 7677–7683.

(28) Donat, F.; Florin, N. H.; Anthony, E. J.; Fennell, P. S. Influence of High-Temperature Steam on the Reactivity of CaO Sorbent for CO2 Capture. *Environ. Sci. Technol.* **2012**, *46*, 1262–1269.

(29) Manovic, V.; Anthony, E. J. Carbonation of CaO-Based Sorbents Enhanced by Steam Addition. *Ind. Eng. Chem. Res.* **2010**, *49*, 9105–9110.

(30) Charitos, A.; Rodriguez, N.; Hawthorne, C.; Alonso, M.; Zieba, M.; Arias, B.; Kopanakis, G.; Scheffknecht, G.; Abanades, J. C. Experimental Validation of the Calcium Looping CO_2 Capture Process with Two Circulating Fluidized Bed Carbonator Reactors. *Ind. Eng. Chem. Res.* **2011**, *50*, 9685–9695.

(31) Alonso, M.; Rodriguez, N.; Grasa, G.; Abanades, J. C. Modelling of a fluidized bed carbonator reactor to capture CO2 from a combustion flue gas. *Chem. Eng. Sci.* **2009**, *64*, 883–891.

(32) Martínez, I.; Grasa, G.; Parkkinen, J.; Tynjälä, T.; Hyppänen, T.; Murillo, R.; Romano, M. C. Review and research needs of Ca-Looping systems modelling for post-combustion CO₂ capture applications. *Int. J. Greenhouse Gas Control* **2016**, *50*, 271–304.

(33) Grasa, G. S.; Abanades, J. C.; Alonso, M.; Gonzalez, B. Reactivity of highly cycled particles of CaO in a carbonation/calcination loop. *Chem. Eng. J.* **2008**, *137*, 561–567.

(34) Symonds, R. T.; Lu, D. Y.; Manovic, V.; Anthony, E. J. Pilot-scale study of CO₂ capture by CaO-based sorbents in the presence of steam and SO₂. *Ind. Eng. Chem. Res.* **2012**, *51*, 7177–7184.

(35) Dieter, H.; Bidwe, A. R.; Varela-Duelli, G.; Charitos, A.; Hawthorne, C.; Scheffknecht, G. Development of the calcium looping CO2 capture technology from lab to pilot scale at IFK, University of Stuttgart. *Fuel* **2014**, *127*, 23–37.

(36) Duelli (Varela), G.; Charitos, A.; Diego, M. E.; Stavroulakis, E.; Dieter, H.; Scheffknecht, G. Investigations at a 10kWth calcium looping dual fluidized bed facility: Limestone calcination and CO_2 capture under high CO_2 and water vapor atmosphere. *Int. J. Greenhouse Gas Control* **2015**, 33, 103–112.