

# Waste Resources Utilization as Stable Supports for Sintering Resistant CaO-Based Sorbents for Calcium Looping CO<sub>2</sub> Capture in Cement Industry

Ismail Salah Ahmed Mohamed

Ismail.mohamed@tecnico.ulisboa.pt

Instituto Superior Técnico, Universidade de Lisboa, Portugal

November 2018

**Keywords:** Calcium looping, CO<sub>2</sub> capture, CaO conversion, sintering, waste-derived supports, fixed bed

## ABSTRACT

Utilization of calcium looping technology in cement industry for CO<sub>2</sub> capture in aim to reduce the 6 % anthropogenic CO<sub>2</sub> emissions produced by cement plants is faced with a major drawback; sintering, which cause a decay in sorbent reactivity with increasing number of CO<sub>2</sub> capture cycles. This work aims to investigate the possibility of using waste-derived materials as a support for CaO sorbents which are utilized for CCS with the advantage of cost reduction and circular economy fulfillment by recycling spent sorbents as raw material for cement production.

In the scope of this research, a natural CaCO<sub>3</sub> was supported with coal fly ash (CFA) and spent fluid catalytic cracking catalyst (SFCC) using different mixing ratios. The CO<sub>2</sub> carrying capacity of sorbents was evaluated in a thermogravimetric analyzer, a fixed bed unit and by in-situ XRD. Sorbents went under three calcination atmospheres and a CO<sub>2</sub> content of 25 % during carbonation. Fresh and used sorbents were characterized by N<sub>2</sub> adsorption, SEM, and XRD to determine their textural and morphological properties and mineralogical composition.

Results obtained showed that addition of CFA and SFCC to natural CaCO<sub>3</sub> improved its CaO conversion by reducing particles agglomeration and maintaining available surface area, also showing that among tested mixing ratios, the blends with 90 % of CaO had the highest CO<sub>2</sub> capture capacity. CO<sub>2</sub> calcination atmosphere proved to have an adverse effect on sorbent capture capacity by increasing sintering, while steam addition proved to enhance carrying capacity by improving product layer diffusion.

## INTRODUCTION

The growing demand of energy was coped with increased production by excessive exploitation of conventional sources of fuel i.e. coal, petroleum, and natural gas, as the rising use of

renewable energy is not capable of covering that need. This utilization of fuels resulted in a rapid growth in emissions, especially CO<sub>2</sub> which consequently lead to climate change that was observed in drastically frequent and higher impact floods, droughts, hurricane, ice glaciers melting, and rising sea level. Reduction of CO<sub>2</sub> emissions has been the main concern for researchers, scientists, and policy makers due to not only its warming potential impact but to the enormous production rate mainly from conventional power plants, steel and cement industries which are accounted for 60% of anthropogenic CO<sub>2</sub> emissions. A first step on the way was by signing Kyoto protocol (1997) on climate change with a target set to reduce emissions for six GHG emissions, then followed by Paris agreement in 2016 after 55 countries accounted for 55% of GHG emissions met conditions of ratification previously agreed on Doha amendment in 2015, which aimed for a long-term goal to maintain the increase of global average temperature to well below 2 °C, alongside countries providing their national climate actions plan for emission reduction and report progressive implementation of their targets.

Development of technologies aiming for CO<sub>2</sub> emission reduction was centered around the concept of sustainable and renewable energy production. Basically, attention was drawn towards three main aspects; first is transition towards clean renewable energy (solar and wind), second is reducing energy consumption by improving energy efficiencies, and the third is implementation of carbon capture and storage (CCS) technologies as a step to capture produced CO<sub>2</sub> emissions. CCS has been divided into three technologies based on their implementation approach to: first, pre-combustion CO<sub>2</sub> capture technology where primary fuels are reformed into syngas by either steam reforming or partial oxidation where gaseous, liquid, or solid fuels are combusted in a lean atmosphere. Produced CO is converted

to CO<sub>2</sub> by water-gas shift process and CO<sub>2</sub> is separated, compressed, and transported to the storage location. Second, Oxy-fuel combustion for CO<sub>2</sub> capture in which oxygen is separated in an air separation unit (ASU) prior to combustion, thus eliminating N<sub>2</sub> presence in flue gas and possibility of NO<sub>x</sub> formation, leaving flue gases with only H<sub>2</sub>O vapor, CO<sub>2</sub>, and excess O<sub>2</sub>. Lastly, post-combustion CO<sub>2</sub> capture technology which focus on removing CO<sub>2</sub> emissions from the flue gas stream thus avoiding making changes to combustion process. This technology is believed to have the capacity for CO<sub>2</sub> emissions cut in future from the stationary power and industrial plants. Basically, this technology has four divisions: capture by adsorption, absorption, cryogenic and membranes. Adsorption separation can be physical through PSA or TSA where it uses solid sorbent ability to adsorb gases by change in pressure or temperature, respectively. While chemical adsorption offers a stronger bond between adsorbate and adsorbent and is more selective towards adsorbed gases. Absorption also has physical and chemical methods, where in chemical solvent like monoethanolamine (MEA) is utilized for its reversibility nature. Physical absorption follows the same method for physical adsorption except for the sorbent where in this case it's a solvent instead of a solid material [1].

Cryogenic works by cooling down flue gas to desublimation temperature (-100 to -135 °C) at which CO<sub>2</sub> solidifies and then it gets separated and compressed. It offers an energy and cost expenses cut of 30 % compared to technologies involving ASU and solvents, as well as a potential water cooling savings and energy storage [2]. For the case of membranes, the principal is to benefit from the pressure difference between membrane sides. It presents a good separation process when gases flow at high pressures and concentration, it requires further improvement to its selectivity since CO<sub>2</sub> has low partial pressure.

The focus of this study will be driven towards chemical adsorption of post-combustion CO<sub>2</sub> capture using calcium looping method.

### Calcium Looping for CO<sub>2</sub> capture

Calcium looping is regarded as the one of the most promising CCS technologies due to its potential high CO<sub>2</sub> capacity which makes it a considerable candidate for implementation into large CO<sub>2</sub> emitting plants and natural availability of CaCO<sub>3</sub> sorbents that offers cost-cut feature. The method benefits from the reversibility of the CaCO<sub>3</sub> reaction that acts to

regenerate the sorbent to allow for much longer utilization for the capture process. A calciner is used to conduct the calcination reaction (Eq. 1) in which CaCO<sub>3</sub> is decomposed to release CO<sub>2</sub> in a pure CO<sub>2</sub> atmosphere and CaO that is transformed to a carbonator in which a carbonation reaction (Eq. 2) is carried out to capture CO<sub>2</sub> from the flue gas stream.



Calcination reaction is carried out at a temperature around 900 °C with addition of energy due to endothermic reaction, while carbonation reaction which is exothermic is carried out under temperature of 600 °C – 700 °C [3]. carbonation reaction undergoes two stages; a fast-controlled stage that is dominant in early cycles accounted for 76 % of CaO conversion and a slow diffusion-limited stage that can raise the CaO conversion up to 96 % (Barker [4]) which dominated after several cycles due to loss of pore volume by pore blockage [5].

### Calcium looping sorbents

Sorbents used for calcium looping can either be natural which assures the cost-effective feature or synthetic that achieve the desired performance enhancement. A deterministic property of sorbents which is required is high capture capacity as it defines the amount of sorbent required for capture process, also sorbents must be highly selective towards CO<sub>2</sub> capture as sometimes they get poisoned by the sulfur content in flue gas or fly ash which affects sorbent regeneration mechanism and consequently reduces sorbent reactivity. On top of that sorbents should maintain a stability and the thermal stress exerted by the carbonation and calcination temperatures as well as mechanical stability against attrition in case of using fluidized bed reactors.

Natural sorbents like limestone, dolomites, and waste marble powder excel in capture capacity beside their abundance in nature. Implementing them in cement industry comes with a key feature as spent sorbents are used as raw material for cement production. Drawbacks of using natural sorbents are embodied in their relatively low thermal resistance and fragile structure which had been a research target to overcome. In contrast, synthetic sorbents succeed to perform better over long cycles due to their altered structure and improved thermal resistance. Different materials were utilized to provide a structural

support to inhibit sintering of sorbent like calcium aluminate and titanium ethoxide. Broda et al. [6] reported that synthesizing CaO-based sorbent with  $Al_2O_3$  using carbon-gel technique resulted in a CaO conversion of 85 % after 30 cycles, while Santos et al. [7] prepared a sorbent with the same sol-gel technique that had a CaO conversion around 74 %.

Sintering of sorbent is considered as a barrier to the utilization of  $CaCO_3$  sorbents through calcium looping. It is caused by the high temperature heating that leads to the loss of sorbent  $S_{BET}$  and  $V_p$ . Sintering occurs during carbonation and mainly calcination were rate of deactivation increases, Erans et al. [3] reported that after 25 cycles sorbent captured only 10 % of its total weight compared to the 30 % in first cycle, a bimodal pore size distribution is created that has small pores and bigger pores from surface energy minimization. During carbonation the reactivity decay arise from closure of small pore by  $CaCO_3$  formation that fails to reopen by calcination as referred by Fennell et al. [8], leading to uncomplete carbonation eventually ending in a poor reactive sorbent recovery according to Lysikov et al. [9].

Researchers investigated different methods to improve the performance of sorbents that leads to higher and long-lasting carrying capacity by reducing the progressive reactivation decay. Manovic et al. [10] studied the effect of thermal pretreatment under temperature range of 800 °C and 1300 °C which reduced initial CaO conversion yet later enhanced the performance as compared to original sorbent. Grinding and repalletizing as a performance enhancement investigated also by Manovic et al. [11] showed a 33 % - 34 % CaO conversion for treated spent sorbent after 30 cycles which is similar to the fresh sorbent. Hydration was also considered for sorbent reactivation as it can be applied to fresh and spent sorbents, it has proved that sorbent can retain around 53 % of capture capacity under 15 cycles following 15 cycles that reduced the capture capacity by 32 % as reported by Yu et al. [12]. A similar effect of changing sorbent composition can be achieved by steam addition where it enhances the reactivity and maximize the calcination and carbonation reaction rates, however, Donat et al. [13] stated that steam presence during calcination enhances sintering but in a way that created pore structure that lead to conversion improvement.

Waste utilization for sorbent capture capacity performance enhancement had emerged as a possibility to implement in cement production

as coal fly ash (CFA) which is a potential waste support is used also for cement production. The unique composition of CFA that mainly contains  $Al_2O_3$  and  $SiO_2$  which have thermally stable structure make CFA a promising support material. Yan et al. [14] studied the performance of CFA-stabilized CaO-based sorbents, different mixing ratios gave improvement to the  $CO_2$  capture capacity, also the decay was minimized and the capture capacity almost stabilized along 30 cycles indicating that CFA worked as a physical barrier preventing CaO agglomeration.

### Calcium looping experimental section

**Sorbents preparation and characterization methods:** a group of three CaO precursors (natural  $CaCO_3$ , commercial  $CaCO_3$  and  $Ca(NO_3)_2 \cdot 4H_2O$  – SIGMA-ALDRICH product-) and two waste-derived supports (coal fly ash CFA and spent fluidized catalytic cracking FCC catalyst) were utilized to prepare sorbents with ratio appears in Table 1, it was based on CaO content (%) of precursors. Natural  $CaCO_3$  was crushed and sieved and grain size range (125 – 355  $\mu m$ ) was used and all sorbents and waste support were kept inside an oven at 120 °C to eliminate moisture capture. Samples were prepared by physically dry mixing using a ball mill (Retsch) with a frequency of 70 Hz for 30 min.

Table 1: Mixing ratios of sorbents and waste derived support

Material		CaO Precursor		
		Commercial $CaCO_3$ / Natural $CaCO_3$ / $Ca(NO_3)_2 \cdot 4H_2O$		
support	CFA / SFCC	90%	75%	60%
		10%	25%	40%

Methods for characterizing fresh and spent sorbents included: thermogravimetric analysis TGA to study sample mass change with temperature.  $N_2$  adsorption technique was used for investigating textural properties of sorbents, also XRD characterization conducted for defining the mineralogical composition and particle size calculations, and finally SEM technique was used to observe morphological change of samples before and after experiments.

### Experimental procedure

**TGA:** the equipment used for test was the TG - DSC setsys Evo 16 - SETARAM analyzer. It consists of a chamber that is supplied with a primary gas (air) and secondary gas (CO<sub>2</sub>) and protected by a protective gas (Ar) and cooling water supply. The mass of sample introduced to the equipment was calculated based on the CaO present in sample with or without support by using equation:

$$m_{sample} = \frac{m_{CaO} * Mr_{CaO precursor}}{Mr_{CaO} * w_{CaO}} \quad Eq. 3$$

where  $m_{sample}$  is the sample mass,  $M_r$  is the molecular weight,  $w_{CaO}$  is the mass fraction of CaO on the mixed sorbent.

The sample is pre-calcined for 20 min under pure air atmosphere, followed by 10 carbonation-calcination cycles. Carbonation was conducted under temperature of 700 °C for 60 min with 75% of air and 25% of CO<sub>2</sub>. Calcination was conducted under temperature of 800 °C for 10 min with 100% of air. The total air flow was 40 ml/min corresponding to 100% of air and 10 ml/min for CO<sub>2</sub> corresponding to 25%. A blank experiment was conducted to eliminate apparatus atmosphere density change. Data acquired was treated using a Microsoft Excel spreadsheet and Origin software to create graphs. Samples were compared based on their CaO conversion which corresponds to the ratio of actual mass of CO<sub>2</sub> captured by a unit mass of sorbent to the theoretical capacity.

**Fixed-bed reactor unit:** it consists of a high temperature resistant quartz reactor with a porous plate placed inside an oven. Three atmospheres were used for experiments in this unit to test pure and blended sorbents. First, a standard atmosphere consisting of 100% of air for calcination and 75% of air with 25% of CO<sub>2</sub> for carbonation. Second, a CO<sub>2</sub> calcination where the carbonation atmosphere remains the same mixture of 75% of air with 25% of CO<sub>2</sub> and for calcination it was 100% of CO<sub>2</sub>. Third, a 5% of steam atmosphere which consist of 95% of air with 5% of steam for calcination and 70% of air with 25% of CO<sub>2</sub> and 5% of steam. The flow of gases was controlled by flowmeters which was calibrated prior to experiments.

A 2 grams samples were used for tests that were run for 20 cycles. With carbonation temperature of 700 °C and calcination temperature of 800 °C for standard conditions and 5% of steam and 900°C for CO<sub>2</sub>

calcination. The pre-calcination temperature was always fixed at 900 °C. calcination was considered finished when the CO<sub>2</sub> detector connected to the exhaust gas would read a concentration below ≤0.05%. while carbonation was completed when the CO<sub>2</sub> detector stabilized around the value of introduced CO<sub>2</sub>, i.e. 25%.

Assessment of data was based on calculating the mass of CO<sub>2</sub> captured during carbonation and validate with the mass of CO<sub>2</sub> released during calcination by finding the integration of areas confined between baseline and CO<sub>2</sub> concentrations (Figure 1). These masses are then used to find the CaO conversion.

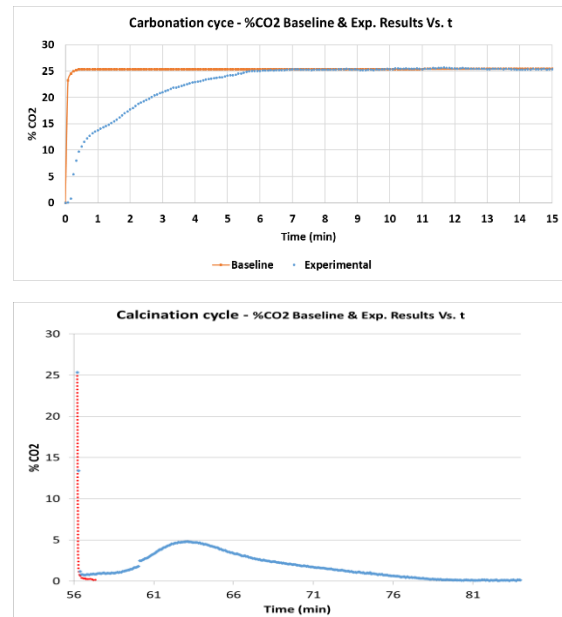


Figure 1: CO<sub>2</sub> captured along carbonation and calcination cycles

## Results and Discussion

**Effect of Ca-precursor and waste-support addition:** Figure 2 shows the results for TGA experiments for different CaO-precursors, pure and mixed with waste-derived supports. For commercial CaCO<sub>3</sub> pure and mixed sorbents, an improvement was observed on CaO conversion due to waste-support addition, i.e. 91% and 96% with 10% of CFA and 10% of SFCC, respectively, compared to 88% with 100% of CaO. This is justified by the structural support given by waste support to prevent sintering during pre-calcination. After the 10<sup>th</sup> cycle, reactivity decay for supported sorbents was lower than that for pure sorbent. Reduction

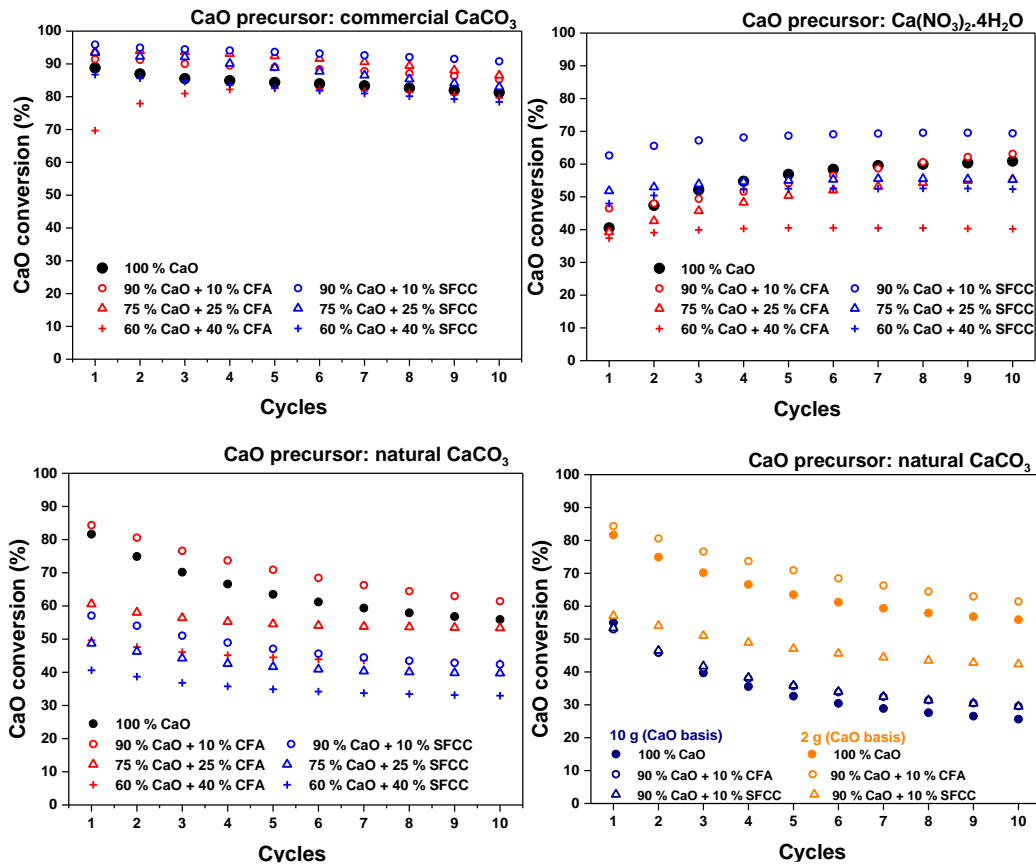


Figure 2: CaO conversion (%) of commercial  $\text{CaCO}_3$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , natural  $\text{CaCO}_3$  sorbents

in CaO conversion was 6% and 5% for 10% of CFA and 10% of SFCC, respectively, while it was 8% reduction for 100% CaO sorbent. This improved performance was continued for the 75% CaO and 25% of support having a final CaO higher than the pure sorbent. CaO conversion for  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  sorbent had a similar behavior of performance enhancement with lower CaO conversion. Broad et al. [15] referred this lower CaO conversion to the fact that  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  melts at lower temperature that hinders pores formation upon  $\text{CaCO}_3$  composition. An investigation present by Yan et al. [14] attributed the continuous increase in CaO conversion to self-reactivation effect.

The CaO conversion profile observed for natural  $\text{CaCO}_3$  was like the WMP profile reported by Pinheiro et al. [16]. Only the 90% of CaO with 10% CFA obtained a better CaO conversion than pure CaO among all supported sorbents. However, all mixture had a lower reactivity decay compared to the 100% CaO sorbent, which decreased as the content of waste support increased. Yan et al. [14] stated that increasing waste support content over 10% weight can result in formation of gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_3$ ) which consumes the active CaO. A different sorbent's masses introduced to the ball milling affected the mixing efficiency which

in return resulted in inconsistency. The last graph on Figure 2 compares the CaO conversion of 2g and 10g (CaO basis) blends with natural  $\text{CaCO}_3$ . The mixture formed with 2g of natural  $\text{CaCO}_3$  with 10% of CFA had better performance due to efficient mixture formed when compared to the mixture with 10% of SFCC, which can be referred to the smaller particle size of CFA in comparison with SFCC as obtained from SEM images. The 10 g samples had lower CaO conversion than the 2 g, while waste supported sorbent performed better than the pure sorbent. The  $\text{CO}_2$  capture deactivation (a relative difference between the 1<sup>st</sup> and 10<sup>th</sup> cycle's CaO conversion) was higher for 10g (CaO basis) sorbents falling between 53% - 44% when compared to the 2g (CaO basis) sorbents, which was between 32% - 26%. In both cases the highest deactivation values occur with the 100% of CaO.

Figure 3 illustrates the CaO conversion of pure natural and commercial  $\text{CaCO}_3$  along with their mixtures with 10% waste support performed on fixed bed unit. As observed on TGA, commercial  $\text{CaCO}_3$  has higher CaO conversion than the natural  $\text{CaCO}_3$  from the 1<sup>st</sup> cycle, i.e. 103% and 91%, respectively. Besides, the commercial  $\text{CaCO}_3$  had lower deactivation compared to natural  $\text{CaCO}_3$ , i.e. 36% and 69%,



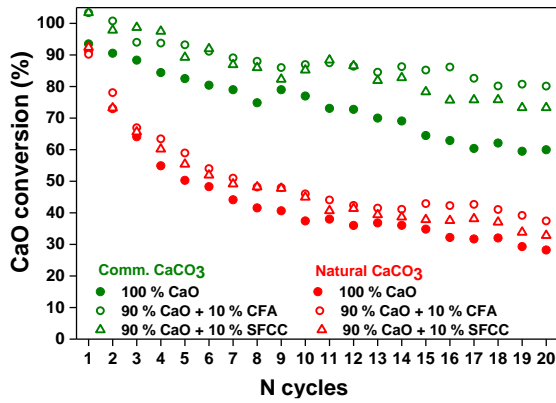


Figure 3: CaO conversion of pure sorbents and CaO sorbents supported with 10 % CFA and SFCC over 20 calcination-carbonation cycles carried on fixed bed

respectively, after 20 cycles. CFA blends had better performance along the cycles indicating reduction of CaO agglomeration from the favorable mixture with the CaO precursors. A 22% and 58% deactivation rate when using CFA with commercial and natural CaCO<sub>3</sub>, respectively. However, this deactivation rate increases in case of commercial and natural CaCO<sub>3</sub> blends with SFCC, i.e. 29% and 64%, respectively. Which can be justified by CFA lower particles that facilitates its dispersion on CaO particle or rather their higher thermal stability resulting from their thermodynamically conversion process.

After 10 cycles, CaO conversion obtained from TGA and fixed bed were different. Which can be attributed to two factors; first, the gas flow nature, and the carbonation-calcination reaction time allowed. In TGA the gas only reaches from top which causes a diffusional limitation of gas flow. However, on the fixed bed unit gas flows through the sample allowing higher interaction between sample and gas. This effect is so evident on fixed bed as it has an initial CaO conversion of 91% compared to 55% on TGA. As Fennell et al. [8] attributed, this is due to development of skeleton structure which defines the carrying capacity. Regarding allowed time, on TGA the time was predefined which appeared to be insufficient for complete carbonation. The diffusional limitation has elongated to time needed for complete carbonation. On fixed bed the time needed was relatively low, and carbonation was considered complete when the CO<sub>2</sub> detector stabilizes around a predefined concentration. Sudden increases of reactivity observed on middle cycles is attributed to the fact that test was conducted along 2 days, with a sample being kept under air flow and turned off oven during night. The initial higher CaO conversion of

Table 2:  $S_{BET}$  (m<sup>2</sup>/g) and  $V_p$  (cm<sup>3</sup>/g) of pure and supported CaO sorbents CFA/ SFCC tested in the fixed bed unit for (0 cy) and 20 carbonation-calcination cycles (20 cy)

CaO-based sorbent		$S_{BET}$ (m <sup>2</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	
Commercial CaCO <sub>3</sub>	100 % CaO	0 cycle	24.6	0.09
		20 cycle	14.4	0.06
	90 % CaO + 10 % CFA	0 cycle	25.6	0.1
		20 cycle	16.9	0.09
	90 % CaO + 10 % SFCC	0 cycle	33.4	0.13
		20 cycle	23.8	0.11
Natural CaCO <sub>3</sub>	100 % CaO	0 cycle	31.1	0.21
		20 cycle	10	0.06
	90 % CaO + 10 % CFA	0 cycle	21.1	0.1
		20 cycle	15.2	0.05
	90 % CaO + 10 % SFCC	0 cycle	27.4	0.15
		20 cycle	15.7	0.05

waste supported commercial CaCO<sub>3</sub> can be justified by their high  $S_{BET}$  (Table 2) obtained by N<sub>2</sub> sorption. The higher values than the pure sorbents explain the role of waste support in hindering CaO particles agglomeration. This effect of higher  $S_{BET}$  can be seen after 20 cycles on CaO conversion enhancement compared to the 100% CaO sorbent. Although natural CaCO<sub>3</sub> had a decrease in  $S_{BET}$  with waste support addition, the increase in pure sorbent  $S_{BET}$  in comparison with the fresh sorbent was higher than the increase of commercial CaCO<sub>3</sub> due to the CO<sub>2</sub> release that obtained higher porous material.

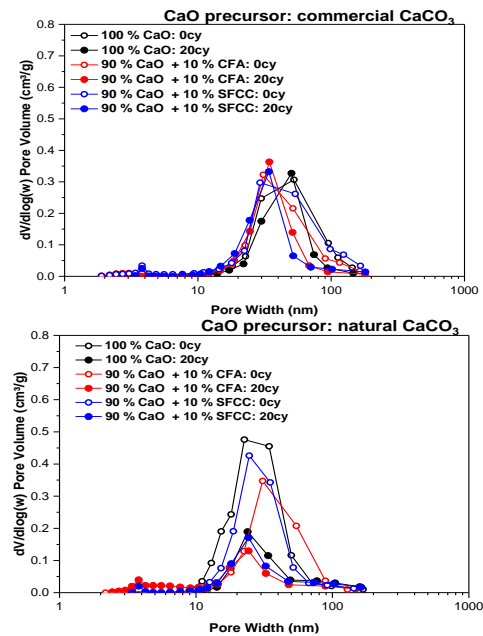


Figure 4: BJH desorption pore size distribution of pure and waste supported CaO sorbents tested in the fixed bed unit after 0 cycle and 20 calcination-carbonation cycles

BJH desorption (Figure 4) shows that commercial  $\text{CaCO}_3$  had almost maintained its pore volume at constant level with small reduction as demonstrated in Table 2, with a pore width falling within mesopores range showing a small presence of macropores for both after 0 and 20 cycles sorbents. For natural  $\text{CaCO}_3$  reduction in  $V_p$  was observed as shown in Table 2, this is due to sintering,  $\text{CaO}$  agglomeration and macropores formation, which had the least effect with CFA presence, i.e. only lost half of its  $V_p$  after 20 cycles.

The lower decrease in  $S_{\text{BET}}$  and  $V_p$  of commercial  $\text{CaCO}_3$  with 10% of CFA (Table 2) corresponds to the decrease in average crystallite size (Figure 5) as CFA appears to inhibit crystallite size growth. Yet the blend with 10% of SFCC had the highest average crystallite size, i.e. 43 nm. The comparatively smaller reduction in  $S_{\text{BET}}$  and  $V_p$  obtained for natural  $\text{CaCO}_3$  was in accordance with an almost stabilized average crystallite size. It was 41 nm for the 100% of  $\text{CaO}$  sorbent and 42 nm for both CFA and SFCC blends.

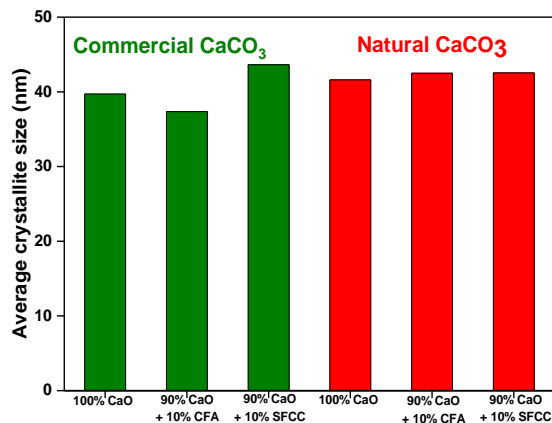


Figure 5:  $\text{CaO}$  crystallite size of Commercial and Natural  $\text{CaCO}_3$  and their blends

**Effect of atmosphere change:** Figure 6 shows the  $\text{CaO}$  conversion after 20 carbonation-calcination cycles under different atmospheres. While a 100%  $\text{CO}_2$  calcination atmosphere had a small negative effect on the initial  $\text{CaO}$  conversion, yet kept on affecting negatively the  $\text{CaO}$  conversion, achieving only 17% final  $\text{CaO}$  conversion. This extensive sintering appears to start after the 5<sup>th</sup> cycle, Yan et al. [14] gave a possible explanation that when  $\text{CO}_2$  calcination starts at 900 °C, the  $\text{CaCO}_3$  phase is still present, due to  $\text{CaCO}_3$  low Tamman temperature (524 °C) comparatively with the  $\text{CaO}$  Tamman temperature (1170 °C), the sintering is promoted. Air or  $\text{N}_2$  atmospheres would mitigate this effect as when the calcination temperature (900 °C) is reached, the  $\text{CaO}$  phase would already exist due to the

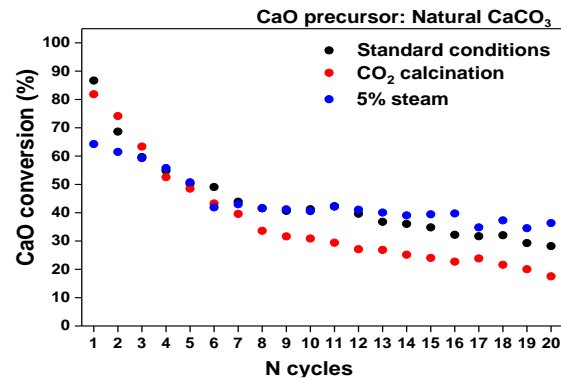


Figure 6:  $\text{CaO}$  conversion of natural  $\text{CaCO}_3$  sorbent tested in a fixed bed unit under different experimental conditions

$\text{CaCO}_3$  decarbonation. Steam presence during calcination shows negative effect on the initial  $\text{CaO}$  conversion. However, steam kept on improving the  $\text{CaO}$  conversion along the cycles resulting in a  $\text{CaO}$  conversion of 36% after 20 cycles, compared to the 28%  $\text{CaO}$  conversion for standard conditions. Donat et al. [13] stated that a possible explanation for the lower initial carrying capacity was observed because steam increases the sintering during calcination and shifts towards higher pores due to higher thermal conductivity and heat capacity of steam compared to air. Similarly, they referred the  $\text{CaO}$  conversion improvement along the cycles to the reduction of diffusion resistance through carbonate layer and generation of small pores which is promoted by steam presence.

The textural properties (Table 3) shows that the  $S_{\text{BET}}$  of sorbent tested under standard conditions lost 67% of its initial value, while sorbent under  $\text{CO}_2$  calcination lost 72% of its initial  $S_{\text{BET}}$ , in agreement with its lower  $\text{CaO}$  conversion profile. After 0 cycles the lower  $S_{\text{BET}}$  and  $V_p$  of sorbent tested under steam corresponds to the  $\text{CaO}$  conversion profile which is affected by sintering enhancement with steam during calcination. After 20 cycles the enhancement imposed by the layer diffusion resulted in improved textural properties.

Table 3:  $S_{\text{BET}}$  and total  $V_p$  of natural  $\text{CaCO}_3$  tested in the fixed bed unit after the activation (0 cy) and 20 carbonation-calcination cycles under different experimental conditions

Experimental condition		$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )
Standard conditions	0 cycle	31.1	0.20
	20 cycles	10	0.06
$\text{CO}_2$ calcination	0 cycle	25	0.17
	20 cycles	6.9	0.05
5 % steam	0 cycle	12.3	0.04
	20 cycles	25	0.08

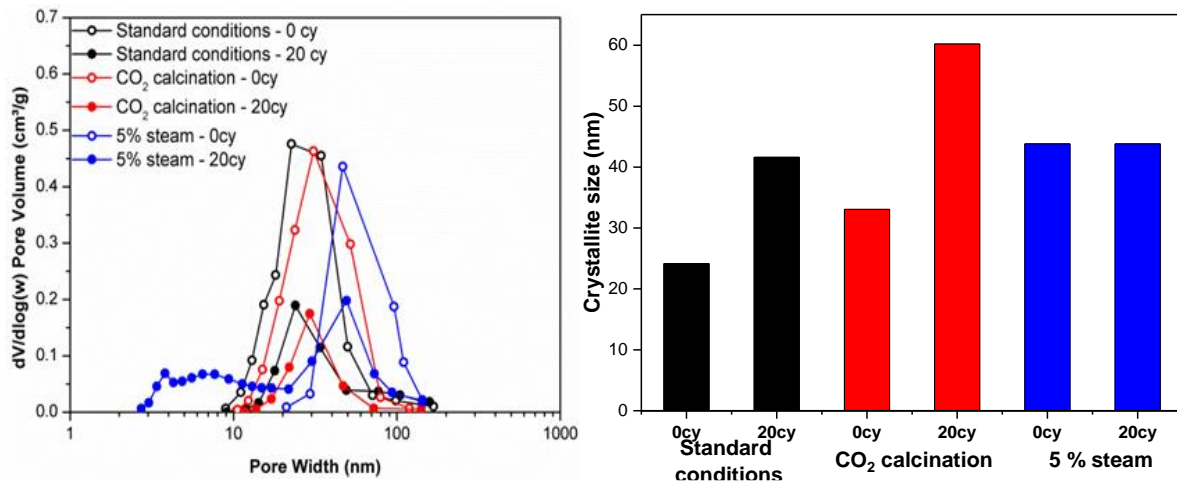


Figure 7: Pore size distributions obtained from N<sub>2</sub> adsorption (PSD from BJH desorption branch) and Crystallite size (nm) obtained from Scherrer equation of natural CaCO<sub>3</sub> tested in the fixed bed unit after the activation (0 cy) and 20 carbonation-calcination cycles (20 cy), under different experimental conditions

Pore size distribution (PSD) obtained with BJH desorption method shows that (Figure 7) regardless of atmosphere conditions the CaCO<sub>3</sub> sorbent lose pore volume after 20 cycles due to sintering. After pre-calcination with standard conditions and CO<sub>2</sub> calcination the CaCO<sub>3</sub> sorbent mainly contains mesopores between 20-30 nm. But sorbent tested under steam developed 50 nm mesopores. Developed macropores after the activation under CO<sub>2</sub> calcination and steam addition is justified by the loss of mesopores due to CaO sintering. The steam addition split the PSD into two populations after 20 cycles, both within the mesopores range. The first have the same average width (50 nm) with a decreasing population and the second is with an increasing population shifted towards lower mesoporosity in the range of 2.5-11 nm, which justifies the increase in S<sub>BET</sub> and V<sub>p</sub> observed earlier.

The average crystallite size obtained from XRD performed on natural CaCO<sub>3</sub> is further supporting the findings presented above. In Figure 7, after activation under standard conditions the average crystallite size was 24 nm. This was much lower than the 33 nm and 43 nm estimated for the CO<sub>2</sub> calcination and steam addition, respectively. Which reinforce the previous explanation that these atmospheres enhance sintering thus particle size growth. The CO<sub>2</sub> calcination obtained the biggest average crystallite size after 20 cycles, which corresponds to its lowest S<sub>BET</sub> and V<sub>p</sub> shown in Table 3. The growth in crystallite size of sorbent under CO<sub>2</sub> calcination was also the highest with 27 nm compared to the 17 nm growth for the sorbent tested under standard conditions. Which agrees with the CaO conversion that higher crystallite size is usually

related to higher sintering degree and lower CO<sub>2</sub> carrying capacity.

The steam addition showed a maintained crystallite size after 20 cycles, i.e. 43 nm. This agrees with the finding that at the beginning the steam contributes to the sintering and fast growth of crystallites, however, this is followed by CaO crystallite size stabilization. This is probably due to increase in S<sub>BET</sub> and V<sub>p</sub> related to diffusional layer changes caused by steam presence.

## Conclusion

TGA results showed that addition of CFA and SFCC had a similar enhanced effect on commercial CaCO<sub>3</sub>, and the 1<sup>st</sup> and 10<sup>th</sup> CaO conversion values were always higher for blends with 10 % and 25% of waste derived sorbents. The blend with 10 % of SFCC observed the highest CaO conversion, that presented an initial CaO conversion of 96 % and after 10 cycles it was 91 %, and the lowest deactivation of 5% only after 10 cycles. The CaO conversion of these sorbents was also very stable. However, increasing the amount of waste-support would affect the CaO capture capacity due to reduced amount of active CaO thus losing the benefits obtained from the anti-sintering physical barrier role of waste on the CaO deactivation.

The Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O sorbent had a continuous increase of its reactivity along the cycles, this phenomenon can be justified by the formation of internal (hard) skeleton that hinders the carbonation due to diffusional limitations, however, along the cycles an external (soft) skeleton is formed that enhances the CaO conversion, this is known as self-reactivation effect. The natural CaCO<sub>3</sub> showed that



introducing the appropriate weight of sorbent and waste-support to the mixing and milling process can have a positive effect on the CaO conversion, as seen in case of 2 g and 10 g samples (CaO basis) preparation. It can be concluded that with commercial sorbents, addition of 10% SFCC gives the highest CaO conversion and stability, while with the natural CaCO<sub>3</sub>, the 10% of CFA mixed sorbents performs better.

CO<sub>2</sub> calcination atmosphere delays the decomposition of CaCO<sub>3</sub> as the sorbent reaches the calcination temperature (900 °C) which enhances sintering due to lower Tammann temperature of CaCO<sub>3</sub> compared to CaO. Subsequently, the sorbent loses its S<sub>BET</sub> (72% reduction after 20 cycles) and V<sub>p</sub> (0.05 cm<sup>3</sup>/g after 20 cycles) in an increased rate, compared to the sorbent tested under standard conditions (68% reduction in S<sub>BET</sub> and V<sub>p</sub> of 0.06 cm<sup>3</sup>/g after 20 cycles). And it obtained an 82% increase in its average crystallite size compared to 72% for the sorbent tested under standard conditions. Steam has a positive effect on stability after 20 cycles, where it has higher CaO conversion than that obtained from sorbent under standard conditions (36% vs 28% of CaO conversion). This positive effect is obtained from steam ability to reduce diffusional resistance through carbonate layer thus improving CaO conversion.

Natural CaCO<sub>3</sub> appears to be the most relevant sorbent for industrial application due to economic and environmental aspects. It was verified that amount of waste-support added, and steam presence are key parameters for CaO conversion and stability enhancement.

### Recommendations

for future work it is recommended to study the behavior of sorbents using different mixing and milling techniques. Also, it's possible to test the effect of CO<sub>2</sub> calcination atmosphere and steam addition on waste-supported sorbents. Besides, investigation of waste-supporting of other natural sorbents like dolomite and WMP.

### References

- [1] P. C. Chiang and S. Y. Pan, "Carbon dioxide mineralization and utilization," *Carbon Dioxide Miner. Util.*, pp. 1–452, 2017.
- [2] L. Baxter, A. Baxter, and S. Burt, "Cryogenic CO<sub>2</sub> Capture as a Cost-Effective CO<sub>2</sub> Capture Process," no. c, 2009.

- [3] M. Erans, V. Manovic, and E. J. Anthony, "Calcium looping sorbents for CO<sub>2</sub> capture," *Appl. Energy*, vol. 180, pp. 722–742, 2016.
- [4] R. Barker, "The reversibility of the reaction CaCO<sub>3</sub> ⇌ CaO+CO<sub>2</sub>," *J. Appl. Chem. Biotechnol.*, vol. 23, no. 10, pp. 733–742, 2007.
- [5] M. Broda, A. M. Kierzkowska, and C. R. Müller, "Synthetic calcium oxide-based carbon dioxide sorbents for calcium looping processes," *Calcium Chem. Looping Technol. Power Gener. Carbon Dioxide Capture*, pp. 51–72, 2015.
- [6] M. Broda and C. R. Müller, "Synthesis of highly efficient, Ca-based, Al<sub>2</sub>O<sub>3</sub>-stabilized, carbon gel-templated CO<sub>2</sub> sorbents," *Adv. Mater.*, vol. 24, no. 22, pp. 3059–3064, 2012.
- [7] E. T. Santos, C. Alfonsín, A.J.S. Chambel, A. Fernandes, A.P. Soares Dias, C.I.C. Pinheiro, M.F. Ribeiro, "Investigation of a stable synthetic sol-gel CaO sorbent for CO<sub>2</sub> capture," *Fuel*, vol. 94, pp. 624–628, 2012.
- [8] P. S. Fennell, R. Pacciani, J. S. Dennis, J. F. Davidson, and A. N. Hayhurst, "The effects of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand," *Energy and Fuels*, vol. 21, no. 4, pp. 2072–2081, 2007.
- [9] A. I. Lysikov, A. N. Salanov, and A. G. Okunev, "Change of CO<sub>2</sub> carrying capacity of CaO in isothermal recarbonation-decomposition cycles," *Ind. Eng. Chem. Res.*, vol. 46, no. 13, pp. 4633–4638, 2007.
- [10] E. J. Anthony, "Thermal Activation of CaO-Based Sorbent and Self-Reactivation during CO<sub>2</sub> Capture Looping Cycles-Manovic.pdf," vol. 42, no. 11, pp. 4170–4174, 2008.
- [11] V. Manovic and E. J. Anthony, "Reactivation and remaking of calcium aluminate pellets for CO<sub>2</sub> capture," *Fuel*, vol. 90, no. 1, pp. 233–239, 2011.
- [12] F. C. Yu, N. Phalak, Z. Sun, and L. S. Fan, "Activation strategies for calcium-based sorbents for CO<sub>2</sub> capture: A perspective," *Ind. Eng. Chem. Res.*, vol. 51, no. 4, pp. 2133–2142, 2012.

- [13] F. Donat, N. H. Florin, E. J. Anthony, and P. S. Fennell, "Influence of high-temperature steam on the reactivity of CaO sorbent for CO<sub>2</sub> capture," *Environ. Sci. Technol.*, vol. 46, no. 2, pp. 1262–1269, 2012.
- [14] F. Yan, J. Jiang, K. Li, S. Tian, M. Zhao, and X. Chen, "Performance of Coal Fly Ash Stabilized, CaO-based Sorbents under Different Carbonation-Calcination Conditions," *ACS Sustain. Chem. Eng.*, vol. 3, no. 9, pp. 2092–2099, 2015.
- [15] M. Broda, R. Pacciani, and C. R. Müller, "CO<sub>2</sub> Capture via Cyclic Calcination and Carbonation Reactions" in *Porous Materials for Carbon Dioxide Capture*, pp. 181–222, 2014.
- [16] C. I. C. Pinheiro, A. Fernandes, C. Freitas, E. T. Santos, and M. F. Ribeiro, "Waste Marble Powders as Promising Inexpensive Natural CaO-Based Sorbents for Post-Combustion CO<sub>2</sub> Capture," *Ind. Eng. Chem. Res.*, vol. 55, no. 29, pp. 7860–7872, 2016.