

Post combustion CO₂ sorbents from carbonate rocks: marble, limestone and dolomite

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ABSTRACT: Portuguese carbonate rocks (marble, limestone and dolomite) wastes were used to produce CaO sorbents for post-combustion carbon capture. The raw materials were crushed, reduced to powder, and calcined at 850°C. The marble and carbonate rock based sorbents were lime whereas dolomite based sorbent was a CaO-MgO mixed material. The cyclic carbon capture of sorbents was assessed by thermogravimetry using CO₂ diluted in N₂ mixtures for both carbonation/calcination steps. All the prepared sorbents showed deactivation due to sinterization as observed by scanning electron microscopy. The dolomite based sorbent showed an improved stability due to the effect of monophasic spacer rolled by MgO

Keywords: CO₂ capture, CCS, calcium looping, lime, sinterization, monophasic spacer, carbonate rocks

1. Introduction

The planet faces huge climate problems due to anthropogenic greenhouse gases (GHG) emissions. Considerable evidence exists that global warming has been caused by human activities, changing the chemical composition of the atmosphere through a buildup of greenhouse gases – primarily carbon dioxide, methane and nitrous oxide (Figure 1).

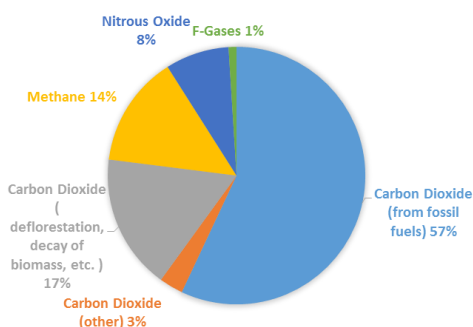


Figure 1 - GHG emissions from human activities in 2007, adapted from [1]

According to IPCC (Intergovernmental Panel to Climate Change), the rising of the average global temperature in more than 2°C could have catastrophic consequences, such as floods, extreme heat waves, and so on. For this reason, the mission is to reduce this rising temperature between now and 2100. To achieve this goal, the Greenhouse Gases (GHG) should be reduced by between 40% and 70% until 2050, and carbon neutrality must be achieved until the end of the century, at least. [2]

Post combustion carbon capture can be performed using the cyclic carbonation of calcium oxide. Such sorbents suffer fast deactivation due to sinterization.

2. Experimental

2.1 Materials and methods

The as received carbonate rocks (marble, limestone and dolomitic limestone; Figure 2) were crushed and reduced to powder (<150 μm).

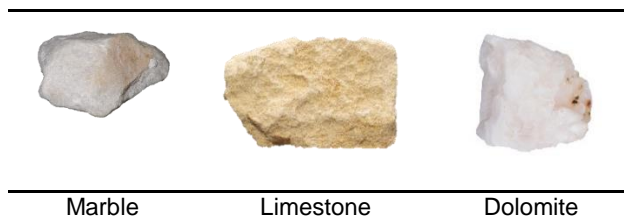


Figure 2 – Raw carbonate rocks used as lime sorbents precursors

The calcination temperature was chosen taking into account the thermal degradation profile obtained by thermogravimetry under air flow (heating rate:20°C/min). In order to evaluate the effect of the calcination temperature the sorbents were calcined in the range 750°C-1100°C for 3h in a muffle. The as prepared sorbents were characterized by X-ray diffraction, HATR-FTIR, and SEM-EDS. The sinterization of the spent sorbents, after 12 or more cycles of carbonation/decarbonation, was assessed by SEM.

The cyclic carbon capture of sorbents was assessed by thermogravimetry using CO₂ diluted in N₂ mixtures for both carbonation/calcination steps. The procedure was carried out using the operating parameter summarised in the Table 1.

Table 1 – Experimental conditions during cyclic carbonation/decarbonation tests

Carbonation	Temperature (°C)	750
	time (s)	1800
	CO ₂ (% V/V)	20
	N ₂ (% V/V)	80
Decarbonation	Temperature (°C)	850
	time (s)	1800
	CO ₂ (% V/V)	20
	N ₂ (% V/V)	80

3. Results and Discussion

The thermograms, under air, for the powdered rocks in the Figure 3 showed decomposition profiles ascribable to CaCO₃ decarbonation for marble and limestone samples. The dolomite sample showed a more complex decomposition profile which is in accordance with previously published results [3]. For all the analyzed samples the decarbonation process started at temperatures slightly lower than 750°C thus 750°C was chosen as the lowest calcination temperature to prepare lime sorbents.

The raw sorbents displayed morphologies similar to those previously published for lime sorbents calcined in similar conditions [4]. The calcination temperature had a major role on the morphology of the prepared sorbents since it promotes sinterization. The elemental analysis performed by EDS during SEM micrographies acquisition showed a high magnesium content for dolomite based sorbents (Table 2). The magnesium of dolomite based sorbents acted as a crystallites spacer [5]. The micrographies for such sorbents showed small crystallites MgO (Fig. 4) surrounding the CaO thus diminishing the CaCO₃ grains limits contact. It is believed that MgO reduces the sinterization phenomena.

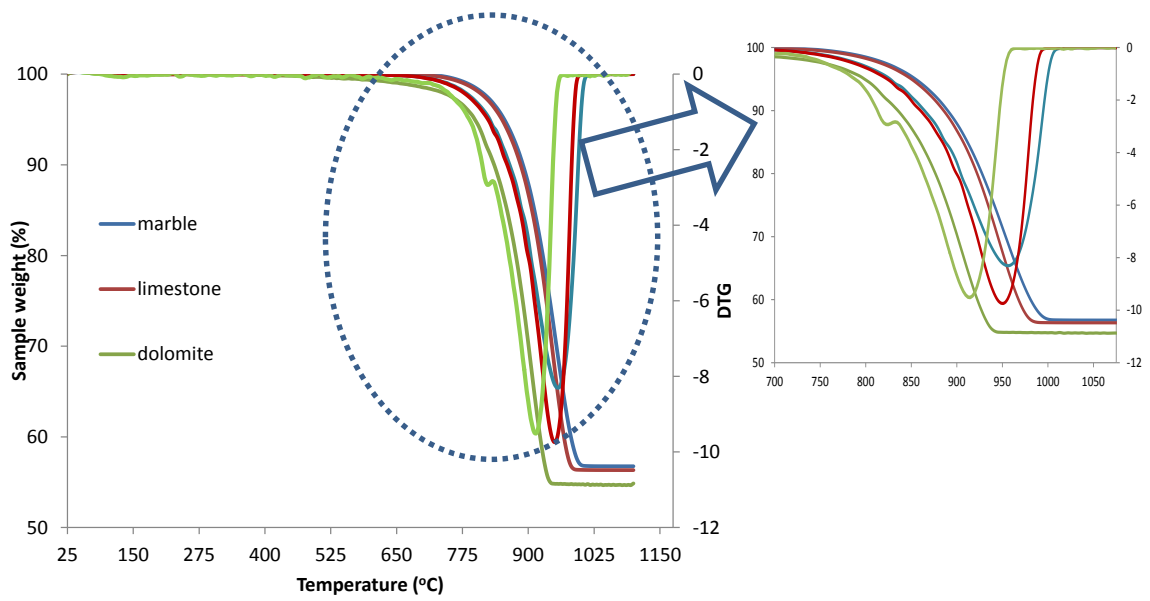


Figure 3 –Thermograms of raw carbonate rocks (air flow; 20°C/min).

Table 2 – EDS elemental analysis of dolomite sorbent calcined at 850°C

Element	Atomic%
C K	5.30
O K	63.48
Mg K	15.20
Ca K	15.25
Au M	0.76
Total	100

Electron Image 1

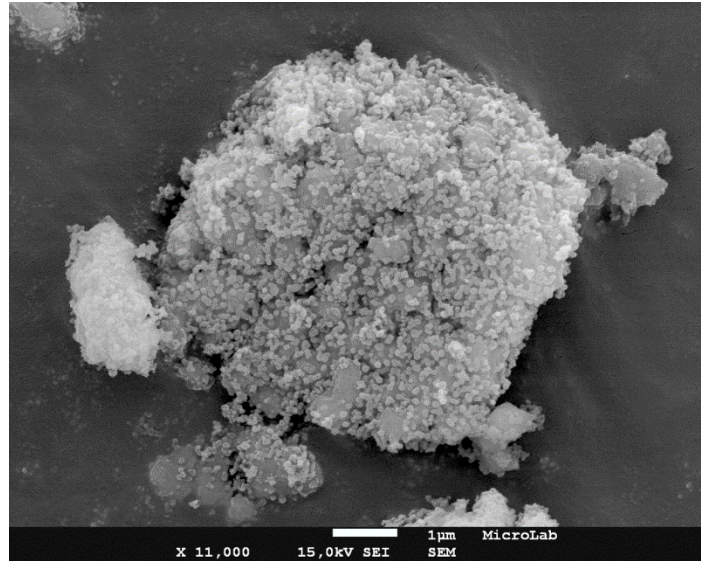


Figure 4 – SEM micrograph of fresh sorbent prepared (calcination temperature) from dolomite (small crystallites of MgO surrounding CaO crystallites)

The tested sorbents prepared from different carbonate rocks showed slightly different initial CO₂ carrying capacities (Fig. 5) mainly due to particles sizes distributions. All the analyzed sorbents showed activity decay in cyclic capture, as referred in

literature, which can be ascribed to sinterization. Such occurrence was confirmed by SEM analysis of the post capture sorbents. The dolomite based sorbent was, as expected, the most stable sorbent due to the MgO spacer effect above referred.

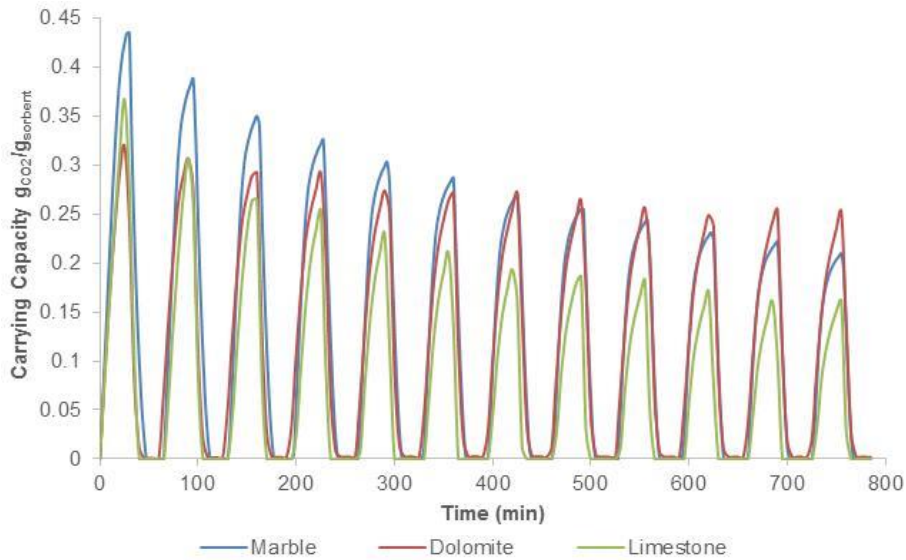


Figure 5 – Carrying capacity of carbonate rocks calcined at 850°C (20% CO₂ in N₂ (V/V); carbonation 750°C; 30 min; decarbonation 850°C; 30 min).

4. Conclusions

Portuguese carbonate rocks (marble, limestone and dolomite) wastes were used to produce CaO sorbents for post-combustion carbon capture. The raw materials were crushed, reduced to powder, and calcined at 850°C. The marble and carbonate rock based sorbents were lime whereas dolomite based sorbent was a CaO-MgO mixed material.

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