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# **Dolomite study for in-situ CO<sub>2</sub> capture for chemical looping reforming**

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## **Dolomite study for in-situ CO<sub>2</sub> capture for chemical looping reforming**

The non- isothermal kinetic and thermal behaviour of a naturally formed dolomite in conditions that approach in-situ CO<sub>2</sub> capture in chemical looping reforming, chiefly the use of the packed bed configuration, were investigated. The performance of this dolomite was studied at micro-scale in 'dry' conditions, as well as at macro-scale in 'dry' and 'wet' conditions to investigate the effects of scale (3mg, 2.5g), partial pressures of CO<sub>2</sub> (<15kPa) and steam, and deactivation upon limited cycling. The carbonation and calcination kinetics were modelled using an improved iterative Coats-Redfern method. Increasing CO<sub>2</sub> partial pressures on the 'dry' macro-scale exacerbated the experimental carbonation conversions in an inversely proportional trend when compared to those at micro-scale. The presence of steam had a positive effect on CO<sub>2</sub> chemisorption. Steam had a negligible influence on the calcination activation energies. The activation energies of carbonation were increased for the experiments at the highest CO<sub>2</sub> partial pressures under wet conditions.

Keywords: dolomite, CO<sub>2</sub> capture, kinetics, modelling, steam

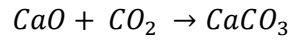
## 1. Introduction

At present, there is an intense interest in chemical looping systems (Blamey *et al.* 2010, Li *et al.* 2008) which have so far been mainly developed for the combustion industry and applied to fluidized bed technology (Chen *et al.* 2011, Sun *et al.* 2008). Lyon and Cole (2000) suggested unmixed combustion which has been lately deployed in the chemical looping technology (Dupont *et al.* 2007, Pimenidou *et al.* 2010a). Furthermore, the reduction of CO<sub>2</sub> emissions is a topic of particular priority in the framework of sustainable energy and low-carbon energy technologies as well as a key issue in today's agenda of most of the developed countries. By incorporating simultaneously the chemical looping reforming and ('in- situ') CO<sub>2</sub> capture (Curran *et al.* 1967, Pimenidou *et al.* 2010b, Giannakeas *et al.* 2012), a high purity H<sub>2</sub> product emerges, without any further separation of unwanted product gases, for direct utilisation i.e. in fuel cells. Calcium looping particularly proved to be the cheapest option for CO<sub>2</sub> capture (Romeo *et al.* 2009) based on CO<sub>2</sub> avoided cost (Abanades *et al.* 2007).

Moreover, materials are sought for CO<sub>2</sub> capture, which will reduce the energy consumption by increasing the production efficiency of the energy carriers. There is a great variety of synthetic CO<sub>2</sub> capture materials currently applied, such as zeolites (e.g. NaX, 5A), which pose some difficulty in adsorbing H<sub>2</sub>O when used to capture CO<sub>2</sub> from gases. Most of synthetic materials are costly to produce (such as zeolites for physisorption and MEA (Monoethanolamine)) when their application is energy consuming (Rao and Rubin 2006). Dolomite and dolomite based sorbents offer smaller efficiency penalties than amine- based post- combustion capture. Calcium oxide (CaO) used for CO<sub>2</sub> capture was first mentioned by DuMotay and Marechal in 1867 who enhanced the gasification of carbon by steam with lime (Barker 1973). The suitability of metal oxides (Me<sub>x</sub>O<sub>y</sub>) in capturing CO<sub>2</sub> at temperatures

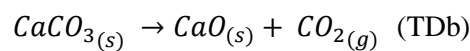
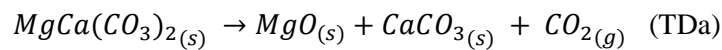
between 550°C and 750°C at atmospheric pressure (101.3 kPa) has been demonstrated in the past six decades (Pimenidou *et al.* 2010b, Hyatt *et al.* 1958, Squires 1967, Dou *et al.* 2010).

The key reaction for the capture of CO<sub>2</sub> by CaO is the following,

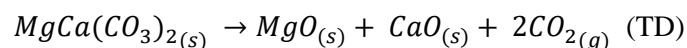


which is considered in post- combustion or in-situ capture of CO<sub>2</sub> processes as well as in energy storage (Aihara *et al.* 2001) with further encounter in flue gas CO<sub>2</sub> separation (Han and Harrison 1994) and hydrocarbon and water gasification for H<sub>2</sub> production (Gupta and Fan 2002). The exothermicity of this reaction has also proven to offer autothermal intervals during in- situ use in chemical looping steam reforming for hydrogen production (Pimenidou *et al.* 2010b).

Calcium oxide may be formed from the thermal decomposition (calcination) of dolomite, which when in a CO<sub>2</sub> environment takes place in two stages (Gupta and Fan 2002, McIntosh *et al.* 1990, Chrissafis *et al.* 2005a, Chrissafis *et al.* 2005b):



MgO gives stability in the sorbent's structure which in the long term gives more durability to this material compared to limestone (Gupta and Fan 2002). The thermal decomposition reaction of  $MgCa(CO_3)_2(s)$  may occur in a single step (McIntosh *et al.* 1990, Samtani *et al.* 2002) in an inert environment as in pure gaseous nitrogen (N<sub>2</sub>),



This step regenerates the 'in- situ' adsorptive material in chemical looping steam reforming like in the exothermic oxidation step of air feed over the reduced Ni- based

catalysts (Dupont *et al.* 1997, Pimenidou *et al.* 2010a, Giannakeas *et al.* 2012, Dou *et al.* 2010). The reversibility of calcination has been confirmed by numerous investigators (Barker 1973, Chrissafis *et al.* 2005b).

Calcined dolomite fulfils the requirements of high carbonation capacity and low cost. When CaO is combined with a metal catalyst in chemical looping reforming, catalyst deactivation is prevented and unfavourable fuels conversion in a rich H<sub>2</sub> syngas is enhanced (Giannakeas *et al.* 2012). However, its stability under repeated calcinations/ carbonation cycles has often been rated as poor mostly based on microbalance and TGA studies ('micro-scale') (Chrissafis *et al.* 2005a), despite exhibiting a higher stability than limestone (Abanades and Alvarez 2003).

The kinetics of the calcination- carbonation reactions were sparsely studied, by L'vov and Ugolkov (2003), Olszak- Humienik and Mozejko (1999), Samtani *et al.* (2002) with regard to the calcinations and by Lee (2004) with regard to the carbonation reaction.

The effect of steam and CO<sub>2</sub> on these metal oxides was investigated in the high CO<sub>2</sub> pressure regime of the reaction (TDa) by Beruto *et al.* (2003). The effect of steam in the DTA analysis of CaCO<sub>3</sub> decomposition in nitrogen as well as in the carbon dioxide atmosphere found in calcite and dolomite was previously examined by McIntosh *et al.* (1990). Ochoa-Fernandez *et al.* (2007) posited that the increase in the kinetics and the carbonation capacity of synthetic ceramic CO<sub>2</sub> sorbents (Li<sub>2</sub>ZrO<sub>2</sub> and Na<sub>2</sub>ZrO<sub>2</sub>) due to the presence of steam was accredited to the increased ion mobility. Hydrotalcites have been reported to be ill-influenced by the presence of steam (Ficilar and Dogu 2006, Ding and Alpay 2000). The effect of steam which enhances the kinetics of carbonation of Ca based sorbents is a known but poorly quantified phenomenon, and is generally attributed to the increased CO<sub>3</sub><sup>2-</sup> ions transport in a steam environment.

In chemical looping reforming, the sorbent needs to exhibit fast kinetics during the CO<sub>2</sub> adsorption at low CO<sub>2</sub> partial pressures, while stability is maintained and capacity is regained. Operating under such conditions creates specific environments for the carbonation and the thermal decomposition of the sorbent. The morphology of CO<sub>2</sub> sorbents should be characterized by large pores with small particles and a large surface area in order to guarantee a long- lasting and efficient performance while sintering is minimized.

This study is focused on the kinetic and thermal study of naturally formed dolomite under conditions which assimilate chemical looping reforming at atmospheric pressure, offering the isolation of the adsorption and regeneration reactions mentioned earlier. These environments of in- situ CO<sub>2</sub> capture, chiefly the use of the packed bed configuration, low CO<sub>2</sub> partial pressure and the presence of steam are investigated and the produced apparent kinetic parameters are also discussed in order to determine optimum conditions of the in- situ employment of naturally formed dolomite in chemical looping reforming. Non- isothermal experiments were performed in a TGA (few milligrams; micro- scale) and lab reactor (few grams; macro- scale) in the absence ('dry' experiments) and in the presence ('wet' experiments) of steam.

## **2. Experimental and numerical section**

### **2.1 Experimental section**

*Material:* Natural dolomite was obtained through WBB Minerals (Warmsworth quarry, West Yorkshire, UK) as a graded aggregate in a fully carbonated form. The chemical analysis of the calcined dolomite, supplied as information data sheet, showed that its composition on a mass basis was: 30.70% CaO, 21.30% MgO, 0.30% SiO<sub>2</sub>, 0.27% Fe<sub>2</sub>O<sub>3</sub>, 0.10% Al<sub>2</sub>O<sub>3</sub> and 47.34% CO<sub>2</sub>. Particles of 1- 1.4 mm size were used in micro- and macro- scale experiments

after manually grinding and sieving (BS410) the as received dolomite. Natural dolomite from Spain of 1- 2 mm particles had been earlier used in packed bed reactor for chemical looping reforming (Dupont *et al.* 2007). For the kinetics study at micro- scale and for the thermal stability study 3 and 10 mg of these particles were used respectively, whereas for the investigation at macro- scale, 2.5 g of the same size ‘fresh’ (fully carbonated) dolomite particles were used.

*Micro- scale (Thermogravimetric analysis (TGA)) set- up:* A thermogravimetric analyzer (Shimadzu TGA-50) was used. Any changes in the weight of the sample were measured and recorded with the TA 60 data collection software while it was heated up at 10 °C min<sup>-1</sup> or cooled down with a cooling blower. Three heating/ cooling cycles were carried out for the kinetic study, at several pressures of gaseous CO<sub>2</sub> ( $P_{CO_2}$  = 5- 15 kPa) at 100 kPa N<sub>2</sub>. The required mass flow rate of each gas in the TGA was controlled by an MKS Instrument Type 247C four channel readout controller and verified by using a CSI 6000 Solid State calibration flow meter. The gas mixture flow rate was set at 50 cm<sup>3</sup> min<sup>-1</sup> (STP). The same heating rate and experimental set- up was also used in the thermal stability study only that an initial mass of 10 mg and a 10 kPa CO<sub>2</sub> pressure was used for both calcination/ carbonation steps.

*Macro- scale set-up:* The set- up of these experiments was performed in a reactor rig as in Pimenidou *et al.* (2010a). The sorbent samples were sandwiched between beds of alumina oxide granules (4-8 mesh; SIGMA ALDRICH). Macro- scale calcination and carbonation runs occurred at a heating rate of 10 °C min<sup>-1</sup> (up to 800 °C) as in the micro- scale experiments. The linearity of the temperature increase in the reactor was verified in the dolomite bed. Temperatures were monitored by 3 thermocouples (Type K) inserted in the sorbent bed; one at the top surface, one in the middle of the sorbent bed and the third one at the bottom surface of the bed. The gases flowed from the bottom end of the reactor and left at



the top end. In both ‘dry’ and ‘wet’ experiments the flow rate of N<sub>2</sub> was 750 cm<sup>3</sup> min<sup>-1</sup> (STP), with the CO<sub>2</sub> flow added to it for the carbonation runs resulting in pressures of 5, 10 and 15 kPa CO<sub>2</sub> ( $P_{CO_2}$ ). Similarly to the micro- scale experiments, the maximum volume of CO<sub>2</sub> which would be required for the full carbonation of the maximum theoretical CaO moles from the fully calcined 2.5 g of the fresh sorbent (MgCa(CO<sub>3</sub>)<sub>2</sub>) was calculated in order to ensure the reactant gas was in excess. This CO<sub>2</sub> volumetric flow rate corresponds to the following molar flow rate,

$$\dot{n}_{CO_2} = \frac{P\dot{V}_{CO_2}}{RT} = \frac{(101.325 \text{ kPa}) \times (0.05 \text{ L min}^{-1})}{(8.314 \text{ L kPa K}^{-1} \text{ mol}^{-1} \text{ 293K})} = 0.021 \text{ moles min}^{-1}$$

which is sufficient for the  $n_{\max (CaO)} = 0.0137$  moles. For the ‘wet’ experiments, deionised water was pumped in a pre-heater situated beneath the reactor and was evaporated at 200°C; the temperature of the reactor was also at 200°C when the steam was initially supplied. During the ‘wet’ runs, the liquid flow rates of deionised water used were: 0.017, 0.045 and 0.073 cm<sup>3</sup> min<sup>-1</sup> for the 5, 10 and 15 kPa CO<sub>2</sub> pressures. This resulted in H<sub>2</sub>O vapor partial pressures of 2.8, 6.8 and 10.1 kPa ( $P_{H_2O}$ ). Steam leaving the reactor was condensed and any left- over moisture was trapped downstream of the condenser using a silica gel trap. A second silica gel trap was used just upstream of the analyzer in order to avoid moisture entering it.

CO<sub>2</sub> content in the effluent gases was monitored online by an NDIR absorption gas analyzer (Uras 14, ABB), connected to a display and control unit. The smallest measurement range for CO<sub>2</sub> was 0-100 ppm. Similarly to the micro- scale thermal stability study, the ‘dry’ and ‘wet’ macro- scale tests were performed for both calcination and carbonation steps at 10 kPa CO<sub>2</sub> during heating at a rate of 10 °C min<sup>-1</sup>. All experiments were conducted at atmospheric pressure in order to avoid resistance of external mass transfer.

## 2.2 Numerical

### 2.2.1 Micro- scale calculations

Conversions of the reactants in the calcination and carbonation reactions under all conditions were calculated based on the absolute CO<sub>2</sub> capacity of the employed mass of sorbent. The final conversion of the reactants, for both calcination/ carbonation reactions, is defined by:

$$a^i(\%) = \frac{M^o}{W_{CO_2}} \cdot \frac{(P_{sorb}^i - P_{sorb}^{f,i-1})}{N_{sorb}^{f,i-1}} \quad (1)$$

$$\text{where } P_{sorb}^i = 100 \times \frac{M_{sorb}^i}{M_{sorb}^{f,i-1}} \quad (2)$$

$P_{sorb}$  is the percentage mass of the sorbent (oxide + carbonate; CaO.CaCO<sub>3</sub>) remaining in the TGA crucible at any time during a specific step of the experiment of index 'i'.  $M^o$  is the initial mass of 'fresh' dolomite in the TGA crucible while  $M_{sorb}^i$  is the mass of sorbent remaining in the TGA at any time during the experiment of index 'i'. The integer superscripts  $i-1$  and  $i$  indicate preceding and present runs (steps) respectively.

By the end of the thermal decomposition the final molecules of CaCO<sub>3</sub> ( $N_{CaCO_3}^{f,i}$ ) and CaO ( $N_{CaO}^{f,o}$ ) in the sample were calculated by equations 3 and 4, when  $(-1)^i < 0$ ,

$$N_{CaCO_3}^{f,i} = \left(1 - \frac{\alpha^{f,i}}{100}\right) \cdot N_{CaCO_3}^{f,i-1} \quad (3)$$

$$N_{CaO}^{f,i} = \left(1 - \frac{\alpha^{f,i}}{100}\right) \cdot N_{CaCO_3}^{f,i-1} + N_{CaO}^{f,i-1} \quad (4)$$

### 2.2.2 Macro- scale calculations

Based on elemental balances for the thermal decomposition of the sorbent, the conversion for  $MgCO_3$  is expressed as:

$$\% \alpha_{MgCO_3}^{TD_i} = 100 \cdot \left( \frac{\Delta N_{CO_2}}{N_{MgCO_3}} \right) \quad \text{for } \frac{\Delta N_{CO_2}}{N_{MgCO_3}} < 1, \quad (5)$$

and

$$\% \alpha_{MgCO_3}^{TD_i} = 100 \cdot \left( \frac{\Delta N_{CO_2} - N_{MgCO_3}}{N_{MgCO_3}} \right) \quad \text{for } \frac{\Delta N_{CO_2}}{N_{MgCO_3}} \geq 1. \quad (6)$$

where  $\Delta N_{CO_2}$  is the net number of  $CO_2$  moles that have evolved from the reactor during the  $i^{th}$  thermal decomposition ( $TD_i$ ) step, and  $N_{MgCO_3}$  is the number of  $MgCO_3$  moles in the ‘fresh’ dolomite.

The conversion ( $\% \alpha_{CaCO_3}^i$ ) for the calcination of  $CaCO_3$ , is,

$$\alpha_{CaCO_3}^i (\%) = 100 \cdot \frac{(\Delta N_{CO_2})}{N_{CaCO_3}^{f,i-1}} \quad \text{for } i > 1 \text{ and } (-1)^i < 0. \quad (7)$$

$\Delta N_{CO_2}$  is given by integrating the number of moles  $dN_{CO_2}$  that are evolved in the reactor over a time interval  $dt$ , which in this case was every 5 s,

$$\Delta N_{CO_2} = \int_{t_0}^t dN_{CO_2} = \int_{t_0}^t x_{CO_2,out} \cdot \dot{N}_{dry,out} dt \quad (8)$$

For the carbonation steps the following equation for  $(-1)^i > 0$ , was used for the calculation of the molar conversion ( $\% \alpha_{CaO}^i$ ),

$$\alpha_{CaO}^i (\%) = 100 \cdot \frac{(\Delta N_{CO_2})}{N_{CaO}^{f,i-1}} \quad (9)$$

The number of  $CO_2$  moles consumed,  $\Delta N_{CO_2}$ , was calculated by the following integral,

$$\Delta N_{CO_2} = \int_{t_0}^t dN_{CO_2} = \int_{t_0}^t (\dot{N}_{CO_2,in} - x_{CO_2,out} \cdot \dot{N}_{dry,out}) dt \quad (10)$$

### 3. Modelling theory

Useful kinetics for modelling purposes include the determination of the activation energy ( $E$ ) and the reaction order ( $n$ ) for the studied reactions. For this reason, the effects of temperature and gas concentration on the selected data were considered.

The improved iterative version of Coats- Redfern method (Urbanovici *et al.* 1999) was applied to evaluate the non- isothermal kinetic parameters. This method includes an iterative procedure which transforms the evaluation of the kinetic parameters ( $E$  and  $A$  (pre-exponential factor)) from a linear regression analysis. Additionally, the  $F$ - test (based on  $F$  – ratio =  $S_{reg}/S_{xy}^2$ , where  $S_{xy}$  : the sum of the squares of residual terms) was used as a complementary statistical criterion to identify the most probable mechanism function ( $g(\alpha)$ ). Residual mean square  $S_{xy}^2$  alone, cannot be used as a statistical criterion for selecting the most probable mechanism function,  $g(\alpha)$ , as suggested by Vyazovkin Lesnikovich (1986).

Reaction equations can potentially give the best simulation ('fit') of the experimental conversions as a temperature function for both micro- and macro- scale calcinations and carbonations based on the iterations' best correlation coefficient ( $r$ ) and  $E$  as well as on the calculated  $n$  when the  $n^{\text{th}}$  order reaction model is applied. The use of the  $F$ - test in the improved iterative Coats- Redfern method (Urbanovici *et al.* 1999) decreased the number of the considered kinetic to the following:

- (1) the Jander (3D) diffusion model,  $g(\alpha) = [1 - (1 - \alpha)^{\frac{1}{3}}]^2$
- (2) the power law,  $g(\alpha) = \alpha^{\frac{1}{m}}$ , for  $m= 1,2,3$  and  $4$
- (3) the  $n^{\text{th}}$  order reaction,  $g(\alpha) = \frac{[1-(1-\alpha)^{1-n}]}{1-n}$  for  $n \neq 1$ ,  $g(\alpha) = -\ln(1 - \alpha)$ .

The Jander model works for solid state processes, which are limited by the diffusion of one of the components through a layer of the product (Jander 1927) and therefore belong to the group of diffusion-limited models. The Jander model is often referred to as being 3D because it is a combination of the parabolic law (1D) and the contracting volume equation for  $n = 3$ . The Jander (3D) diffusion mechanism is well established in describing the kinetics and reaction mechanisms in gas – solid systems, such as hydrogen adsorption, especially for storage materials (Dou *et al.* 2010, Cui *et al.* 2008).

The conversion curves of thermal decompositions in both ‘dry’ and ‘wet’ macro-scale experiments were normalized between 0 and 1 as the minimum and maximum points during this reaction. The normalized conversion fractions ( $\alpha_{normalized}$ ) are calculated by the following equation:

$$\alpha_{normalized} = \frac{\Delta N_{CO_2,t=0} - \Delta N_{CO_2,t}}{\Delta N_{CO_2,t=0} - \Delta N_{CO_2,t,end}}$$

Uncertainties were considered based on an assumed error of 1% on both absolute temperature and conversion.

## 4. Results and discussion

### 4.1 Micro- scale

All calcinations were best described by the  $n^{\text{th}}$  order reaction equation and those following the first carbonations under 5 kPa CO<sub>2</sub> were of order 1.3 (Table 1). The calcinations following the first carbonation steps were harder to initiate compared to the earlier calcination steps as evidenced by the apparent calculated activation energies. The activation energies of the 2<sup>nd</sup> calcination which followed the 1<sup>st</sup> carbonation under all

conditions were higher in value. The larger presence of CaCO<sub>3</sub> in the sorbent, as indicated by the final conversions, reached in the 1<sup>st</sup> carbonation, might have delayed the initiation of the subsequent calcinations.

In the present study, diffusion was the governing kinetic control in the carbonation steps. In particular, the employment of the Jander (3D) integral kinetic equation which described the path of the reaction mechanism was employed and from the calculated kinetic parameters it was found that the conversion curves and the TGA data coincided. Hyatt *et al.* (1958) previously observed that the diffusion of CO<sub>2</sub> through CaCO<sub>3</sub> layers during re-carbonation might occur. Beruto *et al.* (1984) supported that the diffusion of CO<sub>2</sub> through the carbonate product layer on the surface of micropores was restricted by grain boundary layer diffusion. Additionally, it has been suggested that the CO<sub>2</sub> capture performance of Ca-based sorbents is enhanced by improving the diffusion of CO<sub>2</sub> through the product layer (Yi *et al.* 2009). Other researchers suggested that incomplete carbonations occurred due to the fact that the CO<sub>2</sub> reacted close to the exterior surface of a CaO particle, not allowing CO<sub>2</sub> to reach any CaO molecules closer to the particle centre (Chrissafis *et al.* 2005b). Therefore, the thicker the product (CaCO<sub>3</sub>) layer grew, the slower the reaction became. It was observed that during all 2<sup>nd</sup> carbonations, higher activation energies were required. This could accentuate diffusion limited conditions in the reactive system which was further depicted in the final conversions reached (Table 2). Interestingly enough, at the 15 kPa carbonation, the required activation energy in both the 1<sup>st</sup> and 2<sup>nd</sup> carbonations was set in the lowest value scale, compared to those at 5 kPa and 10 kPa CO<sub>2</sub>. In previous works (Sun *et al.* 2008) much lower values of the carbonation at 5 kPa CO<sub>2</sub> were calculated (26 kJ mol<sup>-1</sup>) compared to this study (90.4 kJ mol<sup>-1</sup>). This might be due to the fact that the apparent carbonation activation energy in that earlier work was produced by using the power law kinetic equation (Sun *et al.* 2008) when the present one was based on the Jander (3D) diffusion equation, resulting in more than twice as

large values between the first and second mechanism. Additionally, Urbanovici *et al.* (1999) found that a ratio of 2.7 was obtained in the case of isothermal  $\text{Mg}(\text{OH})_2$  dehydration when the power law equation was used compared to the Jander (3D) diffusion equation.

## 4.2 Macro- scale

No calcinations at macro- scale reached completion ( $\alpha \ll 1$ ), either under ‘dry’ or ‘wet’ conditions (Tables 2 and 3), during the heating up step as shown in the micro-scale study (Table 1). Still, the maximum conversion at macro-scale ‘dry’ conditions seemed to be affected in a positive way by the completeness of the previous carbonation. All calcination steps were set to reach  $800^\circ\text{C}$  in all experimental set- ups, since this is the maximum temperature employed in the air feed step corresponding to oxygen carrier regeneration (Dupont *et al.* 2007, Pimenidou *et al.* 2010a, Pimenidou *et al.* 2010b, Giannakeas *et al.* 2012, Dou *et al.* 2010). Actually, when switching from the air feed step to the fuel feed step, the temperature decreases from  $800^\circ\text{C}$  to  $600^\circ\text{C}$ , and based on the current experimental conversions’ results it was noticed that calcination still took place. Due to the packing effect the sorbent’s bed temperature reached temperatures higher than  $800^\circ\text{C}$ . Calcination steps under ‘dry’ and ‘wet’ conditions concluded during the cooling down intervals possibly as a result of the heat accumulated within the sorbent’s bed which allowed the further thermal decomposition of the material. This is the reason the experimental initial, maximum and final calcination temperatures for the ‘dry’ and ‘wet’ macro- scales in Table 2 are shown.

Despite that calcination steps were performed in an inert environment, a discontinuity in  $\text{CO}_2$  released during these experiments occurred at the same temperature as that observed in the thermal stability ‘dry’ micro- scale calcination which occurred in the presence of  $\text{CO}_2$ . This could have occurred due to self-creation of a  $\text{CO}_2$  atmosphere which resulted from the

larger mass of the sorbent used in the reactor. Such conditions were described by Bandi and Krapf (1976) and were attributed to the effect of the packing of the material. The presence of fines in both samples indicated the evolution of CO<sub>2</sub> during both 'dry' and 'wet' thermal decompositions and resulted in the breaking down of the dolomite particles, or the presence of any grains could have been an effect of calcination which produces more cracked grains as the sorbent decomposes (Figure 1). In previous studies (Silaban *et al.* 1996) it was noticed that the thermal decomposition in pure N<sub>2</sub> results in a more developed morphology, whereas in the presence of CO<sub>2</sub> (100 kPa CO<sub>2</sub>) (Manovic *et al.* 2009) larger grains are developed as larger pore diameters are formed.

The apparent activation energies for the first 'dry' calcinations showed that these reactions were harder to initiate than under 'wet' conditions. Due to the non- isothermal conditions, once the temperatures for the initiation of CaCO<sub>3</sub> thermal decomposition in the sorbent bed were reached, the thermal decomposition of MgCO<sub>3</sub> was terminated. All calcinations were expressed by the reaction order model but with a different order value (Tables 1, 3 and 4). Olszak- Humienik and Możejko (1999) reported activation energies of 219 kJ mol<sup>-1</sup> for the MgCO<sub>3</sub> thermal decomposition when using the Coats- Redfern method based on the diffusion (1D) equation. In that work, the calcination of CaCO<sub>3</sub> was expressed by the random nucleation model resulting in  $E= 390$  kJ mol<sup>-1</sup>. The latter value is in agreement with that of the 2<sup>nd</sup> 'dry' calcination following carbonation at 15 kPa CO<sub>2</sub>.

All first 'dry' carbonations steps showed that the higher the partial pressure of CO<sub>2</sub> was, the lower the final values of conversions reached were. These results do not agree with those of the micro- scale study. Packing of the sorbent in the case of the macro- scale set- up might not allow enough reaction time of the CO<sub>2</sub> with the dolomite particles. The conversion reached by the end of the second carbonation for the middle CO<sub>2</sub> partial pressure (10 kPa)



exhibited the higher drop in value from the respective one in the first carbonation and when compared to the final conversions of the second carbonation steps at 5 and 15 kPa of CO<sub>2</sub>.

Similarly to the present ‘dry’ macro- scale final carbonation conversions, Sun *et al.* (2008) noticed a better performance of carbonations when partial pressures of CO<sub>2</sub> smaller than 10 kPa were used, whereas for  $P_{CO_2} > 10$  kPa the respective performance was limited.

Experimental ‘dry’ carbonation conversions were extremely well reproduced from the iterative method described earlier based on the hypothesis of the Jander (3D) diffusion equation. The highest activation energy among the 1<sup>st</sup> carbonation steps was calculated at the lowest CO<sub>2</sub> partial pressure (5 kPa). This could be attributed to the extent of the preceding calcination ( $\alpha \cong 0.84$ ) which was limited compared to those that preceded the first carbonations at 10 and 15 kPa CO<sub>2</sub> ( $\alpha = 0.96$  and  $0.91$  respectively). Higher energy was needed during the second ‘dry’ carbonation at 10 kPa compared to the respective steps in the other two CO<sub>2</sub> conditions. During the second ‘dry’ carbonation at 15 kPa CO<sub>2</sub> the lowest final conversion for that step was attained which reflected on low apparent activation energies (i.e.  $119 \text{ kJ mol}^{-1}$ ; Table 4).

The calculated conversion curves corresponding to the 1<sup>st</sup> carbonation are superimposable on the experimental curve for the whole range of conversions (Figure 2), while the correlation coefficients indicate an excellent model (Table 3).

#### 4.2.1 The effect of steam

The final conversions of the sorbent’s first calcination (e.g. 0.89 in the lower ‘wet’ CO<sub>2</sub> pressure regime) were not seriously affected by the use of steam when compared to the respective ‘dry’ macro- scale results (e.g. 0.84 at 5 kPa CO<sub>2</sub>) (Table 2). Still the 2<sup>nd</sup> calcination at low partial pressures of steam resulted in an enhanced final conversion during

thermal decomposition (e.g. 2.8-6.8 kPa), but the effect was soon reversed at higher steam partial pressures (10.1 kPa). In past studies such as in McIntosh *et al.* (1990), the effect of steam appeared to have an enhancing impact on the thermal decomposition of Ca sorbents but not to the extent achieved in the present macro- scale study, especially at higher pressure regimes (Table 2). Higher final conversions were reached during the carbonations which might have been assisted by the presence of MgO, which resulted from the initial calcination of dolomite. The mobility of the CO<sub>2</sub> produced on the particles' surface might have been enhanced by the presence of steam resulting in a smaller residence time of the CO<sub>2</sub> produced than under 'dry' calcinations.

The calcinations' experimental conversions were best expressed by the reaction order model. The calculated reaction order was in the same value range in both the 'dry' and 'wet' 2<sup>nd</sup> calcinations following the carbonation in the middle CO<sub>2</sub> concentration range (i.e. 10 kPa CO<sub>2</sub>). Both 'dry' and 'wet' calculated activation energies for these 2<sup>nd</sup> 'dry' and 'wet' calcinations were in the range of 300 kJ mol<sup>-1</sup>. The 1<sup>st</sup> 'wet' calcination at 15 kPa CO<sub>2</sub> was found to be of order 2.9, when the  $n$  for the 2<sup>nd</sup> calcination was calculated to be equal to 1.2. The 2<sup>nd</sup> 'wet' calcination at 15 kPa CO<sub>2</sub> was easier to initiate as evidenced by the calculated activation energies, than the respective 'dry' one. Due to the greater number of available CaCO<sub>3</sub> moles, as indicated by the final conversion reached (Table 2), on the outer layers of the surface of the sorbent particles present in the reactor, a smaller energy supply was necessary for their thermal decomposition. This is the most probable explanation rather than the presence of steam, which did not seem to affect the rest of the 2<sup>nd</sup> 'wet' calcinations as shown in Tables 2 and 3.

The thermal swing regeneration step of the sorbent used in chemical looping reforming process may therefore benefit from the presence of a little steam but too much may prove counterproductive, and thus the safer approach would be to maintain 'dry' conditions

for calcination if possible. This is unlike hydrotalcite sorbents whose regeneration, under the thermal swing generated by steam addition, is recommended.

The 'wet' macro- scale experiments achieved a measurable positive effect on the final experimental absolute CO<sub>2</sub> capacity of the sorbent by increasing the carbonation reaction rate and the final conversions. The first and second carbonation curves in 'wet' conditions exhibited a greater activity than their 'dry macro and micro' counterparts (Figure 2). More specifically, the strongest effect of steam, promoting both the 1<sup>st</sup> and 2<sup>nd</sup> carbonations, was at the lowest and highest 'wet' CO<sub>2</sub> pressure regimes, while the effect of steam was slightly less for the middle 'wet' CO<sub>2</sub> pressure range. Steam could have resulted in a higher flow of the total gases and the better transport of CO<sub>2</sub> to the available CaO sites. For the lowest  $P_{CO_2}$ , the first 'wet' carbonation started at a lower temperature than the 'dry' one. It is worth noting that the temperatures where the carbonations began in this study were significantly lower than those reported in the literature (Abanades *et al.* 2007, Chrissafis *et al.* 2005a). This could be attributed to the non-isothermal conditions of the experiments, which allowed for the kinetic data generation from ambient to high temperatures, as opposed to the kinetic studies so far carried out at high temperature isothermal conditions.

The beneficial effect of steam at high CO<sub>2</sub> pressures was evidenced as carbonations were allowed to reach completeness (Table 2) based on the available CaO moles from the previous step. The catalytic presence of steam might have activated more sites during the carbonation steps which then led to a higher energy demand to reach the higher conversions at the higher 'wet' range of CO<sub>2</sub> pressures.

The kinetic parameters emerging from the micro- and macro- scale carbonation experiments are directly comparable since both were best calculated by the Jander (3D) diffusion equation. Any increase in the activation energies in the 'dry' and 'wet' macro- scale runs compared to those at 'dry' micro- scale is an issue that needs to be considered as it

clearly indicates that at macro- scale more energy is required to initiate carbonations. This might have to do with the larger masses employed and the packing of the material, as discussed earlier, as opposed to micro- scale and despite that in both cases the same size particles were used.

### 4.3 Thermal stability study

In neither the initial 'dry' nor 'wet' macro- scale thermal stability calcinations the sorbent was fully decomposed. The use of CO<sub>2</sub> and the additional CO<sub>2</sub> produced calcination might have retarded the extent of the decomposition of MgCa(CO<sub>3</sub>)<sub>2</sub> into MgO.CaO (Figure 3a). In the past, it was found that the rate of calcination of the CaCO<sub>3</sub> could slow down the overall rate of the dolomite decomposition rather than the MgCO<sub>3</sub> decomposition (Otsuka *et al.* 1986). Furthermore, non-uniform temperature gradients among the mass of the sorbent might have contributed to the incomplete MgCO<sub>3</sub> and CaCO<sub>3</sub> thermal decompositions due to the material's packing and consequently the retention of additional CO<sub>2</sub> around the sorbent's particles. The same trend of incomplete calcinations was followed by all 8 calcinations that succeeded the 9 carbonations, contrary to the micro- scale thermal stability study (Figure 3a).

Two CO<sub>2</sub> peaks during the macro- scale thermal decompositions, which originated from the MgCO<sub>3</sub> and CaCO<sub>3</sub> decompositions respectively, were distinguished (Figure 4a). It was noticed that the CaO carbonation reaction concluded at temperatures close to the initialization temperatures of the MgCO<sub>3</sub> thermal decomposition. These temperatures were confirmed by the earlier determined micro- scale experiments (Figure 4b). In particular, the 'dry' thermal decomposition of MgCO<sub>3</sub> in the TGA at 10 kPa CO<sub>2</sub>, occurred between 643 and 772°C while the 1<sup>st</sup> calcination of CaCO<sub>3</sub> started at 782°C and ended at 828°C. In the 'wet' experiments, the initial temperature of the MgCO<sub>3</sub> decomposition was lower than the

one under 'dry' conditions (587°C) whereas for the CaCO<sub>3</sub> the onset calcination temperature was in the range of 727-827°C.

Over the repeated calcination steps, these two CO<sub>2</sub> peaks tended to merge, forming a single curve with a shallow concavity, which was used to identify the temperature intervals of the two thermal decomposition reactions of MgCO<sub>3</sub> and CaCO<sub>3</sub>. The formation and decomposition temperatures of salts at different CO<sub>2</sub> pressures have already been found, in the literature, to coincide at the temperatures at which the equilibrium pressure is the CO<sub>2</sub> pressure used in the experiment Criado and Dianez (2004). Based on the previous observations, MgCO<sub>3</sub> had completely converted into MgO by the 3<sup>rd</sup> cycle of the 'dry' macro- scale experiments, whereas when in the 'wet' ones, this was achieved by the 2<sup>nd</sup> cycle (Figure 3a). From the same figure it became evident that the presence of steam improved the final experimental conversions reached. Beruto *et al.* (2003) mentioned that steam would accelerate the rate of the first half of the thermal decomposition of dolomite, corresponding to the decomposition of MgCO<sub>3</sub>, which is in agreement with this study. Moreover, the flow of steam could have allowed less residence time of the supplied and produced CO<sub>2</sub> compared to the 'dry' runs, something that promoted the thermal decomposition of MgCO<sub>3</sub>. When natural dolomite is employed on a grams- scale in chemical looping reforming it should preferably be used in a fully decomposed form in order to avoid the incompleteness of the MgCO<sub>3</sub> calcination in order for the CaCO<sub>3</sub> formed during the fuel feed step to benefit from the rapid highly exothermic air feed step (Pimenidou *et al.* 2010b).

An expected decreasing trend of re- carbonation was observed over the repeated cycles, as seen earlier in the 'dry' micro- scale stability runs. Still, the 'dry' macro- scale carbonations from the 3<sup>rd</sup> till the 5<sup>th</sup> cycle performed better than the respective ones at micro- scale. The 'dry' macro- scale carbonations showed a sudden decrease in yield from the 6<sup>th</sup> to the 9<sup>th</sup> cycle, an effect that did not coincide with the micro- scale findings (Figure 3b). Even

though  $\text{MgCO}_3$  was fully decomposed by the 2<sup>nd</sup> cycle under ‘wet’ conditions, the presence of MgO did not prevent sintering and the slow calcination can be attributed to shrunk or blocked passages as opposed to the expected high pore volume of the sorbent’s particles. In Figures 5a and 5b, the surface of the sorbent after the 9<sup>th</sup> carbonation at two magnifications (100  $\mu\text{m}$  and 20  $\mu\text{m}$ ) might not be of high resolution but sintering was obvious even in the smaller magnification. Additionally, in the previous figures the MgO.CaO-  $\text{CaCO}_3$  particles seemed solid and compact as a result of sintering, which limited any further carbonation. Similarly Chrissafis *et al.* (2005a) mentioned that sintering could limit the CaO carbonation over repeated cycles since there could not be sufficient diffusion of  $\text{CO}_2$  through the CaO pores.

In the ‘dry’ macro- scale set- up, the final experimental conversions achieved in early carbonations were greater than the respective ‘wet’ ones. After the completion of the ‘dry’ decomposition of  $\text{MgCO}_3$  which would no longer compete with the carbonation at the low temperature range during the 3<sup>rd</sup>, 4<sup>th</sup> and 5<sup>th</sup> carbonations, the values of the carbonation conversions were higher than in the first and second ones regardless of the extent of the  $\text{CaCO}_3$  calcinations, and hence the higher availability of CaO at the beginning of the carbonation steps. This phenomenon was not noticed under the ‘wet’ conditions even when the  $\text{MgCO}_3$  was fully decomposed. Additionally, under ‘wet’ conditions, the carbonation efficiency was more stable from cycle to cycle despite achieving lower conversions for up to the 8<sup>th</sup> cycle compared to the ‘dry’ carbonations from cycle 1 to 8 (Figure 3b). A similar effect of steam under chemical looping reforming conditions was evidenced by Pimenidou *et al.* (2010b) where the extent of CaO carbonation was stable from cycle 2 to 6. In Figure 3b it can be seen that by the ‘dry’ 9<sup>th</sup> carbonation the conversion fraction was poorer than under the ‘wet’ conditions. Therefore, despite the lower performance of the ‘wet’ carbonations over

the 'dry' ones, the presence of steam actually enhanced the stability of the sorbent over the 9 cycles in terms of CO<sub>2</sub> adsorption.

The repeated cycles of calcination/ carbonation exhibited an asymptotic trend in CO<sub>2</sub> capture performance which could be due to the equilibrium reached between the reduction of the surface area and pore volume (Florin and Harris 2009). In theory, highly sintered dolomite could be a suitable sorbent for SO<sub>2</sub> removal because of the regeneration of macropores during the calcination/ carbonation cycles (Sun *et al.* 2007). When sulphur containing fuels are used, lower effective diffusivity will characterize the CaO based sorbent. Sintering decreases the number of small pores and creates large ones which can accelerate calcination in later stages which enhances SO<sub>2</sub> capture.

## **5. Conclusions**

This study has demonstrated the effect of sample weight, set-up (scale) and steam on the CO<sub>2</sub> capture performance of naturally formed dolomite under conditions imitating those of chemical looping steam reforming. The lab reactor scale indicated that a self-evolving atmosphere of CO<sub>2</sub> during the calcination steps (i.e. regeneration of sorbent) could reduce the extent of production of the desired CaO amount of capturing CO<sub>2</sub> in the carbonation steps (i.e. in steam reforming). Steam appeared to have a positive effect on CO<sub>2</sub> capture at its highest employed pressure regime (i.e. 15 kPa CO<sub>2</sub>/ 10.1 kPa H<sub>2</sub>O).

The carbonation reactions were diffusion limited at all scales and conditions ('dry' and 'wet'), which was evidenced by the shape of the experimental conversion curves and the equation (Jander (3D)) used to reproduce the modelled conversion curves. The calculated activation energies at the highest 'dry' pressure regime of CO<sub>2</sub> at larger scale confirmed that the presence of steam had a positive catalytic effect on the sorbent's final conversions.

Therefore, the use of in- situ CO<sub>2</sub> capture should promote fast kinetics and the CO<sub>2</sub> chemisorption in delivering high H<sub>2</sub> purity, enhance fuel conversion, and lower operational temperatures, better than in the absence of sorbent.

The thermal stability study at both tested scales under all conditions indicated large decay of the sorbent's capture in CO<sub>2</sub> due to sintering of the material. Still, the presence of steam exhibited a stabilisation effect on the sorbents carbonation conversions at the final larger scale cycles.

Overall, the present study showed that the in- situ use of naturally formed dolomite for chemical looping steam reforming could benefit from the absence of steam during the regeneration steps of the sorbent. Full calcination of the sorbent shouldn't be expected as indicated by the present larger scale study and compared to the present and earlier milli- gram scale investigations. On the other hand, the higher CO<sub>2</sub> partial pressures created during the steam reforming steps and the 'wet' conditions are expected to boost the sorbent's CO<sub>2</sub> capture efficiency despite the expected natural decay due to sintering which over repeated cycles should be stabilised.

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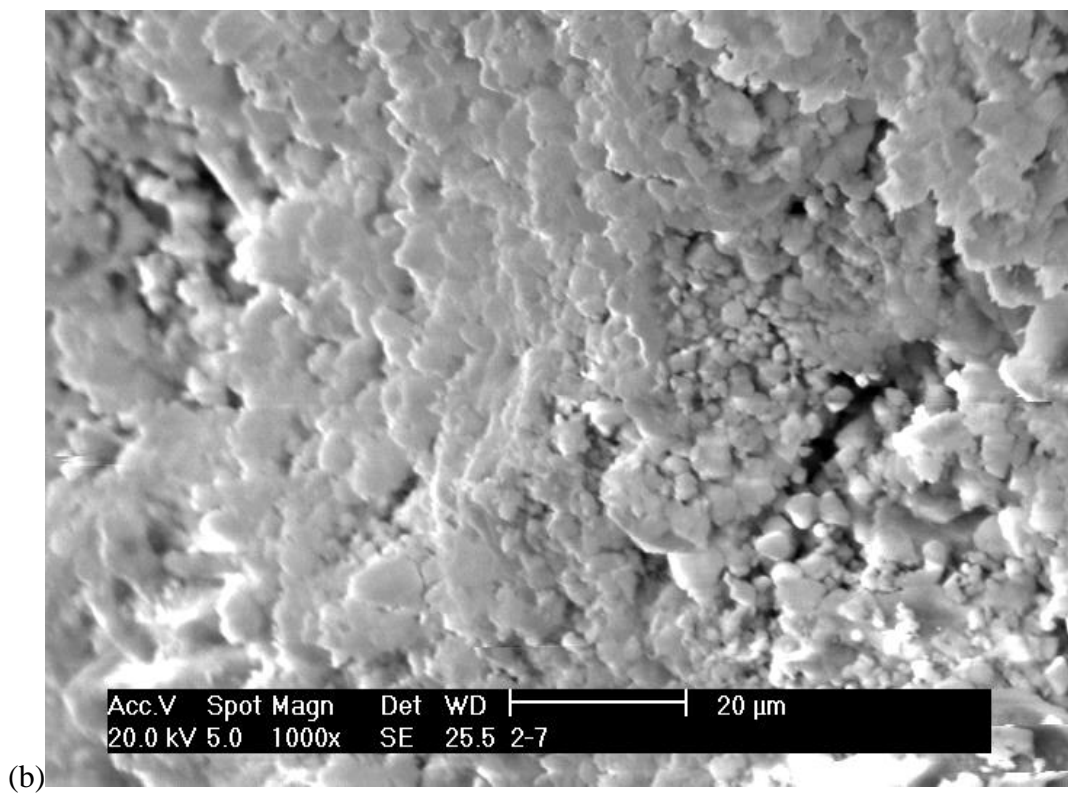
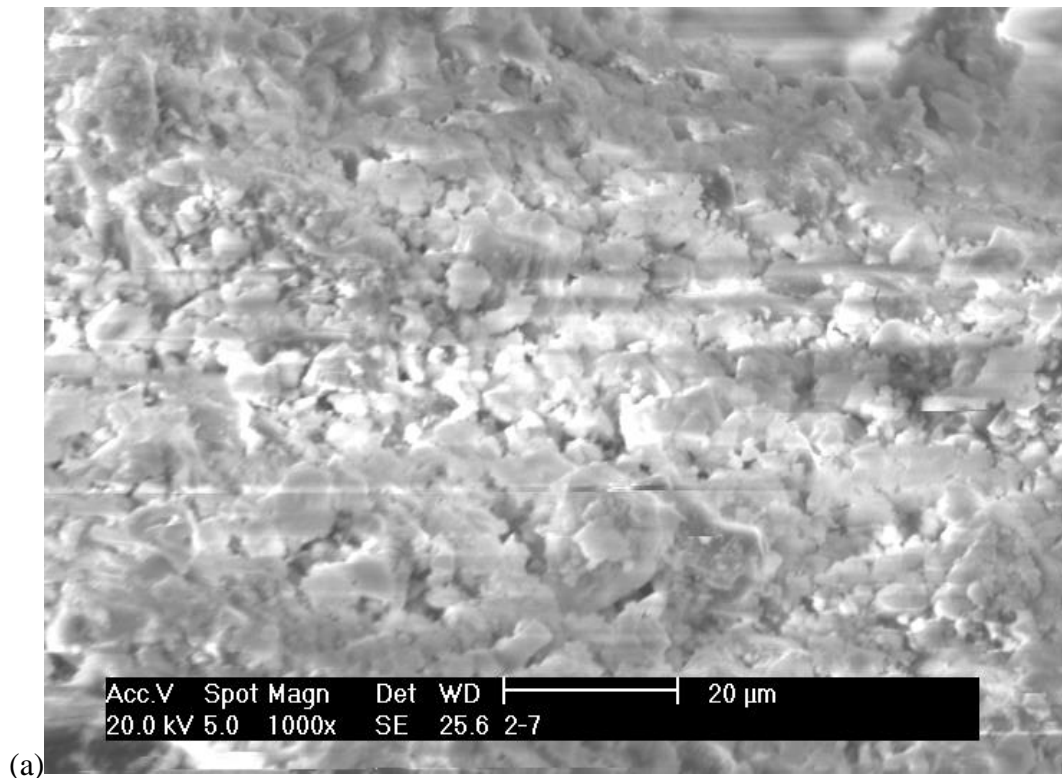
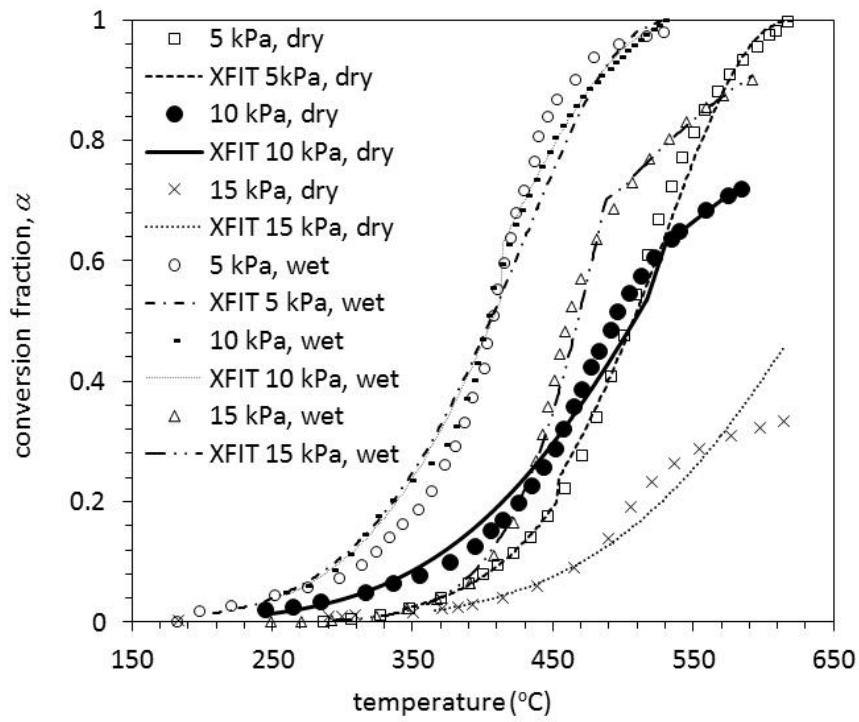
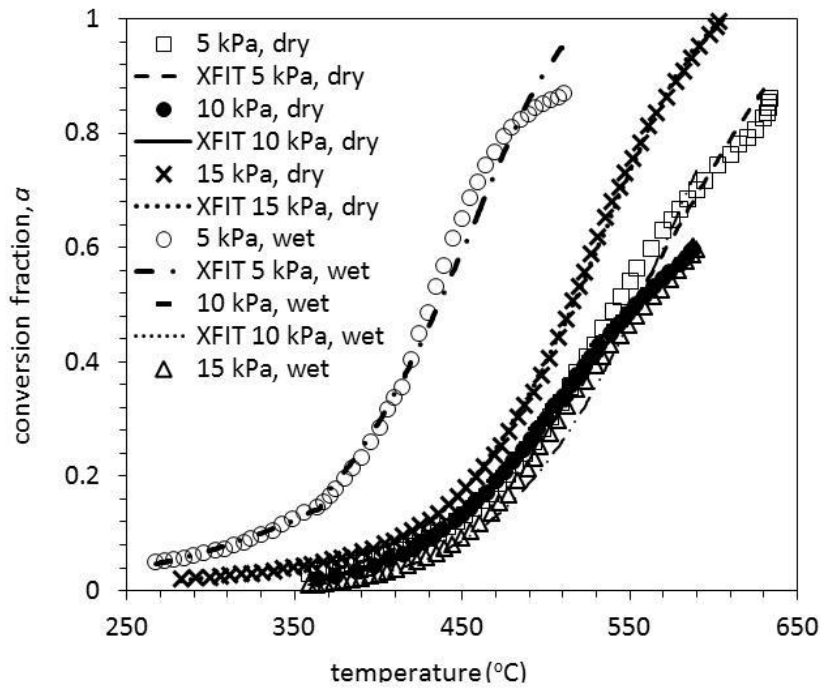


Figure 1. (a) 'Dry' and (b) 'wet' macro- scale SEM images of the sorbent after the 1<sup>st</sup> thermal decomposition at 100 kPa N<sub>2</sub>.

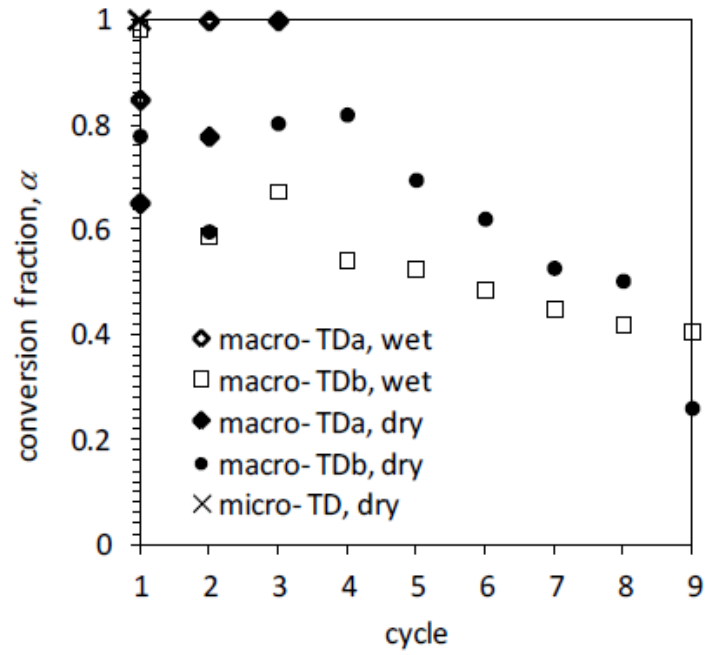


(a)

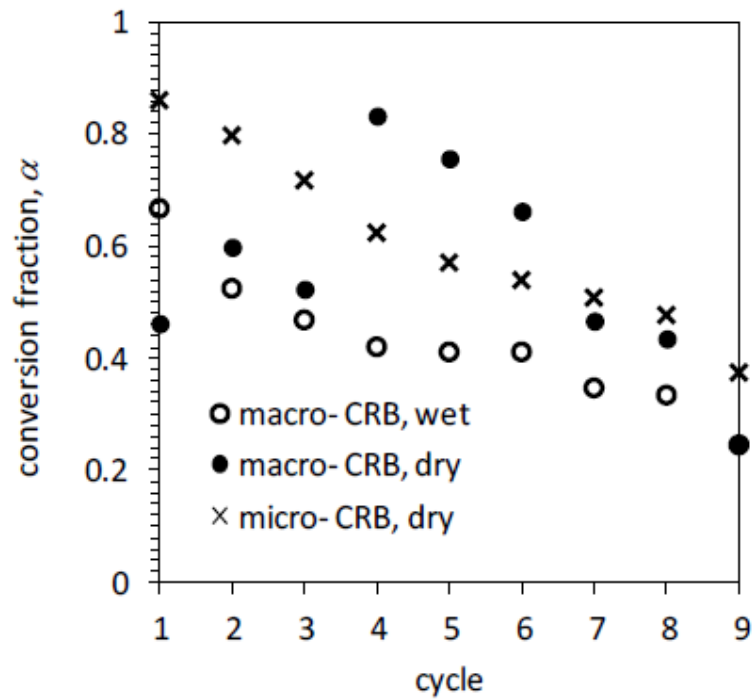


(b)

Figure 2. ‘Dry’ and ‘wet’ macro- scale experimental conversion ( $\alpha$ ) at and model fit ( $\alpha_{FIT}$ ) of the (a) 1<sup>st</sup> and (b) 2<sup>nd</sup> carbonations; at 5, 10 and 15 kPa CO<sub>2</sub> over temperature.



(a)



(b)

Figure 3. Micro- ('dry') and macro- scale ('dry' and 'wet') conversions of 9 consecutive (a) thermal decomposition- (b) carbonation cycles. Carbonations under 'dry' condition at 10 kPa CO<sub>2</sub> and under 'wet' conditions at 10 kPa CO<sub>2</sub>/ 6.8 kPa H<sub>2</sub>O.



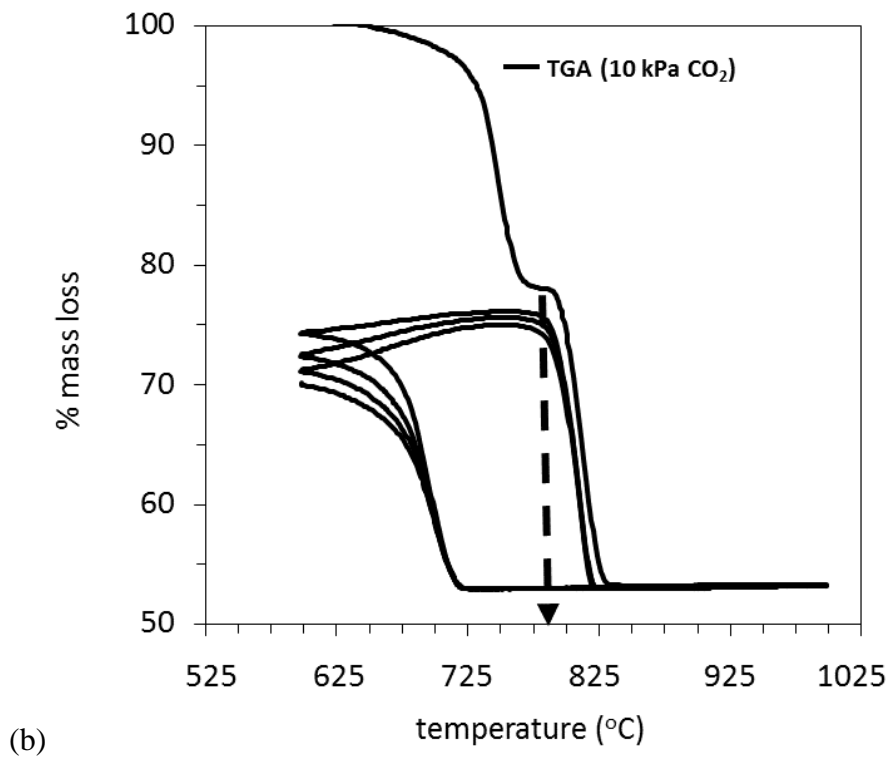
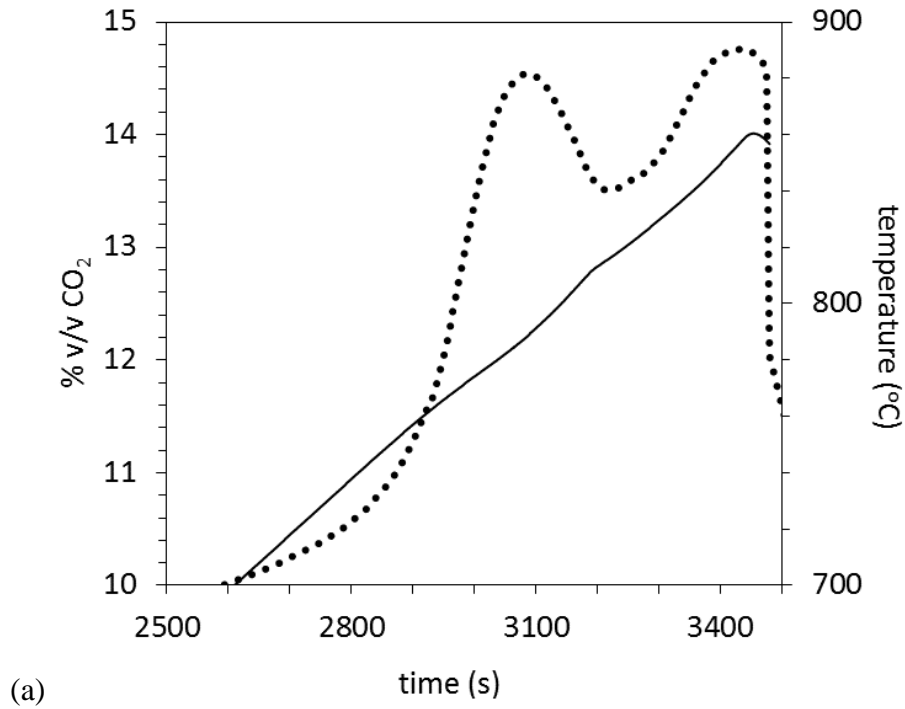


Figure 4. (a) CO<sub>2</sub> concentration (scatter points) and reactor temperature (line) with time. First peak corresponds to the MgCO<sub>3</sub> decomposition; second peak is the CaCO<sub>3</sub> decomposition in macro- scale ('dry') (b) micro- scale (same conditions) temperatures (the arrow indicates the initial temperature of the first thermal decomposition of CaCO<sub>3</sub>).

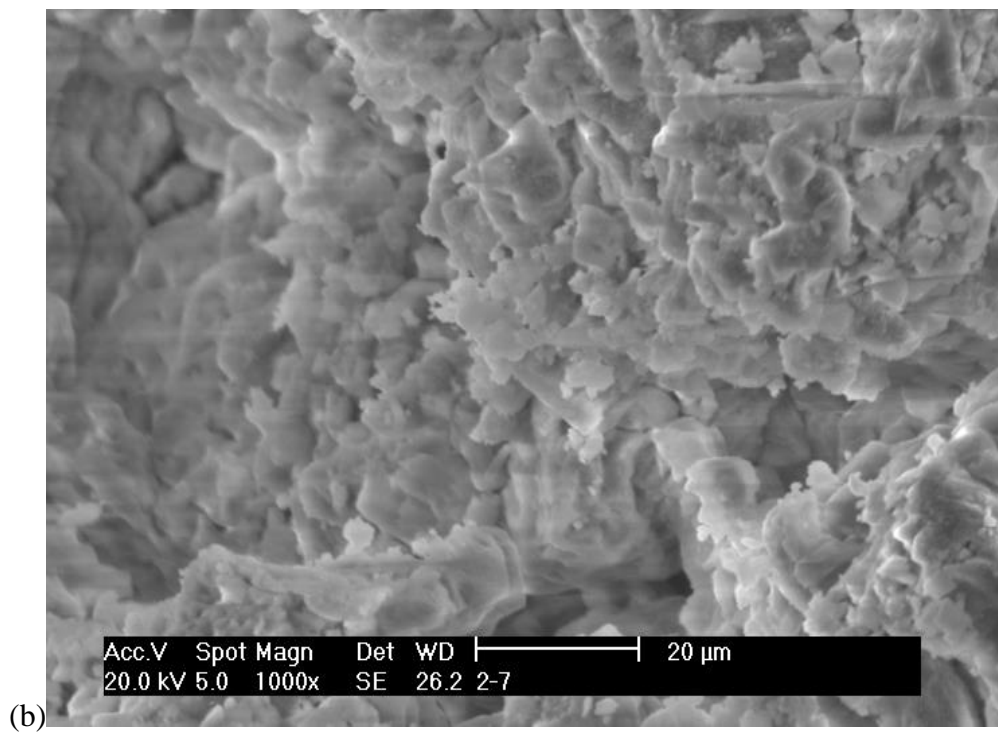
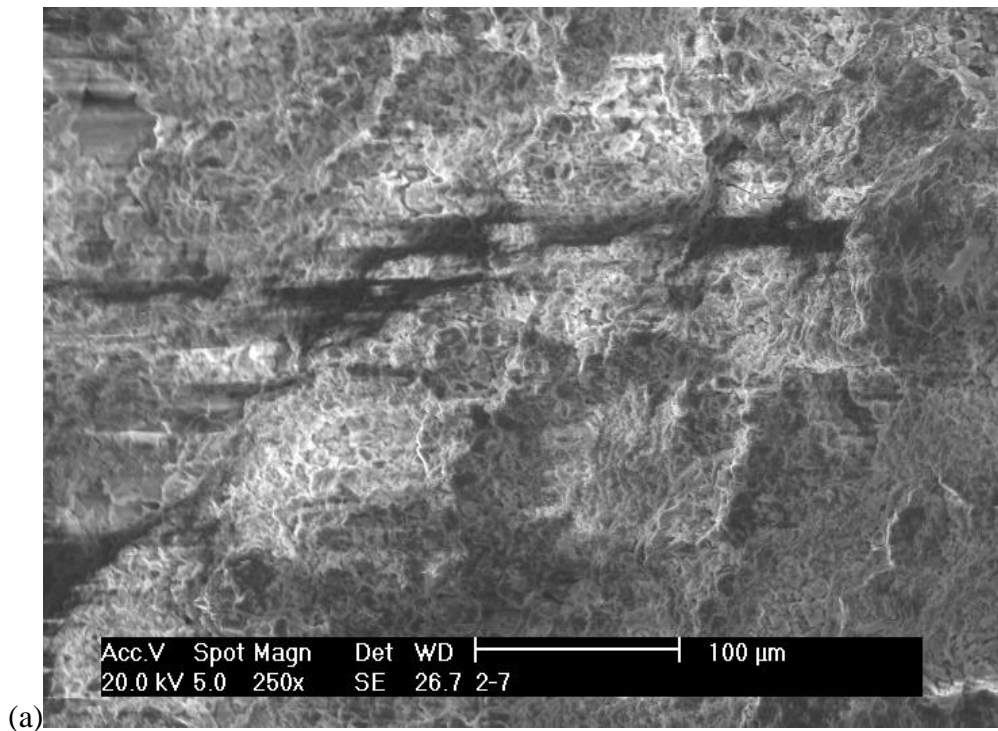


Figure 5. ‘Wet’ macro- scale SEM images of the sorbent after the 9<sup>th</sup> carbonation step at 10 kPa CO<sub>2</sub>/ 6.8 kPa H<sub>2</sub>O at (a) 250x and (b) 1000x magnification.

Table 1. Kinetic parameters for ‘dry’ carbonations at 5 kPa CO<sub>2</sub> at both micro- and macro- scales, ‘wet’ carbonations at 5 kPa CO<sub>2</sub>/ 2.8 kPa H<sub>2</sub>O at macro- scale and thermal decompositions (‘dry’ and ‘wet’) of the sorbent based on the reaction order model  $g(\alpha) = \frac{[1-(1-\alpha)^{1-n}]}{1-n}$  and the Jander diffusion equation  $g(\alpha) = [1 - (1 - \alpha)^{\frac{1}{3}}]^2$ ; correlation coefficient values ( $r$ ) and conversions ( $\alpha$ ) of the applied model.

		1 <sup>st</sup> carbonation						2 <sup>nd</sup> carbonation				
scale	Phase	model ( $g(\alpha)$ )	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit
micro- ‘dry’	PH1	Jander (3D)	90.4±0.8	6.4±7.6	N/A	0.99	0.06-0.82	218±2	25.4±9	N/A	0.99	0.01-0.41
	PH2	Jander (3D)	∅	∅	N/A	∅	∅	31.1±0.8	-5.4±7	N/A	0.97	0.41-0.61
macro- ‘dry’	PH1	Jander (3D)	144.6±3.8	13.5±8.7	N/A	1	0.02-0.19	127.5±9.2	9.9±7.9	N/A	0.99	0.03-0.86
	PH2	Jander (3D)	141.0±2.2	13.3±8.3	N/A	1	0.20-0.99	∅	∅	N/A	∅	∅
macro- ‘wet’	PH1	Jander (3D)	94.7±0.4	8.3±7.6	N/A	0.98	0.02-0.98	59.3±2.2	-0.47±7.5	N/A	0.99	0.00-0.15
	PH2	Jander (3D)	∅	∅	N/A	∅	∅	128.4±2.1	13.43±8.2	N/A	0.99	0.15-0.87
		1 <sup>st</sup> thermal decomposition						2 <sup>nd</sup> thermal decomposition				
scale	Phase	model ( $g(\alpha)$ )	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit
micro- ‘dry’	PH1	reac. ord.	880±37	102±5	1.3	0.99	0.03-0.9	900±96	107±12	1.3	0.99	0.02-0.98
	PH2	reac. ord.	∅	∅	∅	∅	∅	∅	∅	∅	∅	∅
macro- ‘dry’	PH1	reac. ord.	1341.3±327.1	143.4±39.0	2.9	1	0.03-0.48	218.4±3.3	19.6±0.4	1.8	1	0.02-0.81
	PH2	reac. ord.	∅	∅	∅	∅	∅	∅	∅	∅	∅	∅
macro- ‘wet’	PH1	reac. ord.	129.4±1	7.5±0.2	0	1	0.01- 0.6	257.0±4.2	23.7±0.5	1.8	1	0.02-0.83
	PH2	reac. ord.	∅	∅	∅	∅	0.02-0.83	∅	∅	∅	∅	∅

Table 2. Final conversions ( $\alpha$ ) and temperature intervals for the carbonations/ thermal decompositions at ‘dry’ micro- and macro-scales and the ‘wet’ macro- scale set- up used for the calculation of kinetic parameters.

	<b>1<sup>st</sup> carbonation</b> 5 kPa CO <sub>2</sub> - 5 kPa CO <sub>2</sub> / 2.8 kPa H <sub>2</sub> O		<b>2<sup>nd</sup> carbonation</b> 10 kPa CO <sub>2</sub> / 10 kPa CO <sub>2</sub> - 6.8 kPa H <sub>2</sub> O		<b>1<sup>st</sup> carbonation</b> 15 kPa CO <sub>2</sub> / 15 kPa CO <sub>2</sub> - 10.1 kPa H <sub>2</sub> O		<b>2<sup>nd</sup> carbonation</b> 15 kPa CO <sub>2</sub> / 15 kPa CO <sub>2</sub> - 10.1 kPa H <sub>2</sub> O		<b>1<sup>st</sup> carbonation</b> 15 kPa CO <sub>2</sub> / 15 kPa CO <sub>2</sub> - 10.1 kPa H <sub>2</sub> O		<b>2<sup>nd</sup> carbonation</b> 15 kPa CO <sub>2</sub> / 15 kPa CO <sub>2</sub> - 10.1 kPa H <sub>2</sub> O	
<b>scale</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>
<b>micro- ‘dry’</b>	0.83	155-449	0.61	329-616	0.90	245-543	0.73	285-620	0.84	224-553	0.88	284-640
<b>macro- ‘dry’</b>	1	308-656	0.88	302-636	0.72	132-601	0.60	312-588	0.33	160-615	0.26	190-604
<b>macro- ‘wet’</b>	0.98	183-524	0.92	193-547	0.99	218-528	0.86	147-418	0.90	325-591	0.60	377-589
	<b>1<sup>st</sup> thermal decomposition</b>		<b>2<sup>nd</sup> thermal decomposition</b>		<b>1<sup>st</sup> thermal decomposition</b>		<b>2<sup>nd</sup> thermal decomposition</b>		<b>1<sup>st</sup> thermal decomposition</b>		<b>2<sup>nd</sup> thermal decomposition</b>	
<b>scale</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>	<b>(<math>\alpha</math>)</b>	<b>T<sub>i</sub>-T<sub>f</sub> (°C)</b>
<b>micro- ‘dry’</b>	1	705-750	1	690-713	1	724-777	1	685-736	1	717-768	1	626-719
<b>macro- ‘dry’</b>	0.84	493-824-747	0.90	470-823-677	0.96	571-814-680	0.88	627-810	0.91	585-817-596	0.81	656-820
<b>macro- ‘wet’</b>	0.89	577-827-667	0.97	695-829-667	0.89	523-877-657	0.85	693-751-686	0.89	638-861-491	0.64	675-877-695



Table 4. Kinetic parameters for ‘dry’ carbonations at 15 kPa CO<sub>2</sub> at both micro- and macro- scales, ‘wet’ carbonations at 15 kPa CO<sub>2</sub>/ 10.1 kPa H<sub>2</sub>O at macro- scale and thermal decompositions (‘dry’ and ‘wet’) of the sorbent based on the reaction order model

$g(\alpha) = \frac{[1-(1-\alpha)^{1-n}]}{1-n}$  and the Jander diffusion equation  $g(\alpha) = [1 - (1 - \alpha)^{\frac{1}{3}}]^2$ ; correlation coefficient values ( $r$ ) and conversions ( $\alpha$ ) of the applied model.

		1 <sup>st</sup> carbonation						2 <sup>nd</sup> carbonation				
scale	Phase	model ( $g(\alpha)$ )	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit
micro- ‘dry’	PH1	Jander (3D)	77.5± -2.5	3.5±7.8	N/A	0.99	0.07-0.25	103.9± -0.6	7.6±7.7	N/A	0.99	0.02-0.91
	PH2	Jander (3D)	142.1± -2.7	15.1±8.4	N/A	0.99	0.26-0.97	∅	∅	N/A	∅	∅
macro- ‘dry’	PH1	Jander (3D)	135.7±-2.1	10.1±8.2	N/A	0.99	0.03-0.30	119.9±-0.9	6.5±7.9	N/A	0.99	0.01-0.26
	PH2	Jander (3D)	164.2±-16.7	9.4±7.8	N/A	0.99	0.31-0.34	∅	∅	N/A	∅	∅
macro- ‘wet’	PH1	Jander (3D)	206.8±-1.96	25.6±8.7	N/A	1	0.03-0.7	175.1±-1.2	17.1±8.4	N/A	1	0.03-0.6
	PH2	Jander (3D)	43±-3.1	-1.7±7.2	N/A	0.99	0.7-0.9	∅	∅	N/A	∅	∅
		1 <sup>st</sup> thermal decomposition						2 <sup>nd</sup> thermal decomposition				
scale	Phase	model ( $g(\alpha)$ )	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit	E±dE (kJ mol <sup>-1</sup> )	lnA±dlnA (A in s <sup>-1</sup> )	$n$	$r$	conv. fit
micro- ‘dry’	PH1	reac. ord.	360.4±12.8	40±1.6	1.1	1	0.03-0.99	578.5±36.9	66.7±4.7	1.2	0.99	0.03-0.99
	PH2	reac. ord.	∅	∅	∅	∅	∅	∅	∅	∅	∅	∅
macro- ‘dry’	PH1	reac. ord.	1269.7±207.0	138.5±24.2	1.7	0.99	0.04-0.97	412.1±7.6	43.8±0.9	1.5	0.99	0.03-0.99
	PH2	reac. ord.	∅	∅	∅	∅	(normalised)	∅	∅	∅	∅	(normalised)
macro- ‘wet’	PH1	reac. ord.	975±841.2	99.9±235.4	2.9	0.99	0.06-0.19	239.2±4.1	21.7±0.5	1.2	0.99	0.03-1
	PH2	reac. ord.	563.7±242.3	54.9±32.3	2.4	1	0.20-0.40	∅	∅	∅	∅	(normalised)