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

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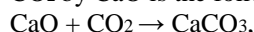
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The non-isothermal kinetic and thermal behaviour of a naturally formed dolomite in conditions that approach in situ CO<sub>2</sub> capture in chemical looping reforming, were investigated. The performance of this dolomite was studied at micro-scale in 'dry' conditions, as well as at macro-scale in 'dry' and 'wet' conditions to investigate the effects of scale (3 mg, 2.5 g), partial pressures of CO<sub>2</sub> (<15 kPa) 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' macroscale exacerbated the experimental carbonation conversions in an inversely proportional trend when compared with 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.

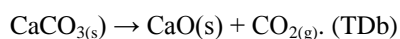
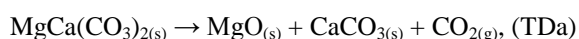
**Keywords:** dolomite; CO<sub>2</sub> capture; kinetics; modelling; steam

## 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 fluidised bed technology (Chen, Grace, and Lim 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, Fink, and Gorin 1967; Giannakeas et al. 2012; Pimenidou et al. 2010b), 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 and 5A), which pose some difficulty in adsorbing H<sub>2</sub>O when used to capture CO<sub>2</sub> from gases. Most of the synthetic materials are costly to produce (such as zeolites for physisorption and 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 (Dou et al. 2010; Hyatt, Cutler, and Wadsworth 1958; Pimenidou et al. 2010b; Squires 1967). The key reaction for the capture of CO<sub>2</sub> by CaO is the following:

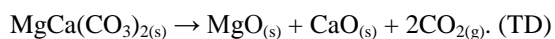


which is considered in post-combustion or in situ capture of CO<sub>2</sub> processes as well as in energy storage (Aihara et al. 2001) with further encounter in flue gas CO<sub>2</sub> separation (Han and Harrison 1994) and hydrocarbon and water gasification for H<sub>2</sub> production (Gupta and Fan 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 (Chrissafis, Dagounaki, and Paraskevopoulos 2005a, 2005b; Gupta and Fan 2002; McIntosh, Sharp, and Wilburn 1990):



MgO gives stability in the sorbent's structure which in the long term gives more durability to this material compared with limestone (Gupta and Fan 2002). The thermal decomposition reaction of MgCa(CO<sub>3</sub>)<sub>2(s)</sub> may

occur in a single step (McIntosh, Sharp, and Wilburn 1990; Samtani, Dollimore, and Alexander 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 (Dou et al. 2010; Dupont et al. 1997; Giannakeas et al. 2012; Pimenidou et al. 2010a). The reversibility of calcination has been confirmed by numerous investigators (Barker 1973; Chrissafis, Dagounaki, and Paraskevopoulos 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 thermogravimetric analysis (TGA) studies ('micro-scale') (Chrissafis, Dagounaki, and Paraskevopoulos 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, Dollimore, and Alexander (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, Vecchiattini, and Giordani (2003). The effect of steam in the Differential Thermal Analysis (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, Sharp, and Wilburn (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 (Ding and Alpay 2000; Ficicilar and Dogu 2006). 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>2</sub><sup>-3</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 characterised by large pores with small particles and a large surface area in order to guarantee a long-lasting and efficient performance while sintering is minimised.

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

#### 2.1.1. 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 1-1.4mm size were used in micro- and macro-scale experiments after manually grinding and sieving (BS410) the as-received dolomite. Natural dolomite particles of 1-2mm from Spain had been earlier used in the 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.

### 2.1.2. Micro-scale (TGA) set-up

A thermogravimetric analyser (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<sub>CO<sub>2</sub></sub> = 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> (Standard Temperature and Pressure (STP)). The same heating rate and experimental set-up were also used in the thermal stability study only that an initial mass of 10 mg and a 10 kPa CO<sub>2</sub> pressure were used for both calcination/carbonation steps.

### 2.1.3. 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 three 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<sub>CO<sub>2</sub></sub>). Similar 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 that the reactant gas was in excess. This CO<sub>2</sub> volumetric flow rate corresponds to the following molar flow rate:  $\dot{n}_{\text{CO}_2} = P \cdot V_{\text{CO}_2} / RT = (101.325 \text{ kPa}) \times (0.05 \text{ L min}^{-1}) / (8.314 \text{ L kPa K}^{-1} \text{ mol}^{-1} \cdot 293 \text{ K}) = 0.021 \text{ mol min}^{-1}$ , which is sufficient for the  $n_{\text{max(CaO)}} = 0.0137 \text{ mol}$ . For the ‘wet’ experiments, deionised water was pumped in a preheater 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 vapour partial pressures of 2.8, 6.8 and 10.1 kPa (P<sub>H<sub>2</sub>O</sub>). 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 analyser in order to avoid moisture entering it. CO<sub>2</sub> content in the effluent gases was monitored online by a Non-Dispersive Infrared Sensor (NDIR) absorption gas analyser (Uras 14, ABB), connected to a display and control unit. The smallest measurement range for CO<sub>2</sub> was 0–100 ppm. Similar 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

$$a^i (\%) = \frac{M^0}{W_{\text{CO}_2}} \cdot \frac{(P_{\text{sorb}}^i - P_{\text{sorb}}^{f,i-1})}{N_{\text{sorb}}^{f,i-1}}, \quad (1)$$

where

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

P<sub>sorb</sub><sup>i</sup> 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<sub>0</sub> is the initial mass of ‘fresh’ dolomite in the TGA crucible, while M<sub>sorb</sub><sup>i</sup> 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<sub>f,i</sub> CaCO<sub>3</sub>) and CaO (N<sub>f,o</sub> CaO) in the sample were calculated by Equations 3 and 4, when (–1)<sub>i</sub> < 0,

$$N_{\text{CaCO}_3}^{f,i} = \left(1 - \frac{\alpha^{f,i}}{100}\right) \cdot N_{\text{CaCO}_3}^{f,i-1}, \quad (3)$$

$$N_{\text{CaO}}^{f,i} = \left(1 - \frac{\alpha^{f,i}}{100}\right) \cdot N_{\text{CaCO}_3}^{f,i-1} + N_{\text{CaO}}^{f,i-1}. \quad (4)$$

### 2.2.2. Macro-scale calculations

Based on elemental balances for the thermal decomposition of the sorbent, the conversion for  $\text{MgCO}_3$  is expressed as

$$\% \alpha_{\text{MgCO}_3}^{\text{TD}_i} = 100 \cdot \left(\frac{\Delta N_{\text{CO}_2}}{N_{\text{MgCO}_3}}\right) \quad \text{for } \frac{\Delta N_{\text{CO}_2}}{N_{\text{MgCO}_3}} < 1, \quad (5)$$

and

$$\% \alpha_{\text{MgCO}_3}^{\text{TD}_i} = 100 \cdot \left(\frac{\Delta N_{\text{CO}_2} - N_{\text{MgCO}_3}}{N_{\text{MgCO}_3}}\right) \quad \text{for } \frac{\Delta N_{\text{CO}_2}}{N_{\text{MgCO}_3}} \geq 1, \quad (6)$$

where  $\Delta N_{\text{CO}_2}$  is the net number of  $\text{CO}_2$  moles that have evolved from the reactor during the  $i$ th thermal decomposition (TD $_i$ ) step, and  $N_{\text{MgCO}_3}$  is the number of  $\text{MgCO}_3$  moles in the ‘fresh’ dolomite. The conversion ( $\% \alpha_{\text{CaCO}_3}$ ) for the calcination of  $\text{CaCO}_3$ , is

$$\alpha_{\text{CaCO}_3}^i (\%) = 100 \cdot \frac{(\Delta N_{\text{CO}_2})}{N_{\text{CaCO}_3}^{f,i-1}} \quad \text{for } i > 1 \text{ and } -(1)^i < 0. \quad (7)$$

$\Delta N_{\text{CO}_2}$  is given by integrating the number of moles  $dN_{\text{CO}_2}$  that are evolved in the reactor over a time interval  $dt$ , which in this case was every 5 s,

$$\Delta N_{\text{CO}_2} = \int_{t_0}^t dN_{\text{CO}_2} = \int_{t_0}^t \chi_{\text{CO}_2,\text{out}} \cdot \dot{N}_{\text{dry,out}} dt \quad (8)$$

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

$$\alpha_{\text{CaO}}^i (\%) = 100 \cdot \frac{(\Delta N_{\text{CO}_2})}{N_{\text{CaO}}^{f,i-1}}. \quad (9)$$

The number of  $\text{CO}_2$  moles consumed,  $\Delta N_{\text{CO}_2}$ , was calculated by the following integral:

$$\Delta N_{\text{CO}_2} = \int_{t_0}^t dN_{\text{CO}_2} = \int_{t_0}^t (\dot{N}_{\text{CO}_2,\text{in}} - \chi_{\text{CO}_2,\text{out}} \cdot \dot{N}_{\text{dry,out}}) dt. \quad (10)$$

## 3. Modeling theory

Useful kinetics for modelling purposes includes 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 the Coats–Redfern method (Urbanovici, Popescu, and Segal 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 (preexponential factor)) from a linear regression analysis. Additionally, the F–test (based on F-ratio =  $S_{reg}/S_{xy}$ , where  $S_{xy}$  is 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  $S_{xy}$  alone cannot be used as a statistical criterion for selecting the most probable mechanism function,  $g(\alpha)$ , as suggested by Vyazovkin and 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 nth order reaction model is applied. The use of the F–test in the improved iterative Coats–Redfern method (Urbanovici, Popescu, and Segal 1999) decreased the number of the considered kinetic to the following:

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

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 (Cui et al. 2008; Dou et al. 2010). The conversion curves of thermal decompositions in both 'dry' and 'wet' macro-scale experiments were normalised between 0 and 1 as the minimum and maximum points during this reaction. The normalised conversion fractions ( $\alpha_{normalised}$ ) are calculated by the following equation:

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

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 nth-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 with the earlier calcination steps as evidenced by the apparent calculated activation energies. The activation energies of the second calcination which followed the first 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 first 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, Cutler, and Wadsworth (1958) previously observed that the diffusion of CO<sub>2</sub> through CaCO<sub>3</sub> layers during re-carbonation might occur. Beruto, Barco, and Searcy (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, Dagounaki, and Paraskevopoulos 2005b). Therefore, the thicker the product (CaCO<sub>3</sub>) layer grew, the slower the reaction became. It was observed that during all second carbonations, higher activation energies were required. This could accentuate diffusion-limited conditions in the reactive system which was further depicted in the final





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.

Scale	First carbonation		Second carbonation		First carbonation		Second carbonation		First carbonation		Second carbonation	
	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)
	5 kPa CO <sub>2</sub> -5 kPa H <sub>2</sub> O		2.8 kPa CO <sub>2</sub> / 2.8 kPa H <sub>2</sub> O		10 kPa CO <sub>2</sub> / 10 kPa H <sub>2</sub> O		6.8 kPa CO <sub>2</sub> -6.8 kPa H <sub>2</sub> O		15 kPa CO <sub>2</sub> / 15 kPa CO <sub>2</sub> -10.1 kPa H <sub>2</sub> O			
Micro- 'dry'	0.83	155-449	0.61	329-616	0.90	245-543	0.73	285-620	0.84	224-553	0.88	284-640
Macro- 'dry'	1	308-656	0.88	302-636	0.72	132-601	0.60	312-588	0.33	160-615	0.26	190-604
Macro- 'wet'	0.98	183-524	0.92	193-547	0.99	218-528	0.86	147-418	0.90	325-591	0.60	377-589
	First thermal decomposition		Second thermal decomposition		First thermal decomposition		Second thermal decomposition		First thermal decomposition		Second thermal decomposition	
Scale	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)	$\alpha$	$T_i - T_f$ (°C)
Micro- 'dry'	1	705-750	1	690-713	1	724-777	1	685-736	1	717-768	1	626-719
Macro- 'dry'	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
Macro- 'wet'	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 3. Kinetic parameters for 'dry' carbonations at 10 kPa CO<sub>2</sub> at both micro- and macro-scale, 'wet' carbonations at 10 kPa CO<sub>2</sub>/6.8 kPa H<sub>2</sub>O at macro-scale and thermal decompositions ('dry' and 'wet') of the sorbent based on the reaction order model  $g(\alpha) = [1 - (1 - \alpha)^{1-n}]/(1 - n)$  and the Jander diffusion equation  $g(\alpha) = [1 - (1 - \alpha)^{1/3}]^2$ ; correlation coefficient values ( $r$ ) and conversions ( $\alpha$ ) of the applied model.

Scale	Phase	Model ( $g(\alpha)$ )	First carbonation			Second carbonation						
			$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit	$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit
Micro- 'dry'	PH1	Jander (3D)	115.1 ± 1.6	10.6 ± 8.1	N/A	1	0.02-0.39	239.4 ± 5.5	29.1 ± 9.4	N/A	0.99	0.02-0.43
	PH2	Jander (3D)	122.7 ± 6.1	12.1 ± 8.8	N/A	0.99	0.41-0.82	40.0 ± 1.8	-3.6 ± 6.9	N/A	0.99	0.44-0.73
Macro- 'dry'	PH1	Jander (3D)	95.2 ± -0.7	6.0 ± 7.7	N/A	0.99	0.03-0.72	160.8 ± 3.1	15.6 ± 8.6	N/A	1	0.02-0.30
	PH2	Jander (3D)	Ø	Ø	N/A	Ø	Ø	89.7 ± -4.5	4.0 ± 8.2	N/A	0.99	0.30-0.60
Macro- 'wet'	PH1	Jander (3D)	97.6 ± -1.4	8.75 ± 7.9	N/A	0.99	0.05-0.60	237.4 ± -1.9	29.89 ± 8.8	N/A	0.99	0.01-0.82
	PH2	Jander (3D)	72.5 ± -2.2	4.50 ± 7.7	N/A	1	0.06-1	Ø	Ø	N/A	Ø	Ø
			First thermal decomposition			Second thermal decomposition						
Scale	Phase	Model ( $g(\alpha)$ )	$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit	$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit
Micro- 'dry'	PH1	Reac. ord.	677.9 ± 58.2	77.9 ± 7.3	1.2	0.99	0.03-0.99	972.8 ± 117.9	113.7 ± 14.8	1.6	0.99	0.03-1
	PH2	Reac. ord.	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø
Macro- 'dry'	PH1	Reac. ord.	1064.8 ± 134.0	115.6 ± 15.6	1.2	0.99	0.03-0.99	318.9 ± 6.0	32.7 ± 0.73	2.6	1	0.03-0.84
	PH2	Reac. ord.	Ø	Ø	Ø	Ø	(normalised)	Ø	Ø	Ø	Ø	Ø
Macro- 'wet'	PH1	Reac. ord.	99.54 ± 1.68	3.30 ± -0.2	0	1	0.03-0.85	323.79 ± 5.4	30.7 ± 0.64	2.9	1	0.02-0.69
	PH2	Reac. ord.	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø

both the first and second carbonations was set in the lowest value scale, compared with those at 5 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 with 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, Popescu, and Segal (1999) found that a ratio of 2.7 was obtained in the case of isothermal Mg(OH)<sub>2</sub> 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 macroscale '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°C in all experimental set-ups, since this is the maximum temperature employed in the air feed step corresponding to oxygen carrier regeneration (Dou et al. 2010; Dupont et al. 2007; Giannakeas et al. 2012; Pimenidou et al. 2010a, 2010b). Actually, when switching from the air feed step to the fuel feed step, the temperature decreases from 800°C to 600°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°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. The experimental initial, maximum and final calcination temperatures for the 'dry' and 'wet' macro-scales are given in Table 2. Despite that calcination steps were performed in an inert environment, a discontinuity in CO<sub>2</sub> 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 CO<sub>2</sub>. This could have occurred due to self-creation of a CO<sub>2</sub> 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).

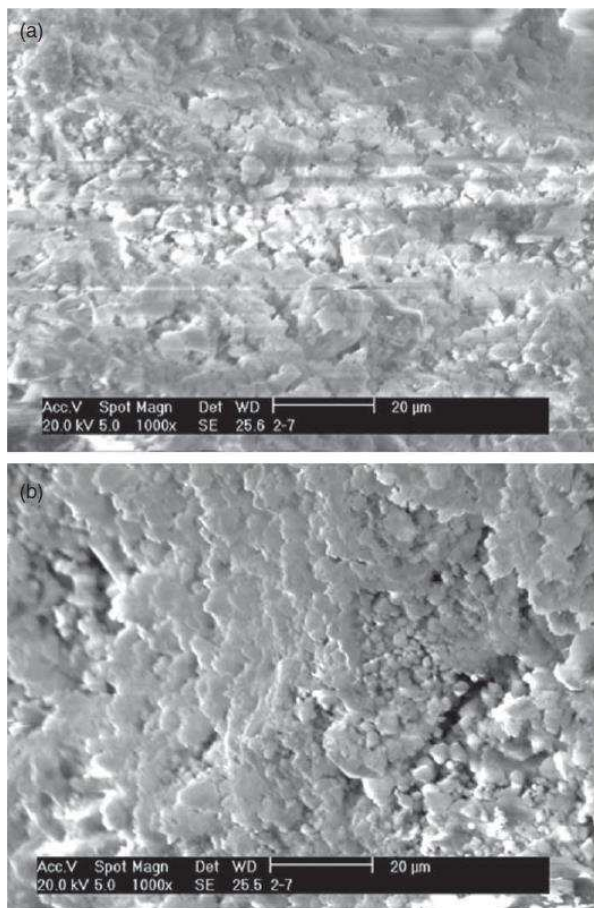


Figure 1. (a) 'Dry' and (b) 'wet' macro-scale SEM images of the sorbent after the first thermal decomposition at 100 kPa N<sub>2</sub>.

In previous studies (Silaban, Narcida, and Harrison 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, Anthony, and Loncarevic 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  $\text{CaCO}_3$  thermal decomposition in the sorbent bed were reached, the thermal decomposition of  $\text{MgCO}_3$  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 Mozejko (1999) reported activation energies of  $219 \text{ kJ mol}^{-1}$  for the  $\text{MgCO}_3$  thermal decomposition when using the Coats-Redfern method based on the diffusion (1D) equation. In that work, the calcination of  $\text{CaCO}_3$  was expressed by the random nucleation model resulting in  $E = 390 \text{ kJ mol}^{-1}$ . The latter value is in agreement with that of the second 'dry' calcination following carbonation at  $15 \text{ kPa CO}_2$ .

All first 'dry' carbonation steps showed that the higher the partial pressure of  $\text{CO}_2$  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  $\text{CO}_2$  with the dolomite particles. The conversion reached by the end of the second carbonation for the middle  $\text{CO}_2$  partial pressure ( $10 \text{ kPa}$ ) exhibited the higher drop in value from the respective one in the first carbonation and when compared with the final conversions of the second carbonation steps at  $5$  and  $15 \text{ kPa}$  of  $\text{CO}_2$ .

Similar to the present 'dry' macro-scale final carbonation conversions, Sun et al. (2008) noticed a better performance of carbonations when partial pressures of  $\text{CO}_2$  smaller than  $10 \text{ kPa}$  were used, whereas for  $P_{\text{CO}_2} > 10 \text{ kPa}$  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 first carbonation steps was calculated at the lowest  $\text{CO}_2$  partial pressure ( $5 \text{ kPa}$ ). This could be attributed to the extent of the preceding calcination ( $\alpha \approx 0.84$ ), which was limited compared with those that preceded the first carbonations at  $10$  and  $15 \text{ kPa CO}_2$  ( $\alpha = 0.96$  and  $0.91$ , respectively).

Higher energy was needed during the second 'dry' carbonation at  $10 \text{ kPa}$  compared with the respective steps in the other two  $\text{CO}_2$  conditions. During the second 'dry' carbonation at  $15 \text{ kPa CO}_2$ , 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 first 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).

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

Scale	Phase	Model ( $g(\alpha)$ )	First carbonation				Second carbonation					
			$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit	$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (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	∅	∅
Second thermal decomposition												
Scale	Phase	Model ( $g(\alpha)$ )	First thermal decomposition				Second thermal decomposition					
			$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (A in s <sup>-1</sup> )	$n$	$r$	Conv. fit	$E \pm dE$ (kJ mol <sup>-1</sup> )	$\ln A \pm d \ln A$ (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)

#### 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 with the respective 'dry' macro-scale results (e.g. 0.84 at 5 kPa CO<sub>2</sub>) (Table 2). Still the second 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, Sharp, and Wilburn \(1990\)](#), 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' second 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 second 'dry' and 'wet' calcinations were in the range of 300 kJ mol<sup>-1</sup>. The first 'wet' calcination at 15 kPa CO<sub>2</sub> was found to be of order 2.9, when the  $n$  for the second calcination was calculated to be equal to 1.2. The second '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's 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 second 'wet' calcinations as shown in Tables 2 and 3.

The thermal swing regeneration step of the sorbent used in the 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 first and second 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<sub>CO<sub>2</sub></sub>, 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, Dagounaki, and Paraskevopoulos 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 with 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 microscale and despite that in both cases the same size particles were used.

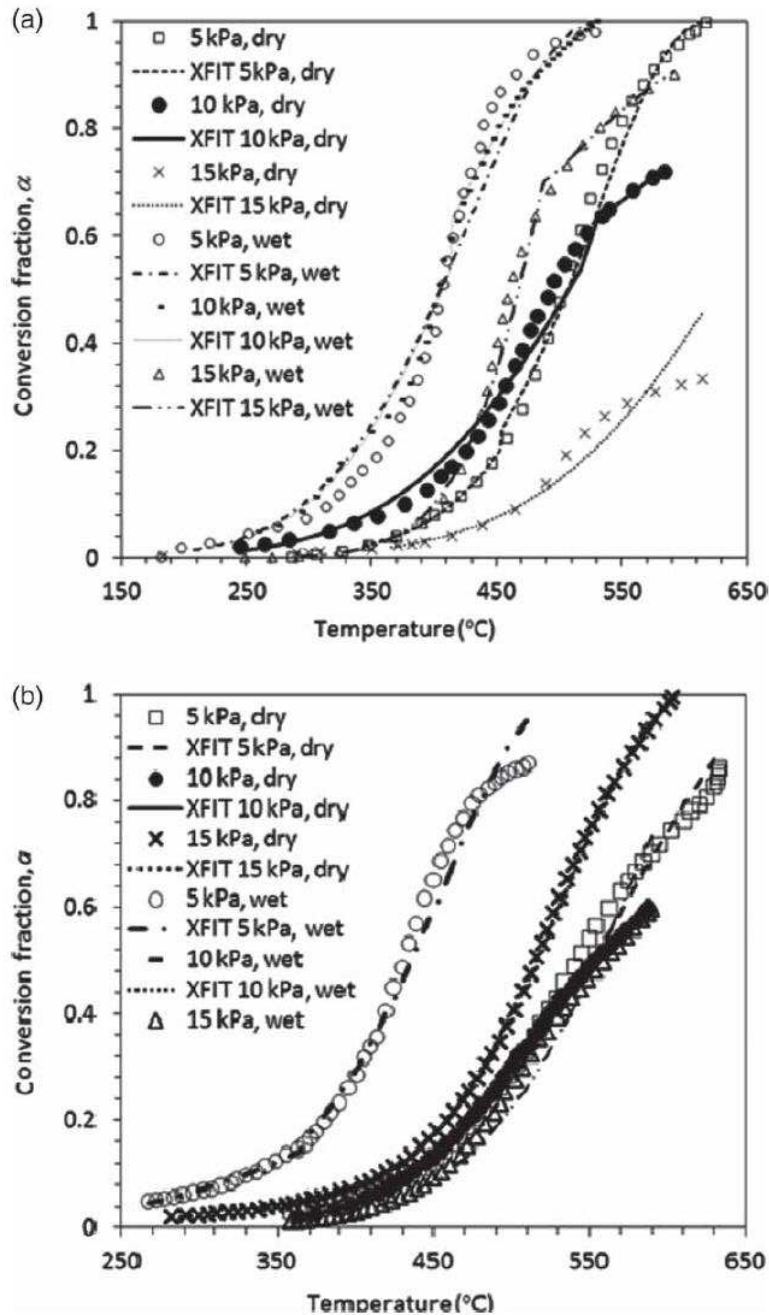


Figure 2. ‘Dry’ and ‘wet’ macro-scale experimental conversion ( $\alpha$ ) at and model fit ( $\alpha_{FIT}$ ) of the (a) first and (b) second carbonations; at 5, 10 and 15 kPa CO<sub>2</sub> over temperature.

#### 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 3(a)). 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 and Nakajima 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 eight calcinations that succeeded the nine carbonations, contrary to the micro-scale thermal stability study (Figure 3(a)).



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 4(a)). It was noticed that the CaO carbonation reaction concluded at temperatures close to the initialisation temperatures of the MgCO<sub>3</sub> thermal decomposition. These temperatures were confirmed by the earlier determined micro-scale experiments (Figure 4(b)). In particular, the 'dry' thermal decomposition of MgCO<sub>3</sub> in the TGA at 10 kPa CO<sub>2</sub> occurred between 643°C and 772°C, while the first 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 Dıanez 2004). Based on the previous observations, MgCO<sub>3</sub> had completely converted into MgO by the third cycle of the 'dry' macro-scale experiments, whereas when in the 'wet' ones, this was achieved by the second cycle (Figure 3(a)). From the same figure, it became evident that the presence of steam improved the final experimental conversions reached. Beruto, Vecchiattini, and Giordani (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 with 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 third till the fifth cycle performed better than the respective ones at micro-scale. The 'dry' macro-scale carbonations showed a sudden decrease in yield from the sixth to the ninth cycle, an effect that did not coincide with the micro-scale findings (Figure 3(b)). Even though MgCO<sub>3</sub> was fully decomposed by the second 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 Figure 5(a) and (b), the surface of the sorbent after the ninth carbonation at two magnifications (100 and 20µm) might not be of high resolution, but sintering was obvious even in the smaller magnification. Additionally, in the previous figures, the MgO · CaO – CaCO<sub>3</sub> particles seemed solid and compact as a result of sintering, which limited any further carbonation. Similarly, Chrissafis, Dagounaki, and Paraskevopoulos (2005a) mentioned that sintering could limit the CaO carbonation over repeated cycles since there could not be sufficient diffusion of CO<sub>2</sub> 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 MgCO<sub>3</sub> which would no longer compete with the carbonation at the low temperature range during the third, fourth and fifth carbonations, the values of the carbonation conversions were higher than in the first and second ones regardless of the extent of the CaCO<sub>3</sub> 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 MgCO<sub>3</sub> 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 eighth cycle compared with the 'dry' carbonations from cycle 1 to 8 (Figure 3(b)). 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 3(b), it can be seen that by the 'dry' ninth 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 nine 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 macro-pores during the calcination/carbonation cycles (Sun et al. 2007). When sulphur containing fuels are used, lower effective diffusivity will characterise 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.

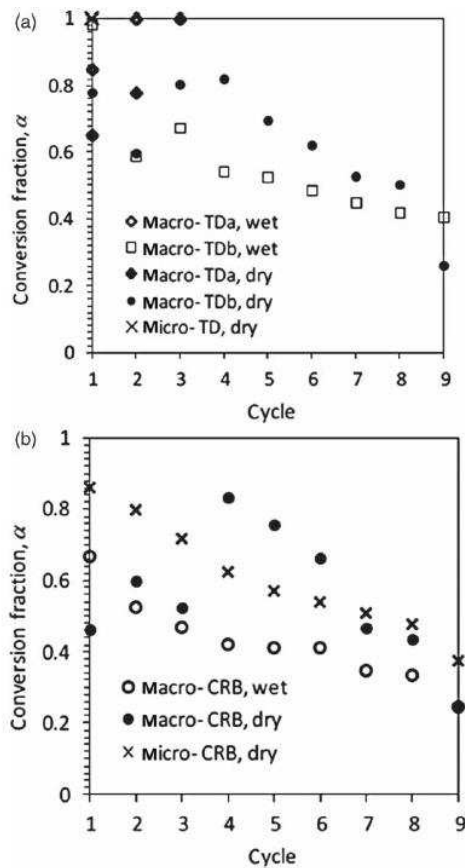


Figure 3. Micro- ('dry') and macro-scale ('dry' and 'wet') conversions of nine consecutive (a) thermal decomposition (b) carbonation cycles. Carbonations under 'dry' condition at 10 kPa CO<sub>2</sub> and under 'wet' conditions at 10 kPa CO<sub>2</sub>/6.8 kPa H<sub>2</sub>O.

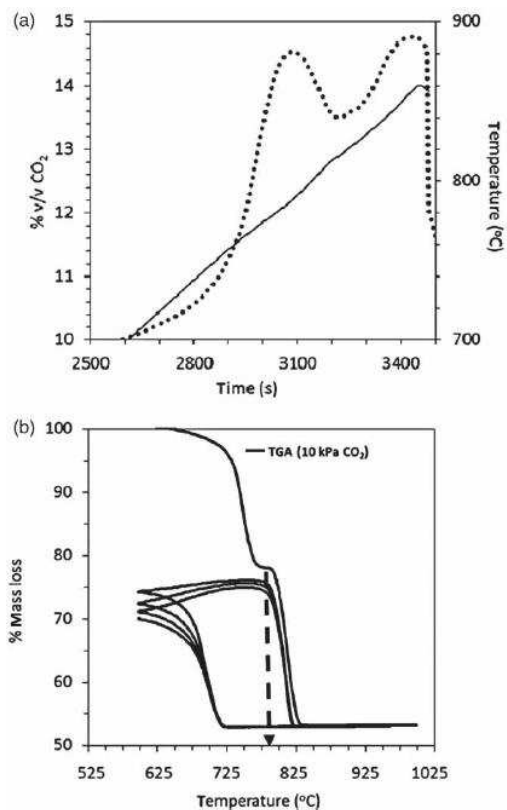


Figure 4. (a) CO<sub>2</sub> concentration (scatter points) and reactor temperature (line) with time. First peak corresponds to the MgCO<sub>3</sub> decomposition; second peak is the CaCO<sub>3</sub> decomposition in macro-scale ('dry') (b) micro-scale (same conditions) temperatures (the arrow indicates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

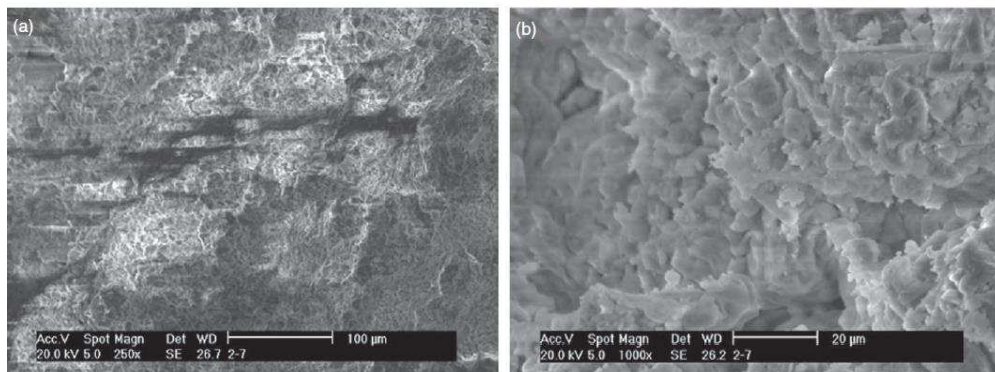


Figure 5. 'Wet' macro-scale SEM images of the sorbent after the ninth carbonation step at 10 kPa CO<sub>2</sub>/ 6.8 kPa H<sub>2</sub>O at (a) 250 $\times$  and (b) 1000 $\times$  magnification.

## 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 should not be expected as indicated by the present larger scale study and compared with 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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