

ADDITIVE EFFECTS OF STEAM ADDITION AND HBr DOPING FOR CaO-BASED SORBENTS FOR CO₂ CAPTURE

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ABSTRACT

Calcium looping is a developing CO₂ Capture and Storage technology that employs the reversible carbonation of CaO (potentially derived from natural limestone). The CO₂ uptake potential of CaO particles reduces upon repeated reaction, largely through loss of reactive surface area and densification of particles. Doping of particles has previously been found to reduce the rate of decay of CO₂ uptake, as has the introduction of steam into calcination and carbonation stages of the reaction. Here, the synergistic effects of steam and doping, using an HBr solution, of 5 natural limestones have been investigated. The enhancement to the CO₂ uptake was found to be additive, with CO₂ uptake after 13 cycles found to be up to 3 times higher for HBr-doped limestones subjected to cycles of carbonation and calcination in the presence of 10% steam, in comparison to natural limestone cycled in the absence of steam. A qualitative discussion of kinetic data is also presented.

Keywords: “Calcium Looping”, “HBr doping”, “Sorbent enhancement”, “Fluidised bed”, “Steam addition effect”.

INTRODUCTION

Carbon Capture and Storage is a technology used to prevent emission of CO₂ into the atmosphere from power stations and other industrial installations (Boot-Handford et al., 2014) to mitigate climate change. Calcium looping is a variety of CCS technology relying upon the reversible reaction between CaO and CO₂ to capture CO₂ (*carbonation* of the CaO) from the exhaust of a process (i.e. this is a *post-combustion* CO₂ capture system) and (via reversal of the reaction, to produce CaO and CO₂, *calcination*). There are inherent thermodynamic advantages to this process, compared to other post-combustion CCS technologies, and a number of researchers have determined that this process imposes an efficiency penalty on a power station significantly lower than that imposed by either oxyfuel combustion or MEA scrubbing, at 6–8% points, as opposed to 10 – 12 points for the latter technologies.(Romeo et al., 2010, Lin et al., 2011, Daval et al., 2011, Martinez et al., 2012) One issue which has received significant attention during previous research is that the ability of CaO produced from natural limestone reduces significantly (from ~ 0.7 mol CO₂/mol CaO) when it is first used to capture CO₂ to a significantly lower level (~0.1 mol CO₂/mol CaO) after 30 cycles of calcination and

carbonation (Fennell et al., 2007a, Blamey et al., 2010a) (hereafter, the number of moles of CO_2 reacted per mole of CaO will be referred to as the *carrying capacity* of the limestone) . The reduction in carrying capacity with the number of cycles has been attributed (Abanades and Alvarez, 2003 Alvarez and Abanades, 2005) to the building up of a product layer on the walls of pores within the CaO, which prevents ready gas-phase diffusion to fresh CaO for reaction. Interesting recent work (Li et al., 2012) indicates that the process may be more complex than the simple picture presented here – with “islands” of CaCO_3 forming and merging to finally produce the product layer discussed above.

The aim of this work is to investigate the synergies between two different methods of improving the reactivity of natural limestones for carbon capture using the calcium looping cycle. It has been shown (Donat et al., 2012, Manovic and Anthony, 2010) that the addition of steam to a calcination / carbonation system can enhance the long-term reactivity of the CaO in the process. It has also been shown (Al-Jeboori et al., 2013) that doping a limestone-based sorbent with HBr (or a number of other halogen-based mineral acids) can significantly enhance the carrying capacity of the sorbent. Here, we investigate, for a number of different natural limestones, whether the effects of doping and the addition of steam are cumulative. This is of particular interest, since if the processes leading to enhanced long-term reactivity were purely physical (i.e. both effects changed the pore structure to an optimal structure, discussed further below), synergistic effects would be less likely to be significant.

Previous authors (Donat et al., 2012, Manovic and Anthony, 2010) have investigated the presence of steam during carbonation and calcination on the capture capacity of CaO-based sorbents. Although there is not a consensus in terms of the effect of steam on the carbonation reaction, previous work (Donat et al., 2012) has shown that the presence of steam in the atmosphere during cycles of carbonation and calcination improves the capture capacity of particles of CaO-based sorbents. It has also been shown that the presence of steam during calcination is beneficial to this process: one hypothesis is the increased rate of sintering of CaO upon steam addition, (Borgwardt, 1989) increases the rate of calcination (MacIntire and Stansel, 1953) and if carefully controlled, assists the formation of pores in the size ranges most conducive to long-term carbonation, previously described as ~ 50 nm diameter (Abanades and Alvarez, 2003, Alvarez and Abanades, 2005) and thereby improves the carrying capacity of the sorbent.

Donat *et al.*,(Donat et al., 2012) showed that steam, when the steam concentration was varied from 0-20%, just 0.1% steam was sufficient to increase the final extent of carbonation – the extent of which depended on the type of limestone used – and that the carrying capacity of Longcliffe limestone did not increase significantly when the amount of steam added was increased above 1%. In general, concentrations above 10% did not produce any improvement in the conversion with respect to the smallest percentages of steam present.

Doping limestone has also been proposed as a method to improve their carrying capacity. Previous work carried out in this group studied the effect of adding different mineral-acid dopants (HBr, HCl, HNO₃, HI) on the performance of the sorbents during cycles of carbonation and calcination.(Al-Jeboori et al., 2012, Al-Jeboori et al., 2013) It was seen that although many of these dopants improved the capture capacity of the sorbents, depending on the combination of limestone and dopant, the extent of improvement was not uniform. It was found that the best value of the residual conversion was obtained for Havelock and Longcliffe limestones when they were doped with a 2 cm³ of HBr solution such that there was 0.167 mol% HBr/CaCO₃.

Since doping with HBr and also the addition of steam to the cycle are both methods to improve the behaviour of the sorbent it is interesting to combine both methods to examine whether there are synergies between them; this is the focus of this study. Following on from previous work, discussed above, 10% steam was the concentration of steam investigated and 0.167 mol% HBr, as steam concentrations and doping conditions that would result in significant enhancement of sorbent carrying capacity. All experiments were carried out using a small, atmospheric-pressure Fluidised-bed reactor and sorbent derived from different limestones sieved to 500-710 µm. Typical experiments consisted of up to 13 cycles of carbonation and calcination with calcination in 15% CO₂, 10% steam and balance N₂ at 900 °C; and, carbonation in 15% CO₂, 10% steam and balance N₂ at 650 °C. The experimental variables investigated here include the effects of doping and steam on five different limestones (from Longcliffe and Purbeck, UK; Cadomin and Havelock, Canada and Compostilla, Spain).

EXPERIMENTAL SECTION

Materials and physical measurements

HBr mineral acid used was Aristar grade purchased from BDH. Havelock (Canada), Longcliffe (United Kingdom), Purbeck (United Kingdom), Compostilla (Spain) and Cadomin (Canada) limestones, sieved to size fractions of 500-710 μm , were investigated in this work. An ADC MGA-3000 was used to detect CO_2 in the off-gas of the reactor. Semi-quantitative XRF analysis for samples was recorded using a Bruker XRF Explorer-S4 analyser. Brunauer-Emmett-Teller (BET) surface areas and pore volume distributions were determined using a Micromeritics Tristar 3000 N_2 sorption analyser.

Physical properties of the sorbent and doping procedure

The chemical compositions of the five limestones, as determined by X-ray fluorescence (Bruker AXS S4 Explorer), are given in Table 1. Samples of the limestones were subsequently doped with HBr using a quantitative wet impregnation method described previously.(Al-Jeboori et al., 2012) This method consists of preparing 2 cm^3 of HBr solution in D.I. water, which is then shaken and poured over 4 g of limestone in a petri-dish and dried in an oven at 100 $^\circ\text{C}$ for an hour. Previous work (Al-Jeboori et al., 2012) demonstrated that the optimum doping concentration was found to be 0.167 mol% HBr/ CaCO_3 , which was found to improve the capture capacity of the sorbents from 0.05 to 0.13 (mol CO_2 /mol CaO) after 50 cycles of carbonation and calcination in a fluidised bed.

Table 1: Chemical composition of limestones in mol-% determined by XRF (n/d denotes not detected).

Component	Havelock	Longcliffe	Purbeck	Compostilla	Cadomin
CaCO_3	93.60	98.89	87.81	93.48	94.34
SrO	0.03	n/d	0.04	0.02	0.02
SiO_2	2.38	0.16	9.87	2.74	2.59
MnO	0.29	0.29	0.05	n/d	0.21
MgO	0.56	0.50	1.28	2.49	2.08

K ₂ O	0.05	0.05	0.08	0.14	0.06
Fe ₂ O ₃	0.10	0.01	0.17	0.22	0.10
S	n/d	n/d	0.15	0.10	n/d
P	n/d	n/d	0.21	n/d	n/d
S	n/d	n/d	0.15	0.10	n/d

Experimental procedure

Doped and undoped samples were subjected to repeated cycles of carbonation and calcination using a fluidized bed reactor (FBR), as described elsewhere, (Blamey et al., 2010b, Donat et al., 2012) both with and without steam. Briefly, the reactor consists of a quartz tube (i.d. 21 mm), located within an externally resistance-heated tube furnace. A small fluidised bed of sand (12.5 ± 0.1 g; sieved to 355-425 μm) was supported upon a porous quartz frit located half-way up the quartz tube. The temperature of the fluidised bed was controlled using a type-K thermocouple, which controlled the power supplied to the furnace. All experiments were carried out with a total fixed flow rate of 170 cm^3/s (800 °C), at atmospheric pressure, such that the U/U_{mf} for the limestone was about 8, as calculated for calcination conditions using a correlation provided by Wen and Yu. (Wen and Yu, 1966) The inlet gas concentration of CO₂ was 15% (v/v). The steam concentration, when used, was set to 10%, following work performed by Donat *et al* (Donat et al., 2012)

The calcination temperature was set to 900 °C and the carbonation temperature to 650 °C, with hold times of 600 s, including the heating and the cooling time at an average rate of about 0.9 °C/s. Upon start-up of the experiment, the sand was added to the bed and the concentration of CO₂ was calibrated against 15% CO₂, balance N₂ (BOC). Once the calcination temperature was reached, 4 ± 0.1 g of limestone was added and the cycling program was started. At the end of the experiment, the contents of the bed were removed in the calcined form, under N₂, and added to a desiccator, before being allowed to cool subsequent to weighing. The mass loss during the experiment was calculated using the assumption that only limestone fines were lost from the bed (i.e., no sand) and the limestone removed remained fully calcined.

Further details of the development of the experimental protocols are available.(Blamey et al., 2010b, Donat et al., 2012)

Thirteen cycles of carbonation and calcination were performed for each experiment; this was the maximum number of cycles possible to be performed in a day (owing to the long time required for stabilisation of steam flowrate). The residual conversion from the Grasa equation (Grasa and Abanades, 2006) has not been calculated, as more cycles is likely to be required to allow accurate projection of residual conversion.

Sorbent morphology (pore volume and surface area) was determined using N₂ adsorption/desorption (Micromeritics Tristar 3000 N₂ Sorption Analyzer). Tests on the sorbent morphology were performed using Longcliffe limestone as an example, after 1 calcination, and 5 and 13 further cycles of carbonation and calcination.

RESULTS AND DISCUSSION

The five limestones, undoped, were first tested under standard experimental conditions (no doping, no steam, calcination temperature of 900 °C, carbonation temperature of 650 °C, carbonation and calcination times of 600 s and an atmosphere of 15% CO₂ in N₂). Figure 1a shows that Purbeck and Compostilla limestones presented the best performance when undoped and without steam, with a carrying capacity of \approx 15% after 13 cycles of carbonation and calcination. This is consistent with previous work.(Donat et al., 2012)

Subsequently, the five limestones, undoped, were cycled under the conditions described above, with the addition of 10% steam during both carbonation and calcination stages. Figure 1b shows that for these experiments, the decay in reactivity was not as abrupt as for the experiments without steam present and a higher carrying capacity was observed at 13 cycles. Cadomin limestone showed the greatest enhancement upon steam addition with an increase in capture capacity in the 13th cycle from 11% to 26%. Similarly, the rest of the limestones showed a significant improvement in their carrying capacity after 13 carbonation/calcination cycles when the steam is present as shown in Table 2.

Table 2: CO₂ carrying capacity (mol CO₂/mol CaO) of the five sorbents studied, after 13 carbonation/calcination cycles.

Condition	Havelock	Longcliffe	Compostilla	Purbeck	Cadomin
undoped, no steam	0.09	0.10	0.15	0.15	0.11
undoped, 10% steam	0.23	0.24	0.25	0.27	0.26
doped HBr, no steam	0.19	0.22	0.16	0.18	0.20
doped HBr, 10% steam	0.27	0.33	0.29	0.37	0.32

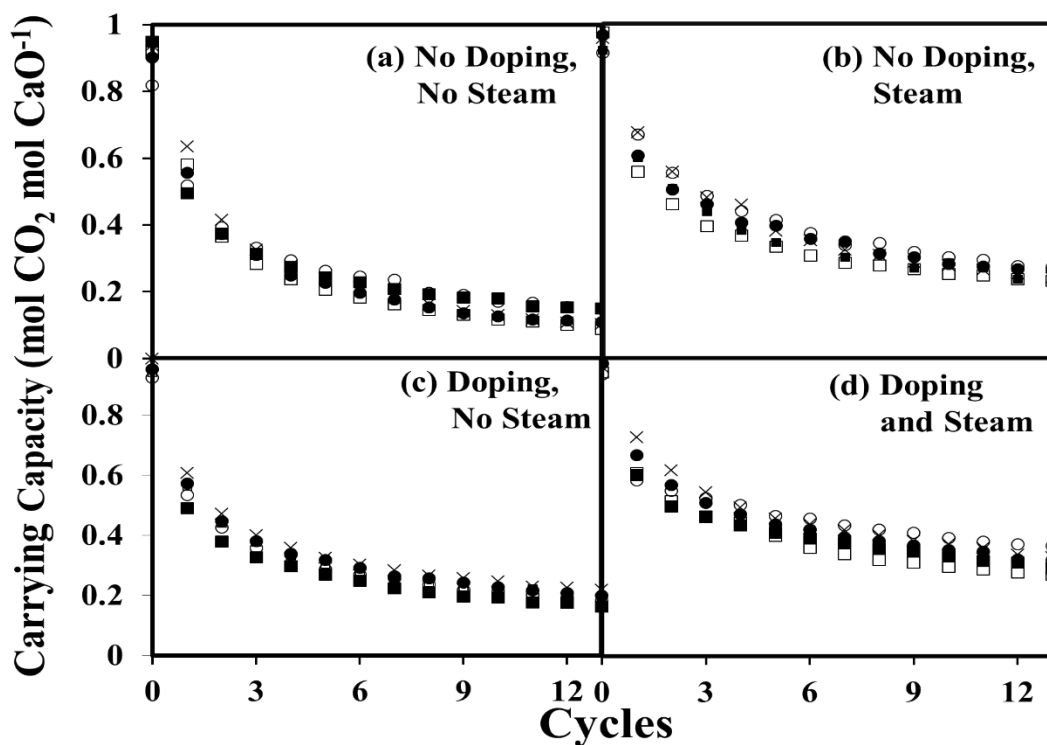


Figure 1: Carrying capacity of the five limestones through 13 carbonation/calcination cycles in standard conditions. calcination temperature of 900 °C, carbonation temperature of 650 °C, carbonation and calcination times of 600 s, 15% CO₂ in N₂. (a) without steam (b) with 10% steam present (c) doped with HBr and no steam (d) doped with HBr with steam present. ■ Compostilla, □ Havelock • Cadomin, ○ Purbeck x Longcliffe.

Figure 1c) shows the sorbent deactivation curves for limestones doped with 0.167 mol% HBr. Longcliffe limestone demonstrated the best performance with a conversion of 22%, which is more than double the carrying capacity of the undoped sorbent. Similarly, the other limestones showed improvements in their capture capacity after 13 cycles of 2% to 10% with respect to the fresh limestones.

Figure 1d) shows the deactivation curves obtained for all the limestones doped with 0.167 mol% HBr in presence of 10% steam. In each case, the enhancements resulting from steam addition and doping were found to be additive, with an average improvement of carrying capacity of up to 3 times relative to the undoped limestones with no steam present (see Table 2). The highest capacity of 37% (mol CO₂/mol CaO) is observed with Purbeck. The results show that the use of doping, together with the presence of steam, can synergistically improve the performance of limestone sorbents, with better results for the combination of both strategies than for either individually.

Figure 2 shows the deactivation curves for Longcliffe limestone in all the scenarios studied to allow comparison of the sequence of improvement in capture capacity from the experiment with the limestone undoped and without steam present with a value of 11.3% of conversion to the 33.15% obtained with the limestone doped with HBr and in presence of steam after 13 cycles. This suggests a synergistic effect when steam and HBr are present at the same time.

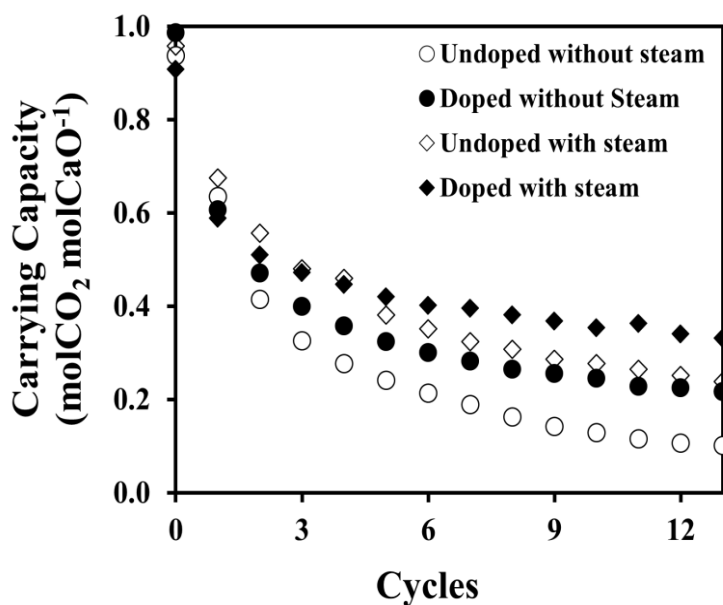


Figure 2: Carrying capacities of sorbent derived from Longcliffe limestone through 13 cycles with and without steam and with and without dopant.

Mechanical stability of sorbents is a factor in determining their observed carrying capacity. The carrying capacity here is considered as the uptake of CO_2 per mole of the *original* sorbent; therefore, any attrition of particles that results in losses of material from the bed will reduce the observed carrying capacity from the actual fractional conversion of the particles in the bed. Attrition has been shown to vary across different limestones and treatment methods and to be problematic in FBRs of a similar scale as the one used for this paper (Blamey et al., 2010b, Fennell et al., 2007b) as well as on a pilot scale (González et al., 2010). Table 3 shows the mass loss data for all the limestones, after 13 cycles, doped and undoped, with or without steam present. As Donat et al (Donat et al., 2012) showed previously, the presence of 10% steam during carbonation and calcination only decreases the mass loss for Purbeck limestone, which could be explained by its higher level of impurities. Doping with an HBr solution has a positive effect on the friability of the limestones, decreasing the mass loss of Cadomin, Purbeck and Longcliffe limestones upon cycling. Although doping is typically found to have a positive effect on the attrition of the sorbents, this effect was found to be negligible for Compostilla and Havelock limestones. In terms of attrition, the experiments upon doped limestone with steam present show similar results to those for the same doped limestone but without steam.

Table 3: Mechanical Stability of the five sorbents studied in terms of the mass lost during 13 reaction cycles.

Condition	<u>final mass loss after 13 cycles (% of initial calcined mass)</u>				
	Havelock	Longcliffe	Compostilla	Purbeck	Cadomin
undoped, no steam	13.3	3.6	2.1	7	4.7
undoped, 10% steam	17.2	5.1	3.7	4.4	6.0
doped HBr, no steam	14.2	1.3	3.0	4.1	2.0
doped HBr, 10% steam	10.8	1.7	3.7	4.9	2.3

The surface areas and porosity associated with small pores were determined by N₂ adsorption/desorption for calcined samples of each limestone after cycling. Longcliffe limestone was selected for additional study given that it has been one of the most studied limestones in previous works carried out in this group and also because of its high reactivity during cycles of carbonation and calcination. Figure 3 compares the evolution of the pore volume of CaO sorbent from Longcliffe limestone after 1 calcination, and following a further 5 and 13 cycles of carbonation and calcination, under all conditions investigated. Both the presence of steam and HBr affect the pore structure by moving the maximum in the plot of dV/dlog (D) vs pore diameter towards larger pores. The peak in the diameter for the undoped limestone without steam corresponds to a value of around 30 nm and when the sorbent is doped with HBr and/or in the presence of steam, the peak moves to a diameter of about 50 nm. Donat et al. (Donat et al., 2012) and Al-Jeboori et al. (Al-Jeboori et al., 2012) have previously shown these effects for steam and doping, though not simultaneously. Here, it is shown that the synergistic effect of both steam and HBr is almost negligible in terms of changes to pore structure when it is compared with the plots for each treatment independently.

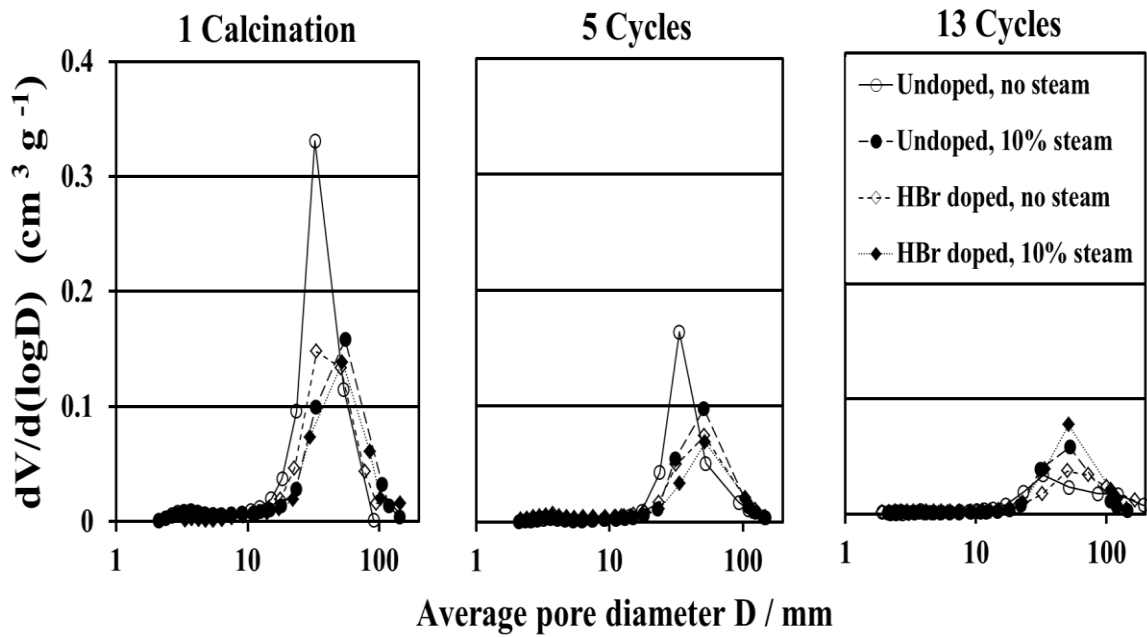


Figure 3: Evolution of pore volume (plotted semi logarithmically) of CaO sorbent derived from Longcliffe limestone, through 13 reaction cycles, undoped and no steam (○), undoped and steam (●), doped with HBr and no steam (□), with steam and doped with HBr (■).

Table 4: BET surface area of CaO sorbent derived from Longcliffe limestone, through 13 cycles, with and without steam, doped and no doped with HBr.

Cycles	BET surface area (m ² /g)			
	No steam, no HBr	10% steam, no HBr	No steam, HBr	10% steam, HBr
Calcination only	16.6	14.7	9.4	9.0
1	8.8	11.8	8.8	7.8
5	6.1	6.6	5.9	6.6
13	3.2	3.7	3.6	5.3

Table 4 shows that a decrease in the BET surface area was observed with increasing cycle number for all treatment methods. The surface area is slightly lower when steam is present after 1 cycle, compared to when it is not present. This reduction is more pronounced when the sorbent is doped with HBr both when cycled with or without steam. Nevertheless, after 5 and 13 cycles, this reduction disappears, such that the BET surface area is very similar for all samples. The rate of decay in the BET surface area is possibly marginally reduced upon addition of steam and/or HBr, resulting in slightly increased BET surface areas for these samples after 13 cycles. A further increase in BET surface is observed when both steam and HBr have been used, resulting in an observed increase in surface area of ~ 50%. Such findings are consistent with those of (Lysikov et al., 2007) and confirmed by (Manovic and Anthony, 2008) who demonstrated that pre-sintering limestones by heating them to a high temperature (> 1200 °C) for long periods of time (up to 24 h), though initially causing significant sintering and loss of reactivity, led to an increase in the long-term reactivity of the limestones. It was hypothesised (Lysikov et al., 2007) that rapid initial sintering of the sample led to the formation of a hard internal skeleton of an optimal pore-size distribution which acted as a support for subsequent cycles of carbonation and calcination.

Reaction rates

One significant purpose of this work is to produce sufficient amounts of sintered material that porosimetry analysis can be conducted. The large samples required lead to complex intra-phase mass transfer in the system (i.e. the potential for significant bubble / emulsion-phase mass transport issues). Furthermore, the drying trap has a significant mixing time, as do the bed and the freeboard. The biggest issue for kinetic studies is that the temperature swing from 900 °C to 650 °C is not instantaneous, so that a substantial proportion of the reaction occurs whilst the temperature is varying. (Donat et al., 2012) This is in contrast to experiments where the concentration of gas into the bed is varied, which can be done in seconds, (Fennell et al., 2007b) but unfortunately does not lead to a realistic decay in carrying capacities, owing to the mild calcination environment. For these reasons, reaction kinetics will only be briefly discussed here qualitatively.

Figure 4 shows the rates of carbonation for doped and undoped Longcliffe particles both with and without steam present, for the first, fifth and thirteenth carbonations. During the first cycle, on average, over the first 60 s of reaction, the undoped particles without steam added actually reacted ~ 1.2 times faster during the initial stage of reaction than the experiments where

solely steam or doping were used. Where both steam and doping was used, the reaction rate was around 1.5 times slower than the basic case. It is most likely that this is because sintering reactions during the first calcination (before the first carbonation), will have reduced the available surface area for reaction for systems where sintering is promoted (i.e., when dopants and/or steam are present). Table 4 indicates that the surface areas for reaction in the first cycle, though following the approximate order in reaction rates of neither steam nor doping > steam > doping > doping + steam do not correlate well in terms of absolute magnitude of reaction rate.

Considering now the initial rate of reaction for the experiments after 5 and 13 cycles, it is clear from Figure 4 that the initial rate of reaction is similar amongst all samples for the first 40 – 60 s, and only diverges significantly after the rate begins to reduce (i.e. when diffusional limitations are beginning to become important). It does appear that the presence of steam or doping can extend the reaction-kinetically limited regime for a short period when diffusion limitations are starting to become important. This contradicts somewhat some previous work (Arias et al., 2012) where only a very limited extension of the kinetically-limited regime was observed when steam was present. The explanation is most likely that diffusion is a more highly activated process than surface reaction, as has been found previously by Grasa *et al.* (Grasa et al., 2009), who adapted the work of Bhatia and Perlmutter (Bhatia and Perlmutter, 1983) and found an initial first-order surface reaction, with an activation energy of 21.3 kJ/mol for Imeco limestone and 19 kJ/mol for Katowice limestone, but an activation energy for the subsequent diffusion reaction of 163 kJ/mol (i.e. around an order of magnitude higher). Owing to the somewhat slow rate of cooling in the fluidised bed used in this work, a high proportion of the reaction occurs at a temperature above the lower set-point of the reactor (650 °C), but in the presence of CO₂. Since the solid-state diffusion reaction is more highly activated than the surface reaction, conducting a significant proportion of the carbonation reaction at a temperature above 700 °C will increase the importance of diffusional effects, so that the effects of moving the pore size distribution so that a large proportion of it lies at around the “optimal” diameter of around 50 nm (Alvarez and Abanades, 2005) is more pronounced in this system, in addition to any improvements to ionic transport through the CaCO₃ layer.

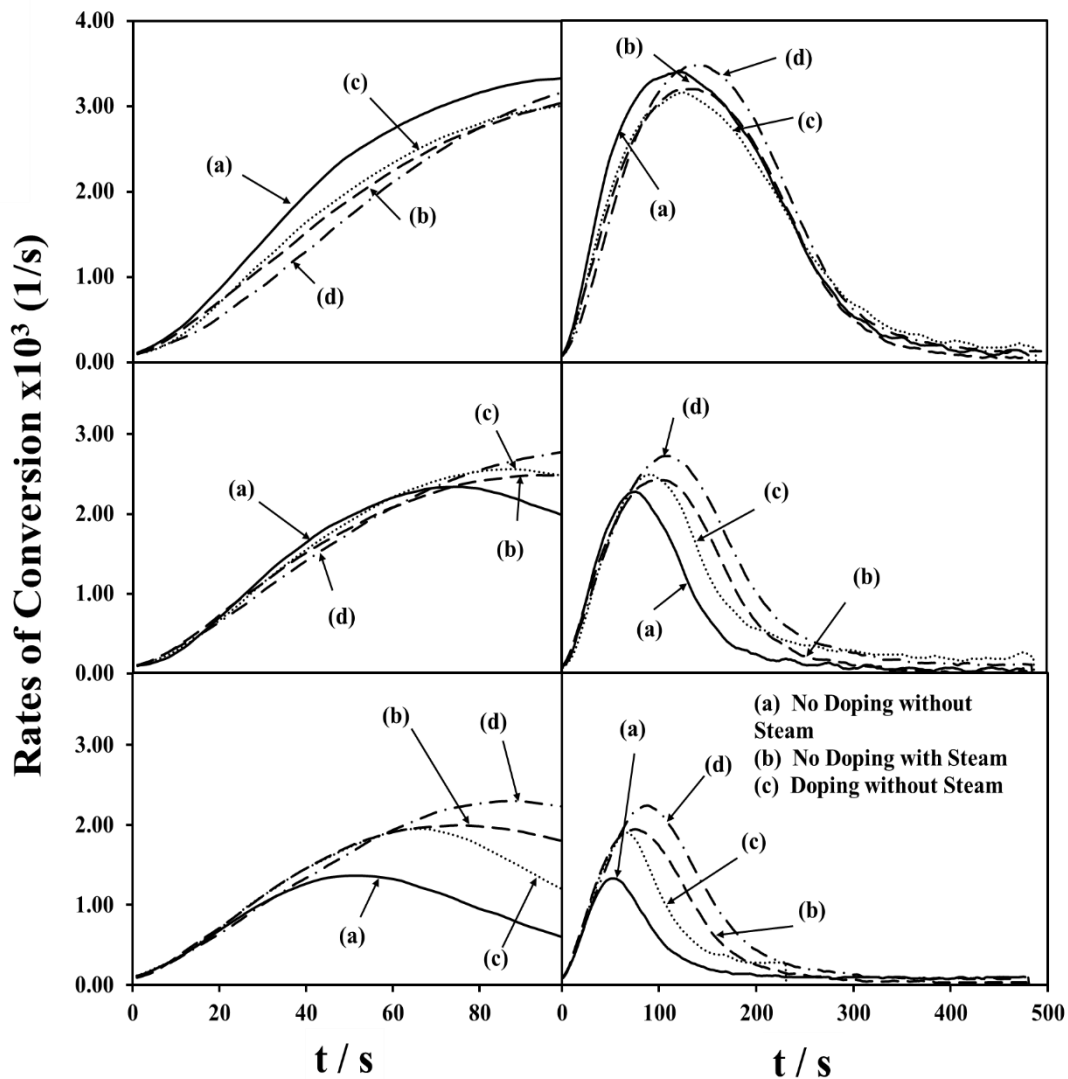


Figure 4: Rate of reaction for the carbonation reaction of Longcliffe limestone in the i th carbonation; cycles in standard conditions. calcination temperature of 900 °C, carbonation temperature of 650°C, carbonation and calcination times of 600 s, 15% CO₂ in N₂; 1st column shows the first 90 s of reaction and the 2nd column shows the first 480 s of reaction.

Economic Drivers for Doping with HBr

Using a framework set out by Romeo et al. (2009) and the experimental data presented here, a case can be made for economic benefits of doping using 0.167 mol% HBr. Romeo et al. (2009) investigated the economic drivers for sorbent enhancement techniques, such as doping, periodic hydration and generation of synthetic sorbents. They established economically competitive investments for enhancing sorbents by 1 percentage point of X_{Ave} (the average conversion to CaCO₃ of all CaO emerging from the carbonator), which were found to be heavily dependent on the solid circulation and purge rates of the solids. For a purge rate

of 1%, economically competitive investments of 1.89 USD/t to 3.04 USD/t to increase X_{Ave} by a percentage point were established for CaO/CO₂ molar ratios of 5 to 1.5; for a higher purge rate of 2.5%, economically competitive investments of 1.39 USD/t to 1.48 USD/t were established (2009 USD converted to October 2014 USD (CEPCI, 2015)). X_{Ave} was calculated for purge rates of 1 and 2.5% in the method proposed by Romeo et al. (2009), using constants determined for the Grasa equation (Grasa et al., 2006) for experimental data for two trials: undoped with steam and doped with steam. The results are shown in Table 5. Upon doping, there is a considerable increase in X_{Ave} of 14.3 and 11.6 percentage points for purge rates of 1% and 2.5% respectively. Doping limestone with 0.167 mol-% HBr would result in an increase to the material cost of sorbents of 4.22 USD/t (using a value of 1500 USD/t for 48% HBr, estimated from alibaba.com). The cost of HBr is significantly lower than the economically competitive investment for the increases of X_{Ave} seen upon doping, especially for lower purge rates. The equipment required to dope with HBr is likely to be simple; if these costs can be kept below ~ 12 USD/t, doping is likely to be an economically competitive investment. Further trials with longer cycle numbers and sulphur present would be required prior to a full economic assessment.

Table 5. Calculated X_{Ave} and Grasa constants, with economically competitive investments for undoped and doped limestone with steam

Limestone Type	Constants for Grasa equation (Grasa et al., 2006)		X_{Ave} , calculated by method proposed by Romeo et al. (2009)		Economically competitive investments (Romeo et al., 2009) [USD/t]	
	Residual capacity, X_r	Decay constant, k	Purge rate = 1%	Purge rate = 2.5%	Purge rate = 1%	Purge rate = 2.5%
Undoped with steam	0.139	0.604	0.192	0.239	n/a	n/a
Doped with steam	0.316	1.883	0.336	0.355	27.1 to 43.6	16.1 to 17.2

CONCLUSIONS

Sorbent reactivation by presence of steam has been shown in the literature to improve sorbent activity in long carbonation/calcination series. Doping limestone with different mineral acids has also been demonstrated to be a potential method to improve the capture capacity of the sorbents. A study of the synergistic effect of steam presence and doping with HBr has been carried out in this work. Previous studies concluded that the presence of 10% steam during carbonation/calcination cycles could significantly increase the carrying capacity of the sorbent, e.g., by a factor of ~ 2 (Al-Jeboori et al., 2013). Here, we have shown that by doping material and cycling in the presence of steam in a small fluidised-bed reactor, the long-term carrying capacity of natural limestone can be increased further, in some cases by more than a factor of 3. We believe that the fluidised bed system utilised, though allowing for the collection of sufficient spent sorbent in order to conduct investigations of the pore size distribution, enhances the effects of solid state diffusion in the system.

ACKNOWLEDGEMENTS

This work was supported by the European Community's Seventh Framework Programme (FP7/2007-2013) under the GA 241302-Caoling project. B.G. acknowledges also the postdoctoral fellowship provided by the PCTI Asturias under the Programme "Clarín".

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