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Carbonation of CaO-Based Sorbents Enhanced by Steam Addition

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The carbonation reaction has recently been intensively investigated as a means of CO₂ capture from gas mixtures such as flue gas produced during fossil fuel combustion. Unfortunately, this gas–solid reaction is limited due to formation of the solid product (CaCO₃) at the reacting surface and sintering, all of which reduce the carrying capacity of the sorbent. In this work the enhancement of carbonation conversion by means of steam addition to the carbonating gas was studied. Seven limestones of different origin and composition as well as one synthetic sorbent (calcium aluminate pellets) were tested. A thermogravimetric analyzer (TGA) was employed for the carbonation tests at different temperatures (350–800 °C) in a gas mixture containing typically 20% CO₂ and 10 or 20% H₂O_(g). The samples tested were calcined under an N₂ (800 °C) or CO₂ (950 °C) atmosphere to explore the influence of different levels of sample sintering, and the results obtained were compared with those seen for carbonation in dry (no steam) gas mixtures. The morphology of samples after carbonation under different conditions was examined by a scanning electron microscope (SEM). It was found that carbonation is enhanced by steam, but this is more pronounced at lower temperatures and for more sintered samples. With increasing temperature and carbonation time, the enhancement of carbonation becomes negligible because the conversion reaches a “maximum” value (~75–80% for samples calcined in N₂) even without steam. Carbonation of samples calcined in CO₂ is enhanced at different levels depending on the sorbent tested. The shape of carbonation profiles and morphology of carbonated samples show that steam enhances solid state diffusion and, consequently, conversion during carbonation.

1. Introduction

Power plants fired with fossil fuels, and in particular coal, are one of the largest sources of man-made CO₂ emitted to the atmosphere. Presently it is believed, with a high level of certainty, that anthropogenic CO₂ is a major contributor to global warming and climate changes.¹ One promising solution to reduce CO₂ emissions is capture from flue gas and subsequent liquefaction and sequestration in the deep oceans or, more likely, in underground geological formations such as saline aquifers or perhaps depleted oil fields.² Among the many new processes for CO₂ capture, the Ca looping cycle technology is considered promising, inexpensive, and environmentally friendly.^{3–6}

This technology is designed for postcombustion CO₂ capture. Solid sorbent, lime (CaO), obtained from natural limestone (CaCO₃) is used in a cyclical process for CO₂ capture. The use of solid sorbent for gas scrubbing means that a fluidized bed (FBC) system can provide the most suitable environment for such capture and regeneration processes,^{5–7} which is somewhat similar to the situation for SO₂ capture, especially for high-sulphur fuels using limestone sorbents.⁸ Therefore, many of the components, which are required for developing and scaling up Ca looping cycles for CO₂ capture, are already commercially available. Moreover, the main reactions (sulphation and carbonation) are similar in that they are both gas/solid reactions involving lime-based sorbents and are deactivated by formation of solid product (CaSO₄ and CaCO₃) at the reacting surface. This means that the extensive knowledge gained from investigation of sulphation can be applied, at least in part, for carbonation.

Carbonation (1) is a reversible reaction



for which equilibrium is described by eq 2⁹

$$\log_{10} P_{\text{CO}_2} [\text{atm}] = 7.079 - \frac{8308}{T[\text{K}]} \quad (2)$$

In practice, use of the carbonation reaction is limited by the maximum temperature that allows CO₂ capture at the desired concentration in cleaned flue gas and the minimum temperature that allows a practical reaction rate. The temperature range, which in real systems simultaneously allows a reasonable reaction rate and low CO₂ concentration in the cleaned gas, is about 600–650 °C.^{3–7} However, in many laboratory studies, this reaction is examined at higher temperatures (sometimes ≥800 °C), in order to simplify experimental procedures, for example to perform carbonation/calcination cycles isothermally.^{10,11} Another simplification typically employed during investigation of carbonation is that gas mixtures used for carbonation tests contain only CO₂ which is usually diluted by N₂. However, real flue gas typically contains steam which originates from both the moisture and hydrogen found in coal or other carbonaceous fuels.

Carbonation involves an initial, fast stage, which is controlled by the kinetics of chemical reaction, and a much slower stage controlled by diffusion through the formed product layer.^{12,13} However, for practical application only the fast stage, which takes place for minutes, is of interest,¹⁵ despite the fact that the sorbent residence time in a typical FBC reactor is longer. Different approaches are being investigated to improve product layer diffusion during reaction between CaO and gaseous compounds. For example, in the case of sulphation, research has suggested that sorbent doping with sodium potentially enhances this diffusion, resulting in higher conversion.¹⁶ A similar effect can be explored for carbonation; however, the presence of Na⁺ ions in the CaO crystal structure enhances sorbent sintering during long series of CO₂ capture cycles, which results in a lower average conversion in that series of cycles.¹⁷

Another way to improve solid state diffusion during carbonation is the presence of gaseous species. It is known that steam enhances sintering, i.e., solid state diffusion in CaO.¹² To date

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Table 1. Elemental Analysis of Limestone Samples Used

compound	Cadomin	Graymont	Havelock	Kelly Rock	Katowice	La Blanca	Purbeck
Al ₂ O ₃ , % wt	0.33	0.49	0.34	1.00	0.24	<0.10	0.21
CaO, % wt	54.91	53.42	51.51	51.61	54.10	54.39	49.32
Fe ₂ O ₃ , % wt	0.09	0.23	0.10	0.37	0.09	<0.01	0.45
K ₂ O, % wt	0.06	0.10	0.12	0.27	0.06	<0.02	0.04
MgO, % wt	0.20	0.61	3.09	0.52	0.89	0.11	0.47
Na ₂ O, % wt	<0.20	<0.20	<0.20	<0.20	<0.20	1.07	<0.20
SiO ₂ , % wt	1.03	1.87	1.07	3.70	0.85	<0.10	10.11
TiO ₂ , % wt	<0.03	<0.03	<0.03	0.06	<0.03	<0.03	<0.03
loss on fusion, % wt	43.09	42.87	43.68	41.69	43.64	44.20	39.19
sum	99.71	99.59	99.91	99.32	99.96	99.77	99.79

there is little available in the literature that suggests the presence of steam in flue gas enhances reactions such as sulphation and carbonation, and it is normally assumed that steam has no such effect. However, recent studies by Wang et al.¹⁸ and Stewart et al.¹⁹ clearly showed a very positive influence of water on sulphation at different temperatures. Similarly, in another study investigating the effects of steam and simulated syngas on CO₂ capture, Symonds et al.²⁰ found that steam significantly promotes absorption of CO₂. In studies by Wang et al.¹⁸ and Symonds et al.²⁰ the authors hypothesized that the reaction is catalyzed by H₂O by means of formation of transient Ca(OH)₂ which is more reactive than is CaO. In other words, they suggested that the fast reaction step, controlled by chemical reaction kinetics, is accelerated in the presence of H₂O. However, this hypothesis has some shortcomings.

Namely, when a chemical reaction mechanism includes several steps, the reaction rate is controlled by the slowest one, i.e., the rate-limiting step. In the case of both sulphation and carbonation, the rate of chemical reaction is significantly higher than the rate of diffusion.^{13,14,21,22} The fast step has lower activation energy and its enhancement is unlikely to contribute significantly to increased overall conversion rate because the reaction is still limited by the slower reaction step. Second, it has also been reported that the activation energy of the intrinsic CaO–CO₂ reaction is higher in the presence of H₂O in syngas (H₂ and CO, water gas shift reaction).²³ This increase of activation energy in the presence of H₂O is inconsistent with the hypothesis that H₂O is a catalyst.

These literature data show that the role of steam during both sulphation and carbonation of CaO needs further exploration. Moreover, such studies as have been done in this area^{20,23} have been done in the presence of H₂ and CO, which may complicate the situation and make it more difficult to draw firm conclusions. Therefore, to properly study the influence of steam on the CaO–CO₂ reaction, the gas mixture employed for carbonation in this work contained only CO₂ as the reactive species and N₂ as an inert gas with the aim of exploring the effects of H₂O on carbonation of different CaO-based sorbents without such potential complications.

2. Experimental Section

Seven limestones of different geographical origin were used in the experiments: Cadomin (formerly called Luscar, 250–425 μ m), Graymont (250–425 μ m), Havelock (250–425 μ m), and Kelly Rock (300–425 μ m), all Canadian limestones; Katowice (400–800 μ m) from Poland (Upper Silesia); La Blanca (400–600 μ m) from Spain; and Purbeck (425–500 μ m) from the United Kingdom (Penrith). The X-ray fluorescence (XRF) elemental analysis of investigated limestones is given in Table 1. It can be seen that the investigated limestones, apart from geographical origin, also differ substantially in composition. This wide range of limestones was tested because our previous experience on

thermal pretreatment¹⁷ showed that conclusions derived by testing one limestone may not be always applicable for another limestone.

Katowice limestone was also used here in pelletized form. Commercial calcium aluminate cement, CA-14, produced by Almatis Inc., was used as binder for pelletization and as a source of Al₂O₃ (70% Al₂O₃ and 28% CaO in cement) for sorbent microstructure enhancement. Pellets were prepared using hydrated lime and 10% of the cement. The mixture, in the form of a gel, was shaped to obtain spheres of ~2 mm size. More details on the pellet preparation method are presented elsewhere.²⁴

Carbonation tests were performed using a Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA). The sorbent sample (~30 mg) was suspended in a quartz tube (i.d. 20 mm) on a platinum pan (i.d. 5 mm). The gas flow rate, controlled by a flowmeter, was 0.04 dm³/min. The temperature and gas used were controlled by Pyris software. Sample mass data during the experiments were monitored, and the degree of carbonation was calculated on the basis of mass change, assuming that mass change occurs only due to formation of CaCO₃.

Before carbonation, the samples were calcined in an N₂ (100%) or CO₂ (100%) atmosphere. The temperature program for calcination in N₂ included heating to 800 °C, followed by an isothermal step at 800 °C for 10 min, and cooling to the desired temperature for carbonation. Calcination in CO₂ included heating to 950 °C and cooling to the carbonation temperature, but during the cooling step CO₂ was switched to N₂ at 900 °C to avoid carbonation before the desired temperature was reached. Both heating and cooling rates were 50 °C/min. A gas mixture (typically 20% CO₂ in nitrogen) was introduced 10 min after the desired temperature was reached, and carbonation was continued for 60 min. Steam (10 or 20%) was introduced in the gas mixture for carbonation tests with steam. Steam was generated by a syringe pump and steam generator. Feed lines containing both steam and the mixed gas were insulated and electrically heat-traced to ensure no steam condensation.

Carbonated samples were collected after the tests and their morphology was observed with scanning electron microscopy (SEM) using a Hitachi S3400 scanning electron microscope with 20 kV of accelerating voltage under high vacuum. The samples were coated with 3 nm of gold/palladium before SEM examination and images obtained by secondary electrons are presented here.

3. Results and Discussion

The first carbonation tests in this study were performed at 800 °C, as has been done in many laboratory studies on CO₂ capture by CaO. However, preliminary results failed to show significant enhancement of carbonation by steam, with such differences as were observed being in the range of experimental error. This result was also in agreement with the study of Sun

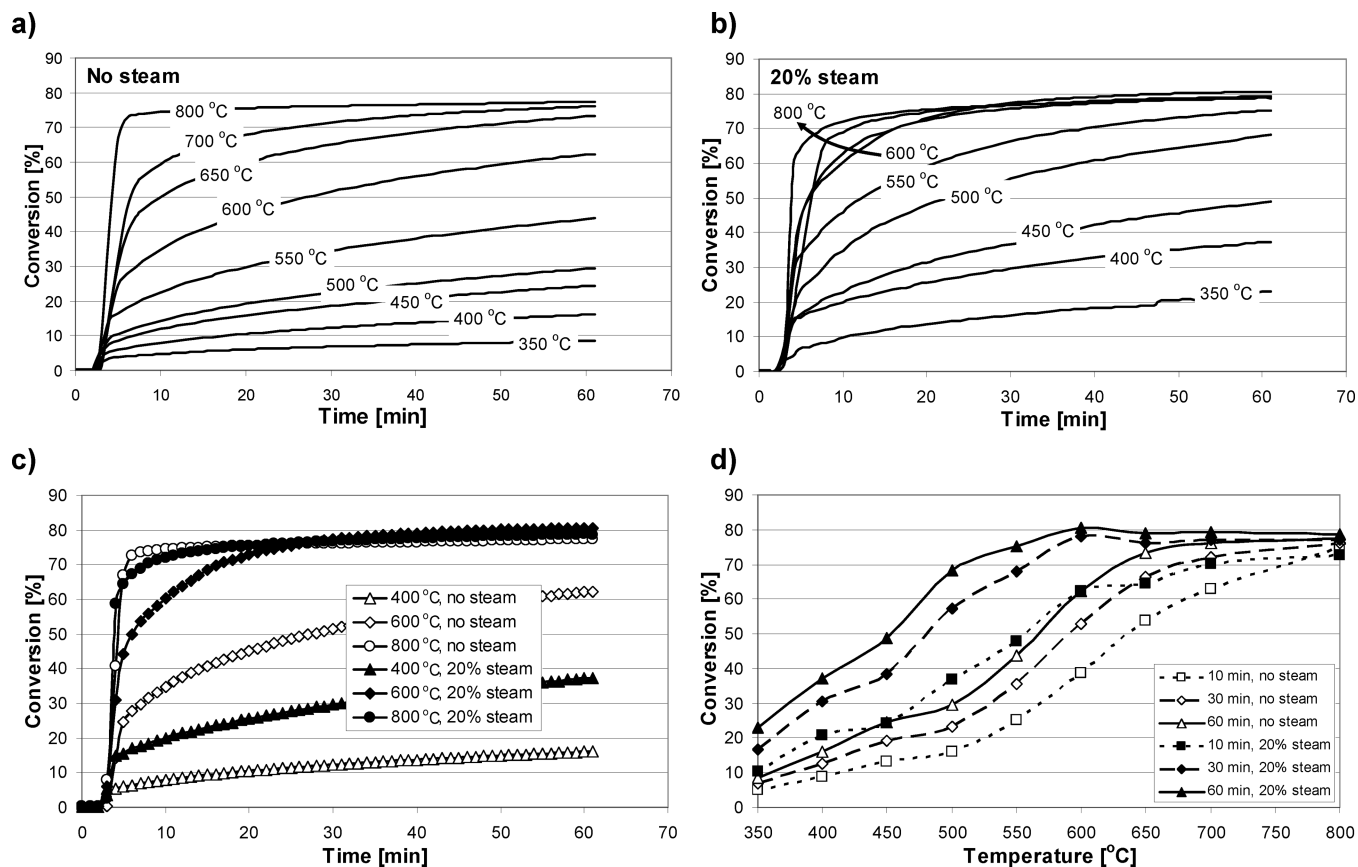


Figure 1. The effect of steam on conversion during carbonation of Kelly Rock lime (300–425 μm) at different temperatures. Conditions: calcination in N_2 (not presented here) and carbonation in 20% CO_2 (N_2 balance): (a) no steam, (b) 20% steam. Comparison: (c) conversion profiles at three temperatures with and without steam, (d) conversions at different temperatures at three carbonation times.

et al.¹¹ who carried out their carbonation steps during calcination/carbonation cycles at 850 °C. However, these results did not agree with the findings of Symonds et al.,^{20,23} who reported strongly positive effects of steam at temperatures of 580–700 °C. Therefore, it was then decided to see how the effect of steam varies with the carbonation temperature.

Tests were done for the temperature range 350–800 °C, and the main results are presented in Figure 1. It can be seen that conversions increase with the temperature, reaching a “maximum” level at ~80% (parts a and b of Figure 1). Moreover, the conversions are higher when steam is present during carbonation, but this difference decreases with the increase of temperature. This can be seen more clearly when conversion profiles for three characteristic temperatures are presented in the same diagram (Figure 1c). The conversion at 400 °C is more than doubled by steam. The difference at 600 °C is lower than that at 400 °C but is still significant. Here it can be seen that this difference increases during the first 20 min. After that, the carbonation supported by steam becomes very slow, reaching ~75%. This high conversion is reached only after 10 min of carbonation at 800 °C, both with and without steam. The profiles almost overlap and this clearly demonstrates why tests on carbonation at ≥ 800 °C failed to show any effect of steam.¹¹

The most important result seen here is that carbonation is greatly enhanced by steam at temperatures around 600 °C, which is the most interesting temperature region for CO_2 capture by Ca looping cycles. Moreover, the effect of steam is very pronounced for shorter carbonation times (~10 min) as can be seen in Figure 1d. These findings can influence the design of dual fluidized bed combustion (FBC) reactors for CO_2 capture which includes hydration of spent sorbent.²⁵ Namely, this means

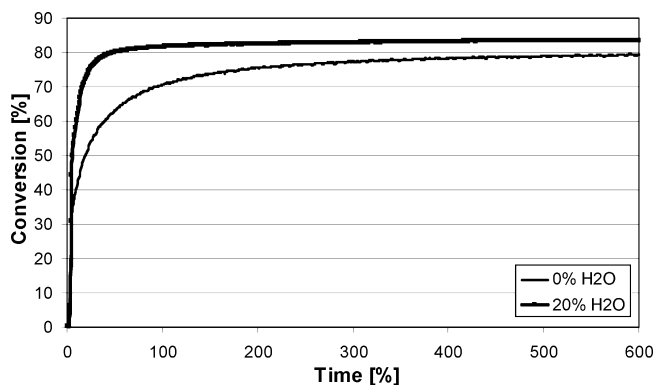


Figure 2. Conversion profiles for carbonation of Kelly Rock at 600 °C for 10 h in 20% CO_2 (N_2 balance) with steam present (20% H_2O) or without steam (0% H_2O).

that hydrated sorbent fed and calcined in a carbonator can release steam during calcination, which subsequently enhances CO_2 capture efficiency.

Another interesting result is that conversions at different temperatures converge to a “maximum” value of about 80%. It appears that steam does not noticeably affect carbonation as this value is approached. This can be clearly seen from results presented in Figure 2 where 10-h carbonation tests are presented. This limit is discussed below in this paper.

The influence of steam concentration was tested at 500 and 600 °C (Figure 3). The tests were performed with both 10 and 20% steam. The results obtained show that increasing steam concentration in this range does not significantly affect the conversion profiles. The curves for 600 °C are almost overlap-

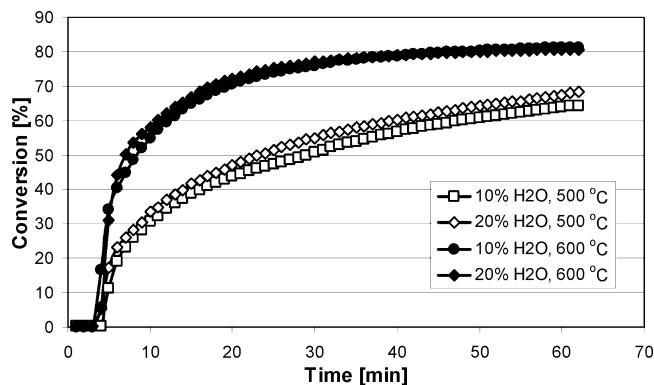


Figure 3. Influence of steam concentration on carbonation of Kelly Rock at 500 and 600 °C, 20% CO₂ (N₂ balance).

ping, and only a small enhancement is noticed at 500 °C at elevated steam concentration.

The purpose of this study was to screen conditions and sorbents with regard to the effect of steam on a single carbonation step. Apart from offering a better explanation of the mechanism, these results can enable us to design better tests and systems, with the ultimate goal of employing the steam effects in Ca looping cycle technology. To ensure that these results are generally valid, a wide range of limestones were tested, and in addition they were explored with the calcination step preformed under different conditions before carbonation to include the possibility that this, too, is important. Taking into account that the temperature of interest for carbonation in looping cycles is about 600 °C and that the effects of steam are very positive at that temperature, further tests in this study were done at 600 °C. However, according to the results presented in Figure 1, the conclusions produced are valid also for lower temperatures.

Carbonation tests with and without steam for six limestones calcined in CO₂ at 950 °C (realistic conditions in a calciner)⁷

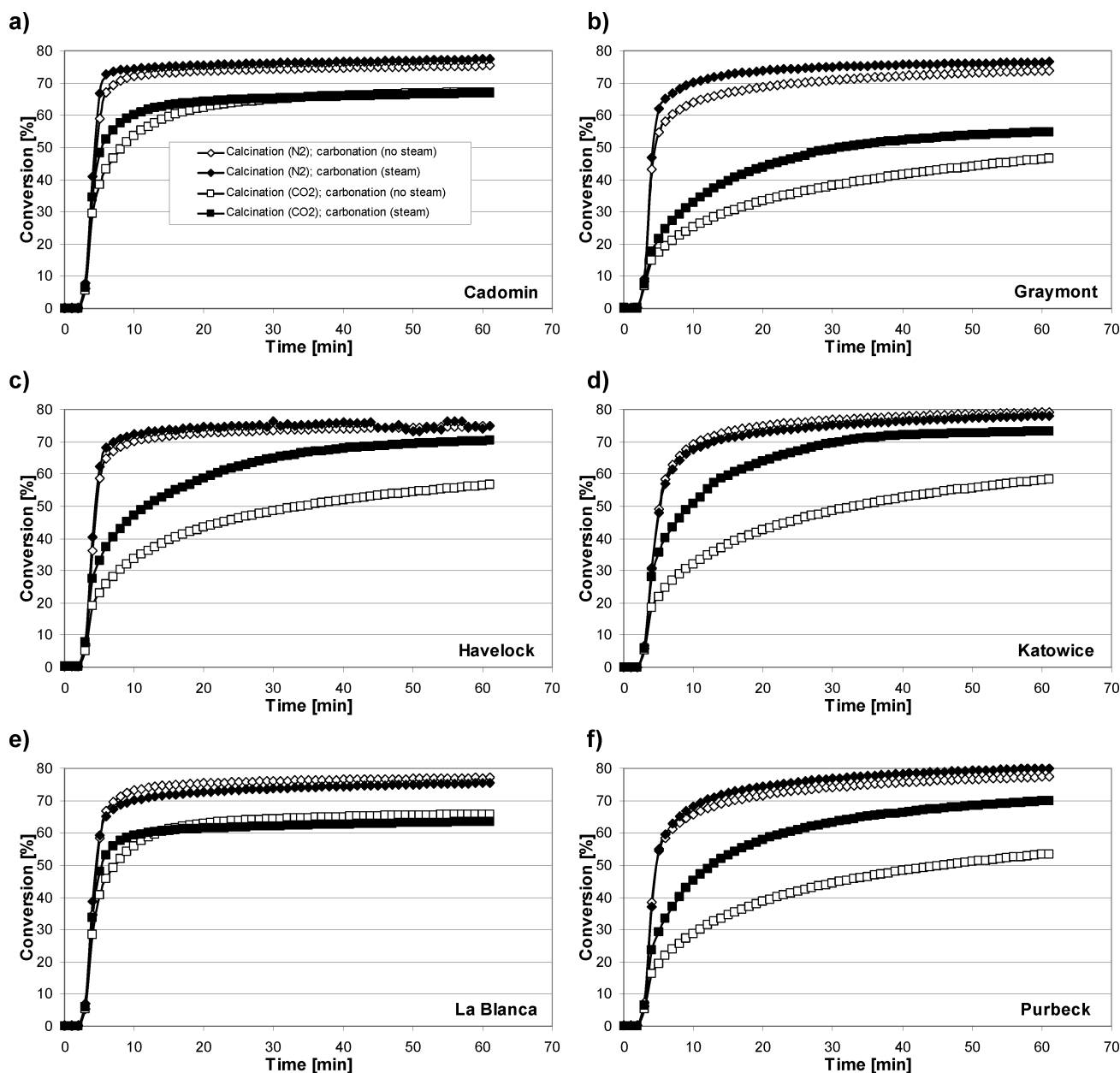


Figure 4. Conversion profiles of six lime samples ((a) Cadomin, 250–425 μm , (b) Graymont, 250–425 μm , (c) Havelock, 250–425 μm , (d) Katowice, 400–800 μm , (e) La Blanca, 400–600 μm , and (f) Purbeck, 425–500 μm). Samples are calcined in N₂ at 800 °C (diamonds) or in CO₂ at 950 °C (squares) and carbonated at 600 °C in 20% CO₂ (N₂ balance), with 10% steam (filled symbols) or without steam (hollow symbols).

and in N_2 at 800 °C (often employed in experimental work) are presented in Figure 4. As is known, calcination conditions affect sorbent morphology and performance during carbonation.²⁶ It can also be seen that lower conversions were obtained when samples were calcined in CO_2 . However, the conversions of these samples are more enhanced by steam than is the case when samples are calcined in N_2 . This is again a promising observation that steam enhances carbonation of more sintered samples that are typical for realistic Ca looping cycle conditions. However, the profiles differ from sample to sample and the exceptions in this work are La Blanca and Cadomin. Here it can be seen that steam does not promote carbonation. It is interesting that La Blanca again behaves differently than many other limestones. Namely, when thermal pretreatment was studied in order to enable better conversion in long series of carbonation/calcination cycles, this limestone after pretreatment showed much poorer conversions, with no self-reactivation effect which was seen for other limestones.¹⁷ That result was explained by its high content of sodium (1.07% Na_2O , Table 1), which enhances solid state diffusion and consequently sintering.²⁷ Carbonation conversion profiles obtained for other limestone samples indicate that steam promotes carbonation via enhancement of solid state diffusion in the product layer. This diffusion is a reaction-rate-controlling step during the slow, diffusion-controlled reaction stage. However, in the presence of Na^+ ions (as in La Blanca) in the product layer, this diffusion is already significantly enhanced, and additional enhancement by steam does not result in any noticeable effect. The content of Na in Cadomin limestone is, however, low (<0.2% Na_2O , Table 1), which means that another effect causes the lack of conversion enhancement by steam, but the reasons cannot be elucidated by results obtained in this study.

The conversions presented in Figure 4 also show that there is a “maximum” value, which is about 75–80% for samples calcined in N_2 , and after that further conversion becomes negligible. It can be seen that, when the fast reaction stage finishes at a conversion close to that value, the presence of steam has little if any conversion improvement effect. This can be explained by the theory that carbonation in the small pores is responsible for the conversion rate during the fast stage.²⁸ When those pores are filled by product ($CaCO_3$), any further carbonation ought to take place at the surface of larger pores. However, their surface area is small and any higher conversion implies a very thick product layer, which is thicker than a critical value.²⁹ Moreover, when all available room in the small pores is filled, carbonation at the surface of large pores, even if it is enhanced by steam, cannot significantly contribute to conversion.

This hypothesis is also supported by results obtained with synthetic calcium aluminate pellets (KT-CA-14), which are presented in Figure 5. This type of sorbent is more porous than a natural limestone after calcination. These pellets have pores in the range of hundreds of nanometres;²⁴ i.e., there is enough space in these small pores for product layer to be stored, allowing quantitative conversion given sufficient carbonation time. Moreover, carbonation can also be noticeably enhanced by steam at conversions >80%, which is presented in Figure 5.

It was already mentioned earlier that the positive effects of steam cannot be easily explained by formation of transient $Ca(OH)_2$, i.e., by a catalytic effect of H_2O . The results presented in this paper support the hypothesis that carbonation of CaO is enhanced via the effect of steam on solid state diffusion. Namely, it can be seen from carbonation profiles presented here that during the initial stage of carbonation, controlled by the kinetics of chemical reaction, conversion rates are fast and

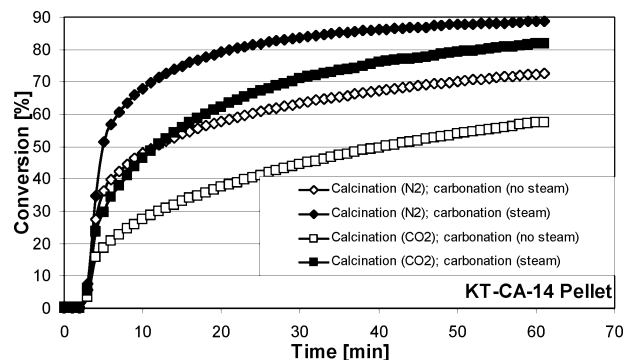


Figure 5. Conversion profiles for synthetic calcium aluminate pellet spheres (2 mm). Test conditions are same as those for Figure 4.

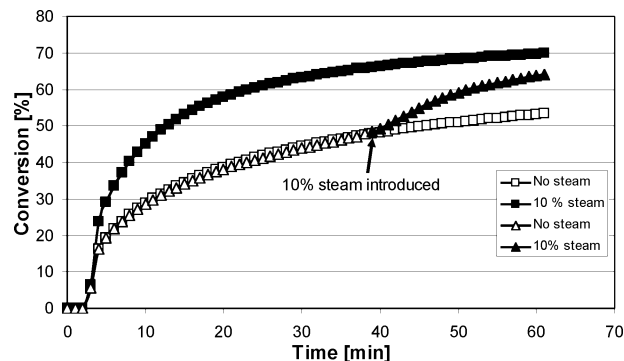


Figure 6. Carbonation of Purbeck limestone calcined in CO_2 at 950 °C with the same carbonation conditions as those used for Figure 4. The run presented by triangles started with no steam and after 40 min 10% steam was introduced.

similar for all tested sorbents and conditions regardless of the presence of steam. This means that steam does not affect reaction rate during the initial, kinetically controlled stage. However, the transition to the slower, diffusion-controlled stage in the presence of steam occurs at higher conversions, i.e., when the product layer is thicker. In other words, the presence of steam enhances diffusion in the product layer, and that diffusion becomes the controlling step later, when thicker product layer is formed. The influence of temperature (Figure 1) also supports this hypothesis. Namely, solid state diffusion is a process of high activation energy and, therefore, greatly influenced by temperature. With increase of temperature, this diffusion becomes more intensive and less limiting, minimizing the effects of steam.

Additional evidence concerning the effect of steam and its mechanism is presented in Figure 6. The runs with steam, no steam, and steam introduced during the diffusion-controlled reaction stage are compared. By contrast to the introduction of steam in the initial reaction stage, where conversion rates are very similar regardless of steam presence, the conversion rate was higher by about 3–4 times when steam was introduced during the slow reaction stage. This is clear proof that steam enhances product layer diffusion, which results in enhanced conversion.

Steam-enhanced solid state diffusion in the product layer also implies different morphology of samples carbonated in the presence of steam vs those with no steam. All samples after carbonation tests were observed by SEM and the most characteristic SEM images are presented in Figure 7. It can be seen that sorbent carbonated with no steam has a grain-subgrain structure, where subgrains form a network of nanosized pores. On the other hand, these pores cannot be seen in sample

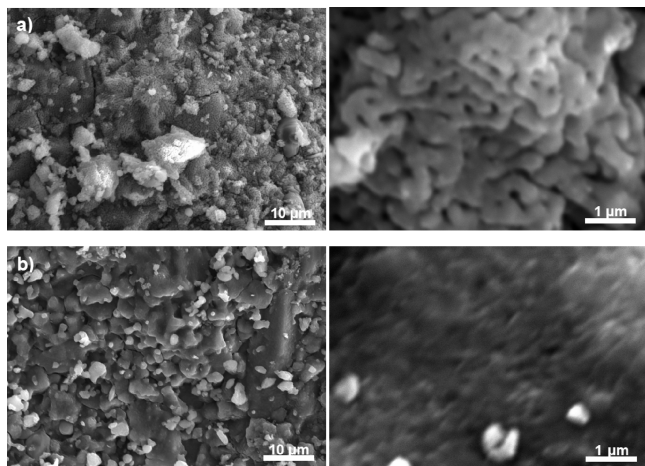


Figure 7. SEM images of carbonated Havelock (see Figure 4c) calcined in CO₂ at 950 °C and carbonated (a) without steam and (b) in the presence of steam.

carbonated in the presence of steam. They are filled by product (CaCO₃) due to higher conversion (71%:57%) and due to enhanced solid state diffusion. The differences in morphology presented in parts a and b of Figure 7 illustrate limits in conversion, even in the presence of steam, which appear when nanosized pores are filled by product. However, before that stage, conversion rate is faster in the presence of steam. This significant difference in sample morphology is a consequence of solid state diffusion enhanced by steam.

4. Conclusions

Screening of sorbents and carbonation conditions with respect to the enhancement of CaO carbonation by steam addition are presented here. It is concluded that steam promotes carbonation *via* enhancement of solid state diffusion in the product layer. This conclusion is supported by the observed temperature dependency of the carbonation rate in the presence of steam, the influence of Na⁺ ions in the sorbent, and by the sorbent morphology observed after carbonation with and without steam present. A general conclusion is that steam is more helpful under conditions when product layer diffusion becomes reaction-rate-limiting earlier, i.e., for sorbents for which their carrying capacity is diminished; this is characteristic for lower temperatures and/or more sintered sorbents. Such results are promising for application of steam for enhancement of CO₂ capture by Ca looping cycles. They also provide a good starting point for design of further carbonation/calcination tests in order to explore the effect of steam on sorbent activity in long series of capture cycles.

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