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Long-Term Calcination/Carbonation Cycling and Thermal Pretreatment for CO₂ Capture by Limestone and Dolomite

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Capturing carbon dioxide is vital for the future of climate-friendly combustion, gasification, and steam-reforming processes. Dry processes utilizing simple sorbents have great potential in this regard. Long-term calcination/carbonation cycling was carried out in an atmospheric-pressure thermogravimetric reactor. Although dolomite gave better capture than limestone for a limited number of cycles, the advantage declined over many cycles. Under some circumstances, decreasing the carbonation temperature increased the rate of reaction because of the interaction between equilibrium and kinetic factors. Limestone and dolomite, after being pretreated thermally at high temperatures (1000 or 1100 °C), showed a substantial increase in calcium utilization over many calcination/carbonation cycles. Lengthening the pretreatment interval resulted in greater improvement. However, attrition was significantly greater for the pretreated sorbents. Greatly extending the duration of carbonation during one cycle was found to be capable of restoring the CO₂ capture ability of sorbents to their original behavior, offering a possible means of countering the long-term degradation of calcium sorbents for dry capture of carbon dioxide.

Introduction

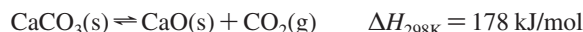
CO₂ emissions produced worldwide by power plants, domestic heating, internal combustion engines, and other energy-related processes have increased rapidly in recent decades, contributing to the greenhouse gas effect (GHG), widely accepted as contributing to climate change. In parallel with the development of technologies which utilize non-carbon-based energy sources, capturing and sequestering CO₂ offer possible means of reducing the emission of greenhouse gases. Capture of CO₂ is an essential first step, typically representing 50–80% of the overall cost of total CO₂ capture and storage costs for power station flue gases.¹ Current technologies for capturing CO₂ are heavily based on liquid solvents. These tend to be expensive and to have serious thermodynamic penalties. Dry sorbents offer significant potential benefits, especially if the sorbents are inexpensive and can remain effective over substantial numbers of calcination/carbonation cycles. The international scientific community is very active in investigating various calcium-based dry sorbents including dolomites, limestones, aragonites, and hydrotalcites. Some recent reviews were reported.^{2–4} Limestone and dolomite have the great advantage of being relatively abundant and cheap, although various other possible sorbents, such as lithium silicates and zirconates, are

Table 1. Chemical Composition Analyses

composition (wt%)	Strassburg limestone	Arctic dolomite
CaO	53.7	30.51
MgO	1.25	21.25
Al ₂ O ₃	0.19	0.17
Fe ₂ O ₃	0.94	1.3
K ₂ O	0.08	0.04
Na ₂ O	0.02	0.15
SiO ₂	0.94	2.12
loss on ignition	42.9	44.4

also under active investigation. Moreover, limestone and dolomite are already widely used as sorbents for capturing sulfur.

At the heart of the limestone looping cycle being investigated for the capture of CO₂ is the calcination/carbonation reaction:



This reaction proceeds forward or in reverse, depending on the partial pressure of CO₂ and the temperature. High temperatures favor the forward (calcination) reaction, whereas high CO₂ partial pressures promote the reverse (carbonation) reaction.

When attempts have been made to capture CO₂ by circulating solid sorbents between a reactor (combustor, gasifier, or steam reformer) where carbonation is made to occur and a calciner where the sorbent is regenerated, there is a loss of reversibility, i.e., the sorbent loses much of its ability to capture CO₂ as cycling progresses. A number of factors influence the sorbent performance and its extent of reversibility for looping calcination/carbonation cycles. These include temperature, pressure, sorbent composition, duration of the carbonation interval, regeneration conditions, and the presence or absence of sulfur.^{3,5}

The rate of carbonation, and hence the extent of carbonation with limited reaction times, are also affected by sintering of

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(1) Steeneveldt, R.; Berger, B.; Torp, T. A. CO₂ capture and storage: closing the knowing-doing gap. *Chem. Eng. Res. Des.* **2006**, *84*, 739–763.

(2) Stanmore, B.; Gilot, P. Review—calcination and carbonation of limestone during thermal cycling for CO₂ sequestration. *Fuel Proc. Technol.* **2005**, *86*, 1707–1743.

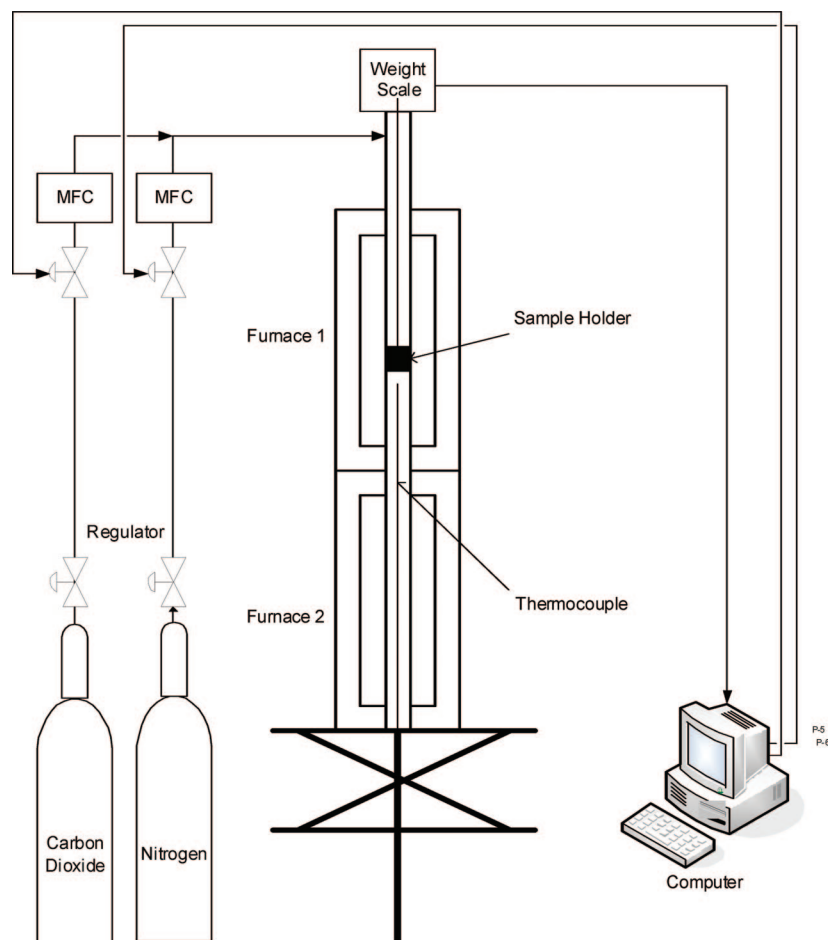


Figure 1. Thermogravimetric reactor setup (One solenoid valve and one mass flow controller MFC for each gas supply, i.e., N_2 and CO_2 . Control signal sent from the computer to the solenoid valves for cyclic calcination–carbonation test.)

the sorbent and by pore plugging, both reducing available surface area and restricting access to the interior of the particles. The pore size distribution of limestone changes after many cycles of calcination/carbonation, producing larger pores. Recent work⁶ has shown a reduction in the volume of pores of diameter $<200\ \mu\text{m}$ for limestone and an increase in pore volume in the $>200\ \mu\text{m}$ range. High-resolution scanning electron microscope (SEM) images and pore size distribution analysis show differences in limestone and dolomite that help to account for differences in their carbonation behavior.⁶ Better results in capturing CO_2 for dolomite can be explained by a reduction in the sintering rate because of the presence of MgO .

Recent work⁷ has demonstrated that prolonged pretreatment, by exposing limestone to temperatures of 1000 or 1100 $^\circ\text{C}$ for 24 h in an inert atmosphere, can significantly improve the utilization efficiency of limestone. However, these tests were only conducted for 30 calcination/carbonation cycles. There is a need to see whether this advantage persists over a much greater

number of cycles, to show whether pretreatment is helpful for dolomite as well as limestone, and to determine whether attrition is affected by the pretreatment. This paper reports on long-term cycling (at least 1000 cycles of calcination/carbonation) with and without thermal pretreatment. Results are also provided with respect to attrition of thermally pretreated sorbents. In addition, we present some results showing the long-term (≥ 1000 cycles) performance of dolomite vs limestone, as well as results elucidating the effect of prolonged carbonation duration on subsequent cycles of calcination/carbonation.

Materials and Methods

Arctic dolomite and Strassburg limestone were compared as sorbents for long-term calcination/carbonation cycling, as these two sorbents have already been tested intensively in previous CO_2 capture tests^{5,6,8,9} as well as in SO_2 capture studies.^{10,11} Table 1 summarizes the chemical composition and loss-on-ignition for both sorbents. The calcined limestone contains 53.7% CaO and only 1.25% MgO , whereas calcined dolomite

(3) Florin, N.; Harris, A. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chem. Eng. Sci.* **2008**, *63*, 287–316.

(4) Anthony, E. Solid looping cycles: a new technology for coal conversion. *Ind. Eng. Chem. Res.* **2008**, *47*, 1747–1754.

(5) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. Removal of CO_2 by calcium based sorbents in the presence of SO_2 . *Energy Fuel* **2007**, *21*, 163–170.

(6) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. The effect of CaO sintering on cyclic CO_2 capture in energy systems. *J. AIChE* **2007**, *53*, 2432–2442.

(7) Manovic, V.; Anthony, E. Thermal activation of CaO -based sorbent and self-reactivation during CO_2 capture looping cycles. *Environ. Sci. Technol.* **2008**, *42*, 4170–4174.

(8) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. Investigation of attempts to improve cyclic CO_2 capture by sorbent hydration and modification. *Ind. Eng. Chem. Res.* **2008**, *47*, 2024–2032.

(9) Sun, P.; Lim, C. J.; Grace, J. R. Cyclic CO_2 capture by limestone-derived sorbent during prolonged calcination/carbonation cycling. *J. AIChE* **2008**, *54*, 1668–1677.

(10) Laursen, K.; Duo, W.; Grace, J.; Lim, C. J. Sulphation and reactivation characteristics of nine limestones. *Fuel* **2000**, *79*, 153–163.

(11) Laursen, K.; Duo, W.; Grace, J.; Lim, C. J. Characterization of steam reactivation mechanisms in limestones and spent calcium sorbents. *Fuel* **2001**, *80*, 1293–1306.

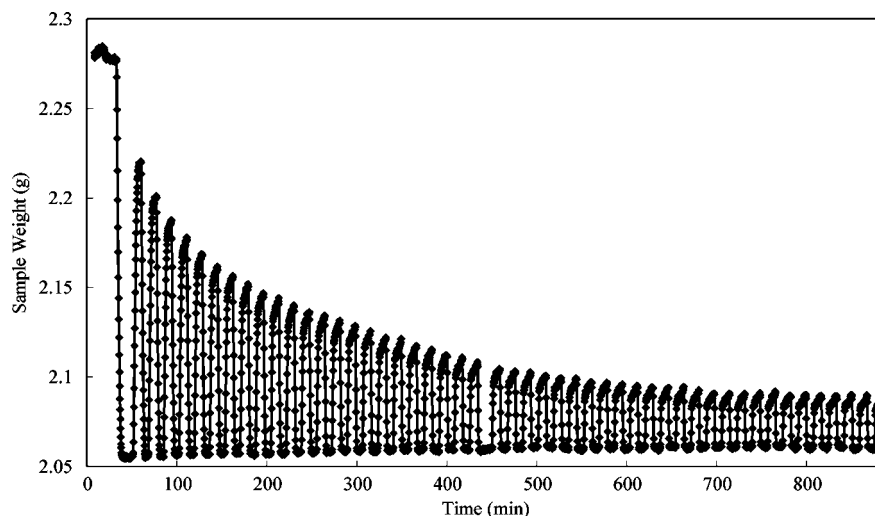


Figure 2. Mass of sample, holder, and wire vs time during early intervals of Strassburg limestone calcination and carbonation during cycling. The somewhat longer period after about 440 min is because the computer resets itself at midnight.

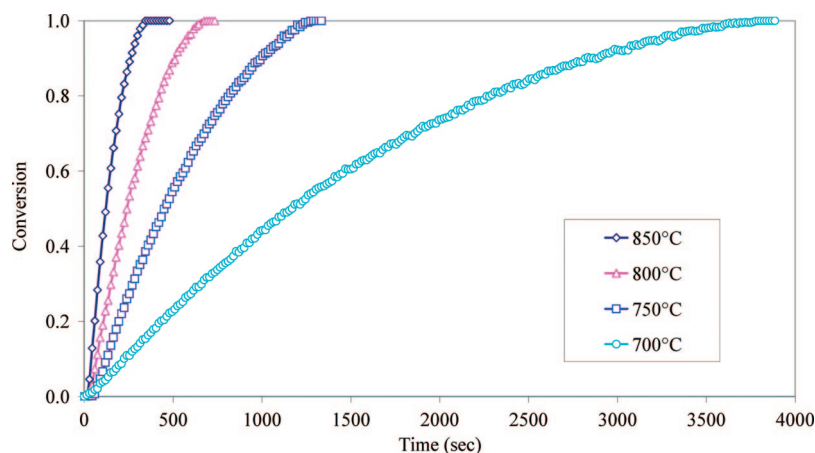


Figure 3. Conversion vs time during initial calcination of Strassburg limestone at different temperatures.

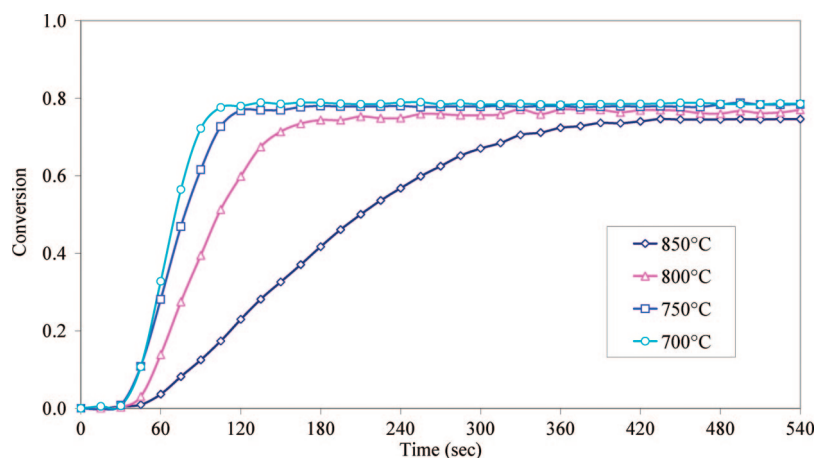


Figure 4. Conversion vs time for initial carbonation of Strassburg limestone in pure CO₂ at different temperatures. (Limestone was 100% calcined before initial/1st carbonation; see Figure 3.)

has only 30.5% CaO, but a greater proportion of MgO, 21.3%. More detailed chemical composition analyses and other properties can be found in previous studies.^{10,11} The thermal pretreatment tests and changes in sorbent carbonation duration focused mainly on Strassburg limestone.

An atmospheric pressure fixed-bed thermogravimetric reactor, shown in Figure 1 and described in detail elsewhere,^{10,11} was used in this work. A pure 40- μ m diameter platinum-wire-mesh sample holder containing 3600 openings/cm² was

utilized to hold 845 ± 5 mg of fresh or pretreated sorbent samples, suspended from a sensitive load cell. Mass flow controllers maintained the desired inlet gas flow rates.

The temperature was maintained constant, in most cases at 850 °C, for both the carbonation and calcination reactions. Switching back and forth between calcination and carbonation was implemented by means of solenoid valves, controlled by a computer, that provided 1.6 L/min flows of either 100% industrial grade N₂ (for calcination) or 100% industrial grade

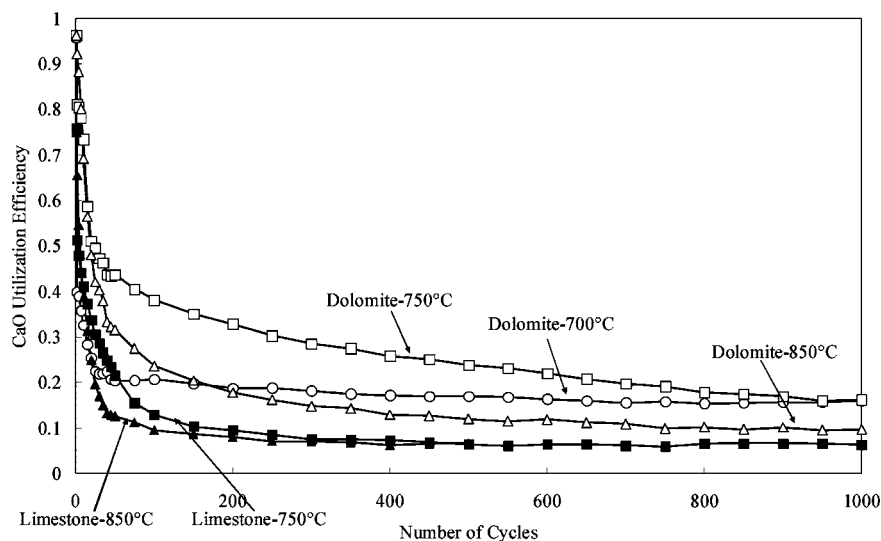


Figure 5. Comparison of long-term calcination/carbonation test results for limestone and dolomite at different temperatures. (Limestone and dolomite were 100% calcined before 1st carbonation.)

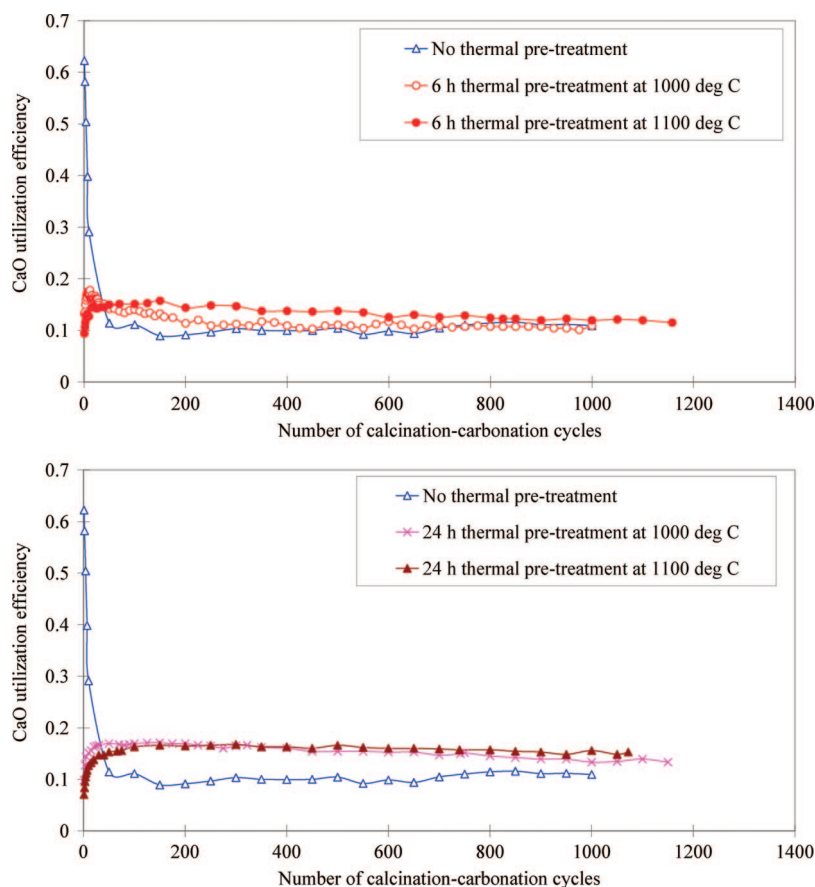


Figure 6. Effect of thermal pretreatment temperature on cyclic CaO utilization efficiency for Strassburg limestone (thermal pretreatment at 1000 and 1100 °C with ~1000 mL/min N₂ for 6 and 24 h; TGR test conditions: 1600 mL/min gas flow, calcination at 100% N₂ for 8 min, carbonation at 100% CO₂ for 9 min, calcination and carbonation temperature both 850 °C).

CO₂ (for carbonation). The lifting table capability of the reactor system was not utilized during the tests described in this paper. The calcination time of each cycle for all runs without and with pretreatment was 8 min, whereas the carbonation duration for all cases, except where specified, was 9 min, as in previous studies.⁹ At least 1000 cycles were completed in each test, many more than in almost all previous studies reported in the literature.

For the runs with pretreatment, sorbents were prepared in a high-temperature programmable furnace with an inert atmo-

sphere provided by a 0.40 L/min flow of 100% nitrogen for heating durations of either 6 or 24 h, cooled, preserving the inert atmosphere, and immediately put in a desiccator before being subjected to long-term cycling in the atmospheric-pressure thermogravimetric reactor.

In one of the runs where the limestone had been pretreated at 1000 °C for 24 h, two of the carbonation intervals were greatly extended, to 12.3 and 59 h, to test the long-term effect of prolonged carbonation, since earlier results⁹ had indicated possible benefits of extended carbonation.

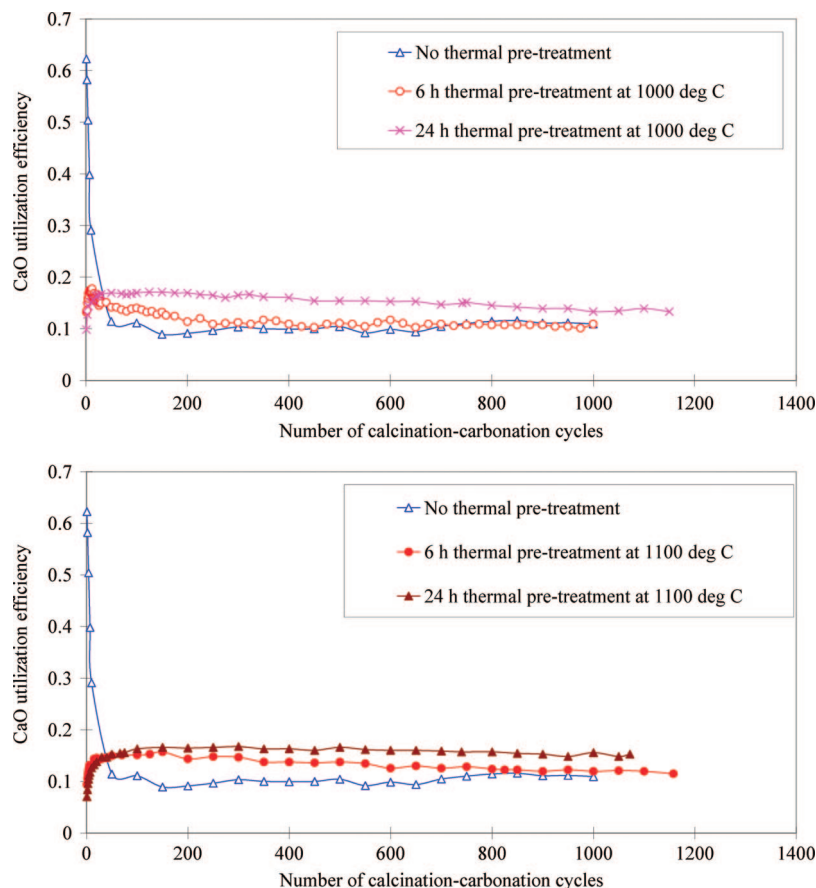


Figure 7. Effect of thermal pretreatment time on cyclic CaO utilization efficiency for Strassburg limestone (thermal pretreatment at 1000 and 1100 °C with ~1000 mL/min N₂ for 6 and 24 h; TGR test conditions: 1600 mL/min gas flow, calcination at 100% N₂ for 8 min, carbonation at 100% CO₂ for 9 min, calcination and carbonation temperature both 850 °C).

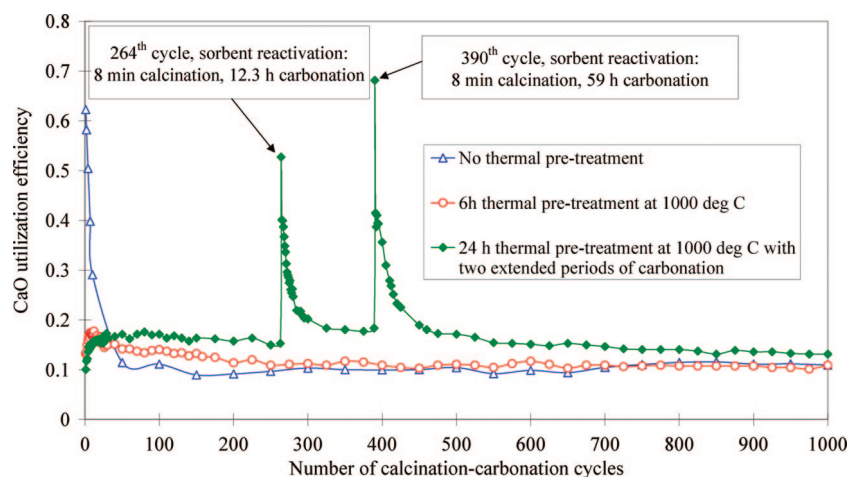


Figure 8. Results of long-term calcination/carbonation cycling with Strassburg limestone without thermal pretreatment, compared with pretreatment at 1000 °C for 6 h and at 1000 °C for 24 h with two extended periods of carbonation. Calcination/ carbonation cycling was at 850 °C in all cases.

For the attrition test, 50 g of thermally pretreated Strassburg limestone or dolomite were subjected to impacts at room temperature in a custom-made attrition-testing chamber¹² where the particles were entrained and accelerated by an air jet with an air velocity of 55 m/s, colliding at nearly right angles with a stainless steel target.

Results and Discussion

A typical trace of sample mass vs time during early calcination/carbonation cycling is shown in Figure 2. Note

that the mass achieved after each period of calcination was almost unchanged, whereas each subsequent carbonation resulted in a noticeably lower mass gain than for the previous cycle, indicating a loss in calcium utilization efficiency.

Figure 3 shows conversion vs time during calcination at different temperatures in the inert (nitrogen) atmosphere. It is seen that the reaction rates were greater at higher temperatures,

(12) Chen, Z.; Lim, C. J.; Grace, J. Study of limestone particle impact attrition. *Chem. Eng. Sci.* **2007**, 62, 867–877.

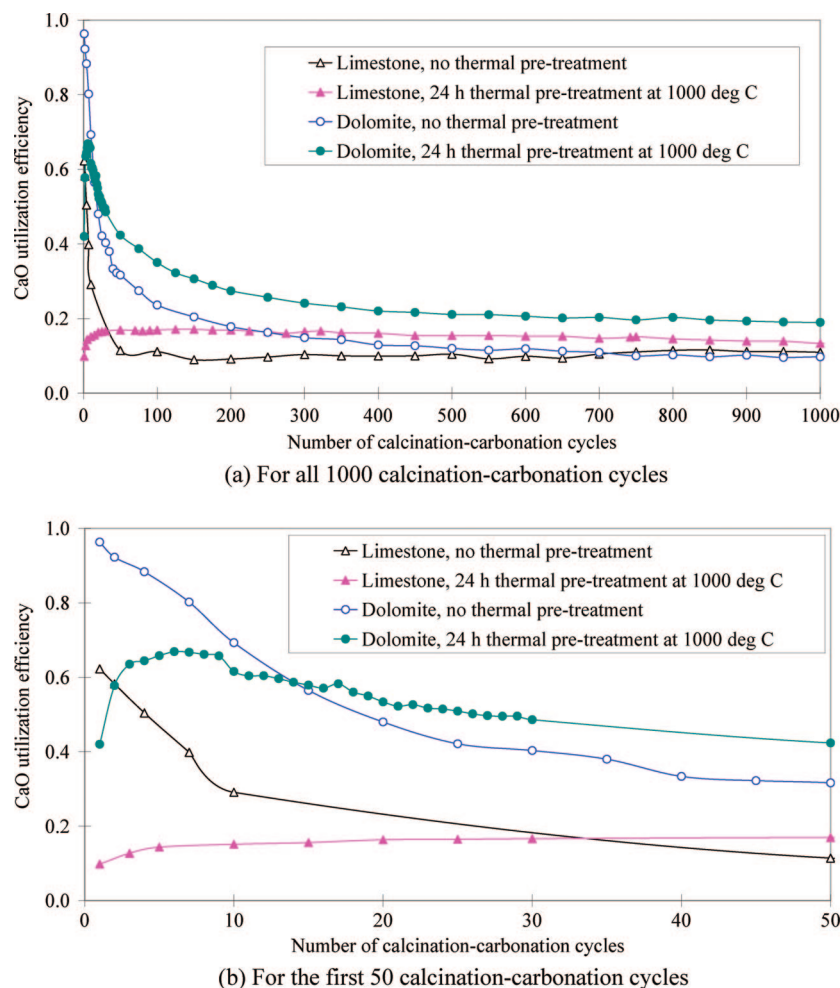


Figure 9. Effect of thermal pretreatment on cyclic CaO utilization efficiency for Arctic dolomite (thermal pretreatment at 1000 °C with ~1000 mL/min N₂ for 24 h; TGR test conditions: 1600 mL/min gas flow, calcination at 100% N₂ for 8 min, carbonation at 100% CO₂ for 9 min, calcination and carbonation temperatures both 850 °C).

Table 2. CaO Utilization Percent Efficiencies for Limestone Long-Term Calcination/Carbonation Cycling after (a) No Thermal Pretreatment; (b) Pretreatment at 1000 °C for 6 h; (c) Thermal Pretreatment at 1000 °C for 24 h; (d) Same as in c but with Two Extended Periods of Carbonation; (e) Thermal Pretreatment at 1100 °C for 6 h; (f) Thermal Pretreatment at 1100 °C for 24 h

cycle no.	no thermal pretreatment	6 h thermal pretreatment at 1000 °C	24 h thermal pretreatment at 1000 °C	24 h thermal pretreatment at 1000 °C ^a	6 h thermal pretreatment at 1100 °C	24 h thermal pretreatment at 1100 °C
1	62.25	13.23	9.83	10.02	9.37	7.05
10	29.10	16.97	15.12	15.42	12.70	12.64
50	11.41	14.16	16.93	17.11	14.97	15.28
100	11.11	14.01	16.93	17.11	15.12	16.31
200	9.12	11.36	16.93	15.73	14.36	16.46
250	9.65	10.90	16.48	14.96	14.81	16.60
264	9.98	11.84	16.36	52.73 ^b	14.86	16.63
300	10.31	11.21	16.48	20.20	14.66	16.75
390	10.13	11.32	15.68	68.15 ^c	14.15	16.49
400	9.94	10.90	16.02	35.62	13.76	16.31
600	9.84	11.67	15.27	15.11	12.55	16.02
800	11.43	10.74	14.51	14.03	12.4	15.72
1000	10.92	10.90	13.30	13.10	11.94	15.58

^a Thermal pretreatment at 1000 °C for 24 h, with two extended periods of carbonation. ^b With 12.3 h carbonation. ^c With 59 h carbonation.

as expected. Lower calcination temperatures required significantly longer calcination times.

On the other hand, carbonation reaction rates decreased with increasing temperature in the 700–850 °C range, as shown in Figure 4. This trend likely resulted from the increasing kinetic rate constant being counterbalanced by a drop in the partial pressure driving force (excess over the equilibrium partial pressure), which increases with temperature. Sintering may also have played a role.⁶

Figure 5 plots the CaO utilization efficiency for CO₂ capture based on total CaO as a function of the number of (8-min) calcination cycles and (9-min) carbonation cycles for both the Strassburg limestone and Arctic dolomite. It is seen that the dolomite lost its ability to capture CO₂ more slowly over the entire 1000-cycle duration. However, the limestone leveled off after ~300 cycles. Hence the relative advantage of the dolomite over the limestone was reduced as the cycling continued.

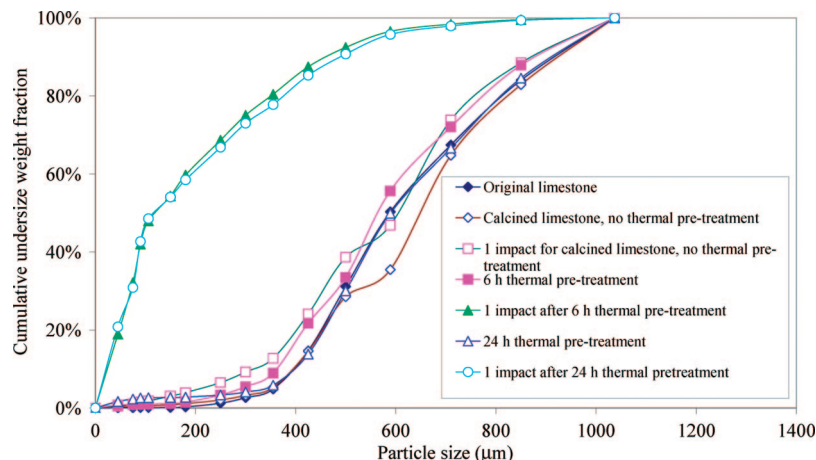


Figure 10. Particle size distributions for original Strassburg limestone, calcined limestone without thermal pretreatment, and 6 and 24 h thermally pretreated lime and impacted (1 cycle) lime (thermally pretreated in a 1000 °C oven with ~1000 mL/min N₂ for 6 and 24 h; calcination at 850 °C for no thermal pretreatment limestone; impact at room temperature with a conveying air velocity of 55 m/s.)

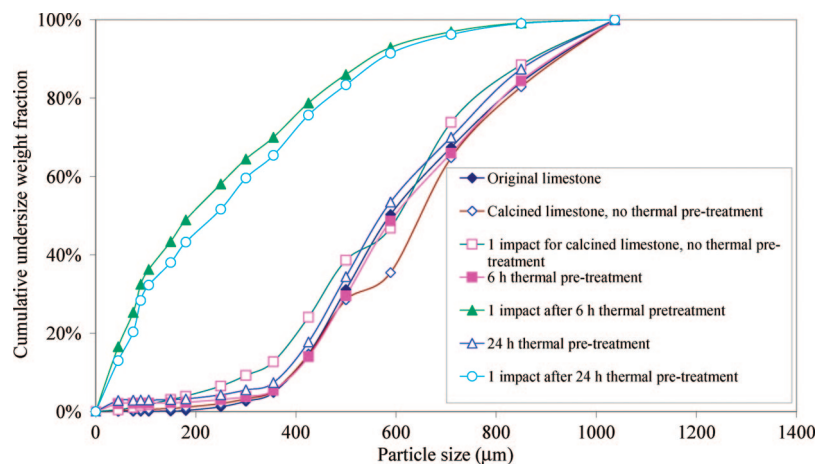


Figure 11. Particle size distributions for original Strassburg limestone, calcined limestone without pretreatment, and 6 and 24 h thermally pretreated lime and impacted (1 cycle) lime (thermally pretreated in an 1100 °C oven with ~1000 mL/min N₂ for 6 and 24 h; calcination at 850 °C for no thermal pretreatment limestone; impact at room temperature with a conveying air velocity of 55 m/s.)

The results in Figure 5 also show the influence of temperature on calcium utilization. For limestone, it is seen that the loss in sorbent reversibility was initially greater when the cycling was carried out at 850 °C than when the thermogravimetric reactor was held at 750 °C, but the two curves eventually become indistinguishable. For the dolomite, a temperature of 750 °C was again more favorable than 850 °C, with a greater difference; the advantage persisted over a greater number of cycles, although the benefit of the lower temperature is clearly diminished and still decreasing after 1000 cycles. In terms of reversibility for the dolomite, 700 °C was initially less favorable than either of the higher temperatures but ultimately led to a higher utilization efficiency.

The effect of the operating temperature on the evolution of sorbent efficiency with the number of calcination–carbonation cycles can be explained in terms of the sorbent physical properties, especially pore volume. With high-temperature calcination or carbonation, sintering occurs, leading to a decrease in sorbent pore volume for carbonation.⁶ On the other hand, with carbonation, the sorbent reactivated itself, especially for a high degree of sintering,⁷ leading to more pore volume. As the number of calcination–carbonation cycles increases, there is a balance between pore volume disappearance and regeneration, resulting in a nearly constant CaO utilization efficiency as shown in Figure 5. The better results in capturing CO₂ for the dolomite

relative to the limestone could be due to a reduction in the sintering rate because of the presence of MgO.⁶

In the thermal pretreatment tests, Strassburg limestone was first held at 1000 °C or at 1100 °C for either 6 or 24 h in a nitrogen atmosphere and then cycled repeatedly (> 1000 cycles) in the thermogravimetric reactor at the base conditions, i.e., 9-min carbonation intervals in pure CO₂ at 850 °C, alternating with 8-min periods of calcination at 850 °C in a pure nitrogen atmosphere. Results are shown in Figures 6 to 8. It is seen that the initial few cycles after the thermal pretreatment were less favorable than without pretreatment. This may be because high-temperature sintering reduced the pore volume for CO₂ capture.^{5,6,8,9} However, after ~20 cycles, the pretreated samples consistently did better than the untreated ones in terms of their ability to capture CO₂, this advantage being retained over 1000 cycles or more. The improved sorbent utilization efficiency results from the self-reactivation of sorbent with repeated carbonation cycles, resulting in an increase in pore volume for CO₂ capture.⁷ Lengthening the pretreatment time from 6 to 24 h resulted in a gain in long-term utilization efficiency, as did an increase in the temperature of pretreatment from 1000 to 1100 °C. For comparison, one thermal pretreatment test was also conducted for Arctic dolomite at 1000 °C for 24 h in a nitrogen atmosphere, followed by 1000 cycles in the thermogravimetric reactor at the same base conditions as for the limestone. Results

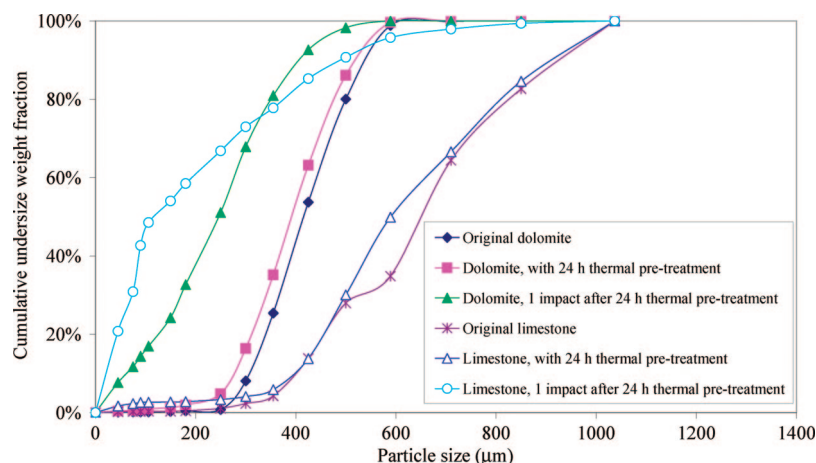


Figure 12. Particle size distributions for both limestone and dolomite before and after thermal pretreatment, and with one impact for thermally pretreated limestone and dolomite (thermally pretreated in a 1000 °C oven with ~ 1000 mL/min N_2 for 24 h; impact at room temperature with a conveying air velocity of 55 m/s.)

are shown in Figure 9. With thermal pretreatment, the initial CaO utilization efficiency was lower and then increased to a maximum after a few cycles (~ 6), followed by a gradual decline in the utilization over the long-term cycling. Overall, compared to limestone, dolomite showed a greater improvement in cyclic performance because of thermal pretreatment.

The solid diamonds in Figure 8 provide results of the run where two of the carbonation intervals were greatly extended (from 9 min to 12.3 h in the 264th cycle, and to 59 h in the 390th cycle.) It is clear that the long-duration carbonation in each case resulted in a substantial recovery in CO_2 capture ability. In the subsequent cycles, the calcium utilization efficiency again declined as the cycling continued, but the post-prolonged-carbonation performance was even better than for the originally pretreated limestone.

Table 2 compares the CaO utilization efficiency during long-term calcination/carbonation cycling for the limestone with and without thermal pretreatment, and with and without extended periods of carbonation. It is clear that the thermal pretreatment is only helpful beyond a limited number of cycles, but it is then possible to maintain the advantage over hundreds (> 1000) of cycles. Thermal pretreatment offers a means of significantly enhancing the net utilization efficiency of the sorbent. Greatly prolonging carbonation periods is also seen to be useful. In this case, the beneficial effects are immediate, and they also appear to be long-lasting. The relatively low values in Table 2 ($< 20\%$) are based on the limited times for calcination (8 min/cycle) and carbonation (9 min/cycle), chosen as representative mean residence times for practical fluidized bed calcination and carbonation reactors.

Thermal pretreatment clearly appears to have benefits for the ability of the sorbent to capture CO_2 , but good sorbent particles should also have other desirable properties, including the ability to be processed, under conditions in which there are mechanical and thermal stresses, without breaking. It was originally planned to subject pretreated samples to repeated impacts in the attrition chamber described above. However, a single impact resulted in such a major increase in attrition, as shown in Figures 10–12, that further impacts were not needed. With or without thermal pretreatment, the calcined limestone (or dolomite) and original limestone (or dolomite) had similar particle size distributions. However, one impact attrition at room temperature with a conveying air velocity of 55 m/s caused a large leftward shift in particle size distribution curves shown in Figures 10–12. It

was immediately clear that the sorbent in this form would very likely be unsuitable for any equipment (e.g., a fluidized bed) where the particles would undergo collisions. More attrition for the thermally pretreated limestone was found than for the thermally pretreated dolomite. The difference could be affected by differences in the initial sizes of the limestone and dolomite, the former being larger. For practical applications, our results indicate that thermal pretreatment, while promising from a calcium utilization point of view, is likely to need to be accompanied by some technique to increase the attrition-resistance of the sorbent particles, e.g., by adding inert carriers to the sorbents. In this paper, the major focus is the effect of thermal pretreatment on the sorbent utilization for CO_2 capture. Ways of reducing attrition of sorbents will be investigated in future work.

Conclusions

When calcium sorbents undergo repeated cycles of calcination and carbonation of limited duration, the ability to capture CO_2 is progressively lost. Dolomite loses less of its capacity to retain carbon than limestone, but its relative advantage was found to decrease as the number of calcination/carbonation cycles increased.

For the range of calcination/carbonation temperatures investigated (700–850 °C), the lower temperatures generally provided better sorbent reversibility, but the advantage tended to be lost as the cycling was prolonged.

Thermally pretreating limestone and dolomite by subjecting particles to an inert atmosphere for extended periods of 6 or 24 h resulted in sustained benefits in terms of the ability of the sorbent to retain carbon in repeated cycles of carbonation and calcination. However, the pretreatment led to a serious decrease in the ability of both sorbents to withstand impact attrition.

Prolonged carbonation was successful in restoring the ability of pretreated limestone, which had undergone multiple cycles of carbonation and calcination, to retain carbon, returning it to performance which was better than that of the original untreated and prior-to-cycling limestone.

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