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Screening of Binders for Pelletization of CaO-Based Sorbents for CO$_2$ Capture[†]

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CaO-based CO$_2$ looping cycle technology is a promising method for separation of CO$_2$ from flue gas and syngas at high temperatures. The process of CO$_2$ capture is expected to take place in fluidized-bed combustion (FBC) systems, which implies significant attrition and elutriation of the solid sorbent. Hence, both reactivation of spent sorbent and preparation of modified CaO-based sorbent may be required to maximize the performance of the sorbent. One of the more promising methods to achieve reactivation, namely, hydration, seems to produce very fragile particles, which are unlikely to be suitable for FBC applications. Thus, it is expected that pelletization of the obtained powder may be required. In this paper, we present initial results on the screening of suitable binders for pelletization. Two types of bentonite (Na- and Ca-bentonite) and four types of commercial calcium aluminate cements (CA-14, CA-25, Secar 51, and Secar 80) were investigated here, with a primary focus of maintaining a high CO$_2$-capture capacity over 30−35 cycles. The tests were carried out using a thermogravimetric analyzer (TGA), and the results showed that the presence of bentonites led to faster decay in activity as a result of the formation of calcium-silica compounds with low melting points, which leads to enhanced sintering. This is confirmed by scanning electron microscopy (SEM) and also X-ray diffraction (XRD), which showed the presence of spurrite [Ca$_5$(SiO$_4$)$_2$CO$_3$] as the dominant compound in the pellet after this series of cycles. Better results were obtained with no binder, i.e., by hydration of lime, where Ca(OH)$_2$ plays the role of the binder. Promising results were obtained also with calcium aluminate cements, where no effect of sintering because of the presence of these binders was noticed. Thus, on the basis of this study, the use of calcium aluminate cements for pelletization of CaO-based sorbent is recommended.

1. Introduction

It is widely accepted that global warming and climate changes are being exacerbated by increasing concentrations of greenhouse gases, in particular CO$_2$. Fossil fuel (especially coal) combustion power plants represent a major source of anthropogenic CO$_2$. One possible mitigation step is the capture of CO$_2$ from flue gas followed by its sequestration in geological formations.[1−3] The goal of CO$_2$ capture from flue gases is the production of a concentrated stream of CO$_2$ at high pressure that can be readily transported to a storage site. The capture/separation step for CO$_2$ from large point sources is a critical one with respect to the technical feasibility and cost of the overall carbon sequestration scenario, because the CO$_2$ separation is both the most technically challenging and energy-intensive step. Thus, much research is targeted at improving current technologies or developing new approaches of CO$_2$ separation and capture.[4]

Solid looping cycles offer an important new class of technologies for CO$_2$ separation.[5] These cycles employ a solid carrier to bring oxygen to the fuel or remove CO$_2$ from combustion or gasification gases to be released as a pure CO$_2$ stream, with subsequent regeneration of the O$_2$ (O$_2$ cycles) or CO$_2$ (CO$_2$ cycles) carrier. CO$_2$ looping cycles, which employ a solid CaO-based carrier, may inexpensively and effectively remove CO$_2$ from combustion (or gasification) gases, allowing it to be regenerated as a pure CO$_2$ stream suitable for sequestration.[5,6] The use of solids also means that, in many cases, fluidized-bed combustion (FBC) systems will represent optimal technology for such processes. Preliminary economic analyses[7−9] suggest that such processes are economically attractive, and an important advantage of using CaO is that limestone (CaCO$_3$) is an abundant and relatively inexpensive material when used at the industrial scale.

CO$_2$ capture by CaO-based sorbents is based on the reversible chemical reaction

$$CaO_{(s)} + CO_{2(g)} = CaCO_{3(s)} \quad \Delta H < 0 \quad (1)$$

CO$_2$ separation from flue gas is possible in a multicycle process in a dual FBC reactor. This involves reaction of CaO

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(1) Metz, B.; Davidson, O.; de Coninck, H.; Loos, M.; Meyer, L. *Special Report on Carbon Dioxide Capture and Storage*, Intergovernmental Panel on Climate Change; Cambridge University Press: New York, 2005.

(2) Herzog, H. What future for carbon capture and sequestration? *Environ. Sci. Technol.* **2001**, *35*, 148–153.

(3) Bachu, S. CO$_2$ storage in geological media: Role, means, status, and barriers to deployment. *Prog. Energy Combust. Sci.* **2008**, *34*, 254–273.

(4) Yang, H.; Xu, Z.; Fan, M.; Gupta, R.; Slimane, R. B.; Bland, A. E.; Wright, I. Progress in carbon dioxide separation and capture: A review. *J. Environ. Sci.* **2008**, *20*, 14–27.

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

(6) Stanmore, B. R.; Gilot, P. Review—Calcination and carbonation of limestone during thermal cycling for CO$_2$ sequestration. *Fuel Process. Technol.* **2005**, *86*, 1707–1743.

(7) Abanades, J. C.; Grasa, G.; Alonso, M.; Rodriguez, N.; Anthony, E. J.; Romeo, L. M. Cost structure of a postcombustion CO$_2$ capture system using CaO. *Environ. Sci. Technol.* **2007**, *41*, 5523–5527.

(8) MacKenzie, A.; Granatstein, D. L.; Anthony, E. J.; Abanades, J. C. Economics of CO$_2$ capture using the calcium cycle with a pressurized fluidized bed combustor. *Energy Fuels* **2007**, *21*, 920–926.

(9) Abanades, J. C.; Rubin, E. S.; Anthony, E. J. Sorbent cost and performance in CO$_2$ capture system. *Ind. Eng. Chem. Res.* **2004**, *43*, 3462–3466.

with CO_2 from flue gas/syngas in a carbonator and regeneration of sorbent and obtaining of concentrated CO_2 stream in a calciner.[10] However, attrition of sorbent is a significant problem for FBC systems,[11] leading to significant sorbent elutriation from the reactor, as was demonstrated in our recent pilot-scale demonstration of the CO_2 looping cycle using a dual FBC reactor.[12] Along with decay of sorbent-carrying capacity as a result of sintering and sulfation, attrition is one of the major challenges in further developing CaO-based CO_2 looping cycle technology. Attrition is expected to be more important than in normal FBC operations because, apart from the mechanical stresses experienced by circulating sorbent particles, thermal stresses also occur as a result of different temperatures employed in the carbonator and calciner, which also enhance attrition.

Pelletization of the elutriated sorbent powder is one potential solution to reuse sorbent. Grinding sorbents and pelletizing them using pressure has been used to improve limestone reactivity.[13] The use of sodium carbonate (Na_2CO_3) and bentonites as binders, to increase the strength of pelletized particles, has been investigated in our recent preliminary study.[14] These binders, when heated with limestone, can form local eutectic melts, which improve sorbent strength and enhance the mobility of ions in the sorbent, increasing the rate of solid-state diffusion. This in turn improves reactivity in the case of gas−solid reactions (such as sulfation and carbonation) with the formation of solid product at the reacting surface. However, the increased mobility also leads to enhanced sintering, resulting in modification of the pore size distribution in both the pellet and the particles comprising the pellet.

Unlike sulfation, loss of surface area and falloff of reactivity are more important for such cycles, because of the fact that the sorbent must survive multiple reaction cycles. A faster falloff in the CO_2-carrying capacity over multiple cycles because of the presence of silicate and aluminosilicate impurities has already been reported.[15,16] This led us to a further investigation of pellets prepared with bentonite binders because our preliminary study[14] examined only a small number of cycles (typically five or less), while the economics of CaO-based CO_2 looping cycle technology depend upon achieving high capacity over many cycles, to reduce the need for sorbent makeup.[7−9] Here, we also examined calcium aluminate cements as binders. These materials have extremely low costs and excellent refractory properties, i.e., possibility of use at high

Table 1. Elemental Composition of Limestone Samples Used

component	Cadomin (L1), $< 75 \mu m$	Cadomin (L2), $> 250 \mu m$
SiO_2 (wt %)	11.68	5.47
Al_2O_3 (wt %)	3.08	1.54
Fe_2O_3 (wt %)	0.71	0.61
TiO_2 (wt %)	0.14	< 0.03
P_2O_5 (wt %)	0.03	< 0.03
CaO (wt %)	45.71	50.67
MgO (wt %)	0.76	0.55
SO_3 (wt %)	0.17	< 0.10
Na_2O (wt %)	< 0.20	< 0.20
K_2O (wt %)	0.74	0.35
Ba (ppm)	1366	618
Sr (ppm)	246	272
V (ppm)	< 50	< 50
Ni (ppm)	< 50	< 50
Mn (ppm)	1344	1132
Cr (ppm)	< 50	< 50
Cu (ppm)	142	36
Zn (ppm)	170	78
loss on fusion (wt %)	36.67	40.48
sum (wt %)	99.99	99.98

Table 2. Elemental Composition of Bentonites Used

component (wt %)	sodium bentonite	calcium bentonite
CaO	0.65	3.14
SiO_2	63.02	60.50
Al_2O_3	21.08	18.20
Fe_2O_3	3.25	5.52
FeO	0.35	< 0.01
Na_2O	2.57	0.20
K_2O	< 0.02	0.14
SO_3	< 0.10	< 0.10
trace	0.72	nd
loss on ignition (LOI)	5.64	4.85
loss on fusion (LOF)	nd	nd

temperatures; moreover, it has been shown that the presence of alumina in CaO-based sorbents improves CO_2-capture performance over many cycles.[17,18]

2. Experimental Section

2.1. Materials. Cadomin limestone (Canada) was used to prepare pellets. The crushed limestone sample (< 1.4 mm) was sieved, and particle sizes $< 75 \mu m$ (sample L1) and $> 250 \mu m$ (sample L2) were used for preparation of pellets. The potential to use particle size $< 75 \mu m$ can be potentially important in FBC systems because such small particles are typically rapidly elutriated. However, Table 1 demonstrates that an interesting difference between small and large limestone particles is the difference in chemical composition, with significantly higher impurity content in samples $< 75 \mu m$.

Bentonites are hydrated aluminosilicate clay primarily composed of montmorillonite, $(Na,Ca)_{0.33}(Al_{1.67},Mg_{0.33})Si_4O_{10}(OH)_2 \cdot nH_2O$. Substitution of a portion of Al^{3+} with Mg^{2+} alters the crystal charge, which can be balanced by cations, such as Na^+ (Na-bentonite) and Ca^{2+} (Ca-bentonite). These are used as binders in this work, and their elemental composition is given in Table 2.

Another type of binder used here is calcium aluminate cements, the main active constituent of which is monocalcium aluminate ($CaAl_2O_4$). They usually contain other calcium aluminates as well as a number of less reactive phases deriving from impurities in the raw materials (limestone and bauxite) used for their manufacture. Rather a wide range of Al_2O_3/CaO ratios and impurities is

(10) Abanades, J. C.; Anthony, E. J.; Wang, J.; Oakey, A. Fluidized bed combustion systems integrating CO_2 capture with CaO. *Environ. Sci. Technol.* **2005**, *39*, 2861–2866.

(11) Jia, L.; Hughes, R.; Lu, D.; Anthony, E. J.; Lau, I. Attrition of calcining limestones in circulating fluidized bed systems. *Ind. Eng. Chem. Res.* **2007**, *46*, 5199–5209.

(12) Lu, D. Y.; Hughes, R. W.; Anthony, E. J. Ca-based sorbent looping combustion for CO_2 capture in pilot-scale dual fluidized beds. *Fuel Process. Technol.* **2008**, *89*, 1386–1395.

(13) Gupta, H.; Iyer, M.; Sakadjian, B. B.; Fan, L. Reactive separation of CO_2 using pressure pelletised limestone. *Int. J. Environ. Technol. Manage.* **2004**, *4*, 3–19.

(14) Lu, D. Y.; Hughes, R. W.; Reid, T.; Anthony, E. J. Hydration and pelletization of $CaCO_3$-derived sorbents for in-situ CO_2 capture. The 20th International Conference on Fluidized Bed Combustion, Xi'an, China, May 18−20, 2009.

(15) Manovic, V.; Anthony, E. J. Steam reactivation of spent CaO-based sorbent for multiple CO_2 capture cycles. *Environ. Sci. Technol.* **2007**, *41*, 1420–1425.

(16) Manovic, V.; Charland, J.-P.; Blamey, J.; Fennell, P. S.; Lu, D. Y.; Anthony, E. J. Influence of calcination conditions on carrying capacity of CaO-based sorbent in CO_2 looping cycles. *Fuel* **2009**, *88*, 1893–1900.

(17) Wu, S. F.; Li, Q. H.; Kim, J. N.; Yi, K. B. Properties of a nano CaO/Al_2O_3 CO_2 sorbent. *Ind. Eng. Chem. Res.* **2008**, *47*, 180–184.

(18) Manovic, V.; Anthony, E. J.; Grasa, G.; Abanades, J. C. CO_2 looping cycle performance of a high-purity limestone after thermal activation/doping. *Energy Fuels* **2008**, *22*, 3258–3264.
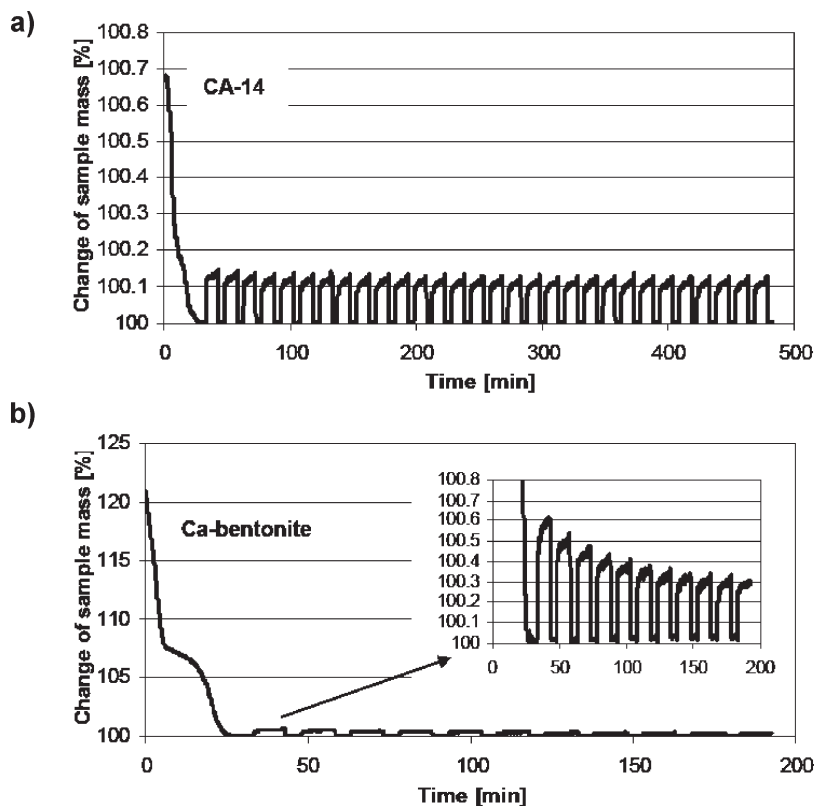
Figure 1. Calcination/carbonation cycles with original binders: (a) CA-14 calcium aluminate cement and (b) Ca-bentonite.

encountered, depending upon the application and purity of the aluminum source used.[19] They are produced in large quantities, are inexpensive, and are used preferably when refractory properties are required, as well as resistance to corrosion and chemicals and rapid setting. These properties are also desirable if they are to be used as binders for CaO-based pellets. Four commercial calcium aluminate cements were used in this study. CA-14 and CA-25 were produced by Almatis, Inc. and differ in content of Al_2O_3, ≥ 70 and $\geq 80\%$, respectively. Secar 51 and Secar 80 are produced by Kerneos, Inc., and they have been chosen because of their wider difference in Al_2O_3 content, ≥ 50 and $\geq 80\%$, respectively.

2.2. Pellet Preparation and Testing. Pellets were prepared using a powdered limestone (or hydrated lime) sample and binders in the desired ratios. When hydrated lime was used, the limestone was calcined at 850 °C for 2 h before hydration. Bentonite pellets were prepared containing 2 and 5% binder, while calcium aluminate pellets contained 5, 10, 20, and 40% by weight of cement. These percents are related to solid material ratios (binder and limestone). Weighed amounts of limestone/ hydrated lime and binder, 10 g in total mass, were mixed in a glass beaker, and water was added and stirred to obtain a gel, similar to mortar. This gel was extruded through a 1.0 mm sieve to obtain uniform pellet diameters. The resulting pellets were then air-dried for 24 h, and the final pellet diameters were typically ∼0.8 mm.

CO_2-carrying capacities for pellets were determined with a Perkin-Elmer TGA-7 apparatus using ∼30 mg samples suspended in a quartz tube (20 mm inner diameter) on a platinum pan (5 mm inner diameter). The gas flow rate, controlled by a flowmeter, was 0.04 dm³/min, and the temperature and gas used were controlled by Pyris software. Data on sample mass during the experiments were monitored, and conversions were calculated on the basis of mass change, assuming that mass change occurs only because of the formation/decomposition of $CaCO_3$.

Both carbonation and calcination were performed isothermally at 850 °C: carbonation in 100% CO_2 for 10 min and calcination in 100% N_2 for 10 min.

The sample morphologies were observed with a Hitachi S3400 scanning electron microscope (SEM) with 20 kV of accelerating voltage under high vacuum. The calcined samples were coated with gold/palladium before SEM examination, and images obtained by secondary electrons are presented here.

3. Results and Discussion

The binders contain CaO as silicates, aluminosilicates, aluminates, etc.; however, this CaO is considered to be inactive with regard to its use in CO_2 capture, but this hypothesis was also verified by subjecting the binders with no limestone addition to CO_2-capture cycles. Both the original binders and those treated by water addition and drying in air were cycled. Typical results are given in Figure 1 for CA-14 cement and Ca-bentonite. It can be seen that mass increase of the binders during the carbonation stage in the case of the cement is ∼0.1%. This means that the mass change of pellets during CO_2 cycles because of contribution of the binder is on the order of magnitude of 0.01%, which is negligible. In the case of Ca-bentonite, in the first cycle, mass increase is 0.6%, but this falls to 0.3% after 10 cycles, which confirms a negligible contribution (∼0.01%) to the capture from these binders.

Our recent study[14] on pelletization using bentonites and Na_2CO_3 as binders showed promising results when ≤ 5 CO_2 cycles were performed with pellets. Using a standard model for sorbent deactivation,[20] these results were extrapolated to 50 cycles and calculated conversions, in the case of pellet with 5% Na_2CO_3, were predicted as 57%. However, it has been

(19) Taylor, H. F. W. *Cement Chemistry*; Academic Press: New York, 1990; p 317.

(20) Abanades, J. C.; Alvarez, D. Conversion limits in the reaction of CO_2 with lime. *Energy Fuels* **2003**, *17*, 308–315.
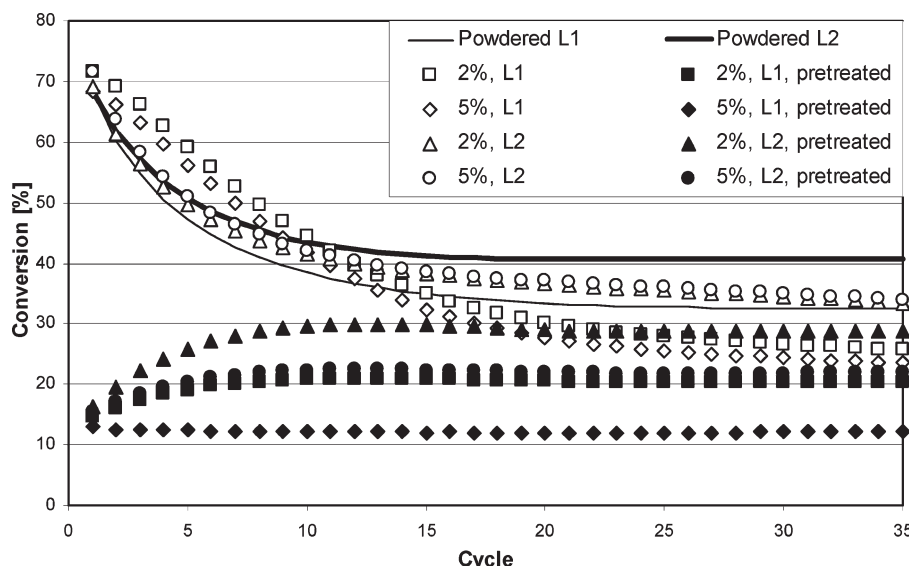
Figure 2. Carbonation conversion of CaO-based pellets prepared from powdered Cadomin limestone samples (original particle size before powdering: L1, $< 75\,\mu$m; L2, $> 250\,\mu$m) and Ca-bentonite binder (2 and 5%). Thermal pretreatment, 6 h at 1000 °C in 100% CO_2; calcination, 100% N_2; and carbonation, 100% CO_2 (both isothermally at 850 °C for 10 min).

shown[18] that the presence of Na^+ ions causes poorer performance for La Blanca (Spanish) limestone during CO_2 cycles, especially in the case of thermal pretreatment. Moreover, doping of Kelly Rock (Canadian) limestone by Na_2CO_3 also caused poorer CO_2-capture activity in a longer series of cycles, and it was shown that the porous structure of the sorbent was destroyed after multiple cycling.[18] It should be mentioned that there is some evidence available in the literature[21] indicating that doping with very small amounts of Na_2CO_3 (by washing with very dilute solutions of Na_2CO_3) might be favorable for long-term reactivity. However, our experience showed that such results are not important for this work because such small amounts of Na_2CO_3 cannot significantly contribute to producing the necessary strength development required for pellet formation. This consideration led us to the decision to cease further investigation of Na_2CO_3 here as a binder for CaO-based sorbents for cyclic CO_2 capture.

Previous research[22–27] showed that changes in CO_2-capture capacity of modified CaO-based sorbents along reaction cycles often did not follow predictions obtained by different equations presented in the literature.[20,28–30] These formulas are mainly designed by fitting sorbent activity results for natural sorbents with monotonic decay of activity along reaction cycles. However, modified sorbents often show slower decay in the initial cycles as a result of the presence of "doped ions", which enhance solid-state diffusion and improve carbonation conversions. On the other hand, they enhance sintering, which is a cumulative effect and results in faster activity decay in later cycles. Moreover, thermally pretreated sorbents can even experience increased activity in the initial cycles. These uncertainties with regard to the behavior of bentonite-bonded pellets in a longer series of CO_2 cycles led us to their additional investigation.

The bentonite pellets examined here were prepared using two bentonites (Ca- and Na-bentonite), two different binder/limestone ratios (2 and 5%), and two limestone particle size fractions with very different elemental composition ($< 75\,\mu$m, L1; $> 250\,\mu$m, L2), using powdered limestone and hydrated lime. The original and thermally pretreated pellets were subjected to a series of 35 calcination/carbonation cycles. The results for pellets prepared with limestone powders using Ca-bentonite are shown in Figure 2. It can be seen that there is a large difference between pretreated and original pellet samples. The activities of the pellets are very low after pretreatment and do not significantly recover with increasing numbers of reaction cycles. The increase of both binder content and content of impurities in the samples (see Table 1) causes an unfavorable effect for CO_2-carrying capacity with increasing numbers of reaction cycles. A similar effect can be seen when original (no pretreatment) pellet samples from two powdered limestone samples (L1 and L2) are compared. In the case of Na-bentonite use, similar qualitative results were obtained but are not presented here in the interest of brevity.

(21) Fennell, P. S.; Pacciani, R.; Dennis, J. S.; Davidson, J. F.; Hayhurst, A. N. The effects of repeated cycles of calcination and carbonation on a variety of different limestones, as measured in a hot fluidized bed of sand. *Energy Fuels* **2007**, *21*, 2072–2081.

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

(23) Lysikov, A. I.; Salanov, A. N.; Okunev, A. G. Change of CO_2 carrying capacity of CaO in isothermal recarbonation–decomposition cycles. *Ind. Eng. Chem. Res.* **2007**, *46*, 4633–4638.

(24) Chen, Z.; Song, H. S.; Portillo, M.; Lim, C. J.; Grace, J. R.; Anthony, E. J. Long-term calcination/carbonation cycling and thermal pretreatment for CO_2 capture by limestone and dolomite. *Energy Fuels* **2009**, *23*, 1437–1444.

(25) Martavaltzi, C. S.; Lemonidou, A. A. Parametric study of the $CaO-Ca_{12}Al_{14}O_{33}$ synthesis with respect to high CO_2 sorption capacity and stability on multicycle operation. *Ind. Eng. Chem. Res.* **2008**, *47*, 9537–9543.

(26) Li, Y.; Zhao, C.; Chen, H.; Liang, C.; Duan, L.; Zhou, W. Modified CaO-based sorbent looping cycle for CO_2 mitigation. *Fuel* **2009**, *88*, 697–704.

(27) Lu, H.; Khan, A.; Pratsinis, S. E.; Smirniotis, P. G. Flame-made durable doped-CaO nanosorbents for CO_2 capture. *Energy Fuels* **2009**, *23*, 1093–1100.

(28) Abanades, J. C. The maximum capture efficiency of CO_2 using a calcination/carbonation cycle of $CaO/CaCO_3$. *Chem. Eng. J.* **2002**, *90*, 303–306.

(29) Wang, J. S.; Anthony, E. J. On the decay behavior of the CO_2 absorption capacity of CaO-based sorbents. *Ind. Eng. Chem. Res.* **2005**, *44*, 627–629.

(30) Grasa, G. S.; Abanades, J. C. CO_2 capture capacity of CaO in long series of carbonation/calcination cycles. *Ind. Eng. Chem. Res.* **2006**, *45*, 8846–8851.
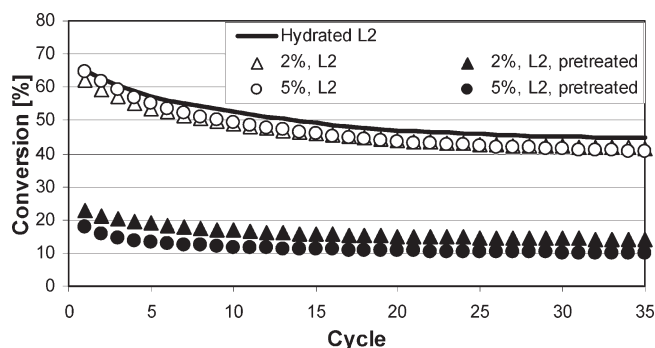
Figure 3. Carbonation conversion of CaO-based pellets prepared from calcined (850 °C for 2 h) and hydrated (liquid water) Cadomin limestone samples (original particle size: L2, >250 μm) and Ca-bentonite binder (2 and 5% calculated to limestone mass before calcination). Thermal pretreatment, 6 h at 1000 °C in 100% CO_2; calcination, 100% N_2; and carbonation, 100% CO_2 (both isothermally at 850 °C for 10 min).

The better performance of the purer limestone sample (>250 μm) caused us to use it for preparation of all subsequent pellets to avoid the negative influence of SiO_2 from the sample <75 μm. Significantly better carrying capacities were obtained when hydrated lime was used for pellets when samples were not pretreated (Figure 3). These results are in agreement with data on the superior performance of hydrated CaO-based sorbents.[15,31,32] Unfortunately, the effect of binder addition was again unfavorable and especially pronounced when pellets were thermally pretreated. This means that presintering of bentonite-based CaO pellets to improve their strength, which has been seen when natural sorbent was used,[33] would be impractical because of the drastic drop in CaO-capture activity, which, according to results presented here, does not recover with increasing numbers of reaction cycles.

The cause for poor activity of pretreated bentonite-based CaO pellets can be seen in Figure 4. The SEM image in Figure 4a, obtained from pretreated hydrated lime (5%, L2, pretreated, Figure 3) after 35 cycles, shows a very sintered structure compared to that seen for the hydrated lime sample (Figure 4b) after undergoing the same cycling conditions. The enhanced sintering seen here is in close agreement with our previous research on the influence of impurities on local melting in CaO particles during carbonation/calcination cycles,[16] which is explained by enhanced solid-state diffusion.[34−36] The SEM−energy-dispersive X-ray (EDX) analyses showed that local melted areas at the particle surfaces correlate with the presence of silica, which is explained by the formation of
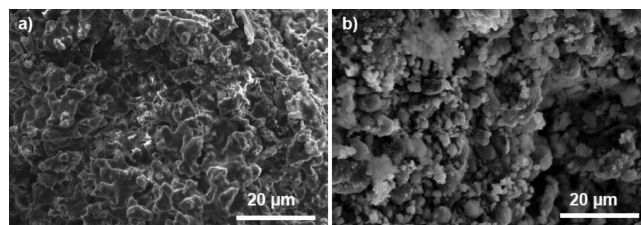

Figure 4. SEM images of pellet particles after 35 calcination/carbonation cycles (see Figure 3): (a) 5%, L2, pretreated and (b) hydrated L2.

eutectic mixtures and reaction of SiO_2 with active CaO. It is interesting to note that similar results with regard to the unwanted effect of SiO_2 have also been seen for other metal oxides, when used in chemical looping cycles.[37]

Apart from the formation of eutectic mixtures that destroy the porous structure of CaO-based sorbent, another effect that contributes to sintering has been noticed and examined in more detail. Namely, after calcination in each cycle (*n*), sample mass was higher than after calcination in the previous cycle (*n* − 1). This effect was more pronounced with an increase in the bentonite content and in the content of impurities coming from limestone, as well as for pellets prepared with hydrated lime and pellets thermally pretreated before CO_2 cycles. From the results given in Figure 5, it can be seen that the cumulative mass increase is 2% after 35 cycles. Because N_2 and CO_2 were the only two gases in contact with sample during cycles and given that N_2 is inert under conditions employed here, it is reasonable to suppose that low-melting compound(s) containing CO_2 were also being formed. Hence, we chose to examine this phenomenon by X-ray diffraction (XRD), using the sample after 35 cycles (Figure 5).

The XRD spectrum shown in Figure 6 indicates the presence of about 36.2% of an amorphous phase. However, a significant amount (18.8%) of CaO is bound with SiO_2 in lamite, $Ca_2(SiO_4)$. The mass increase during CO_2 cycles seen in Figure 5 is fully explained by the formation of spurrite, $Ca_5(SiO_4)_2CO_3$. The calculated content of CO_2 in the sample that originates from spurrite is 2.6%, which is in close agreement with the sample mass increase seen in Figure 5 (2.0%). A somewhat higher value determined by XRD may be due to the formation of spurrite during calcination and pretreatment of the original pellet at 1000 °C for 6 h in 100% CO_2, i.e., before the calcination/carbonation cycles. From Figure 5 (top right chart, 35th cycle), it can also be seen that calcination is almost finished within 2−3 min, which represents decomposition of $CaCO_3$. However, more detailed examination of the calcination step (bottom right chart, 35th calcination) shows a very slow additional mass decrease that is most likely due to decomposition of spurrite. The final result of the formation of lamite and spurrite is that only 18.3% of the sample is free CaO that can react with CO_2.

The results presented in Figure 4a show very sintered morphology, with melted areas caused by the formation of eutectic mixtures and compounds, such as those seen by XRD (Figure 6). These mixtures and compounds enhance sintering and loss of sorbent surface area, but, on the other hand, they enhance solid-state diffusion. The final effect on carbonation conversion can be seen in Figure 7, where typical differences

(31) Manovic, V.; Lu, D.; Anthony, E. J. Sulphation and carbonation properties of hydrated sorbents from a fluidized bed CO_2 looping cycle reactor. *Fuel* **2008**, *87*, 2923–2931.

(32) Fennell, P. S.; Davidson, J. F.; Dennis, J. S.; Hayhurst, A. N. Regeneration of sintered limestone sorbents for the sequestration of CO_2 from combustion and other systems. *J. Energy Inst.* **2007**, *80*, 116–119.

(33) Marquard-Moellenstedt, T.; Specht, M.; Zuberbuehler, U.; Koppatz, S.; Pfeifer, C.; Rauch, R.; Soukup, G.; Hofbauer, H.; Koch, M. Transfer of the absorption enhanced reforming (AER) process from the pilot scale to an 8 MWth gasification plant in Guessing, Austria. 16th European Biomass Conference and Exhibition, Valencia, Spain, June 2−6, 2008.

(34) Bhatia, S. K.; Perlmutter, D. D. Effect of the product layer on the kinetics of the CO_2−lime reaction. *AIChE J.* **1983**, *29*, 79–86.

(35) Borgwardt, R. H.; Bruce, K. R.; Blake, J. An investigation of product-layer diffusivity for CaO sulfation. *Ind. Eng. Chem. Res.* **1987**, *26*, 1993–1998.

(36) Florin, N. H.; Harris, A. T. Screening CaO-based sorbents for CO_2 capture in biomass gasifiers. *Energy Fuels* **2008**, *22*, 2734–2742.

(37) Zafar, Q.; Mattisson, T.; Gevert, B. Integrated hydrogen and power production with CO_2 capture using chemical-looping reforming redox reactivity of particles of CuO, Mn_2O_3, NiO, and Fe_2O_3 using SiO_2 as a support. *Ind. Eng. Chem. Res.* **2005**, *44*, 3485–3496.
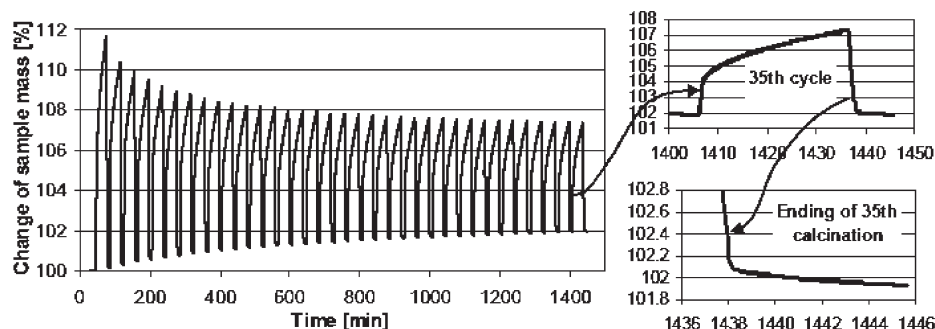
Figure 5. Changes of sample mass during 35 calcination/carbonation cycles with pellet prepared from calcined and hydrated Cadomin limestone ($< 75\ \mu$m) and 5% Ca-bentonite. Pretreatment, 6 h at 1000 °C in 100% CO_2; carbonation, 30 min in 100% CO_2 at 850 °C; and calcination, 10 min in 100% N_2 at 850 °C.

Chemical compound	Content [%]
1. Lime, syn, CaO	18.3
2. Spurrite, $Ca_5(SiO_4)_2CO_3$	26.7
3. Larnite, syn, $Ca_2(SiO_4)$	18.8
Crystallinity (%)	63.8
Amorphous content (%)	36.2
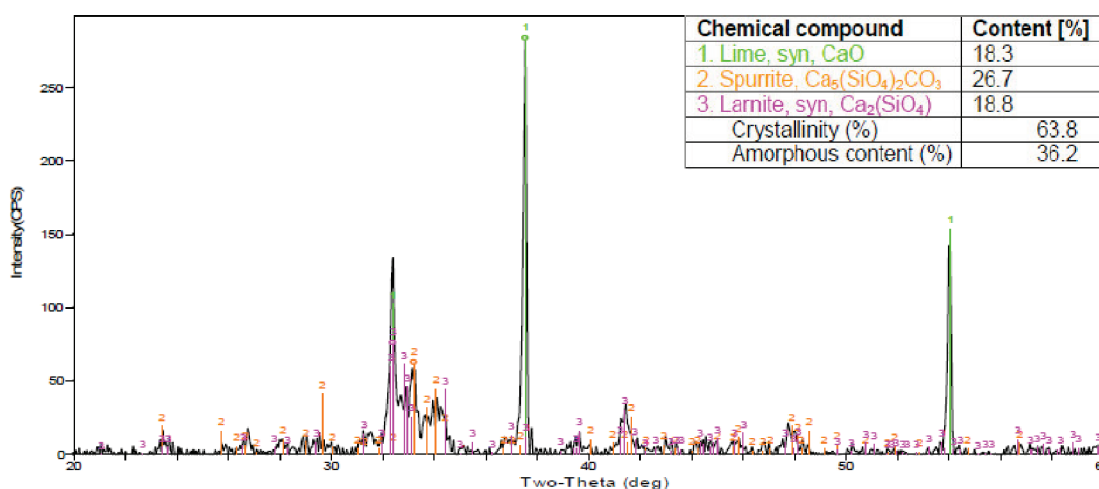
Figure 6. XRD of the pellet sample after 35 calcination/carbonation cycles (presented in Figure 5).

between the conversion profile for the original limestone and those for bentonite-based CaO pellets are shown. It can be seen that the conversion rate of the original limestone is faster during first-stage carbonation, which is due to a larger surface area. However, after ~2 min, the conversion rate is controlled by solid-state diffusion and is faster for bentonite-based CaO pellets.

Unfortunately, unlike sulfation of CaO-based sorbents/pellets, where only one "cycle" occurs, here multicycling is required. During these cycles, processes that lead to sintering are cumulative. This is clearly illustrated in Figure 5, where mass increase because of the formation of spurrite increases cumulatively with an increasing number of reaction cycles. These results with pellets prepared using bentonites as binder show significant deficiencies, such as poorer CO_2-capture capacity in a longer series of CO_2 cycles. This is a similar effect to that seen in the case of doping of CaO by Na_2O.[18]

The problems arising because of the use of Na_2CO_3 and bentonites highlight the fact that a desirable binder should not contain such elements as seen in these binders; i.e., one should avoid Si, Na, and K. In contrast, desirable elements must, in addition to acting as a binder, also stabilize sorbent morphology, leading us to consider high-purity calcium aluminate cements as promising candidates for binders. Namely, they are high-alumina cements, which also contain CaO bonded in aluminates, and typically have minimal impurities. They also have refractory properties, required in the case of high-temperature CO_2 capture, and finally, there is evidence of a favorable effect of alumina compounds on the CO_2-carrying capacity of CaO-based sorbents.[17,18]
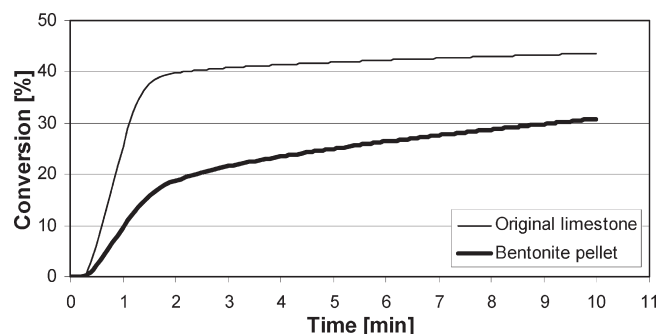

Figure 7. Typical difference in conversion−time profile during carbonation of original limestone and pellets prepared with bentonite binder.

Figure 8 shows conversion changes along calcination/carbonation cycles for pellets prepared with varying amounts of CA-14 calcium aluminate cement. The results obtained are significantly better than those seen for bentonite binder (Figure 2). This enhancement is especially significant for pretreated samples. The conversions of pretreated samples are 41−46% in the first cycle and increase about 7−8% for cycles 2 and 3. After that, conversions of pretreated samples decrease but somewhat slower than those for the original pellets, achieving conversions of ~30% in the 30th cycle. This is ~10% lower than for the original powdered sample (L2). These lower conversions of pellets than those for limestone powder can be explained by the particle size of the sorbents
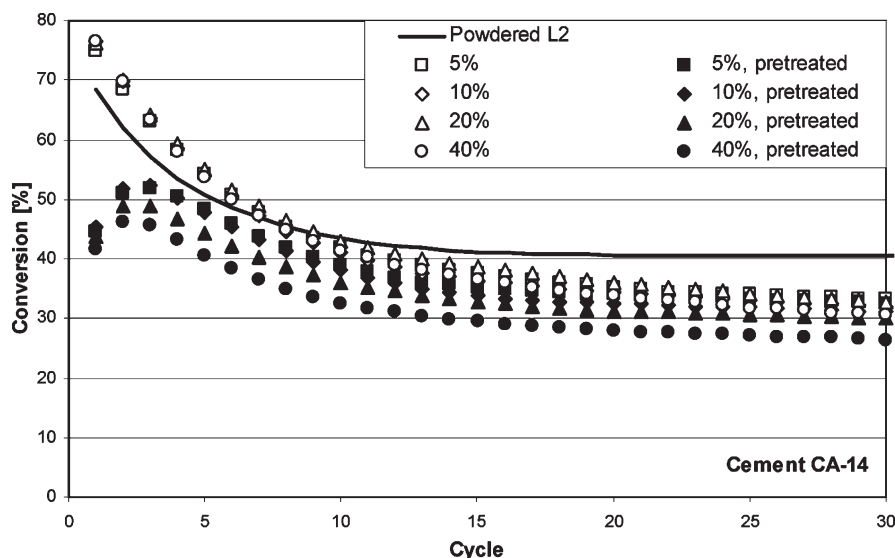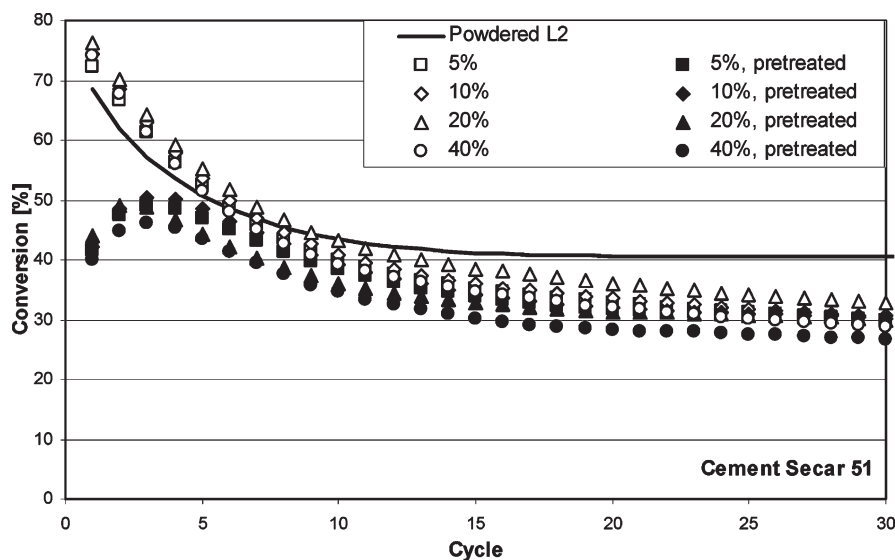
Figure 8. Carbonation conversion of CaO-based pellets prepared from powdered Cadomin limestone samples (original particle > 250 μm, sample L2) and CA-14 aluminate cement (5, 10, 20, and 40%). Thermal pretreatment, 6 h at 1000 °C in 100% CO_2; calcination, 100% N_2; and carbonation, 100% CO_2 (both isothermally at 850 °C for 10 min).

Figure 9. Carbonation conversion of CaO-based pellets prepared from powdered Cadomin limestone samples (original particle > 250 μm, sample L2) and Secar 51 aluminate cement (5, 10, 20, and 40%). Thermal pretreatment, 6 h at 1000 °C in 100% CO_2; calcination, 100% N_2; and carbonation, 100% CO_2 (both isothermally at 850 °C for 10 min).

rather than the unwanted influence of compounds from the cement. Namely, the particle size of limestone powder was of the order of micrometers to tens of micrometers, while the pellet particle diameter was ~0.8 mm. The decrease in conversion with increased concentration of the cement is less pronounced; i.e., increasing the cement content from 5 to 40% caused a drop in conversion in the 30th cycle of only about 5%.

The influence of the cement type is also negligible and nearly in the range of experimental error. Thus, additional results are presented only in the case of Secar 51 cement, which comes from another manufacturer and differs from the other three cements investigated here. The main difference is a smaller content of Al_2O_3 (~50%) and a higher content of impurities. However, the results for this cement, presented in Figure 9, are very similar to those seen in Figure 8 for CA-14 cement.

These results with aluminate cements are very promising when pelletization of CaO-based sorbent for CO_2 capture is considered. The improved performance of CaO-based sorbents supported by Al_2O_3 seen here is in close agreement with that reported in previous studies,[38,39] which was explained by the formation of mayenite ($Ca_{12}Al_{14}O_{33}$). SEM examination of the samples obtained showed that sorbent morphology is very similar to that presented in Figure 4b. Here, it is also important to note that no effect of increased sample mass after calcination with cycles (that is presented in Figure 5 for

(38) Feng, B.; An, H.; Tan, E. Screening of CO_2 adsorbing materials for zero emission power generation systems. *Energy Fuels* **2007**, *21*, 426–434.

(39) Li, Z. S.; Cai, N. S.; Huang, Y. Y.; Han, H. J. Synthesis, experimental studies, and analysis of a new calcium-based carbon dioxide absorbent. *Energy Fuels* **2005**, *19*, 1447–1452.

bentonite-bound pellets) is seen. Moreover, the difference in carbonation profiles between the original powder and pellet prepared with bentonite, which is presented in Figure 7, is also not seen here for aluminate cements. The pellets themselves have pronounced strength; thus, use of hydrated lime for additional strength development has not been tested here, although this can be considered if it is desired to take advantage of the enhanced activity of sorbents derived from $Ca(OH)_2$.[15,31,32]

The results presented in this study show that pelletization of CaO-based sorbents for CO_2 capture is feasible. Taking into account that limestone and other natural sorbents are inexpensive and abundant, any modification of the original sorbent or reuse of spent material is subject to tight limitations of cost. However, the materials used here for pelletization are less expensive than materials used for preparation of similar synthetic sorbents in previous studies,[17,38,39] which offers a significant advantage. It should also be considered that purging too much material from the CO_2-capture system can aggravate the problem of disposal of the rejected sorbent, which makes any means of reducing the volume of purge most welcome. Finally, the use of spent pelletized material, for instance in the cement industry, may be also feasible, especially when calcium aluminate cements are used as binders.

4. Conclusions

Possible binders for pelletization of CaO-based sorbents were examined in this study. It has been shown that Na_2CO_3 and bentonites, which possess appropriate binding properties for pellet formation, are not suitable for pellets that are to be used in a longer series of calcination/carbonation cycles. They cause enhanced sorbent sintering and loss of CO_2-capture capacity, because of the formation of local eutectic mixtures and compounds, such as $Ca_2(SiO_4)$ and $Ca_5(SiO_4)_2CO_3$, as shown by XRD. On the other hand, pelletization using calcium aluminate cements shows very promising results and these materials do not enhance sintering as other binders appear to do. These results with calcium aluminate cements are particularly promising for practical application because these cements have a number of very favorable properties, such as fast setting and good refractory properties, and finally, they are inexpensive and easily obtained commercially in large quantities.