Competition of Sulphation and Carbonation Reactions during Looping Cycles for CO, Capture by CaO-Based Sorbents

2 AUTHORS:

Vasilije Manovic
Cranfield University
91 PUBLICATIONS **1,974** CITATIONS

SEE PROFILE

Edward Anthony
Cranfield University
260 PUBLICATIONS **7,159** CITATIONS

SEE PROFILE

Competition of Sulphation and Carbonation Reactions during Looping Cycles for CO₂ Capture by CaO-Based Sorbents[†]

Vasilije Manovic and Edward J. Anthony*

CanmetENERGY, Natural Resources Canada, 1 Haanel Drive, Ottawa, Ontario, Canada K1A 1M1

Received: November 4, 2009

Two types of sorbents are investigated here (natural limestone and highly reactive calcium aluminate pellets) to elucidate their reactivity in terms of sulphation and carbonation and determine the resulting effect on looping cycles for CO₂ capture. The sorbents are tested in a thermogravimetric analyzer (TGA) apparatus using typical synthetic flue gas mixtures containing 15% CO₂ and various concentrations of SO₂. The sulphation and carbonation conversions were determined during sulphation/carbonation/calcination cycles. The sorbent morphology and its changes were determined by means of a scanning electron microscope (SEM). The results showed that sulphation, that is, the formation of CaSO₄ at the sorbent surface, is a cumulative process with increasing numbers of reaction cycles, which hinders sorbent ability to capture CO₂. In the case of high sorbent reactivity, as determined by its morphology, the unfavorable effect of sulphation is more pronounced. Unfortunately, any increase in the temperature in the carbonation stage accelerates sulphation more than carbonation as a result of higher activation energy for the sulphation reaction. The SEM analyses showed that although sulphation and carbonation occur during cycles involving calcination, an unreacted core/partially sulphated shell sorbent particle pattern is formed. The main outcomes of this research indicate that special attention should be paid to the sulphation when more reactive and more expensive, synthetic CaO-based sorbents are used for CO₂ capture looping cycles. Desulphurization of flue gas before CO₂ capture appears to be essential because CO₂ looping cycles are so strongly affected by the presence of SO₂.
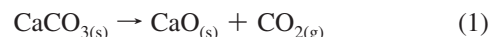
1. Introduction

The use of fossil fuels for energy production purposes causes a wide spectrum of undesired environmental impacts. The negative environmental effects of such combustion represent a growing problem because the utilization of fossil fuels such as coal is increasing, and this can be expected to continue for the near-to-medium term future.[1,2] Earlier on, the main environmental issues of coal utilization were considered to be the emissions of SO$_x$ and NO$_x$ as well as the production/disposal of solid wastes. Recently, studies on global warming and climate changes caused by greenhouse gases[3,4] have focused attention on CO₂ emissions, and this is increasingly being regarded as the principal problem related to coal combustion.

Technologies to limit successfully emissions of nitric oxides and sulphur dioxide include fluidized bed combustion (FBC).[5,6] Reduction of SO₂ emissions in FBCs is based on in situ SO₂ retention by natural sorbents: limestones and dolomites.[7] These materials are abundant and relatively inexpensive (<\$10/t), which represents their main advantage because their use as solid sorbents is affected by their relatively low conversion, which is typically <45%.[7] The high level of production of ash rich in unreacted CaO can perhaps be mitigated by means of hydration of partially reacted sorbent and its further use for SO₂ retention.[8,9]

Currently FBC technology is being considered as a suitable technology for CO₂ capture using CaO-based sorbents.[10–12] This technology for CO₂ capture has been demonstrated at the pilot plant scale,[13] and its economics have been explored in several studies.[14–17] Again, as with sulphation, one of its main potential advantages is low cost, which has been estimated to be <\$20/t avoided CO₂, which would be very competitive with CO₂ postcombustion scrubbing using amine-based sorbents, such as monoethanolamine (MEA), which is the CO₂ capture technology closest to market.[18] The main goal of CO₂ capture is to obtain a concentrated CO₂ stream ready for liquefaction and storage in geological formations[19] or marketing for use in enhanced oil recovery. CaO-based CO₂ capture technology employing fluidized beds is based on the cyclic carbonation/calcination process. Sorbent utilization here is also an issue, and unfortunately it decreases with increasing numbers of reaction cycles,[20,21] which is believed to be a consequence of sintering and loss of sorbent surface area.[22–24] Given that sulphation and carbonation are similar reactions, similar methods to improve sorbent utilization have been investigated,[25] of which the most promising were hydration,[26,27] thermal preactivation,[21,28] and sorbent doping, particularly by Al₂O₃.[29,30]

Sorbent utilization in a CO₂ capture system begins with calcination

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{1}$$

The calcined sorbent (lime) reacts with SO₂ (sulphation) in the presence of O₂ (always present in flue gas)

$$CaO_{(s)} + SO_{2(g)} + 1/2 O_{2(g)} \rightarrow CaSO_{4(s)} \tag{2}$$
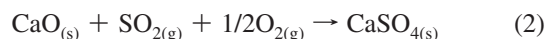
and also reacts with CO₂ (carbonation), when chemical equilibrium allows

---

$$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)} \qquad (3)$$

Direct sulphation also occurs in systems with high CO_2 partial pressure, such as oxy-fuel combustion systems[31]

$$CaCO_{3(s)} + SO_{2(g)} + 1/2 O_{2(g)} \rightarrow CaSO_{4(s)} + CO_{2(g)} \qquad (4)$$
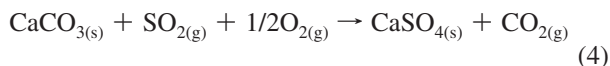
For CO_2 capture, a typical temperature during the capture step is 650−700 °C,[10−13] which thermodynamically also allows both reactions to take place simultaneously. Both of these are typical heterogeneous gas−solid reactions, and deactivation due to sulphation occurs because of solid product formation at the reacting surface.[32,33] Moreover, $CaSO_4$ is thermodynamically stable at temperatures of interest for sorbent regeneration (>900 °C) and obstructs carbonation during the carbonation/calcination cycles. CaO is both chemically bound as $CaSO_4$ and also physically hindered from reacting with CO_2 because of the formation of a $CaSO_4$ product layer. Recently, it was found that carbonation/calcination cycles enhance sulphation for both natural[34,35] and synthetic sorbents,[36] which is explained by the formation of larger pores during the cycles. Namely, during carbonation/calcination cycles, because of sintering, small pores are transformed into larger ones. This prevents the closure of small pores at the sorbent particle surface and hence reduces the chance of formation of unreacted core.

The sulphation, which hinders CO_2 capture activity of the sorbent, becomes more important when developing new, more efficient and durable synthetic CaO-based sorbents for CO_2 capture[29,30] because these sorbents are always more expensive than natural ones. A recent study[37] showed very high reactivity of these sorbents, with almost quantitative sulphation, at higher temperature (900 °C) expected for sorbent regeneration (calcination) during CO_2 capture cycles. This means that the presence of SO_2 must be avoided in this stage of the CO_2 capture process, and various solutions were proposed such as direct heating[11] or the use of nonsulfur fuels for the calcination stage.

If CaO-based CO_2 looping cycle technology is to be deployed with fossil fuels such as coal, SO_2 will always be present in the flue gas to be decarbonated. This requires exploration of sulphation activities of CaO-based sorbent at lower temperatures (650−700 °C) typical for the carbonation stage, where simultaneous carbonation takes place. The literature[38] suggests that direct sulphation of the limestone takes place at 600 °C, resulting in 10% conversion after 5000 s when 1920 ppm SO_2 is present in the gas. Ryu et al.[39] also demonstrated that CO_2 capture activity in their simultaneous CO_2/SO_2 capture FBC tests fell faster when SO_2 was present in carbonating gas, proportional to its concentration. Moreover, Li et al.[40] showed that partially sulphated limestone particles can capture CO_2, and the ability of sorbent to capture SO_2 increases after carbonation and recalcination.

This study examines the effects of the simultaneous sulphation and carbonation on the activity of CaO-based sorbents during many CO_2 capture cycles. The competitiveness of the two reactions is examined in a single simultaneous sulphation/carbonation step. Two types of sorbents were compared: natural limestone and pellets prepared with hydrated lime and calcium aluminate cements.

2. Experimental Section

Materials. Cadomin limestone (CD) from Canada (0.25 to 1.4 mm) was used here as a typical natural material examined in numerous studies as a CaO-based sorbent for both SO_2 and CO_2 capture. This sorbent was tested here as is and also used in pelletized form. Commercial calcium aluminate cement, CA-14, produced by Almatis Inc., was used at the same time as binder for pelletization and as a source of Al_2O_3 (70% Al_2O_3 in cement) for sorbent microstructure enhancement. Pellets were prepared using hydrated CD lime and 10% of the cement, with a final particle size of ∼0.8 mm. More details of the limestone and pellets, their composition, and pellet preparation method are presented elsewhere.[30]

Sulphation/Carbonation/Calcination Cycles. A Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA) was used for the sulphation/carbonation/calcination cycles. The sample was suspended in a quartz tube (i.d. 20 mm) on a platinum pan (i.d. 5 mm). The temperature and gas used were controlled by Pyris software. The temperature program included heating to 950 °C, cooling from 950 to 700 or 650 °C (calcination step), and then keeping the temperature at 700 or 650 °C (sulphation/carbonation was investigated at these two temperatures) for 35 min (sulphation/carbonation step). The program started with the introduction of N_2, which was replaced with synthetic flue gas mixture (15% CO_2, 3% O_2, different concentrations of SO_2, and N_2 balance) 5 min after the temperature reached 700 or 650 °C. The period of 5 min was to stabilize the temperature at the desired level after the cooling step. Therefore, the sulphation/carbonation step was for 30 min. The heating/cooling rate was 30 °C/min, which means that the calcination step was for 20 + 5 min when the carbonation temperature was 650 °C and 16.67 + 5 min when it was 700 °C. The gas flow rate during runs was controlled with a flowmeter at 40 cm³/min.

Up to 30 sulphation/carbonation/calcination cycles were performed, depending on the activity of the sorbent sample and SO_2 concentration in the reacting gas. Namely, with higher sorbent reactivity and higher SO_2 concentration, higher sulphation conversion and loss of carbonation activity were previously achieved; these experiments were terminated after a lower number of cycles. Apart from the investigation of the activity during the cycles, the sulphation/calcination conversions were also examined in single cycles. In these experiments, the sulphation/calcination stage was stopped at different times (up to 5 h) and followed by calcination, which enabled the calculation of sorbent conversions at that time and hence sorbent sulphation and carbonation activity.

Data on sample mass during the experiments were monitored, and conversions were calculated on the basis of mass change, assuming that mass change occurred only because of the formation of $CaSO_4$ and the formation/decomposition of $CaCO_3$, as are presented in Figure 1. It was assumed that sample mass increased in the sulphation/carbonation stage because of the formation of both $CaSO_4$ and $CaCO_3$, but individual contributions could not be identified. However, at the end of a cycle during cyclic experiments, these contributions were determined by mass loss because of decomposition of $CaCO_3$ during subsequent calcination. In single-cycle sulphation/carbonation experiments, sulphation and carbonation conversions were determined in the same manner, but calcination was started after different durations to explore the conversions rate of both reactions.

The sample morphologies after sulphation/carbonation/calcination cycles were observed with a Hitachi S3400 scanning electron microscope (SEM) with 20 kV of accelerating voltage under high vacuum. The samples were coated with 3 nm gold/palladium before SEM examination, and images obtained by secondary electrons are presented here.
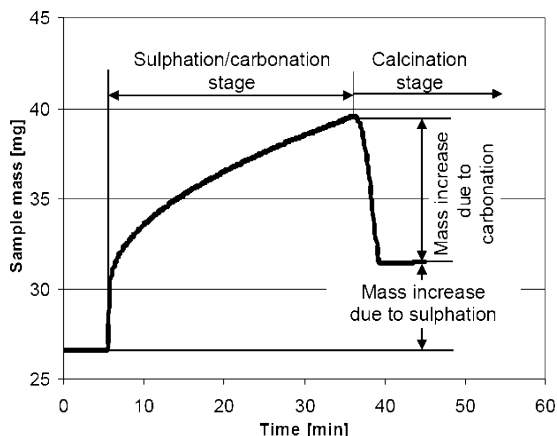
Competition of Sulphation and Carbonation Reactions

J. Phys. Chem. A, Vol. 114, No. 11, 2010 **3999**

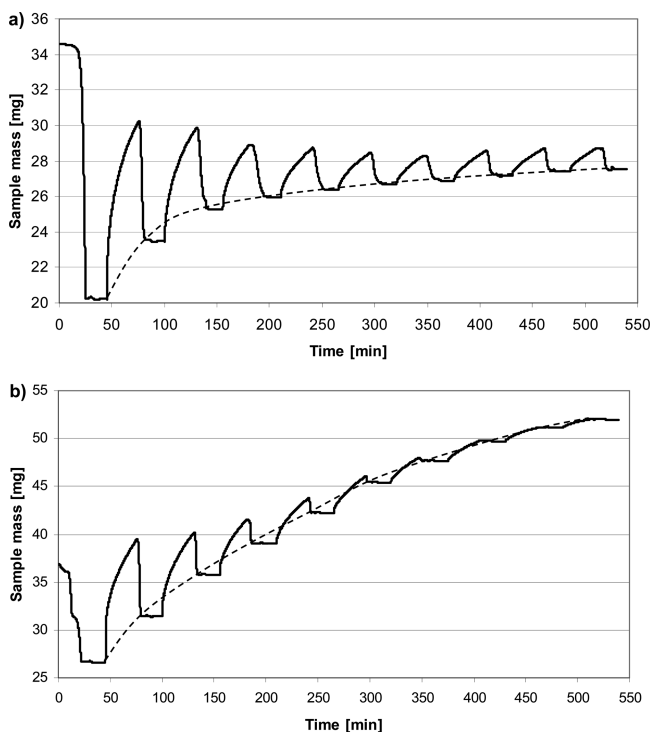**Figure 1.** Mass change during a sulphation/carbonation/calcination cycle.

Figure 2. Sample mass changes during sulphation/carbonation/calcination cycles of (a) CD limestone and (b) calcium aluminate pellets. Conditions: sulphation/carbonation with 15% CO_2, 3% O_2, 0.5% SO_2, and N_2 balance for 30 min at 700 °C; calcination under 100% N_2 for 25 min at temperature 700–950–700 °C.

3. Results and Discussion

Figure 2 presents mass change during sulphation/carbonation/calcination cycles of (a) CD limestone and (b) calcium aluminate pellets. Both experiments were done under the same conditions as described above. The concentration of SO_2 was 0.5%, which is a realistic flue gas value for coal containing ~2% sulphur. A drastic drop in carbonation conversion during cycles was seen, especially pronounced for the aluminate pellets. In this case, it can be seen that the sorbent has effectively lost carbonation activity as early as the sixth cycle, and any mass increase in further cycles was only due to sulphation. This means that modifications of CaO-based sorbent to increase its CO_2 capture activity also has the unfortunate effect of enhancing its sulphation activity, which is an irreversible process, at least under CO_2 looping cycle conditions, and results in an irretrievable loss of the sorbent from further cycles.
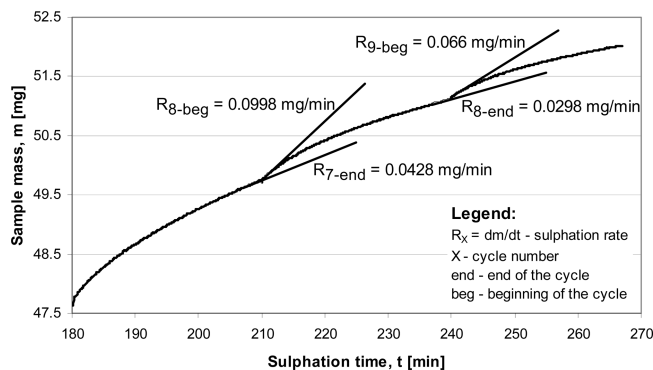

Figure 3. Sulphation rates before and after calcination stage. Note that sample masses in the calcination stages were constant (see Figure 2b, cycles 7–9), and they are omitted in this diagram.

The dashed lines in Figure 2 connect sample mass after each calcination, which determines sulphation conversions. Very high sulphation activity can be seen, taking into account that the experiments were done at 700 °C, which is significantly lower than the optimal temperature for sulphation (850–900 °C).[7] It was calculated that sulphation conversion after nine cycles was 30 and 89%, respectively, for limestone and aluminate pellets. These values were comparable to those when continuous sulphation tests were done with the same sorbents using 0.5% SO_2 at 900 °C.[37] It should be noted that samples were exposed to the atmosphere containing SO_2 for 270 min in comparison with 360 min in a previous study[37] when similar conversions were obtained. These high conversions at significantly lower temperature were additional evidence of CO_2 looping cycles enhancing sulphation, as already presented in the literature.[34–36]

An additional parameter that contributes to the sulphation is heating the sample to 950 °C in the calcination stage. Namely, sulphation is deactivated by product layer, $CaSO_4$, which covers the available surface area of the sorbent, and diffusion through the product layer becomes the limiting step for the process. Research[41,42] has suggested that ion diffusion occurs in the layer formed. Here it is believed that this type of solid-state diffusion in the product layer, responsible for limiting the conversion rate, can occur even with no SO_2 present in the surrounding gas. Moreover, solid-state diffusion is a process with high activation energy, and it is significantly enhanced with increased temperatures. Therefore, the higher temperature during the calcination step enhances the diffusion of CaO (Ca^{2+} and O^{2-} in a coupled manner) through the product layer and increases the concentration of CaO at the product layer surface, which increases the sorbent activity after the calcination stage. This can be clearly seen in the case of aluminate pellets when sulphation rates in cycles 7–9 are observed, as presented in Figure 3. It should be noted that only the sulphation/carbonation stages from Figure 2 are presented. Taking into account that sample mass did not change during calcination, it is considered that the mass increase was only due to sulphation. It can be seen that the sulphation rate after the calcination stage was more than twice as high as that observed at the end of the previous cycle, that is, before calcination. It is also important to note that this means a higher sulphation rate in the CO_2 capture stage than could be expected solely on the basis of the relatively lower temperature (650–700 °C) in that stage in real CO_2 capture systems. Solid-state (ion) diffusion, important for sulphation, occurs in the calcination stage and is enhanced at the higher temperatures (>900 °C) necessary to produce a concentrated stream of CO_2. This results in higher sulphation reactivity after calcination stages and higher sulphation conversions.
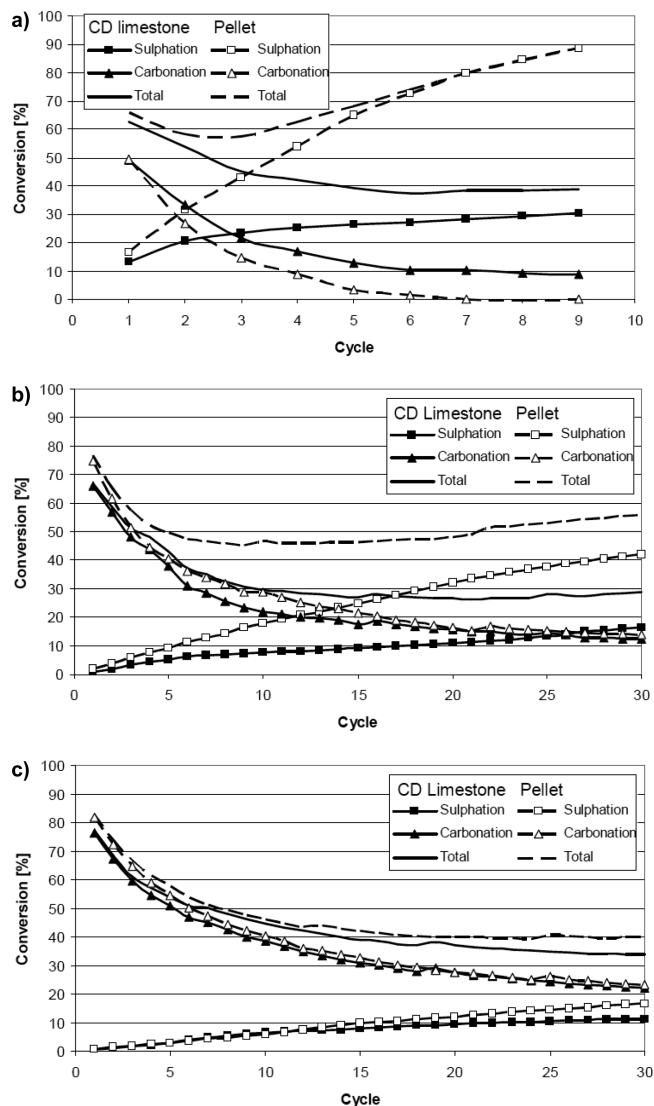
Figure 4. Conversions during sulphation/carbonation/calcination cycles with different concentrations of SO_2: (a) 0.5, (b) 0.05, and (c) 0.01%.

The results presented here show that aluminate pellets experience a total loss of carbonation activity after six cycles when 0.5% SO_2 is present in the carbonation stage. The somewhat better performance of natural limestone is not much more promising because after nine cycles, carbonation conversion is only 9%, which would not be sufficient to produce an economic looping cycle process.[14–17] This means that relatively high concentrations of SO_2 in flue gas should be avoided in the carbonator during CO_2 capture cycles, which requires desulphurization of the gas before it enters the carbonator. This could be efficiently achieved by using spent[35] or reactivated sorbent from CO_2 looping cycles[43,44] for sulphur removal upstream of the carbonator. Therefore, it was interesting to explore how sorbents behave under lower SO_2 concentrations (to simulate precleaned, i.e., desulphurized flue gas), and a number of cycles were carried out with synthetic flue gas containing 0.05 and 0.01% SO_2.

Figure 4 presents conversions during cycles with different SO_2 concentrations for the two investigated sorbents. It can be seen that sulphation conversions, as expected, decreased with decreased SO_2 concentration. Consequently, carbonation activity of both sorbents was higher when gas with lower SO_2

concentration was used. The influence of SO_2 is significantly more pronounced in the case of pellets.

It is interesting that total conversion had a minimum value for both sorbents when concentration of SO_2 was 0.5 or 0.05% (Figure 4a,b). After that minimum, total conversion increased during cycles, which was especially pronounced for pellets with 0.5% SO_2. This increase in total conversion during cycles can be explained by enhanced sulphation that is a result of the favorable influence of CO_2 cycles on sulphation activity of the sorbents.[34–36] This effect cannot be seen in the case when SO_2 concentration was 0.01% (Figure 4c) because there was insufficient SO_2 in the reacting gas. Namely, the maximum possible sulphation conversion after 30 cycles was ~17%, taking into account the total amount of SO_2 in the flue gases and the amount of CaO in the samples. It has been calculated that >70% SO_2 was retained by the limestone sample. Aluminate pellets retained >95% SO_2 from the reacting gas. An almost straight sulphation conversion line was obtained in this case, confirming the high reactivity of aluminate cements with SO_2. Here it should be noted also that carbonation conversions of aluminate pellets were slightly higher than those for limestone. This is an important result, which shows that at lower concentrations of SO_2 in the carbonation stage, aluminate cement can retain a higher carbonation activity than that of natural sorbents. Moreover, these results showed that desulphurization of flue gas before CO_2 capture can effectively protect highly efficient sorbents from undesirable sulphation.

Figure 5 presents SEM images of sorbent particles, which were broken after cycles to study their morphology for both the outer surface and interior of the particles. There is a significant difference between the two examined sorbents. The particles originating from limestone (Figure 5a,b) have clearly defined core−shell patterns, formed regardless of SO_2 concentration. However, it was noticeable that the shell was thicker in the case of higher SO_2 concentration (Figure 5a). Very different morphology was seen in the aluminate pellets (Figure 5c,d) after a number of reaction cycles. In the aluminate pellets, there was some evidence of a very thin shell forming despite the sorbent's much higher sulphation conversion. It can also be seen that the sorbent structure is very porous, independent of even high sulphation conversions (Figure 5c). Similar morphologies have been seen when sulphation with similar samples was done at 900 °C,[37] which is further evidence that higher temperatures employed here for calcination (700−950−700 °C) enhance sulphation at lower temperature (700 °C).

The results presented in Figure 4 show sulphation and carbonation conversions at the end of cycles during multicycle tests. However, it was interesting to explore how conversions change during a single-cycle test. To achieve this in the sulphation/carbonation stage, N_2 was introduced at different times to create calcination conditions, and this allowed us to determine conversions, as schematically presented in Figure 1.

It can be seen in Figure 6 that carbonation conversion is higher during the first 10 min for limestone than for the aluminate pellets. After that, conversion is similar, with slightly higher carbonation conversion for the pellet, when it reaches a maximum. The decrease in carbonation conversion after the maximum is clearly a result of direct sulphation of $CaCO_3$. The higher carbonation conversion at the end of the test was obtained for limestone, because it has more available CaO in the sample; that is, there is less CaO bound as $CaSO_4$. Total conversion of aluminate pellets is higher at the end of the experiment because of their favorable morphology that enables high CaO utilization (>95%).
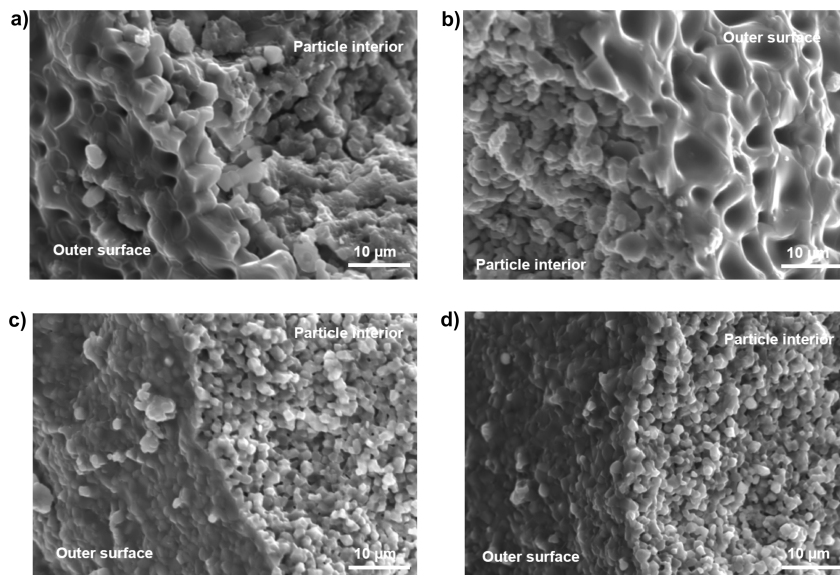
Competition of Sulphation and Carbonation Reactions

J. Phys. Chem. A, Vol. 114, No. 11, 2010 **4001**

Figure 5. SEM images of residues after sulphation/carbonation/calcination cycles: (a,b) CD limestone and (c,d) aluminate cement. SO_2 concentration in the sulphation/carbonation stage (a,c) 0.5%, nine cycles and (b,d) 0.01%, 30 cycles.
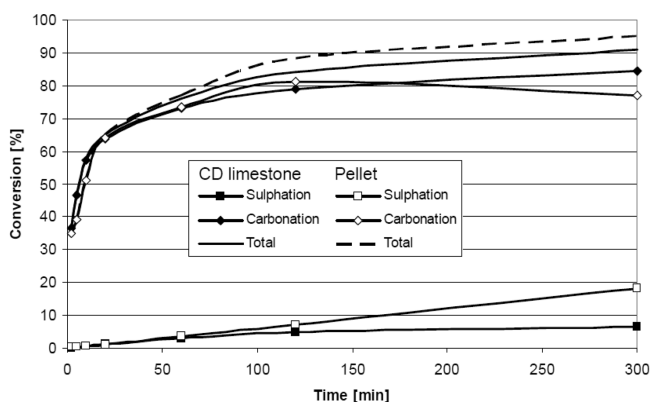

Figure 6. Conversions during sulphation/carbonation of two investigated sorbents at 700 °C, 0.05% SO_2 concentration.

Figure 7. Conversions during sulphation/carbonation of aluminate pellets at different temperatures (650 and 700 °C), 0.05% SO_2 concentration.

Most of the tests in this study were done at 700 °C, which serves as a higher limit in CO_2 capture systems because of chemical equilibrium for carbonation/calcination reactions. Decreasing the temperature leads to lower CO_2 equilibrium concentration, but it also affects conversion rate. However, it can decrease the sulphation rate (because of the high activation energy for product layer diffusion, 120 kJ/mol[41]), which here is the undesirable reaction. The test at lower temperature (650 °C) gave lower sulphation conversion for the aluminate pellets (Figure 7). However, this did not help carbonation conversion because this reaction was slower at lower temperature. In other words, it can be supposed that product (here both $CaCO_3$ and $CaSO_4$ should be considered) layer diffusion at lower temperature also affects carbonation, and thus temperature decrease is not very effective in achieving separate sulphation and carbonation reactions. This also showed that the most effective (and in this stage of our research, the only possible) way to protect highly efficient CaO-based sorbent is desulphurization of flue gas before the CO_2 capture stage.

4. Conclusions

A Ca looping system employs conditions suitable for both sulphation and carbonation, which will occur simultaneously. Their kinetics and the thermodynamic conditions in the capture system and solid sorbent proper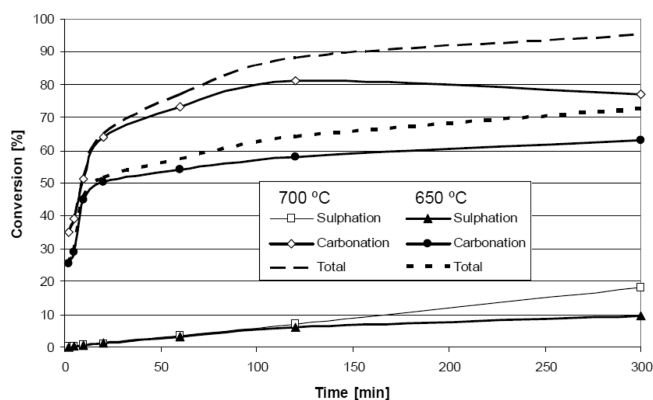ties determine the extent of these reactions. Here it is shown that they are competitive reactions when CaO-based sorbents are used for cleaning flue gas. The increase in reactivity of a CaO-based sorbent for CO_2 capture typically leads to an increase in its activity toward SO_2, which is an undesirable reaction for CO_2 looping cycle technology, especially when more efficient and more expensive sorbents are used in CO_2 capture systems. In this study, it was shown that the chemistry in CO_2 capture systems is extremely complex when SO_2 is present. Sorbent reactivity with SO_2 is increased because a more favorable morphology for reaction with SO_2 is formed during carbonation/calcination cycles. Moreover, at the end of the calcination stage, sorbent is activated by high temperature in that stage, which results in a faster sulphation rate at the beginning of the sulphation/carbonation stage.

Results presented here show that a reduction of SO_2 concentration to a very low level in the sulphation/calcination stage is perhaps the only possible way to protect sorbent from sulphation and a significant loss of activity toward the carbonation reaction. It is possible to achieve this using spent/reactivated sorbent from CO_2 capture cycles, which is highly reactive toward SO_2 and can ensure a very low concentration of SO_2 in flue gas entering the carbonator.

References and Notes

(1) Mohr, S. H.; Evans, G. M. Forecasting Coal Production until 2100. *Fuel* **2009**, *88*, 2059–2067.

(2) Hook, M.; Aleklett, K. Historical Trends in American Coal Production and a Possible Future Outlook. *Int. J. Coal Geol.* **2009**, *78*, 201–216.

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

(4) Herzog, H. What Future for Carbon Capture and Sequestration. *Environ. Sci. Technol.* **2001**, *35*, 148–153.

(5) Oka, S. *Fluidized Bed Combustion*; Marcel Decker: New York, 2004.

(6) Anthony, E. J. Fluidized Bed Combustion of Alternative Solid Fuels; Status, Successes and Problems of the Technology. *Prog. Energy Combust. Sci.* **1995**, *21*, 239–268.

(7) Anthony, E. J.; Granatstein, D. L. Sulfation Phenomena in Fluidized Bed Combustion Systems. *Prog. Energy Combust. Sci.* **2001**, *27*, 215–236.

(8) Laursen, K.; Duo, W.; Grace, J. R.; Lim, J. Sulfation and Reactivation Characteristics of Nine Limestones. *Fuel* **2000**, *79*, 153–163.

(9) Anthony, E. J.; Bulewicz, E. M.; Jia, L. Reactivation of Limestone Sorbents in FBC for SO_2 Capture. *Prog. Energy Combust. Sci.* **2007**, *33*, 171–210.

(10) Shimizu, T.; Hirama, T.; Hosoda, H.; Kitano, K.; Inagaki, M.; Tejima, K. A Twin Fluid-Bed Reactor for Removal of CO_2 from Combustion Processes. *Chem. Eng. Res. Des.* **1999**, *77*, 62–68.

(11) 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.

(12) Anthony, E. J. Solid Looping Cycles: A New Technology for Coal Conversion. *Ind. Eng. Chem. Res.* **2008**, *47*, 1747–1754.

(13) 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.

(14) 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.

(15) 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.

(16) Romeo, L. M.; Lara, Y.; Lisbona, P.; Escosa, J. M. Optimizing Make-up Flow in a CO_2 Capture System using CaO. *Chem. Eng. J.* **2009**, *147*, 252–258.

(17) Romeo, L. M.; Lara, Y.; Lisbona, P.; Martínez, A. Economical Assessment of Competitive Enhanced Limestones for CO_2 Capture Cycles in Power Plants. *Fuel Process. Technol.* **2009**, *90*, 803–811.

(18) Aaron, D.; Tsouris, C. Separation of CO_2 from Flue Gas: A Review. *Sep. Sci. Technol.* **2005**, *40*, 321–348.

(19) Bachu, S. CO_2 Storage in Geological Media: Role, Means, Status, and Barriers to Deployment. *Prog. Energy Combust. Sci.* **2008**, *34*, 254–273.

(20) 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.

(21) 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.

(22) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. The Effect of CaO Sintering on Cyclic CO_2 Capture in Energy Systems. *AIChE J.* **2007**, *53*, 2432–2442.

(23) Abanades, J. C.; Alvarez, D. Conversion Limits in the Reaction of CO_2 with Lime. *Energy Fuels* **2003**, *17*, 308–315.

(24) 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.

(25) Manovic, V.; Anthony, E. J. Improvement of CaO-Based Sorbent Performances for CO_2 Looping Cycles. *Therm. Sci.* **2009**, *13*, 89–104.

(26) 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.

(27) 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.

(28) 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.

(29) 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.

(30) Manovic, V.; Anthony, E. J. CaO-Based Pellets Supported by Calcium Aluminate Cements for High-Temperature CO_2 Capture. *Environ. Sci. Technol.* **2009**, *43*, 7117–7122.

(31) Jia, L.; Tan, Y.; Wang, C.; Anthony, E. J. Experimental Study of Oxy-Fuel Combustion and Sulphur Capture in a Mini-CFBC. *Energy Fuels* **2007**, *21*, 3160–3164.

(32) Prasannan, P. C.; Ramachandran, P. A.; Doraiswamy, L. K. A Model for Gas-Solid Reactions with Structural Changes in the Presence of Inert Solids. *Chem. Eng. Sci.* **1985**, *40*, 1251–1261.

(33) Duo, W.; Sevill, J. P. K.; Kirkby, N. F.; Clift, R. Formation of Product Layers in Solid-Gas Reactions for Removal of Acid Gases. *Chem. Eng. Sci.* **1994**, *49*, 4429–4442.

(34) Grasa, G. S.; Alonso, M.; Abanades, J. C. Sulfation of CaO Particles in a Carbonation/Calcination Loop to Capture CO_2. *Ind. Eng. Chem. Res.* **2008**, *47*, 1630–1635.

(35) Manovic, V.; Anthony, E. J.; Loncarevic, D. SO_2 Retention by CaO-Based Sorbent Spent in CO_2 Looping Cycles. *Ind. Eng. Chem. Res.* **2009**, *48*, 6627–6632.

(36) Pacciani, R.; Muller, C. R.; Davidson, J. F.; Dennis, J. S.; Hayhurst, A. N. Performance of a Novel Synthetic Ca-Based Solid Sorbent Suitable for Desulfurizing Flue Gases in a Fluidized Bed. *Ind. Eng. Chem. Res.* **2009**, *48*, 7016–7024.

(37) Manovic, V.; Anthony, E. J. Sulphation Performance of CaO-based Pellets Supported by Calcium Aluminate Cements Designed for High-Temperature CO_2 Capture. *Energy Fuels*, in press.

(38) Liu, H.; Katagiri, S.; Kaneko, U.; Okazaki, K. Sulfation Behavior of Limestone under High CO_2 Concentration in O_2/CO_2 Coal Combustion. *Fuel* **2000**, *79*, 945–953.

(39) Ryu, H.; Grace, J. R.; Lim, C. J. Simultaneous CO_2/SO_2 Capture Characteristics of Three Limestones in a Fluidized-Bed Reactor. *Energy Fuels* **2006**, *20*, 1621–1628.

(40) Li, Y.; Buchi, S.; Grace, J. R.; Lim, C. J. SO_2 Removal and CO_2 Capture by Limestone Resulting from Calcination/Sulfation/Carbonation cycles. *Energy Fuels* **2005**, *19*, 1927–34.

(41) 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.

(42) Hsia, C.; St. Pierre, G. R.; Raghunathan, K.; Fan, L.-S. Diffusion Through $CaSO_4$ Formed during the Reaction of CaO with SO_2 and O_2. *AIChE J.* **1993**, *39*, 698.

(43) Manovic, V.; Anthony, E. J. SO_2 Retention by Reactivated CaO-Based Sorbent from Multiple CO_2 Capture Cycles. *Environ. Sci. Technol.* **2007**, *41*, 4435–4440.

(44) Manovic, V.; Anthony, E. J. Sequential SO_2/CO_2 Capture Enhanced by Steam Reactivation of a CaO-Based Sorbent. *Fuel* **2008**, *87*, 1564–1573.