

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/245234836>

Sulfation Performance of CaO-Based Pellets Supported by Calcium Aluminate Cements Designed for High-Temperature CO₂ Capture

ARTICLE *in* ENERGY & FUELS · FEBRUARY 2010

Impact Factor: 2.79 · DOI: 10.1021/ef900943h

CITATIONS

15

READS

18

2 AUTHORS:



Vasilije Manovic

Cranfield University

91 PUBLICATIONS 1,974 CITATIONS

SEE PROFILE



Edward Anthony

Cranfield University

260 PUBLICATIONS 7,171 CITATIONS

SEE PROFILE

Sulfation Performance of CaO-Based Pellets Supported by Calcium Aluminate Cements Designed for High-Temperature CO₂ Capture

Vasilije Manovic and Edward J. Anthony*

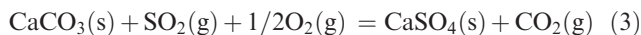
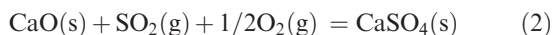
CanmetENERGY, Natural Resources Canada, 1 Haanel Drive, Ottawa, Ontario, Canada K1A 1M1

Received August 29, 2009. Revised Manuscript Received November 4, 2009

CaO-based sorbents supported by calcium aluminate cements were originally prepared as sorbents for CO₂ capture in looping cycles. However, their high affinity for CO₂ at high temperatures suggests that they will readily react with any SO₂ present in flue gases to be decarbonated. Thus, the sulfation performance of these pellets was investigated in this study using a synthetic flue gas in a thermogravimetric analyzer (TGA). The results obtained showed that after 6 h in gas containing 0.5% SO₂ at 900 °C the pellets prepared from hydrated lime and cement were > 90% sulfated. They showed the highest sulfation affinity among the sorbents tested here. Namely, Cadomin limestone was < 30% sulfated and the corresponding hydrated lime < 70%. The pellets prepared from limestone powder and cement had significantly lower sulfation (~65%) in comparison to that for pellets obtained from hydrated lime and cement. The scanning electron microscope (SEM) images of sulfated samples clearly showed the presence of a sulfated shell at the surface of original limestone particles, while the calcium aluminate pellets had porous morphology even after almost 100% sulfation. The X-ray diffraction (XRD) analyses showed that mayenite (Ca₁₂Al₁₄O₃₃), which is responsible for the good CO₂ capture performance of these pellets, was not present after sulfation. Pellets after 30 carbonation/calcination cycles displayed significantly reduced affinity for SO₂, with sulfation conversions at ~15%, but they easily recovered this capacity with ~80% sulfation levels after hydration. These results clearly show that, for the pellets to perform well, the presence of SO₂ must be avoided during looping cycles at least during sorbent regeneration at high temperatures.

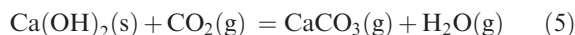
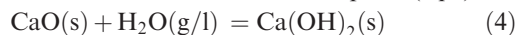
1. Introduction

Natural CaO-based materials, limestones and dolomites, are used extensively as cheap SO₂ sorbents with fluidized bed combustion (FBC) technologies¹ firing high-sulfur coals and petroleum coke. The sulfation process can occur after calcination (eq 1) with lime (eq 2) or directly with limestone (eq 3) when the CO₂ partial pressure is high enough to prevent CaCO₃ decomposition:²



The main shortcoming of the sulfation process in FBC is its relatively low sorbent utilization, which is typically below 45%.¹ This results in extra sorbent use and requires disposal of larger amounts of partially unreacted sorbent, which is environmentally and economically disadvantageous. Possible solutions are hydration (eq 4) of unreacted lime³ and its use for

further SO₂ retention or carbonation and disposal (eq 5).⁴



Recently, anthropogenic global warming and climate changes have created interest in CO₂ capture and storage (CCS) for fossil fuel-fired power plants.⁵ For CCS the most challenging step is CO₂ separation from flue gases to obtain a concentrated CO₂ stream suitable for liquefaction and geological storage.^{6,7} As a result, different solutions for CO₂ capture have received increased attention: precombustion CO₂ capture,^{8,9} oxyfuel combustion,^{2,10} and postcombustion CO₂ capture.^{11,12} Looping cycles involving solid CaO-based

*To whom correspondence should be addressed. E-mail: banthony@nrcan.gc.ca. Telephone: (613) 996-2868. Fax: (613) 992-9335.

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

(2) 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.

(3) Anthony, E. J.; Bulewicz, E. M.; Jia, L. Reactivation of Limestone Sorbents in FBC for SO₂ Capture. *Prog. Energy Combust. Sci.* **2007**, 33, 171–210.

(4) Rao, A.; Anthony, E. J.; Manovic, V. Sonochemical Treatment of FBC Ash: A Study of the Reaction Mechanism and Performance of Synthetic Sorbents. *Fuel* **2008**, 87, 1927–1933.

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

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

(7) Bachu, S. CO₂ Storage in Geological Media: Role, Means, Status, and Barriers to Deployment. *Prog. Energy Combust. Sci.* **2008**, 34, 254–273.

(8) Harrison, D. P. Sorption-Enhanced Hydrogen Production: A Review. *Ind. Eng. Chem. Res.* **2008**, 47, 6486–6501.

(9) Florin, N. H.; Harris, A. T. Enhanced Hydrogen Production from Biomass with in situ Carbon Dioxide Capture using Calcium Oxide Sorbents. *Chem. Eng. Sci.* **2008**, 63, 287–316.

(10) Buhre, B. J. P.; Elliott, L. K.; Sheng, C. D.; Gupta, R. P.; Wall, T. F. Oxy-Fuel Combustion Technology for Coal-Fired Power Generation. *Prog. Energy Combust. Sci.* **2005**, 31, 283–307.

(11) Gupta, H.; Fan, L.-S. Carbonation-Calcination Cycle using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas. *Ind. Eng. Chem. Res.* **2002**, 41, 4035–4042.

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

CO₂ carriers can be used in both processes: pre- and post-combustion. The process of CO₂ capture is based on the reversible heterogeneous reaction, carbonation, which is the reverse of calcination (eq 1). The process of CaO capture is cyclic, which means that a quantity of sorbent is used a number of times for capture after regeneration. In principle, regeneration occurs at higher temperatures, > 900 °C, in order to obtain a concentrated stream of CO₂, ready for sequestration.

The most prominent challenge for these processes is the loss of sorbent activity with increasing numbers of reaction cycles caused by sintering.^{13,14} The sorbent deactivation demands increased fresh sorbent makeup. As this is the main parameter determining the economic competitiveness of any proposed CaO-based CO₂ capture technology scheme,^{15–17} different methods for sorbent enhancement are under intense investigation, including hydration,^{18,19} thermal pretreatment,^{20,21} and doping with alumina compounds.^{22–25}

The methods for sorbent enhancement were mainly based on producing changes in sorbent morphology. On the other hand, carbonation (reverse of eq 1) and sulfation (eqs 2 and 3) are similar reactions, both heterogeneous, and both affected by changes in sorbent porous structure. SO₂ is typically present in flue gas, and simultaneous SO₂ and CO₂ capture has been investigated.^{26,27} CaSO₄ formation is irreversible (under SO₂/CO₂ capture conditions), and moreover CaSO₄ fills small pores and covers the surface of larger pores, preventing contact of CO₂ with unreacted CaO and causing

a marked decrease in performance of the sorbent for CO₂ capture. It has also been shown that many natural sorbents subjected to calcination/carbonation cycles have better reactivity to SO₂ than that of the original sorbents.^{27–29} This is due to formation of larger pores in the sorbent as a result of sintering, which prevent pore filling and formation of unreacted core/sulfated shell or network patterns, allowing SO₂ diffusion and further reaction with unreacted CaO.^{30,31}

The most promising modification of CaO-based sorbents for CO₂ capture is doping/syntheses with alumina compounds.^{22–25} These materials showed promising performance and the best CO₂ carrying stability among CaO-based sorbents investigated to date. Our recent study³² showed that a very promising method for pelletization involves the use of calcium aluminate cements. The pellets obtained showed good mechanical performance and high CO₂ carrying capacities during a series of 1000 carbonation/calcination cycles, with a residual activity of 28%.³³ The main characteristic of some synthetic sorbents as well as calcium aluminate pellets is the presence of mayenite (Ca₁₂Al₁₄O₃₃), which is believed to be responsible for ensuring a favorable sorbent morphology, by maintaining the microporosity, through many CO₂ cycles.

CaO-based pellets prepared with calcium aluminate cements have also been used for desulfurizing hot gases.^{34,35} A recent study on sulfation properties of synthetic sorbent (85 wt % CaO and 15 wt % Ca₁₂Al₁₄O₃₃) highlights its enhanced reactivity to SO₂ in comparison to that of natural sorbents.³⁶ It also appears that mayenite may react with SO₂ even at low/moderate temperatures.³⁷ These results have led us to an investigation of the sulfation behavior of highly efficient calcium aluminate pellets prepared for CO₂ capture.^{32,33} It is very important to explore how such sorbents behave in the presence of SO₂ for at least two reasons. First, SO₂ is typically present in flue gas that is subjected to decarbonation and/or in the concentrated CO₂ stream during sorbent regeneration, if sulfur-containing fuels are used in the regeneration step. Second, high sorbent reactivity to SO₂ suggests that spent sorbents could be used for sulfur removal before their disposal at the end of their CO₂ capture life. These aspects were examined in this study and are presented here.

(13) Abanades, J. C.; Alvarez, D. Conversion Limits in the Reaction of CO₂ with Lime. *Energy Fuels* **2003**, *17*, 308–315.

(14) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. The Effect of CaO Sintering on Cyclic CO₂ Capture in Energy Systems. *AIChE J.* **2007**, *53*, 2432–2442.

(15) Abanades, J. C.; Rubin, E. S.; Anthony, E. J. Sorbent Cost and Performance in CO₂ Capture System. *Ind. Eng. Chem. Res.* **2004**, *43*, 3462–3466.

(16) Romeo, L. M.; Lara, Y.; Lisbona, P.; Escosa, J. M. Optimizing Make-up Flow in a CO₂ 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 CO₂ Capture Cycles in Power Plants. *Fuel Process. Technol.* **2009**, *90*, 803–811.

(18) Fennell, P. S.; Davidson, J. F.; Dennis, J. S.; Hayhurst, A. N. Regeneration of Sintered Limestone Sorbents for the Sequestration of CO₂ from Combustion and Other Systems. *J. Energy Inst.* **2007**, *80*, 116–119.

(19) Manovic, V.; Anthony, E. J. Steam Reactivation of Spent CaO-Based Sorbent for Multiple CO₂ Capture Cycles. *Environ. Sci. Technol.* **2007**, *41*, 1420–1425.

(20) Lysikov, A. I.; Salanov, A. N.; Okunev, A. G. Change of CO₂ Carrying Capacity of CaO in Isothermal Recarbonation-Decomposition Cycles. *Ind. Eng. Chem. Res.* **2007**, *46*, 4633–4638.

(21) Manovic, V.; Anthony, E. J. Thermal Activation of CaO-Based Sorbent and Self-Reactivation during CO₂ Capture Looping Cycles. *Environ. Sci. Technol.* **2008**, *42*, 4170–4174.

(22) 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.

(23) Wu, S. F.; Li, Q. H.; Kim, J. N.; Yi, K. B. Properties of a Nano CaO/Al₂O₃ CO₂ Sorbent. *Ind. Eng. Chem. Res.* **2008**, *47*, 180–184.

(24) Martavaltzi, C. S.; Lemonidou, A. A. Parametric Study of the CaO-Ca₁₂Al₁₄O₃₃ Synthesis with Respect to High CO₂ Sorption Capacity and Stability on Multicycle Operation. *Ind. Eng. Chem. Res.* **2008**, *47*, 9537–9543.

(25) Dennis, J. S.; Pacciani, R. The Rate and Extent of Uptake of CO₂ by a Synthetic, CaO-Containing Sorbent. *Chem. Eng. Sci.* **2009**, *64*, 2147–2157.

(26) Ryu, H.; Grace, J. R.; Lim, C. J. Simultaneous CO₂/SO₂ Capture Characteristics of Three Limestones in a Fluidized-Bed Reactor. *Energy Fuels* **2006**, *20*, 1621–1628.

(27) Li, Y.; Buchi, S.; Grace, J. R.; Lim, C. J. SO₂ Removal and CO₂ Capture by Limestone Resulting from Calcination/Sulfation/Carbonation Cycles. *Energy Fuels* **2005**, *19*, 1927–1934.

(28) Grasa, G. S.; Alonso, M.; Abanades, J. C. Sulfation of CaO Particles in a Carbonation/Calcination Loop to Capture CO₂. *Ind. Eng. Chem. Res.* **2008**, *47*, 1630–1635.

(29) Manovic, V.; Anthony, E. J.; Loncarevic, D. SO₂ Retention by CaO-Based Sorbent Spent in CO₂ Looping Cycles. *Ind. Eng. Chem. Res.* **2009**, *48*, 6627–6632.

(30) Hartman, M.; Coughlin, R. W. Reaction of Sulfur Dioxide with Limestone and the Influence of Pore Structure. *Ind. Eng. Proc. Des. Dev.* **1974**, *13*, 248–253.

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

(32) Manovic, V.; Anthony, E. J. CaO-Based Pellets Supported by Calcium Aluminate Cements for High-Temperature CO₂ Capture. *Environ. Sci. Technol.* **2009**, *43*, 7117–7122.

(33) Manovic, V.; Anthony, E. J. Long-Term Behavior of CaO-Based Pellets Supported by Calcium Aluminate Cements in Long Series of CO₂ Capture Cycles. *Ind. Eng. Chem. Res.* **2009**, *48*, 8906–8912.

(34) Akiti, T. T., Jr.; Constant, K. P.; Doraiswamy, L. K.; Wheelock, T. D. Development of an Advanced Calcium-Based Sorbent for Desulfurizing Hot Coal Gas. *Adv. Environ. Res.* **2001**, *5*, 31–38.

(35) Wheelock, T. D.; Akiti, T. T., Jr. Core-in-Shell Sorbent for Hot Coal Gas Desulfurization, U.S. Patent No. 6,689,714, February 10, 2004.

(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) Chen, Q.; Yoshida, K.; Yamamoto, H.; Uchida, M.; Sadakata, M. Investigation on the Application of C12A7 in Flue Gas Desulfurization at Low-Moderate Temperature. *Energy Fuels* **2007**, *21*, 3264–3269.

Table 1. XRF Elemental Analyses of Limestone Samples Used

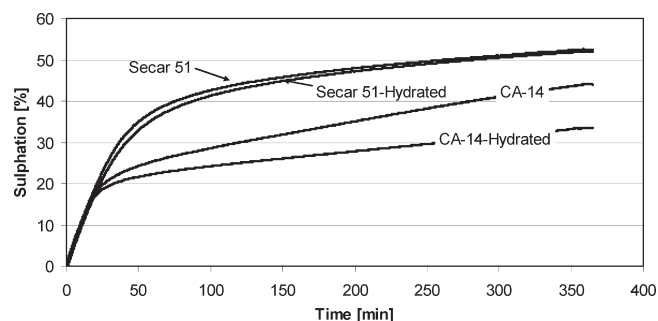
component	Cadomin (CD)	Havelock (HV)	Katowice (KT)
SiO ₂ , wt %	5.47	0.95	0.85
Al ₂ O ₃ , wt %	1.54	0.25	0.24
Fe ₂ O ₃ , wt %	0.61	0.40	0.09
TiO ₂ , wt %	< 0.03	< 0.03	< 0.03
P ₂ O ₅ , wt %	< 0.03	< 0.03	< 0.03
CaO, wt %	50.67	54.31	54.10
MgO, wt %	0.55	0.54	0.89
SO ₃ , wt %	< 0.10	< 0.10	< 0.10
Na ₂ O, wt %	< 0.20	< 0.20	< 0.20
K ₂ O, wt %	0.35	0.02	0.06
Ba, ppm	618	< 250	< 250
Sr, ppm	272	141	287
V, ppm	< 50	< 50	< 50
Ni, ppm	< 50	< 50	< 50
Mn, ppm	1132	573	72
Cr, ppm	< 50	< 50	< 50
Cu, ppm	36	< 30	< 30
Zn, ppm	78	< 30	45
loss on fusion, wt %	40.48	43.45	43.64
sum, wt %	99.98	99.98	99.96

2. Experimental Section

Materials. Three limestones: Cadomin (CD) and Havelock (HV) from Canada and Katowice (KT) from Poland (Upper Silesia) were used for pelletization. Particle sizes used were CD and HV limestones, 0.25–1.4 mm and KT, 0.4–0.8 mm. The elemental analysis of the limestones used is given in Table 1. The distinguishing feature in the elemental compositions is the high SiO₂ (5.47%) and Al₂O₃ content (1.54%) in CD limestone, indicating the presence of silicate and aluminosilicate impurities. Four commercial calcium aluminate cements were used here. CA-14 and CA-25, produced by Almatris Inc., have Al₂O₃ contents of ~70 and ~80%, respectively. Secar 51 and Secar 80, produced by Kerneos Inc., were chosen because of their wider difference in Al₂O₃ content, ~50 and ~80%, respectively.

Pellet Preparation. Pellets were prepared using powdered limestone or hydrated lime and 10% of the cement, calculated on the initial (before calcination and hydration) limestone mass. When hydrated lime was used, the limestone was calcined at 850 °C for 2 h before hydration. Weighed amounts of limestone (or lime after calcination) and cement were mixed in a glass beaker, and water was added with stirring to obtain a gel, similar to mortar. When lime was used, water was added slowly to minimize the effects of heat release due to the exothermic hydration process. The gel obtained was then extruded through a 1.0 mm sieve to produce uniform pellet diameters. Two other pellet sizes were also prepared, with diameters of 2 and 4 mm, and these were shaped by hand, using protective gloves, to obtain spheres. More details on the materials used and the pellet preparation method are presented elsewhere.^{32,38}

Sulfation. A Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA) was used for the sulfation experiments. 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 900 °C (30 °C/min) and then keeping the temperature at that level for 370 min. The program started with the introduction of N₂, which was replaced with the gas mixture of synthetic flue gas (15% CO₂, 3% O₂, 0.5% SO₂ and N₂ balance) 10 min after the temperature reached 900 °C. Sulfation was performed for 360 min. The gas flow rate during runs was controlled with a flowmeter at 40 cm³/min. 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 due to formation of CaSO₄.

**Figure 1.** Sulfation of original and hydrated samples of calcium aluminate cements.

Sample Characterization. The sample morphologies 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.

Identification/quantification of compounds in the pellet samples before and after sulfation was done by X-ray diffraction (XRD). XRD data were collected on a Bruker D5000TT diffractometer over the angular range 10–80° (2θ) in 0.02° steps and 20 s per step. The phases were identified, and quantitative analyses of the samples were obtained using α-alumina (Al₂O₃) as an internal spiking standard.

3. Results and Discussion

Calcium aluminate cements contain significant amounts of various calcium compounds, with CaO content 20–40% in cements used for pellets examined in this study. To define sulfation conversions, it is important to explore whether CaO from calcium aluminate cements reacts with SO₂. Recently, we showed that CaO from cement does not take place in carbonation/calcination cycles.³⁸ Moreover, it has been shown³² that Al₂O₃ from cement reacts with some of the CaO from limestone to form mayenite (Ca₁₂Al₁₄O₃₃). Thus, to explore the fate of CaO from cement, sulfation tests of both original and hydrated CA-14 and Secar 51 cements were carried out and results are presented in Figure 1. It can be seen that up to half of the CaO from cement reacted with SO₂; hence, CaO in the cement should be considered as active during sulfation, and conversions are calculated on the basis of total CaO in the pellet.

At the end of the CO₂ cycles, mayenite was determined by XRD, as it was considered the compound responsible for maintaining sorbent morphology suitable for carbonation.³² However, reaction of CaO from cement with SO₂ means that, during sulfation of pellets, competition between mayenite and CaSO₄ formation must occur. The pellets prepared from CD hydrated limestone and CA-14 aluminate cement (HP-CA-14) were characterized by XRD before and after sulfation in the TGA. To collect enough sulfated pellet sample for quantitative XRD analysis, the TGA sulfation test was repeated several times. The diffractograms obtained are presented in Figure 2. It can be seen that the main alumina compound present in the crystal phase of the pellet before sulfation (Figure 2a) is katoite, (CaO)₃Al₂O₃(H₂O)₆. The most intensive peaks in this diffractogram belong to portlandite, Ca(OH)₂. The most pronounced crystal phase in the sample after sulfation (Figure 2b) is anhydrite, CaSO₄. The only identified alumina compound is calcium aluminum silicate, Ca₁₂Al₁₀Si₄O₃₅, i.e., mayenite is not identified. These

(38) Manovic, V.; Anthony, E. J. Screening of Binders for Pelletization of CaO-Based Sorbents for CO₂ Capture. *Energy Fuels* 2009, 23, 4797–4804.

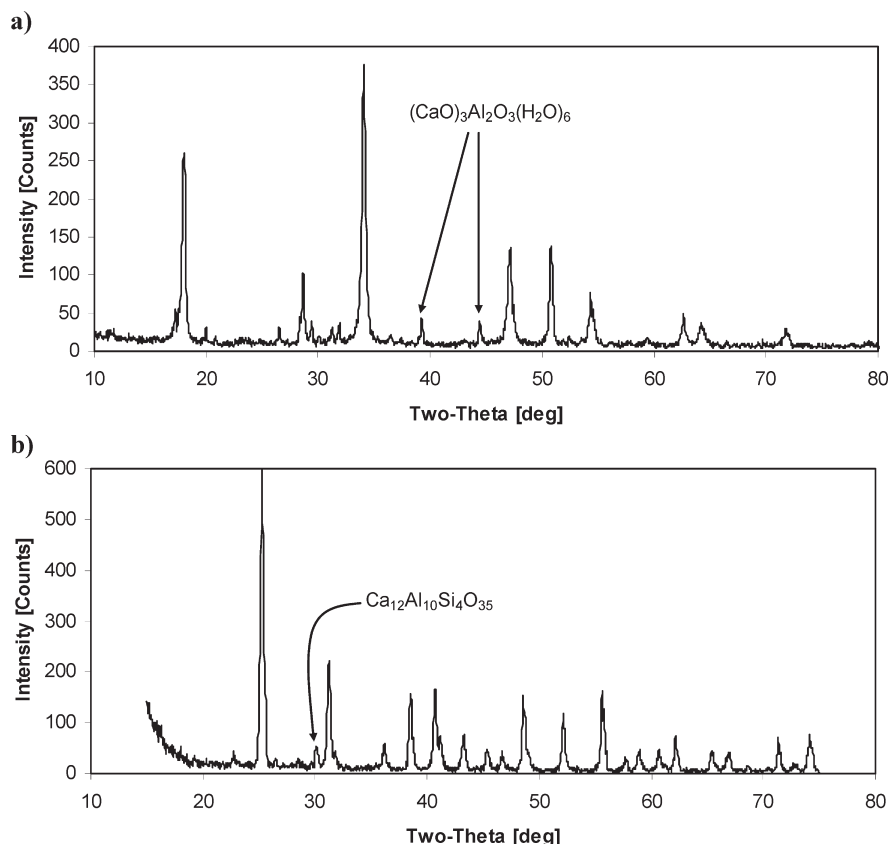


Figure 2. XRD spectra of pellet sample (hydrated HV lime and 10% CA-14 cement) before (a) and after (b) sulfation in TGA.

Table 2. XRD Analysis of Pellet Sample (Hydrated HV Lime and 10% CA-14 Cement) before and after Sulfation in TGA

compound	before sulfation	after sulfation
portlandite, $\text{Ca}(\text{OH})_2$, wt %	65.8	
katoite, $(\text{CaO})_3\text{Al}_2\text{O}_3(\text{H}_2\text{O})_6$, wt %	17.3	
calcium aluminum silicate, $\text{Ca}_3\text{Al}_6\text{Si}_2\text{O}_{16}$, wt %	1.9	
calcite, CaCO_3 , wt %	3.0	
gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, wt %	3.6	
quartz, SiO_2 , wt %	2.5	3.9
anhydrite, CaSO_4 , wt %		89.3
calcium aluminum silicate, $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}$, wt %		3.9
lime, CaO , wt %		1.2
mayenite, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, wt %		
crystallinity (%)	94.1	98.3
amorphous content (%)	5.9	1.7

results show that CaO from aluminate cement reacts with SO_2 and either prevents the formation of mayenite or if mayenite is formed as an intermediate, it completely and preferentially reacts with SO_2 , which is in agreement with earlier findings on mayenite reactivity with SO_2 .³⁷

Other compounds identified in the crystal phase of the sample, along with their amounts, are given in Table 2. It can be seen that the material achieves a very high level of sulfation, with 89.3% of CaSO_4 in the sample and only 1.2% of unreacted CaO remaining. These results also show that CaO, both from limestone and cement, was sulfated. Analysis of the original pellets showed that mayenite was not found prior to sulfation, because its generation demands that the pellet be exposed to high-temperature CO_2 cycles.³²

The comparison of conversion vs time profiles of the original CD limestone, its corresponding hydrated lime, and

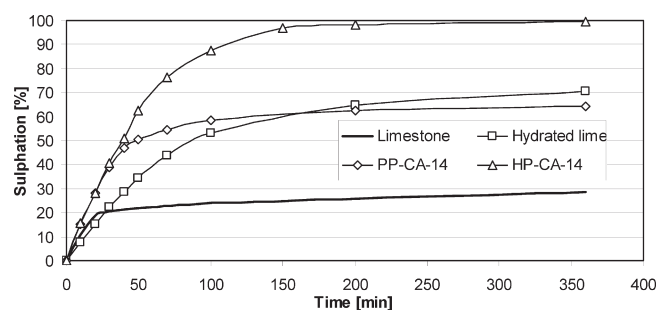


Figure 3. Sulfation tests in TGA of original CD limestone (particle size 0.25–1.4 mm) and pellets (~1 mm) prepared from CA-14 cement and hydrated CD lime, powdered CD limestone (PP-CA-14), and hydrated CD lime (HP-CA-14). Conditions: 900 °C, synthetic flue gas (15% CO_2 , 3% O_2 , 0.5% SO_2 and N_2 balance).

pellets prepared from CA-14 cement and powdered limestone (PP-CA-14) or hydrated lime (HP-CA-14) is presented in Figure 3. The large differences in both conversion profiles and final conversions after 6 h can be seen. The original limestone did not reach 30% sulfation, and this result is in agreement with results available in the literature^{1,30,31} for other limestones. This low conversion of CD limestone can be explained by formation of an unreacted core/partially sulfated shell pattern,^{30,31} and this is clearly illustrated in Figure 4. Large CaSO_4 grains in the shell at the particle surface can be seen. In the interior of the particles are much smaller grains of unreacted CaO, with enough room between them to accommodate more CaSO_4 . However, the outer shell prevents diffusion of SO_2 toward the unreacted CaO core.

The differences between the particle surface and morphology of the particle interior for various sorbents are presented

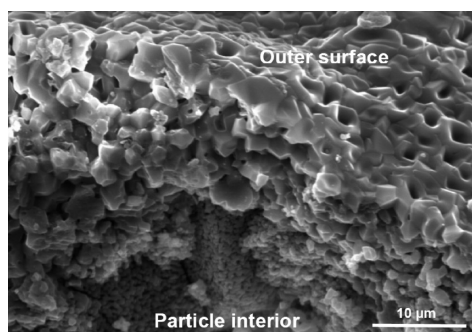


Figure 4. SEM image of a broken partially sulfated CD limestone particle.

in Figure 5. The almost total conversion of HP-CA-14 pellet, as determined by XRD (Table 2) and TGA measurement (Figure 3), can be explained by the SEM image of its particle surface (Figure 5c, left). Here, there are much smaller grains and visible open pores at the particle surface. This means that alumina doping (here by means of aluminate cement) keeps the sorbent morphology stable even during sulfation at high temperature and prevents formation of large product grains at the particle surface (seen in the case of the original limestone, Figure 5a). Sulfation of hydrated lime falls between these two cases (Figure 5b). In this case, somewhat larger pore volume in the particle is observed because of calcination of voluminous $\text{Ca}(\text{OH})_2$. However, large CaSO_4 grains close to the particle surface are formed during sulfation, preventing diffusion of SO_2 and further sulfation. Thus, the particle size was expected to be an important parameter when hydrated pellets were prepared with no aluminate cement, as is seen in the experiment presented in Figure 6, where with an increase of particle size from 1 to 4 mm, the final sulfation dropped by a half.

The sulfation performance of calcium aluminate pellets and morphology seen in Figure 5c imply that particle size should not be an important parameter, at least in terms of final conversion. This is confirmed in Figure 7, where high final levels of sulfation ($\sim 90\%$) were reached regardless of the pellet size but the conversion rate of larger particles was slower, which is a result of increased resistance to diffusion of SO_2 in larger particles. These results are in very close agreement with results obtained with synthetic sorbents³⁶ where an influence of pellet size was also not observed. Moreover, a very similar qualitative performance of pellets prepared with different cements can be seen in Figure 7. This is expected given that CaO from cement also reacts with SO_2 , as seen in this study, which effectively reduces or eliminates any influence of the difference between the various cements used and their different CaO contents. Similar performance was observed for pellets prepared with CA-25 and Secar 51 and other investigated limestone samples; however, the results are not presented here in the interest of brevity. The results of Figure 7 are important because they clearly show that residue from carbonation/calcination cycles in FBC may be successfully hydrated, pelletized, and used for SO_2 retention prior to disposal.

It should be noted here that pellets used in this study had larger diameters than those suitable for use in FBC systems with solid circulation. However, they can be used in a packed bed, which is an advantage if attrition phenomena during their use in FBC systems is important. It is also important to note that there are no restrictions on preparing smaller pellets suitable for solid circulation in FBC systems. According to

Table 3. Hydration and Carbonation Levels (Determined by TGA) of Pellets after 30 CO_2 Cycles and Hydration by Moist Air at Room Temperature for 24 h

sample	hydration [wt %]	carbonation [wt %]
C#4-CA-14-2 mm	18.10	3.86
C#4-CA-14-4 mm	16.51	4.13
HV-Secar-51-4 mm	17.02	8.51
HV-Secar-80-4 mm	9.33	21.33

results for their sulfation activity (Figure 7) and carbonation activity,³² which are higher for smaller pellets, reducing the pellet particle size can be considered as an advantage rather than as a shortcoming.

It was also interesting to explore sulfation of pellets immediately after CO_2 looping cycles. These tests were done with samples after 30 cycles in the TGA and results are presented in Figure 8. These results were different than those obtained with natural sorbents, whose sulfation reactivity typically increases as a result of carbonation/calcination cycles.^{28,29} The sulfation conversion of spent calcium aluminate pellets was drastically lower (13–23%) in comparison with $> 90\%$ obtained for the same pellets before CO_2 cycles (Figure 8 vs Figure 3). A drop in sulfation conversion, albeit not so drastic, after CO_2 capture cycles has already been reported for a synthetic sorbent.³⁶

The loss of sulfation activity of pellets is important from two points of view: (i) it affects the potential for use of pellets spent in CO_2 cycles for SO_2 retention or (ii) it implies the loss of highly efficient sorbent for CO_2 capture during cycles when SO_2 is present in the carbonation/calcination gas. The second aspect is evidently potentially important because calcium aluminate pellets are more expensive than natural sorbents for SO_2 retention and, to ensure economic competitiveness, they must survive more CO_2 cycles.

The significant loss of SO_2 capture activity of pellets treated by means of carbonation/calcination cycles is an interesting and encouraging result from the point of view that appropriate treatment of the pellets before use for CO_2 capture may reduce their affinity to SO_2 , since it would be desirable in order to increase sorbent selectivity toward CO_2 . However, if sulfation of spent pellets is required, this can be enhanced by hydration, for example, by simple exposure to moist air.¹⁸ The pellets produced here react readily with moisture, and highly hydrated samples (9–18%) were obtained even after simple exposure to air (Table 3). Evidently, some of the $\text{Ca}(\text{OH})_2$ also continued to react with CO_2 from the air, resulting in significant carbonation levels (4–21%). The hydration of samples after 30 carbonation/calcination cycles resulted in the recovery of sulfation performance. The results in Figure 9 show $> 80\%$ conversion regardless of the material used for pellet preparation and particle size.

The high sulfation activities of aluminate pellets explored in this study are important from two aspects. The first is the possibility of using the original and, more appropriate, reactivated spent pellets for desulfurizing flue gas, representing a clear advantage of these pellets. On the other hand, original pellets react with SO_2 during their regeneration (calcination), which reduces their CO_2 carrying capacity. Some CaO in the sorbent is irretrievably lost (as CaSO_4) from CO_2 capture cycles, and activity of unreacted CaO is reduced because of the formation of a CaSO_4 product layer. This highlights the need for sorbent regeneration in non- SO_2 -containing conditions, which is feasible using nonsulfur-containing fuels, such as natural gas and biomass or through direct heating during the

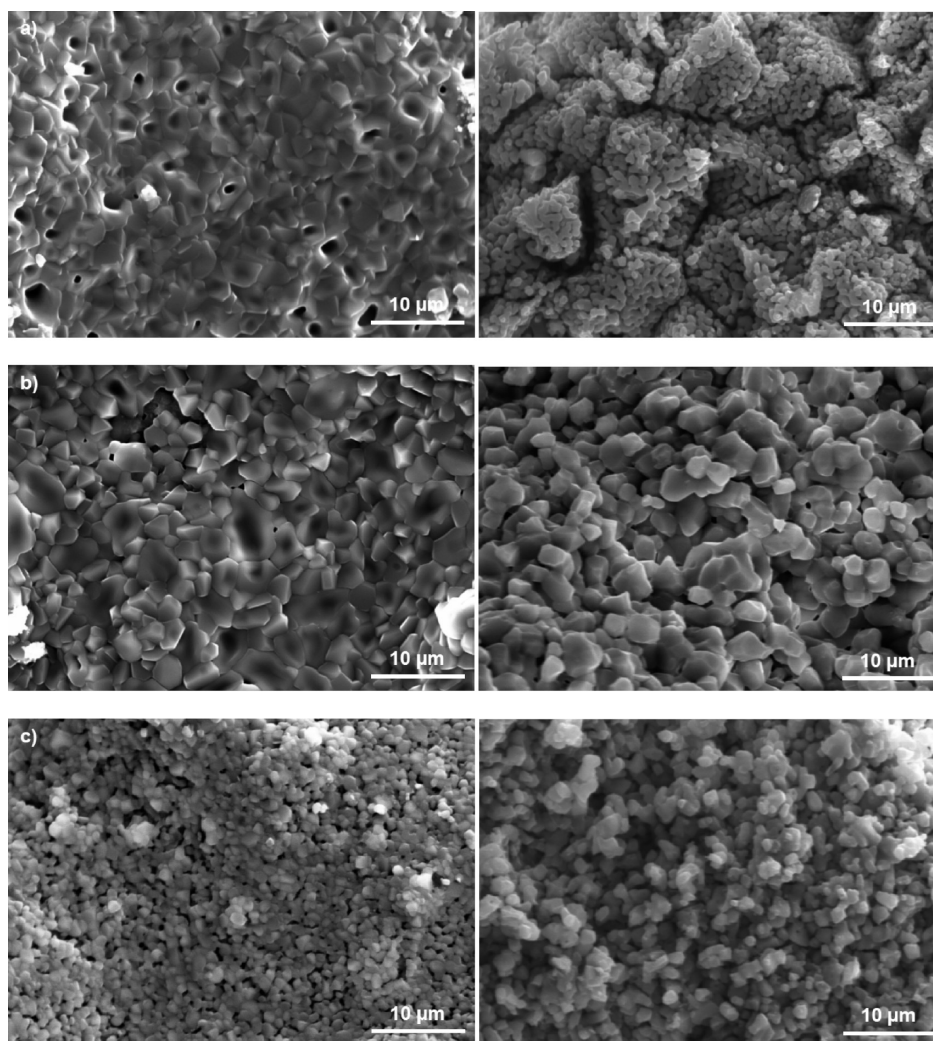


Figure 5. SEM image of broken partially sulfated particles after sulfation in TGA (Figure 3): (a) CD limestone, (b) hydrated CD lime, and (c) HP-CA-14 pellet. Left column, particle surface; right column, inside of particle.

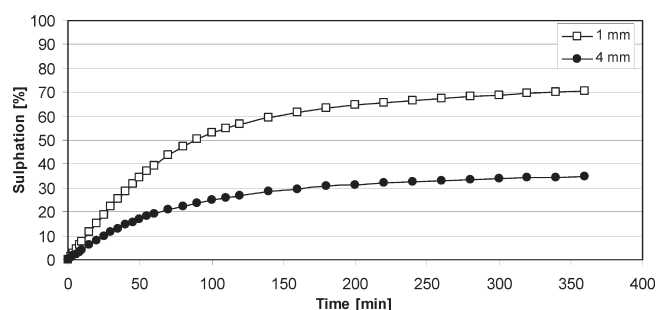


Figure 6. Sulfation performance of different-sized pellets (1 and 4 mm) prepared from hydrated CD lime with no cement.

calcination stage.⁴⁰ The heat obtained from natural gas is somewhat more expensive than that from coal, and it might introduce some additional economic penalties. However, it should be noted that only ~30% of the total heat is required for regeneration in the calciner (~70% is generated in the main

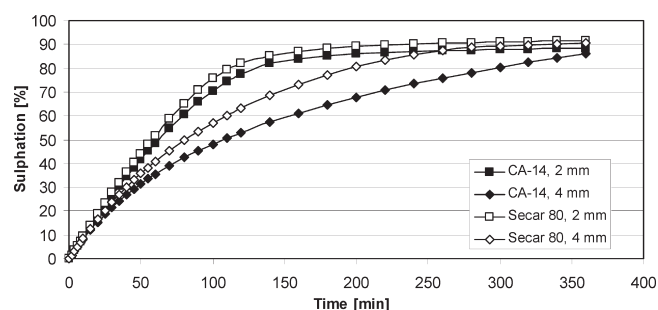


Figure 7. Sulfation profiles of different-sized pellets (2 and 4 mm) prepared from hydrated spent sorbent from a pilot plant FBC reactor (sample designated as Carbonator No. 4,³⁹) and different cements: CA-14 and Secar 80.

combustor).⁴⁰ Moreover, economic studies⁴¹ have shown that 30-year levelized costs for a calciner associated with CO₂ capture in a 360 MW power plant are mainly from sorbent costs (\$11.469/ton, i.e., 41.7%, when limestone is considered), while other factors are operating (\$9.588/ton, including O₂ plant) and capital costs (\$5.776/ton). Only \$0.692/ton (2.5%)

(39) Manovic, V.; Lu, D.; Anthony, E. J. Steam Hydration of Sorbents from a Dual Fluidized Bed CO₂ Looping Cycle Reactor. *Fuel* **2008**, *87*, 3344–3352.

(40) Abanades, J. C.; Anthony, E. J.; Wang, J.; Oakey, A. Fluidized Bed Combustion Systems Integrating CO₂ Capture with CaO. *Environ. Sci. Technol.* **2005**, *39*, 2861–2866.

(41) MacKenzie, A.; Granatstein, D. L.; Anthony, E. J.; Abanades, J. C. Economics of CO₂ Capture Using the Calcium Cycle with a Pressurized Fluidized Bed Combustor. *Energy Fuels* **2007**, *21*, 920–926.

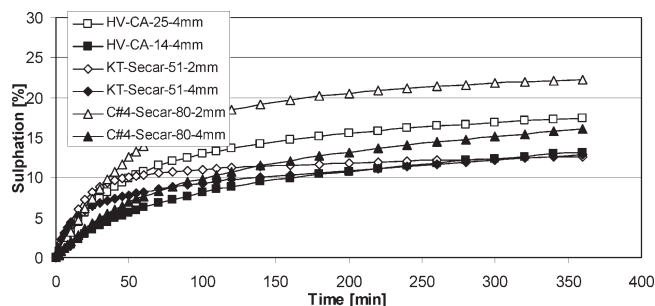


Figure 8. Sulfation profiles of pellets after 30 carbonation/calcination cycles. Conditions during cycles: carbonation in 100% CO₂, calcination in 100% N₂, both for 10 min, isothermally at 850 °C. Pellets were prepared from hydrated lime (HV, KT, and C#4, sample from a pilot plant FBC reactor designated as Carbonator No. 4)³⁹ and 10% cement (CA-14, CA-25, Secar 51, and Secar 80); particle sizes, 2 and 4 mm.

of captured CO₂ is related to fuel (coal and petroleum coke were considered). It is clear that somewhat more expensive nonsulfur-containing fuel cannot significantly affect the feasibility of the total process from an economic viewpoint. The sorbent costs are >40% of the total costs, and protection of sorbent (especially more expensive and reactive types) from SO₂ by means of using nonsulfur-containing fuels in the calciner would have a significant net beneficial effect.

The use of non/low-sulfur-containing fuels in the calciner, when more expensive and more reactive sorbents are used, is also important from the point view of solids accumulation due to ash from fuels such as coal. The calculated purge required to offset the high price of synthetic sorbent is technically forbidding. The mass fraction of the inert material in the solid internal circulation flow grows exponentially at low purge values, and the amount of solids moving in the system can no longer be handled.¹⁶ Thus, an additional advantage of natural gas is the lower purge of solid material necessary from the system. The use of biomass as fuel is beneficial because it leads to a net reduction of CO₂, i.e., “negative” CO₂ emissions. However, this fuel contains low-melting ash compounds, which at higher temperatures in the calciner can cause agglomeration problems.⁴² Moreover, low-melting compounds enhance sintering and loss of CO₂ capture activity

(42) Grubor, B. D.; Oka, S. N.; Ilic, M. S.; Dakic, D. V.; Arsic, B. T. Biomass FBC Combustion-Bed Agglomeration Problems. Proceedings of 13th International Conference on Fluidized Bed Combustion, Orlando, FL, May 7–10, 1995; ASME: New York, 1995; pp 515–522.

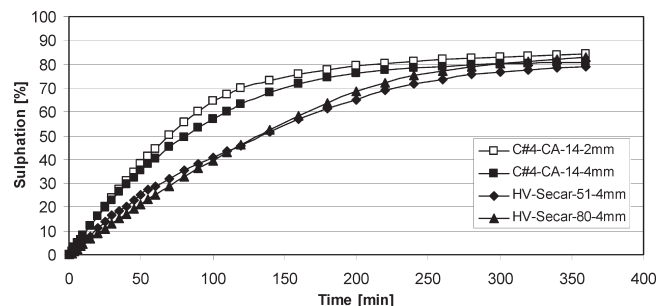


Figure 9. Sulfation profiles of hydrated (moist air for 24 h)¹⁸ pellets after 30 carbonation/calcination cycles. Conditions and designations are the same as those for Figure 8.

of the sorbent,⁴³ which diminish the advantages of using biomass in the calciner.

4. Conclusions

The sulfation performance of CaO-based pellets prepared using calcium aluminate cements was investigated in this study, and it was shown that the pellets readily react with SO₂, which can reduce their excellent performance in carbonation/calcination cycles during CO₂ capture. These results highlight the need to avoid high SO₂ concentrations, especially during calcination where higher temperatures enhance sulfation. This is possible using nonsulfur-containing fuels in the calciner or direct heat transfer from a combustor to the calciner.⁴⁰ While carbonator temperatures are lower (650–700 °C), the high reactivity of the pellets may also cause their sulfation under such conditions. Possible solutions could be desulfurization of the gas before entrance to the carbonator using spent²⁹ or reactivated⁴⁴ sorbent. In this study, pellets subjected to carbonation/calcination cycles show reduced reactivity with SO₂, which means that a suitable sorbent treatment could shift their selectivity toward CO₂. However, sulfation performance can be recovered by hydration if the sorbents are to be used for sulfur removal at the end of their carbonation lifetime.

(43) Manovic, V.; Lu, D.; Anthony, E. J.; Charland, J.-P.; Blamey, J.; Fennell, P. S. Influence of Calcination Conditions on Carrying Capacity of CaO-Based Sorbent in CO₂ Looping Cycles. *Fuel* **2009**, *10*, 1893–1900.

(44) Manovic, V.; Anthony, E. J. SO₂ Retention by Reactivated CaO-Based Sorbent from Multiple CO₂ Capture Cycles. *Environ. Sci. Technol.* **2007**, *41*, 4435–4440.