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Influence of Water Vapor on the Direct Sulfation of Limestone under Simulated Oxy-fuel Fluidized-Bed Combustion (FBC) Conditions

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Oxy-fuel combustion of fossil fuel is one of the most promising methods for producing electricity, together with a stream of concentrated CO₂ ready for sequestration. Oxy-fuel fluidized-bed combustion (FBC) can also use limestone as a sorbent for *in situ* capture of sulfur dioxide. However, although a limited number of studies have been performed on sulfation of limestone under oxy-fuel combustion conditions, there are still a number of important but unanswered questions. Here, the effect of water vapor on the sulfation of limestone was studied, because it has not been examined in detail in previous sulfation studies and past studies on direct sulfation of limestone in FBC either did not explore the influence of H₂O or did so under unrealistic conditions for oxy-fuel FBC. The purpose of this study is to identify the effect of water vapor on direct sulfation of limestone under simulated oxy-fuel circulating FBC (CFBC) conditions. Direct sulfation of three limestones was conducted in a thermogravimetric analyzer (TGA) apparatus at 800 and 850 °C. The limestone particle sizes used were 75–125, 125–150, 150–250, and 250–425 μm, and tests were carried out in a synthetic flue gas atmosphere, consisting of 80% CO₂, 15%, 10% or 0% H₂O, 4% O₂, 5000 ppm SO₂, and balance N₂. Water always improved limestone sulfation, especially at 850 °C. In addition, for some limestones, such as Kelly Rock (Nova Scotia, Canada), when the reaction gas contained no H₂O, the calcium conversion ratio was higher at 800 °C than at 850 °C. However, when the reaction gas contained 10% H₂O, the conversion ratio and the sulfation reaction rate were always higher at 850 °C than at 800 °C. Because coal-fired boiler flue gases always contain water vapor, the role played by H₂O in the limestone sulfation reaction should always be considered in future studies.

Introduction

CO₂ accounts for about 50% of the anthropogenic greenhouse effect, and currently about 28 gigatons of CO₂ are produced from fossil fuels each year.¹ Burning the fuel in nominally pure oxygen allows one to produce a flue gas that is primarily composed of CO₂, H₂O, small quantities of O₂, Ar, N₂, and trace gases, such as SO₂ and NO_x. The resulting flue gases can be relatively easily treated to produce a stream of liquid CO₂ ready for sequestration.^{2–7}

Oxy-fuel-fired pulverized fuel (PF) units require high flue gas recirculation ratios to maintain acceptable furnace

temperatures. In contrast, circulating fluidized-bed combustors (CFBCs) circulate large quantities of solids, and oxy-fuel-fired CFBC can take advantage of this capability and use external solid heat exchangers to remove heat from the system, significantly reducing the amount of recycled flue gas needed to keep combustor temperatures at reasonable levels.⁸

The reduced flue gas recirculation ratio should result in significant boiler island cost savings. This unique feature of FBCs means that much higher percentages of oxygen can be used in the recycled flue gas/oxygen mixtures than would be possible in PF oxy-fuel-firing applications. This allows for the design and construction of more compact, relatively less expensive CFB boilers. Economic analysis indicates that oxy-fuel-firing technology in CFB boilers could be developed and deployed economically in the near future.⁹

To control the SO₂ emissions from CFB, limestone is usually used as a sorbent. For oxy-fuel combustion in CFB, the concentration of CO₂ will be more than 80%, and for the operating temperature of coal-fired CFBs, which is normally ~850 °C, limestone calcination will not occur at

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(1) International Energy Agency (IEA). *IEA World Energy Outlook*; IEA: Paris, France, 2008.

(2) Tan, Y.; Croiset, E.; Douglas, M. A. Combustion characteristics of coal in a mixture of oxygen and recycled flue gas. *Fuel* **2006**, *85*, 507–512.

(3) Murphy, J. J.; Shaddix, C. R. Combustion kinetics of coal chars in oxygen-enriched environments. *Combust. Flame* **2006**, *144*, 710–729.

(4) Chui, E. H.; Majeski, A. J.; Douglas, M. A.; Tan, Y.; Thambimuthu, K. V. Numerical investigation of oxy-coal combustion to evaluate burner and combustor design concepts. *Energy* **2004**, *29*, 1285–1296.

(5) 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.

(6) Liu, H.; Okazaki, K. Simultaneous easy CO₂ recovery and drastic reduction of SO_x and NO_x in O₂/CO₂ coal combustion with heat recirculation. *Fuel* **2003**, *82*, 1427–1436.

(7) Liu, H.; Zailanib, R.; Gibbs, B. M. Pulverized coal combustion in air and in O₂/CO₂ mixtures with NO_x recycle. *Fuel* **2005**, *84*, 2109–2115.

(8) Tan, Y.; Jia, L.; Hughes, R.; Lu, D.; Anthony, E. J. Oxy-fuel combustion with recycled flue gas on a mini CFB combustor. *Proceedings of the 31st International Technical Conference on Coal Utilization and Fuel Systems*; Clearwater, FL, May 21–25, 2006.

(9) ALSTOM Power, Inc. *Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers—Phase II*; ALSTOM Power, Inc.: Windsor, CT, Oct 27, 2004.

(10) Illerup, J. B.; Dam-Johansen, K. High-temperature reaction between sulfur dioxide and limestone—VI. The influence of high pressure. *Chem. Eng. Sci.* **1993**, *48* (11), 2151–2157.

this temperature. Thus, the sulfation of sorbent under these conditions can be expressed by the following overall reaction:



This reaction is usually referred to as direct sulfation.

The direct sulfation reaction of limestone can be significantly influenced by various parameters, such as temperature, limestone (source and particle size), gas concentrations, etc. The negative influence of the sintering of limestone particles on sulfation has already been demonstrated by Illerup and Dam-Johansen¹⁰ and Zevenhoven and Yrias,¹¹ and it was observed that the limestone particles partially lost their reactivity after heat treatment at 1123 K. Illerup and Dam-Johansen and Zevenhoven and Yrias suggested that pore closing by sintering might be the reason for this behavior, while Liu et al.^{12,13} observed pore size increases with an increasing temperature. This pore structure variation with an increasing temperature can significantly influence the sulfation reaction because of its influence on diffusion in the product layer.

The influence of the SO₂ concentration on the direct sulfation of limestone has also been studied, and the observed apparent reaction order of SO₂ varies from 0.4 to greater than 1.^{12,14–17} Some researchers evaluated the reaction orders by studying the initial reaction rate, while others evaluated them at high conversions. However, few authors have tried to explain the reaction order that they observed.

In addition, the rate of the direct sulfation reaction can be significantly reduced by higher CO₂ concentrations.^{18–20} Ulerich et al.¹⁹ suggested that the lower sulfation rates caused by higher CO₂ concentrations were related to slower diffusion of the formed CO₂ away from the limestone particles. Tullin et al.²⁰ suggested that the negative effect of higher CO₂ concentrations was related to the reverse reaction of the dissociation of the limestone. Another explanation for the effect of the

CO₂ partial pressure on the direct sulfation is its influence on solid-state mobility, as shown by Tetard et al.²¹ and Beruto et al.²² Finally, limestones show different reactivities, and Alvarez and Gonzalez²³ and Zevenhoven and Yrias¹¹ discussed this problem in terms of the effect of various impurities in limestone. It was also found that porous limestones often show higher sulfation rates than dense limestones.^{13,24} Despite a great deal of work performed in this area, Hu and Dam-Johansen²⁵ summarized the situation in their review paper as “except that the final product is CaSO₄, nothing else is confirmed”.

In coal-fired utility- or industrial-scale CFBC boilers, the flue gas will inevitably contain H₂O. However, very few investigations have considered the influence of H₂O on the direct sulfation of limestone. Hajaligol and Longwell¹³ investigated the effects of water vapor on the sulfation of CaCO₃ at 900 °C and, for 10–12 μm particles, found that H₂O could promote the direct sulfation of limestone; however, this would not be possible at atmospheric pressure, as is the case for oxy-fuel firing. However, this particle size is clearly not appropriate for CFBC operation, because the limestone size for CFBC is usually in the range of 75–500 μm.³³ In addition, to introduce water into the gas stream, the gases were saturated with water vapor at 40 and 50 °C, which means that water levels were lower than might be expected for a combustion situation. Finally, these workers did not offer any explanations about the H₂O effect observed. In a more recent study, Hu et al.²⁶ studied the effect of water on sulfation and found that it significantly enhanced the sulfation rate and influenced the order of reaction. However, in their study, the maximum water level was 7.5% (which is still lower than might be expected in a practical combustion situation), although the particle sizes here were realistic. Moreover, to ensure direct sulfation in their system, the temperature range explored was from 450 to 700 °C, because the highest CO₂ levels were 50% in their gases, and these temperatures are significantly lower than operational temperatures in a real CFBC boiler.

In this investigation, the influence of H₂O on direct sulfation of limestone was tested under what we believe are more realistic oxy-fuel CFBC conditions. Other parameters considered included temperature, particle size, and limestone type.

Experimental Section

Three limestones were sulfated in a Cahn thermogravimetric analyzer (TGA). The compositions of the limestones are given in Table 1, while Table 2 gives the experimental conditions. All experiments followed the same procedure: a known amount of limestone sample (about 20 mg) was loaded into the TGA in a shallow platinum sample pan (12.7 mm in diameter and 2 mm deep). The TGA was first flushed with pure CO₂ at 300 mL/min

Table 1. Analysis of the Three Limestones (wt %)

compound	Kelly Rock	Havelock	Calpo
SiO ₂	3.45	1	1.59
Al ₂ O ₃	1.11	0.13	1.1
Fe ₂ O ₃	0.15	0.19	<0.55
TiO ₂	0.05	<0.0165	<0.04
P ₂ O ₅	<0.03	<0.011	<0.02
CaO	51.28	51.33	50.83
MgO	0.48	3.14	2.61
SO ₃	<0.10	<0.100	0.37
Na ₂ O	<0.20	<0.096	<0.17
K ₂ O	0.245	0.13	0.16
loss on fusion	41.78	43.73	43.37

(11) Zevenhoven, R.; Yrias, P. Sulfur dioxide capture under PFBC conditions: The influence of sorbent particle structure. *Fuel* **1998**, *77* (4), 285–292.

(12) Liu, H.; Katagiri, S.; Kaneko, U.; Okazaki, K. Sulfation behavior of limestone under high CO₂ concentration in O₂/CO₂ coal combustion. *Fuel* **2000**, *79* (8), 945–953.

(13) Hajaligol, M. R.; Longwell, J. P. Analysis and modeling of the direct sulfation of CaCO₃. *Ind. Eng. Chem. Res.* **1988**, *27* (12), 2203–2210.

(14) Spartinos, D. N.; Vayenas, C. G. Kinetics of sulfation of limestone and precalcined limestone. *Chem. Eng. Process.* **1991**, *30* (2), 97–106.

(15) Iisa, K.; Hupa, M.; Yrjas, P. Product layer diffusion in the sulfation of calcium carbonate. *Proceedings of the 24th International Symposium on Combustion*; The Combustion Institute: Pittsburgh, PA, 1992; pp 1349–1356.

(16) Krishnan, S. V. Sulfation of high purity limestones under simulated PFBC conditions. *J. Chem. Eng.* **1993**, *71* (2), 244–255.

(17) Zhong, Q. Direct sulfation reaction of SO₂ with calcium carbonate. *Thermochim. Acta* **1995**, *260*, 125–136.

(18) Dam-Johansen, K. Absorption of SO₂ on dry limestone. Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark, Lyngby, Copenhagen, Denmark, 1987.

(19) Ulerich, N. H.; Newby, R. A.; Keairns, D. L. A thermogravimetric study of the sulfation of limestone and dolomite—Prediction of pressurized and atmospheric fluidized-bed desulfurization. *Thermochim. Acta* **1980**, *36*, 1–16.

(20) Tullin, C.; Nyman, G.; Ghardashkhani, S. Direct sulfation of CaCO₃: The influence of CO₂ partial pressure. *Energy Fuels* **1993**, *7* (4), 512–519.

(21) Tetard, F.; Bernache-Assollant, D.; Champion, E. Pre-eutectic densification of calcium carbonate doped with lithium carbonate. *J. Therm. Anal. Calorim.* **1999**, *56* (3), 1461–1473.

(22) Beruto, D.; Giordani, M.; Botter, R. Microstructure development of Li₂CO₃–CaCO₃ eutectic mixture in CO₂(g) and N₂(g) environments. *J. Phys., Colloq.* **1986**, *47* (2), 527–531.

for 15 min. Then, the flow rate of CO₂ was decreased to 150 mL/min, and the sample was heated at 30 °C/min. The limestone sample was heated under a pure CO₂ stream to prevent calcination. All gas flow rates were determined at room temperature and atmospheric pressure. Once the preset temperature was reached, the TGA gas supply was switched to synthetic flue gas containing CO₂, O₂, H₂O, and N₂. The gas flow rate was maintained at 150 mL/min throughout the test period. The sample weight and temperature were monitored and recorded continuously. Experiments were performed in multiple duplicates at several test conditions, and repeatability of the tests was good (within ±10%). Separate tests verified that sample size and/or gas flow rate used in the TGA have no effect on the overall calcium conversion ratio.

Results and Discussion

Kelly Rock limestone (Nova Scotia, Canada) with a particle size of 125–150 μm was first used to investigate the influence of H₂O on the direct sulfation of limestone in oxy-fuel combustion. The tests were performed at two temperatures (800 and 850 °C). Figure 1 shows the sulfation results. Here, the conversion ratio is defined as the amount of Ca converted to CaSO₄ divided by the total amount of Ca available in the sample. For comparison purposes, sulfation of Kelly Rock limestone without H₂O is also shown in Figure 1.

Several interesting phenomena can be seen in Figure 1. First, at both temperatures (800 and 850 °C), the calcium conversion ratio of Kelly Rock limestone was always higher when the reaction gas contained H₂O than that obtained without H₂O, especially at 850 °C, when the conversion ratio almost doubled with 10% H₂O. This shows that H₂O has a strong effect on sulfation of limestone, at least under oxy-fuel FBC conditions. H₂O improves the sulfation of limestone, and the influence is more pronounced at 850 °C than at 800 °C. The data also indicated that, when the H₂O concentration increased from 10 to 15%, the calcium conversion ratio of Kelly Rock limestone increased further.

Table 2. Experimental Conditions (Gas Concentration in vol %)

temperature (°C)	800–850
CO ₂ concentration (%)	80
O ₂ concentration (%)	4
SO ₂ concentration (ppmv)	5000
H ₂ O vapor concentration (%)	0, 10, and 15
N ₂ concentration (%)	0.5–5.5

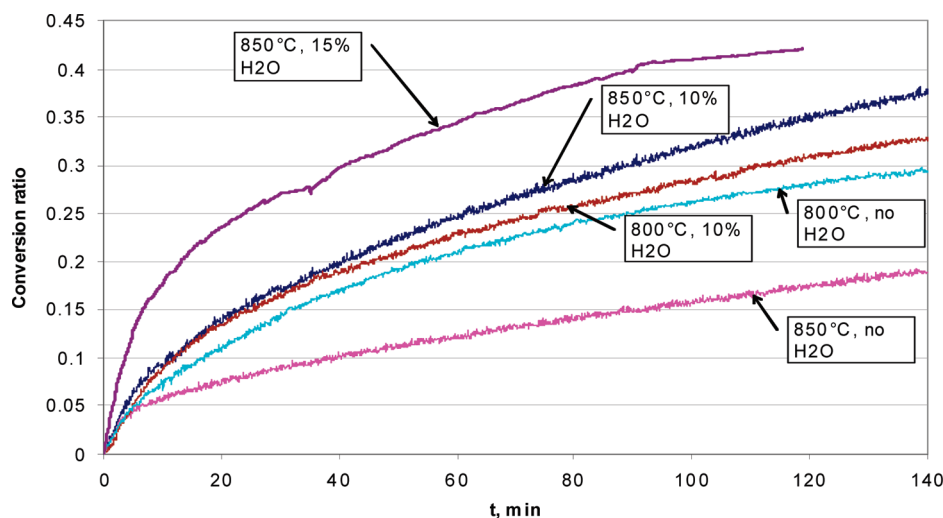


Figure 1. Calcium conversion ratio of Kelly Rock limestone (125–150 μm).

Another interesting phenomenon noted in Figure 1 was that, in the absence of H₂O, the calcium conversion ratio of Kelly Rock limestone was higher at 800 °C than at 850 °C at any given time. However, when the reaction gas contains 10% H₂O, the conversion ratio and sulfation reaction rate of Kelly Rock limestone obtained at 850 °C were always higher than at 800 °C. Because flue gas from real coal-fired boilers always contains some water vapor, these results clearly suggest that the role of H₂O should be considered when studying the direct sulfation of limestone under oxy-fuel combustion conditions.

Kelly Rock limestone in three additional size ranges, 75–125, 150–250, and 250–425 μm, was also used in the sulfation tests, and the results are shown in Figures 2–4. Sulfation patterns similar to those seen in Figure 1 were observed for these limestone size ranges; i.e., sulfation was improved by the presence of H₂O. The sulfation rate and conversion ratio of limestone at 800 °C without H₂O were always higher than those at 850 °C. However, when reaction gas contained 10% H₂O, higher conversion ratios were always obtained at 850 °C rather than at 800 °C. The reason for this phenomenon is not clear at this time, although one could argue that this supports a solid-state diffusion mechanism, which is enhanced at higher temperatures. More studies with different types of limestone are clearly needed. The particle size also played an important role in determining the sulfation of limestone. As expected, with or without H₂O, higher calcium conversion ratios were achieved as the particle size decreased, because smaller limestone particles experience less pore plugging and have a larger surface area.

As shown above, the influence of H₂O on direct sulfation of limestone has been demonstrated with Kelly Rock limestone at two temperatures and four particle size ranges. To determine if the observed H₂O effect is limestone-specific, two other Canadian limestones, Havelock and Calpo (both from New Brunswick, Canada), were also tested. For Havelock limestone, two particle size ranges: 250–425 and 75–125 μm, were tested at 800 and 850 °C. Calpo limestone particles (75–125 μm) were tested at 850 °C. Results are shown in Figures 5–7. It is clear from these tests that the H₂O effect on sulfation is not limited to one particular limestone. It was noted that, for Havelock limestone of 250–425 μm in size, when 10% water is present in the synthetic flue gas, the calcium conversion ratio was higher initially at 800 °C than

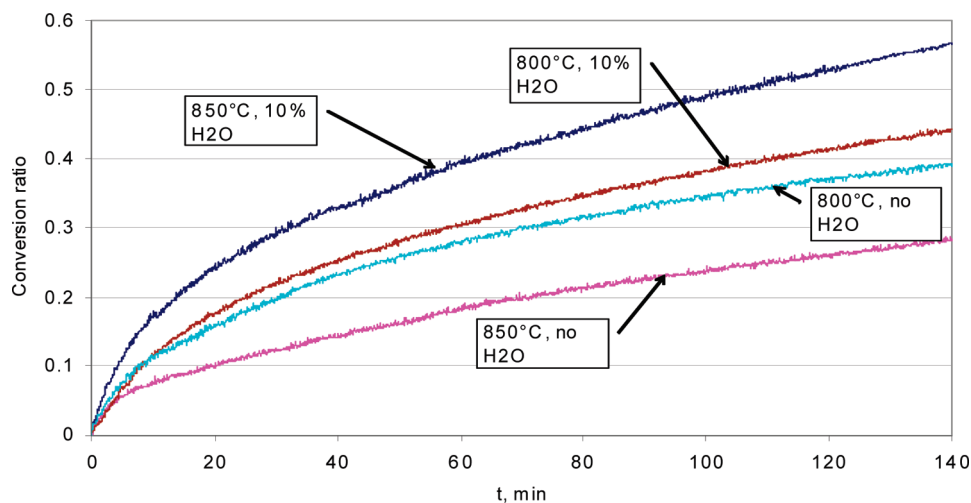


Figure 2. Calcium conversion ratio of Kelly Rock limestone (75–125 μm).

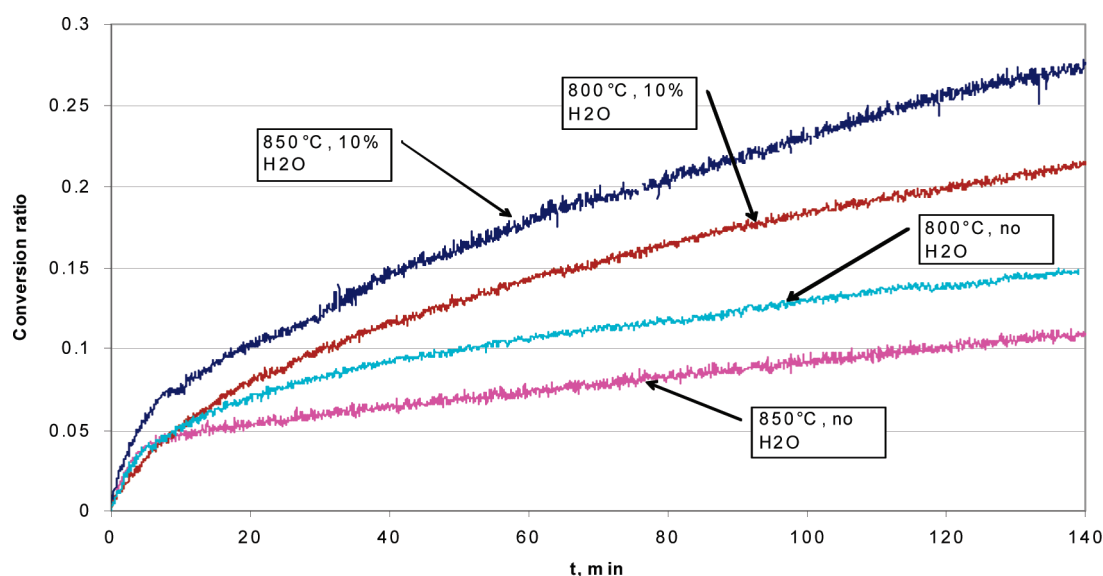


Figure 3. Calcium conversion ratio of Kelly Rock limestone (150–250 μm).

at 850 °C. A higher calcium conversion at 800 °C was maintained until about 100 min into the tests.

Additionally, when there was no water in the synthetic flue gas, Havelock and Kelly Rock limestone with a particle size of 250–425 μm behaved similarly, with the calcium conversion ratio slightly higher for Havelock limestone. In the situation with 10% water in the synthetic flue gas, Kelly Rock and Havelock sulfated to the same extent at 140 min at 850 °C. At 800 °C, Havelock limestone performed better than Kelly Rock limestone. In comparison of calcium conversion ratios at 850 °C of Kelly Rock, Havelock, and Calpo limestones with the same particle size of 75–125 μm both with and without water in the synthetic flue gas (Figures 2, 6,

and 7), the behavior of these limestones was also similar. The difference in the conversion ratio was likely caused by differences in composition and physical structure of these limestones.

Discussion of the H₂O Effect Mechanism. Because H₂O has been shown to play an important role in determining the direct sulfation of limestone under oxy-fuel CFBC conditions and real coal combustion flue gases inevitably contain H₂O, the sulfation of limestone may not be as simple as expressed in reaction 1. In addition to reaction 1, there are a number of possibilities, either an effect on solid-state diffusion involving H₂O, as suggested by Hu et al.,²⁶ or alternatively transient formation of Ca(OH)₂. For CaCO₃ under oxy-fuel CFBC conditions, the dynamic equilibrium below always exists



If a H₂O molecule meets a CaO molecule, Ca(OH)₂ may be transiently formed



(23) Alvarez, E.; Gonzalez, J. F. High pressure thermogravimetric analysis of the direct sulfation of Spanish calcium-based sorbents. *Fuel* **1999**, 78 (3), 341–348.

(24) Yrjas, P.; Iisa, K.; Hupa, M. Comparison of SO₂ capture capacities of limestones and dolomites under pressure. *Fuel* **1995**, 74 (3), 395–400.

(25) Hu, G.; Dam-Johansen, K. Review of the direct sulfation reaction of limestone. *Prog. Energy Combust. Sci.* **2006**, 32, 386–407.

(26) Hu, G.; Dam-Johansen, K.; Wedel, S.; Hansen, J. P. Direct sulfation of limestone. *AIChE J.* **2007**, 53, 948–960.

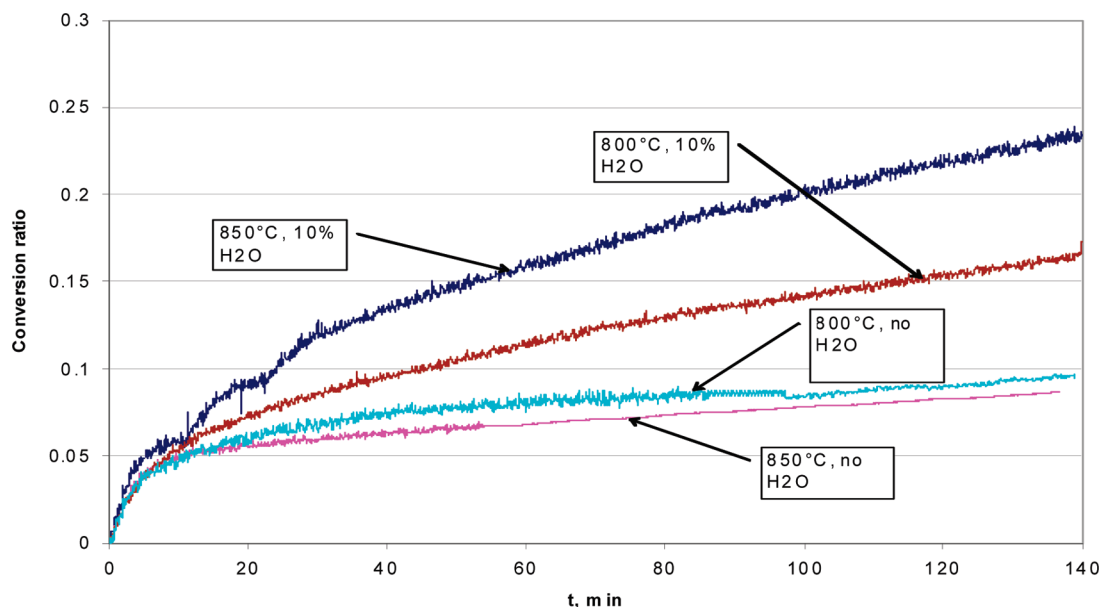


Figure 4. Calcium conversion ratio of Kelly Rock limestone (250–425 μm).

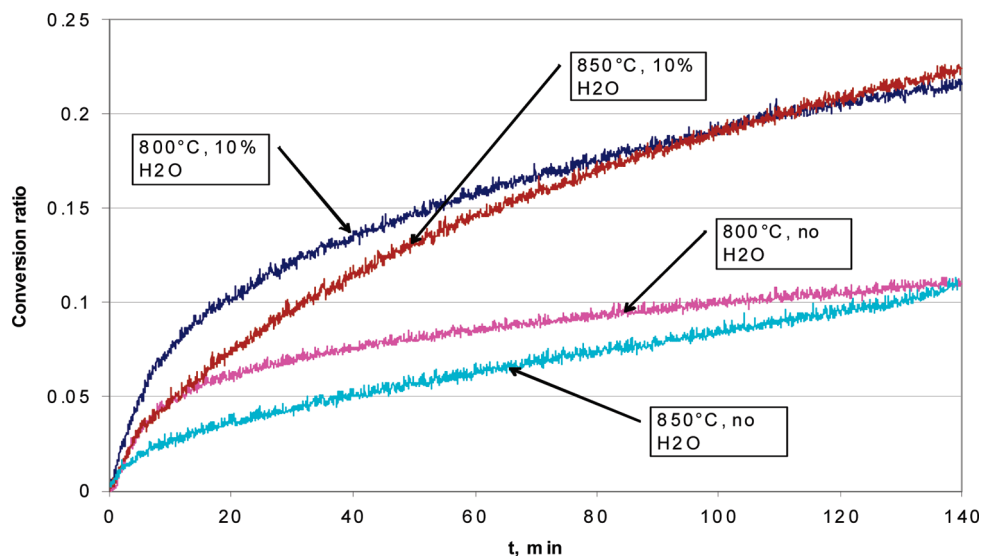
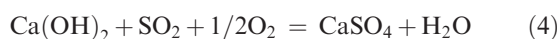


Figure 5. Calcium conversion ratio of Havelock limestone (250–425 μm).

Sulfation of $\text{Ca}(\text{OH})_2$ occurs



Overall, these reactions are equivalent to reaction 1.

$\text{Ca}(\text{OH})_2$ is not thermodynamically stable at normal oxy-fuel CFBC temperatures. Therefore, if formed, $\text{Ca}(\text{OH})_2$ can only exist as a transient species. However short that duration might be, if a SO_2 molecule contacts a $\text{Ca}(\text{OH})_2$ molecule, reaction 4 will most likely occur. Reaction 4 is faster than reaction 1, and many investigations have verified that reaction 4 has lower activation energy than reaction 1. For example, for the reaction of $\text{Ca}(\text{OH})_2$ and SO_2 , in the investigation of Izquierdo et al.,²⁷ an apparent activation energy of 32 kJ/mol has been estimated. In addition,

Jorgensen et al.²⁸ found that the conversion rate is increased moderately with temperature, in agreement with the activation energy of 25 kJ/mol. Ruiz-Alsop and Rochelle²⁹ found that the activation energy of reaction 4 was ~ 12 kJ/mol. However, for reaction 1, Hajaligol and Longwell¹³ found, at low conversions, the activation energy was 68.7 kJ/mol and, at high conversions, the activation energy was 146.5 kJ/mol. Also, Qiu and Lindqvist³⁰ found, at low conversions, the activation energy was 96.8 kJ/mol and, at high conversions, the activation energy was 144 kJ/mol. One may consider that

(28) Jorgensen, C.; Chang, J. C. S.; Brna, T. G. Evaluation of sorbents and additives for dry sulfur dioxide removal. *Proceedings of the Spring National American Institute of Chemical Engineers (AIChE) Meeting*, New Orleans, LA, 1986.

(29) Ruiz-Alsop, R.; Rochelle, G. T. Effect of relative humidity and additives on the reaction of sulfur dioxide with calcium hydroxide. *Report Prepared for the United States Environmental Protection Agency (U.S. EPA)*; U.S. EPA: Washington, D.C., 1987.

(30) Qiu, K.; Lindqvist, O. Direct sulfation of limestone at elevated pressures. *Chem. Eng. Sci.* **2000**, *55*, 3091–3100.

(27) Izquierdo, J. F.; Fite, C.; Cunill, F.; Iborra, M.; Tejero, J. Kinetic study of the reaction between sulfur dioxide and calcium hydroxide at low temperature in a fixed-bed reactor. *J. Hazard. Mater.* **2000**, *113*–123.

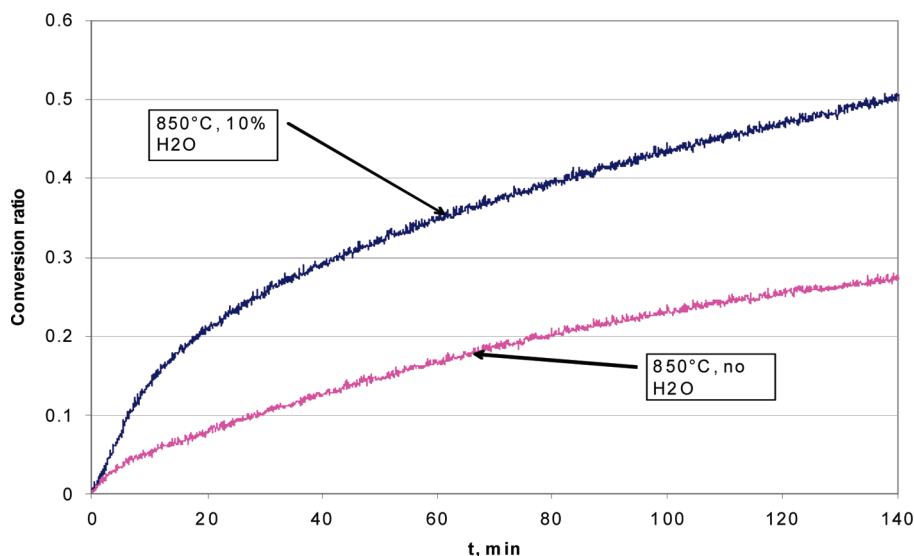


Figure 6. Calcium conversion ratio of Havelock limestone (75–125 μm).

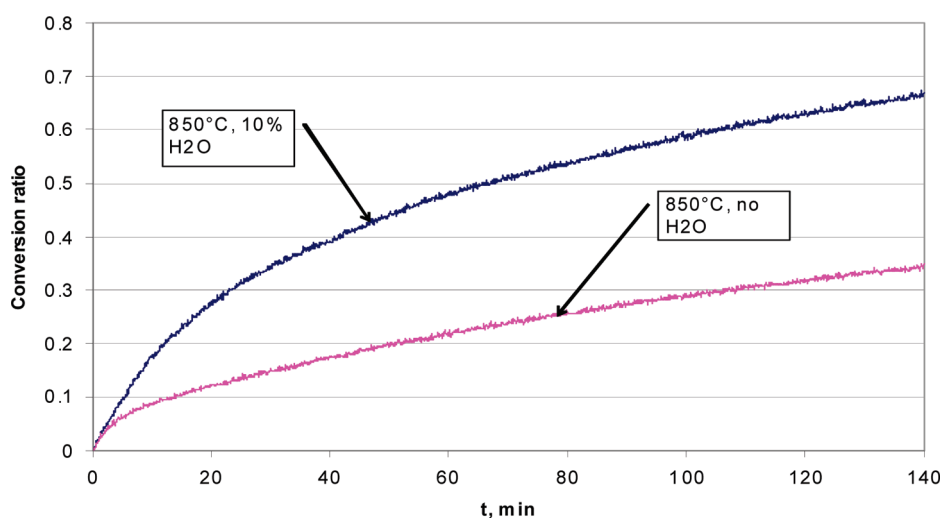


Figure 7. Calcium conversion ratio of Calpo limestone (75–125 μm).

Table 3. Activation Energy for Direct Sulfation of Kelly Rock Limestone (kJ/mol)

particle size (μm)	75–125	125–150	150–250	250–425
with 10% H_2O	118	57.1	97.4	138
with no H_2O	–164	–207	–143	–138

H_2O acts as a catalyst during the direct sulfation of limestone under oxy-fuel combustion conditions, improving the sulfation process.³¹

To support the idea that water is catalyzing the sulfation process, the activation energy was calculated using the following equation:²⁹

$$\ln \frac{t_1}{t_2} = \frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

where t_1 and t_2 are reaction times, T_1 and T_2 are reaction temperatures (in K), E is the activation energy (in J/mol), and R is the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$). The calculated

activation energies are given in Table 3. Table 3 shows that the activation energy of sulfation for the Kelly Rock limestone used in this work with 10% H_2O is between 57 and $138 \text{ kJ mol}^{-1} \text{ K}^{-1}$. Without H_2O , the activation energies were in the range from -138 to $-206 \text{ kJ mol}^{-1} \text{ K}^{-1}$ because the temperature has a negative effect on the overall conversion of calcium in the temperature range of 800 – 850°C . This is consistent with experimental observations, shown in Figures 1–4.

In Haul and Stein's investigation³² on the exchange of carbon-13 dioxide between calcite crystals and gaseous carbon dioxide, it was found that water vapor enhanced the exchange appreciably. They thought the exchange might occur by a mechanism in which a carbonate ion momentarily breaks up into a carbon dioxide molecule, leaving an oxygen ion in the site. This carbon dioxide molecule then passes to

(32) Haul, R. A. W.; Stein, L. H. Exchange of carbon-13 dioxide between calcite crystals and gaseous carbon dioxide. *Nature* **1953**, *171*, 619–620.

(33) Takeshita, M. *Environmental Performance of Coal-Fired FBC*, IEACR/75; International Energy Agency (IEA) Coal Research: London, U. K., 1994.

(31) Levenspiel, O. *Chemical Reaction Engineering*, 3rd ed.; Wiley: New York, 1998.

a neighboring site similarly vacated and combines with the oxygen ion to reform a carbonate ion. In accordance with the findings by Haul and Stein's study, the crystal defect theory could potentially explain how the presence of H₂O influences the direct sulfation of limestone. However, only limited data are currently available, and to draw definite conclusions, further work is needed.

Conclusions

Three Canadian limestones were used to study direct sulfation under simulated oxy-fuel CFBC conditions, using realistic particle sizes and temperature ranges. In agreement with other researchers, it was found that the presence of H₂O always improved the sulfation of limestone, at least for the limestones tested in this study. The degree of improvement may vary for different temperatures, particle size ranges, and limestone types. The influence of H₂O on the sulfation of limestone at 850 °C is more pronounced than that at 800 °C.

The limestone particle size also affected the sulfation of limestone, in that smaller particles displayed consistently better calcium conversion under the same sulfation conditions. When the direct sulfation of limestone in industrial-scale processes was evaluated, the influence of H₂O should be taken into account. A mechanism has been suggested, involving the steps: CaCO₃—Ca(OH)₂—CaSO₄, but the question cannot be considered resolved. The activation energy of sulfation with 10% H₂O present was calculated, and it was shown that the presence of water lowers the activation energy for the sulfation process.

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