

# Effect of sulfation during carbonation on CO<sub>2</sub> capture in calcium looping cycle

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**Abstract:** Two Canadian limestones with different properties were tested to determine the effect of SO<sub>2</sub> during the carbonation of sorbent on the CO<sub>2</sub> capture performance in Ca-looping. When the reaction gas is mixed with SO<sub>2</sub>, the carbonation ratio of the sorbent is always lower than that without SO<sub>2</sub> for each cycle under the same conditions, and the sulfation ratio increases almost linearly with the increase in the cycle times. At 650 °C, there is little difference in the carbonation ratio of the sorbent during the first four cycles for the two carbonation time, 5 and 10 min at 0.18% SO<sub>2</sub>. The indirect sulfation reaction that occurs simultaneously with the carbonation of CaO is responsible for the degradation of the sorbent for CO<sub>2</sub> capture, and the carbonation duration is not the main factor that affects the ability of the sorbent. 680 °C is the best carbonation temperature among the three tested temperatures and the highest carbonation ratio can be obtained. Also, the sulfation ratio is the highest. The probable cause is the different effects of temperature on the carbonation rate and sulfation rate. A higher SO<sub>2</sub> concentration will decrease the carbonation ratio clearly, but the decrease in the carbonation capability of the sorbent is not proportional to the increase of the SO<sub>2</sub> concentration in flue gases.

**Key words:** Ca-based sorbent; carbonation; sulfation; looping; CO<sub>2</sub> capture

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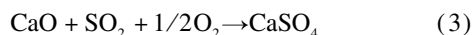
Calcium looping is an emerging technology for high-temperature post-combustion CO<sub>2</sub> capture<sup>[1-5]</sup>. It has experienced the fastest developing pace due to the strong similarities and synergies with existing combustion technology in circulating fluidized beds, including recent oxy-fired CFB development<sup>[6]</sup>. Both carbonation and calcination reactions are carried out at very high temperatures, around 650 °C for carbonation,



and over 900 °C for calcination in a rich atmosphere of CO<sub>2</sub>,

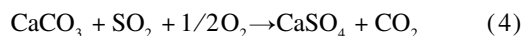


However, there is some SO<sub>2</sub> in coal fired flue gases. Limestone has great potential for capturing sulphur dioxide, despite SO<sub>2</sub> concentrations being two orders of magnitude lower than that of CO<sub>2</sub>. The desulphurization of the combustion flue gases is achieved via the following reaction under the atmospheric conditions:



which is usually called the indirect sulfation of limestone.

In combustion systems where the partial pressure of CO<sub>2</sub> is high enough that CaCO<sub>3</sub> is not calcined to CaO, the removal of SO<sub>2</sub> can be realized via direct sulfation, i. e., direct reaction of the gaseous SO<sub>2</sub> with calcium carbonate in the presence of O<sub>2</sub>:



Sulfation is irreversible under typical FBC conditions, although it proceeds at a much slower rate than carbonation. As sulfation proceeds, the CaSO<sub>4</sub> formed leads to pore blockage due to the high volume per unit mass occupied by the primary sulfation product compared to the calcine<sup>[7]</sup>. Pore closure mainly occurs on the surface of the particles, obstructing direct contact with the interior calcine<sup>[7-10]</sup>. Since the pore of CaO will be blocked and the CaSO<sub>4</sub> product layer will be resistant to CO<sub>2</sub> diffusion on the surface of the sorbents, the SO<sub>2</sub> will bring a negative effect on the CO<sub>2</sub> capture for this process. Ryu et al.<sup>[11-13]</sup> suggested that the presence of SO<sub>2</sub> leads to the fast deterioration of limestone CO<sub>2</sub> capture, mainly due to the competition between carbonation and both sulfation reactions. Basinas et al.<sup>[14]</sup> found that the sorbents sulphated via the un-reacted core mode converted more available calcium, but this adversely affected the reversibility of cyclic CO<sub>2</sub> capture. The reversibility strongly deteriorated when a higher total pressure was combined with increasing SO<sub>2</sub> partial pressure. The effect of the presence of SO<sub>2</sub> was also studied by Coppola et al.<sup>[15]</sup>. Results showed that the presence of SO<sub>2</sub> in the flue gas significantly decreased the sorbent CO<sub>2</sub> capacity, most likely because of the formation of an impervious CaSO<sub>4</sub> layer at the periphery of the

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particle<sup>[16]</sup>.

As tested, the CO<sub>2</sub> capture capacity for all sorbents calcined in CO<sub>2</sub> in the presence of SO<sub>2</sub> was effectively eliminated after 2 to 3 cycles. These results suggest that the presence of SO<sub>2</sub> must be avoided if the object is CO<sub>2</sub> capture from flue gas<sup>[17]</sup>. In this study, the sulfation following the carbonation of CaO is tested. The effect factors, such as the carbonation temperature, SO<sub>2</sub> concentration etc, are tested. Especially the influence of duration is tested, which is hoped to obtain the best balance between CO<sub>2</sub> capture and SO<sub>2</sub> negative

effects. Also, a high SO<sub>2</sub> concentration of 0.18% was tested, aiming to find how much negative effect of SO<sub>2</sub> exists only in the carbonation stage on the Ca-sorbents utilization.

## 1 Experimental Procedure

Two limestones, Massieci and Kelly Rock, were used for the test. Prior to the sorption test, both limestones were milled and sieved to ensure the particle size ranging from 250 to 425 μm for all the tests performed. The main components of the sorbents are presented in Tab. 1.

**Tab. 1** The component of the two limestones

Component	w(SiO <sub>2</sub> )	w(Al <sub>2</sub> O <sub>3</sub> )	w(Fe <sub>2</sub> O <sub>3</sub> )	w(TiO <sub>2</sub> )	w(P <sub>2</sub> O <sub>5</sub> )	w(CaO)	w(MgO)	w(SO <sub>3</sub> )	w(Na <sub>2</sub> O)	w(K <sub>2</sub> O)	Loss on fusion
Massieci	1.74	0.59	0.12	<0.03	0.21	52.80	0.51	0.22	<0.20	0.10	42.67
Kelly Rock	3.45	1.11	0.15	0.05	<0.03	51.28	0.48	<0.10	<0.20	0.245	41.78

TherMax 700 TGA was used for testing. The temperature and the weight of the sample were recorded continuously, and the flow rate was kept at 50 mL/min for both calcination and carbonation. The initial calcination of the limestone occurred under the non-isothermal conditions as the temperature was raised from room temperature to 850 °C. The samples were then maintained at this temperature for a sufficient time (5 min) to ensure complete calcination, and then it was cooled down to the carbonation temperature. Pure nitrogen was used for the calcination process in all cases. When the furnace temperature reached the set carbonation temperature, the gas was switched to the mixed gases containing SO<sub>2</sub> for specified duration. After carbonation duration, the inlet gas was then switched back to pure nitrogen, and it was heated to 850 °C in N<sub>2</sub>. The cyclic process was repeated 8 times. The testing conditions are shown in Tab. 2.

**Tab. 2** Testing conditions

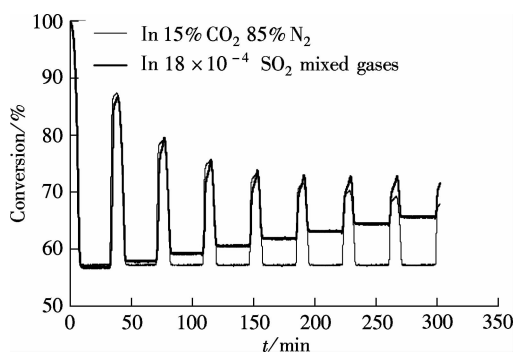
Conditions	Carbonation	Calcination
T/°C	620, 650, 680	850
φ(SO <sub>2</sub> )/10 <sup>-6</sup>	0, 900, 1 800	
φ(CO <sub>2</sub> )/%	15	
φ(O <sub>2</sub> )/%	3	
φ(N <sub>2</sub> )/%	Balance	100
Duration/min	5, 10	5

## 2 Results and Discussion

### 2.1 Effect of SO<sub>2</sub> on carbonation kinetics and conversion

Massieci limestone is chosen for testing the effect of SO<sub>2</sub> on the carbonation first, and the carbonation temperature is 650 °C. For comparison, the carbonation in 15% CO<sub>2</sub> and 85% N<sub>2</sub> (without SO<sub>2</sub>) was also tested. The carbonation duration for both tests is 5 min, as shown in Fig. 1.

The most common characteristic shown in Fig. 1 is that when the reaction gas is without SO<sub>2</sub>, the limestone calcined to CaO completely, and this can be found from the



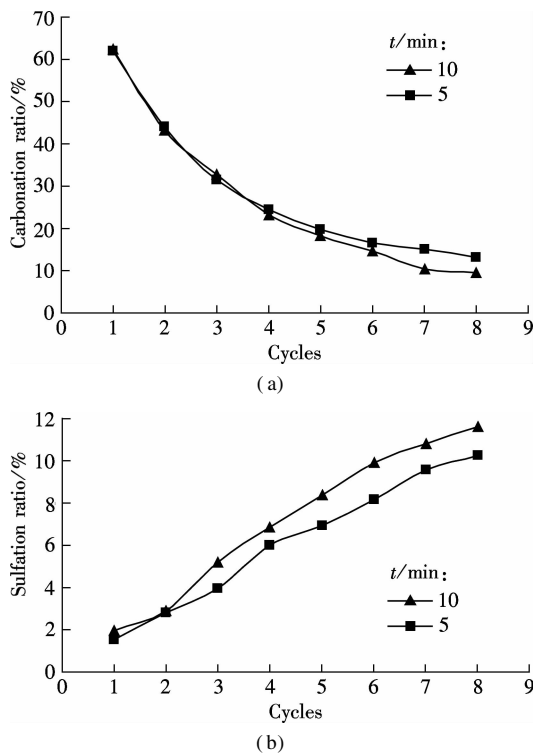
**Fig. 1** Effect of SO<sub>2</sub> on the conversion of Massieci limestone in Ca-looping at 650 °C

same degree of decomposition for every cycle although the ability of capture CO<sub>2</sub> always decreases with the increase in the cycle times. However, when the reaction gas contains 0.018% SO<sub>2</sub>, the final conversion degree increases with the increase in the cycles' times. For example, for the first cycle, the conversion degree is 56.8% and it is 65.8% for the 8th cycle. The only reason for this is that CaSO<sub>4</sub> is formed during CaO carbonation, and this will degrade the capability of the sorbent for capturing CO<sub>2</sub>.

### 2.2 Effect of duration on conversion of carbonation and sulfation

To obtain a good carbonation utilization of sorbent, a suitable carbonation duration should be evaluated. The carbonation duration of 5 and 10 min are tested, and the testing conditions are the same as those in Fig. 1 (see Fig. 2).

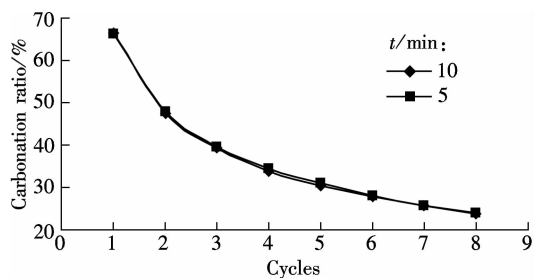
As shown in Fig. 2(a), the difference in the carbonation ratio between the two carbonation durations, 5 and 10 min are not obvious for all the eight cycles. Also, a similar tendency occurs for the sulfation ratio of sorbents for the two durations, as shown in Fig. 2(b). For example, 11.65% for 10 min and 10.29% for 5 min at the 8th cycle. It seems that a longer carbonation duration (5 and 10 min) will not greatly decrease the carbonation ratio.



**Fig. 2** The carbonation and sulfation ratio of Massieci limestone at 5, 10 min carbonation duration. (a) Carbonation ratio; (b) Sulfation ratio

To verify this further, the carbonation ratio under the conditions without SO<sub>2</sub> in reaction gases are tested, as shown in Fig. 3.

Fig. 3 shows that there is little difference in the carbonation ratios between the two durations. It can be speculated that the difference in carbonation ratios between the two durations (see Fig. 2) is mainly caused by SO<sub>2</sub> rather than carbonation duration. Since the sulfation reaction occurring after 5 min is direct sulfation which is very slow at 650 °C, it will not produce seriously adverse effects on the carbonation of CaO even after a longer carbonation duration. So, the carbonation duration is not an influential factor that affects the ability of the sorbent at 650 °C in the calcium looping cycles.

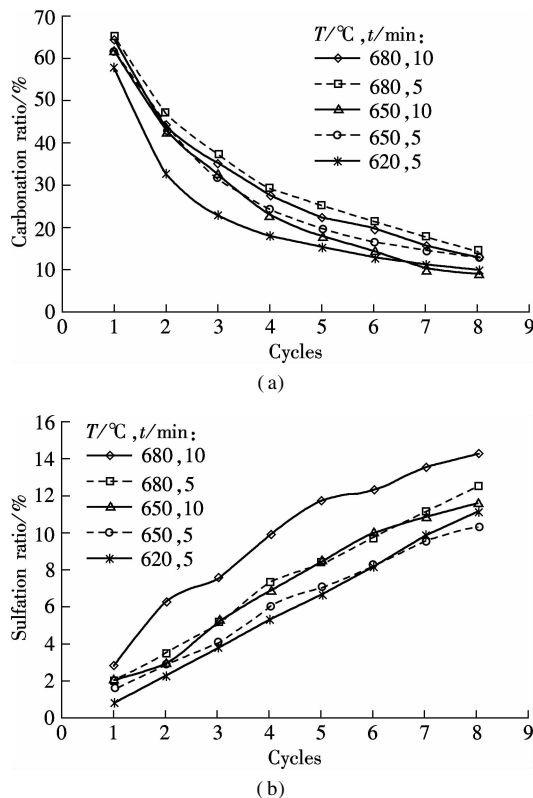


**Fig. 3** The carbonation ratio of Massieci limestone without SO<sub>2</sub> at 650 °C

### 2.3 Effect of temperature on conversion of carbonation and sulfation

Fig. 4 shows the carbonation and sulfation characteris-

tics of sorbent at temperatures of 620, 650 and 680 °C, respectively, and the SO<sub>2</sub> concentration is 0.18%.



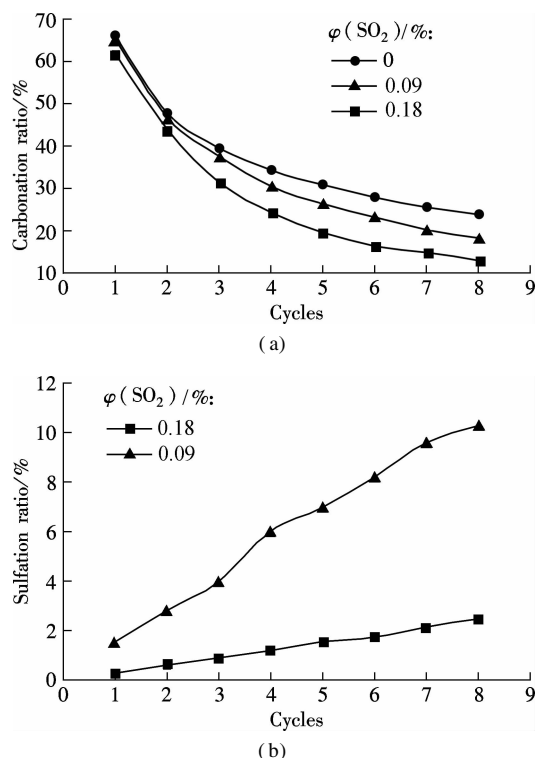
**Fig. 4** Effect of carbonation temperature on carbonation and sulfation ratios of Massieci limestone in 0.18% SO<sub>2</sub> mixed gases. (a) Carbonation ratio; (b) Sulfation ratio

As shown in Fig. 4(a), for the 5 min carbonation duration, the best carbonation is obtained at 680 °C, then at 650 °C, and the worst is at 620 °C. For the tests of 10 min duration, the carbonation ratio is higher at 680 °C than that at 650 °C. It shows that temperature is an important factor that determines the carbonation of the sorbent, and 680 °C is the best carbonation temperature among the three testing temperatures. However, as a negative influence on carbonation, the sulfation ratio is the highest at 680 °C, as shown in Fig. 4(b). Since the sulfation reaction of sorbent can retard the carbonation of the sorbent, the highest sulfation ratio of sorbent should result in the lowest carbonation ratio. A probable reason for this phenomenon is that the increase in the carbonation ratio caused by the increasing temperature is greater than the negative effect caused by sulfation reaction. Although sulfation will be enhanced by high temperatures, the carbonation improvement will be more obvious.

### 2.4 Effect of SO<sub>2</sub> concentration on conversion of carbonation and sulfation

As known from Fig. 1, 0.18% SO<sub>2</sub> will bring a negative effect on the capability of sorbent for CO<sub>2</sub> capture. For the low sulphur content coal, the SO<sub>2</sub> concentration in flue gas is less than 0.18%, and the effect of a relatively

low concentration  $\text{SO}_2$  is investigated. The mixed gas with 0.09%  $\text{SO}_2$  is used for the next test at the carbonation temperature of 650 °C (see Fig. 5).



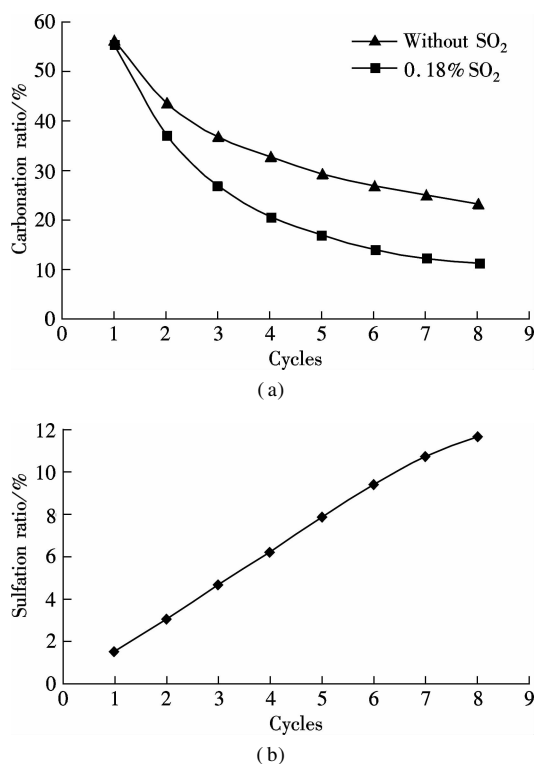
**Fig. 5** Carbonation and sulfation ratio vs cycles in 0.09% and 0.18%  $\text{SO}_2$  mixed gases. (a) Carbonation ratio; (b) Sulfation ratio

It can be seen from Fig. 5(a) that a higher concentration of  $\text{SO}_2$  will greatly decrease the carbonation ratio, especially from the second cycle. For example, the carbonation ratio is 18.33% at 0.09%  $\text{SO}_2$  and only 13.06% at 0.18%  $\text{SO}_2$  for the 8th cycle, and the difference is 5.27%. However, the relative sulfation ratio difference is greater than that of the carbonation ratio, as shown in Fig. 5(b). For example, the sulfation ratio is 10.29% for 0.18%  $\text{SO}_2$  and only 2.47% for 0.09%  $\text{SO}_2$  at the 8th cycle. It shows that the decrease in the carbonation capability of the sorbent caused by  $\text{SO}_2$  is not proportional to the increase of the  $\text{SO}_2$  concentration in flue gases, and even a little  $\text{CaSO}_4$  product formed in the carbonation will lead to a decrease in the capability of the sorbent for  $\text{CO}_2$  capture.

## 2.5 Effect of different limestones

Another limestone, Kelly Rock limestone, was tested to check if the phenomena occurring above are only applicable to one specific limestone. For comparison, the carbonation in 15%  $\text{CO}_2$  and 85%  $\text{N}_2$  at the carbonation temperature of 650 °C is also tested (see Fig. 6). As shown in Fig. 6, when the reaction gases are mixed with 0.18%  $\text{SO}_2$ , the carbonation ratio of the sorbent is always lower than that without  $\text{SO}_2$  for each cycle. For example, the carbonation ratio is 23% without  $\text{SO}_2$  and only 11.17% with

in 0.18%  $\text{SO}_2$  mixed gases. The sulfation occurred along with the carbonation of sorbent brings more negative effect with more looping cycles, just like that of Massieci limestone. Also, the sulfation ratio of sorbent increases with the cycles almost linearly, from the first cycle of 1.51% up to 11.71% of the 8th cycle.



**Fig. 6** Carbonation and sulfation ratio of Kelly Rock limestone at 5 min carbonation duration. (a) Carbonation ratio; (b) Sulfation ratio

## 3 Conclusion

When reaction gases are mixed with 0.18%  $\text{SO}_2$ , the carbonation ratio of the sorbent is always lower than that without  $\text{SO}_2$  for each cycle. The carbonation ratio of the sorbent decreased with cycles whether with  $\text{SO}_2$  or not, but a fast decrease occurred when the reaction gases contained  $\text{SO}_2$ . Sulfation of the sorbent occurred during carbonation and will bring more negative effect with more looping cycles. The difference in carbonation ratios between the sorbent at 5 and 10 min durations at 650 °C is not very clear, which shows a long duration will not bring great effect on the carbonation at 650 °C and in 0.18%  $\text{SO}_2$ . Sulfation that occurred simultaneously with the carbonation of  $\text{CaO}$  is responsible for the degradation of the sorbent for  $\text{CO}_2$  capture. 680 °C is the optimal carbonation temperature among the three temperatures. However, the sulfation ratio is also the highest at this temperature. A probable cause for this is that the effect of temperature on carbonation is stronger than that of sulfation for this kind of sorbent. The negative effect will be increased with more  $\text{SO}_2$ , and the decrease in the carbonation capability

of the sorbent by SO<sub>2</sub> is not proportional to the increase of the SO<sub>2</sub> concentration in flue gases.

## References

- [1] Lasheras A, Ströhle J, Galloy A, et al. Carbonate looping process simulation using a 1D fluidized bed model for the carbonator[J]. *International Journal of Greenhouse Gas Control*, 2011, **5**(4): 686–693.
- [2] Zhao M, Andrew I M, Harris T. Review of techno-economic models for the retrofitting of conventional pulverised-coal power plants for post-combustion capture (PCC) of CO<sub>2</sub>[J]. *Energy and Environmental Science*, 2013, **6**(1): 25–40.
- [3] MacKenzie A, Granatstein D L, Anthony E J, et al. Economics of CO<sub>2</sub> capture using the calcium cycle with a pressurized fluidized bed combustor[J]. *Energy and Fuels*, 2007, **21**(2): 920–926.
- [4] Martínez I, Murillo R, Grasa G, et al. Integration of a Ca looping system for CO<sub>2</sub> capture in existing power plants[J]. *Aiche Journal*, 2011, **57**(9): 2599–2607.
- [5] Ariasa B, Diego M E, Abanades J C. Demonstration of steady state CO<sub>2</sub> capture in a 1.7 MWth calcium looping pilot[J]. *International Journal of Greenhouse Gas Control*, 2013, **18**: 237–245.
- [6] Myöhänen K, Hyppänen T, Pikkarainen T, et al. Near zero CO<sub>2</sub> emissions in coal firing with oxyfuel CFB boiler[J]. *Chemical Engineering and Technology*, 2009, **32**(3): 355–363.
- [7] Krishnan S V, Sotirchos S V. Effective diffusivity changes during calcination, carbonation, recalcination, and sulfation of limestones[J]. *Chemical Engineering Science*, 1994, **49**(8): 1195–1208.
- [8] Stanmore B R, Gilot P. Review-calcination and carbonation of limestone during thermal cycling for CO<sub>2</sub> sequestration[J]. *Fuel Process Technology*, 2005, **86**(16): 1707–1743.
- [9] Cheng L M, Chen B, Liu N, et al. Effect of characteristic of sorbents on their sulfur capture capability at a fluidized bed condition[J]. *Fuel*, 2004, **83**(7/8): 925–932.
- [10] Laursen K, Duo W, Grace J R, et al. Sulfation and reactivation characteristics of nine limestones[J]. *Fuel*, 2000, **79**(2): 153–163.
- [11] Ryu H J, Grace J R, Lim C J. Simultaneous CO<sub>2</sub>/SO<sub>2</sub> characteristics of three limestones in a fluidized-bed reactor[J]. *Energy and Fuels*, 2006, **20**(4): 1621–1628.
- [12] Sun P, Grace J R, Lim C J, et al. Removal of CO<sub>2</sub> by calcium-based sorbents in the presence of SO<sub>2</sub>[J]. *Energy and Fuels*, 2007, **21**(1): 163–170.
- [13] Sun P, Grace J R, Lim C J, et al. Simultaneous CO<sub>2</sub> and SO<sub>2</sub> capture at fluidized bed combustion temperatures[C]//18th International Conference on Fluidized Bed Combustion. Toronto, Canada, 2005: 22–25.
- [14] Basinas P, Wu Yinghai, Grammelis P, et al. Effect of pressure and gas concentration on CO<sub>2</sub> and SO<sub>2</sub> capture performance of limestones[J]. *Fuel*, 2014, **122**: 236–246.
- [15] Coppola A, Scala F, Salatino P, et al. Fluidized bed calcium looping cycles for CO<sub>2</sub> capture under oxy-firing calcinations conditions: Part 1. Assessment of six limestones[J]. *Chemical Engineering Journal*, 2013, **231**: 537–543.
- [16] Coppola A, Montagnaro F, Salatino P, et al. Fluidized bed calcium looping: the effect of SO<sub>2</sub> on sorbent attrition and CO<sub>2</sub> capture capacity[J]. *Chemical Engineering Journal*, 2012, **207/208**: 445–449.
- [17] Ridha F N, Manovic V, Macchi A, et al. The effect of SO<sub>2</sub> on CO<sub>2</sub> capture by CaO-based pellets prepared with a kaolin derived Al(OH)<sub>3</sub> binder[J]. *Applied Energy*, 2012, **92**: 415–420.

## 碳酸化过程中硫化反应对钙基吸收剂循环捕集 CO<sub>2</sub> 的影响

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**摘要:** 采用 2 种不同特性的加拿大石灰石来研究钙基吸收剂循环煅烧碳酸化捕集 CO<sub>2</sub> 过程中硫化反应对碳酸化反应的影响。当反应气氛中有 SO<sub>2</sub> 时, 每次循环中钙的碳酸化转化率都要低于没有 SO<sub>2</sub> 的循环, 而且钙的硫酸化转化率几乎随着循环次数线性增长。在 650 ℃, 0.18% SO<sub>2</sub> 的环境中, 对 5 和 10 min 这 2 种碳酸化时间而言, 前 4 次循环的碳酸化转化率几乎没有区别。与碳酸化过程同时发生的间接硫化反应是导致吸收剂捕集 CO<sub>2</sub> 能力下降的原因, 而碳酸化时间并不是影响吸收剂脱碳的主要影响因素。在所测试的 3 个温度中, 680 ℃ 是最佳碳酸化温度, 在此温度下碳酸化转化率最高, 而此温度下硫化转化率最大, 则可能是由于温度对碳酸化和硫化反应速率的作用不同而造成的。碳酸化转化率随 SO<sub>2</sub> 浓度的增加而减小, 但两者之间并不是线性关系。

**关键词:** 钙基吸收剂; 碳酸化; 硫化; 循环; CO<sub>2</sub> 捕集

**中图分类号:** TK16