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SORBENT REACTIVITY STUDIES FOR CO₂ AND SO₂ CO-CAPTURE BY CALCIUM LOOPING PROCESS

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ABSTRACT

Limestone samples were analyzed in a thermo gravimetric analyser (TGA) at a calciner and carbonator operating conditions for CO₂ and SO₂ co-capture in a typical Calcium Looping (CaL) process. The CaSO₄ formed in the sample at both reactor operating conditions, accumulated over the number of carbonation and calcination cycles and hence effectively reduced its CO₂ capture potential. Subjected to hydration, a multi cycled DFB (dual fluidized bed) sample was found to be highly reactive like a fresh limestone with SO_2 and CO_2 Simultaneous carbonation and sulfation tests were performed, depicting the carbonator operating conditions, to optimize the CO₂ capture in presence of SO₂. Analysis of carbonation to sulfation ratio against the residence time revealed that the smaller the residence time better the CO_2 capture efficiency. Out of the two tested carbonation temperatures of 650°C and 700°C, the former one was found to be favorable towards CO_2 separation. Finally sulfation-only rates were measured at both reactor temperatures. No significant difference was observed for up to 80 minutes. However the sulfation of freshly carbonated limestone was faster than the original limestone. Lime (CaO) sulfation was the fastest among all three cases.

NOMENCLATURE

X _{CO2}	CaO to CaCO ₃ conversion	[mol-%]
X _{SO2@carb.}	CaO to CaSO ₄ conversion @	[mol-%]
	carbonator	
X _{SO2@calc.}	CaO to CaSO ₄ conversion @	[mol-%]
	calciner	
CaL	Calcium Looping process	[-]
CCS	Carbon Capture and Storage	[-]
GHG	Greenhouse Gases	[-]
CFB	Circulating Fluidized Bed	[-]
TGA	Thermo-gravimetric Analyser	[-]
DFB	Dual Fluidized Bed	[-]

INTRODUCTION

Fossil fuel combustion is the single largest human influence on climate, accounting for about 80% of anthropogenic greenhouse gas emissions [1]. More than one third of these emissions originate from stationary power generation plants/point sources spread all over the world. CCS is now widely accepted as a GHG mitigation strategy that would promote the fossil fuel power generation as an environmental friendly process. CO_2 separation, compression, transport and storage are the three main steps of a CCS process. However, CO_2 separation is the most costly process to date. Numbers of technologies are on development to address the cost factor. Calcium looping (CaL) is one among them. A detailed description of this process and the cost analysis is available in literature [2-4].

There are two primary reactions that involve in a CaL process. One is carbonation which takes the CO_2 from the flue gases and the second is calcination to releases the CO_2 and regenerate the sorbent.

Carbonatio : $CaO + CO_2 \rightarrow CaCO_3$

Calcination: $CaCO_3 \rightarrow CaO + CO_2$

As shown in figure 1, CaL process can be realized in industrial scale with two interconnected, atmospheric circulating fluidized bed (CFB) reactors, namely calciner and carbonator. The carbonator operates at 600°C - 700°C and the calciner is above 900°C. Pilot scale studies concerning the CaL process are also reported recently [5]. In the same literature the effect of important operating parameters in the CaL process was investigated and characterized, namely the space time and the sorbent looping ratio.



FIGURE 1. PROCESS FLOW DIAGRAM SHOWING THE MAIN COMPONENTS OF A CaL PROCESS.

For viability of a CaL process, it is necessary that the naturally occurring calcium sorbents maintain a reasonable reactivity over multiple capture and release cycles. Previous studies report a loss of reactivity with increasing number of cycles and calcination temperatures [2, 6-8]. These studies were carried out in CO₂/N₂ environment that simulates the flue gases from a combustion power plant. However, in reality, the flue gases especially from a coal power plant contain SO₂ in the stream. This will also react with the sorbents in these reactor conditions. Lime (CaO) sulfation has been extensively studied in the past and found to contain SO2 emissions from the fluidized bed combustion systems. In these studies it was focused on maximizing the SO₂ capture. On the other hand, in the case of CaL, it is the CO₂ capture that has to be optimized. There are studies reported on sequential SO₂ and CO₂ capture [9, 10]. However, simultaneous carbonation and sulfation that occur in a typical carbonator conditions require further investigations. There are two previous studies on simultaneous capture found in the literature. One concerning the high reactivity CaO[7] at 700°C and the other with natural limestones and dolomite at 850°C[11].

Therefore this study is focused on the sulfation of naturally occurring calcium sorbents in both the calciner and carbonator of a CaL based CO₂ separation process. Thermo-gravimetric analyses were carried out on two limestone samples and a multi cycled spent sample in a simulated environment that prevail in those two reactors. Simultaneous sulfation and carbonation experiments representing the carbonator reactions two different temperatures were an important part of this work. This is to identify the process conditions at which the carbonation could be maximized in the presence of SO_2 .

EXPERIMENTAL METHODS

The two limestone samples used in this study originate from different locations in Germany and Greece. Both contain more than 94 wt-% of CaCO₃ and referred as limestone 1 and limestone 2 hereafter. The third sample which was used in limited experiments was taken from a continuously operating $10kW_{th}$ DFB which is located at the Institute of Combustion and Power plant Technology (IFK) at the University of Stuttgart. These samples were collected from the stream leaving the fluidized bed carbonator at steady state operating conditions. The carbonator temperature was 650°C and the calciner was at 875°C. In fact the DFB was operated with the limestone 1, electrically heated and synthetic flue gas of 15 mol-%CO₂ in N₂. The samples were studied in a thermo gravimetric analyzer (TGA, Linseis STA PT1600) supplied by Linseis® Messgeraete GmbH. The detailed description of this TGA and the custom designed sample holder can be found in a previous work of these authors[12].

Samples of 500 - 600 mg in the size range of 200 - 300 μ m were used in all the analyses. Initial and final weights of the samples were measured in an external microbalance for comparison. The samples were then loaded to the TGA and heated at 10 degrees per minute. The gas box and the TGA were operated with two different programs provided by the supplier. The test parameters were fed to the programs beforehand. A 100 ml/min reaction gas mixture was continuously supplied to the reaction chamber at desired gas concentrations in adiabatic conditions. Another flow of 50 ml/min N₂ purge was supplied to the housing of the measuring system to protect from corrosive gases (SO₂, CO₂ etc.). The change in weigh and the temperature were logged to the system for every second.

RESULTS AND ANALYSIS

Apart from the CO₂ that reacts with the lime (CaO), the flue gas from a typical coal fired power plant also contains H_2O and SO_2 that react with both the lime and the limestone at certain concentrations and temperatures. Following is the list of reactions that could occur in a CaL process;

Hydration: $CaO + H_2O \rightarrow Ca(OH)_2$

Sulfation 1: $CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$

Sulfation 2 : $CaCO_3 + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4 + CO_2$

In the carbonator and calciner (both operate above 600°C and atmospheric pressure) the hydration reaction will never happen according to the thermodynamic equilibrium analysis found in the literature[7]. However the sulfation 1 and 2 will occur in carbonators, while in the calciners only sulfation 1. Hence experimental investigations are required to understand the sulfation reactions and to optimize the carbonation reaction in the presence of SO₂. This study concerning the influence of sulfation over the CaL process was divided into two parts: the sulfation at calciner conditions and the sulfation at carbonator conditions - that means a simultaneous carbonation and sulfation. In the last section of this work sulfation rates are analyzed and discussed at various conditions. The experimental parameters such as the temperature and the gas concentrations were chosen according to the prevailing conditions in the carbonator and the calciner.

Figure 2 is a typical TGA curve showing several calcination, sulfation and carbonation cycles at both the calciner and carbonator conditions. The sample weight change

and the temperature are plotted together. In this particular case the calcination occurred at 900° C in 100% N₂ (p-q of the weight change curve) followed by sulfation in 3000ppm SO₂ and 5%O₂ (q-r of the weight change curve) and at 650° C the simultaneous carbonation and sulfation in 10%CO₂, 2700ppm SO₂ and 4.5%O₂ (r-s of the weight change curve). From p to s the weight change curve represents one complete cycle.



FIGURE 2. A TIPICAL TGA CURVE SHOWING SEVERAL CYCLES OF CALCINATION, SULFATION AND SIMULTANIOUS CARBONATION AND SULFATION (p-q-r-s OF THE WEIGHT CHANGE CURVE REPRESENTS A COMPLETE CYCLE).

The degree of sulfation achieved at the calciner, $X_{SO2@cal.}(900^{\circ}\text{C})$ and carbonator, $X_{SO2@car.}(650^{\circ}\text{C})$ conditions-in mol% can be determined as follows,

$$X_{SO2@cal.} = \left[\frac{(m_r - m_q)/80}{m_q/56}\right] \times 100$$
$$X_{SO2@car.} = \left[\frac{(m_r - m_r)/80}{m_q/56}\right] \times 100$$

The degree of carbonation achieved at the carbonator, X_{CO2} (650° C) is as follows,

$$X_{CO2.} = \left[\frac{(m_s - m_t)/44}{m_q/56}\right] \times 100$$

where $m_q/56$ is the initial number of moles of CaO in the sample, $(m_r - m_q)/80$ is the number of moles of CaSO₄ formed at calciner conditions, $(m_t - m_r)/80$ is the number moles of CaSO₄ formed at carbonator conditions and $(m_s - m_t)/44$ is the number moles of CaCO₃ formed.

1. INFLUENCE OF SULFATION AT CALCINER CONDITIONS

The samples were first calcined at 900°C followed by 20 minutes sulfation at the same temperature and then cooled down to 650°C for carbonation in 15 mol-%CO₂ for another 20 minutes. The same procedure was repeated four times. The tests were carried out primarily with one variant of changing the type of samples. Figure 3 shows the comparison of sulfation achieved by limestone 1 and 2 in 20 minutes at a typical calciner condition. Both samples show similar degrees of conversion in the first two cycles while in the 3rd and 4th cycle limestone 2 begins to trail. The difference in conversion also increases with increasing the number of cycles. It can be observed that the degree of sulfation at the second cycle is higher than at the first cycle.



FIGURE 3. CaO TO CaSO₄-MOL% CONVERSION OF LIMESTONE 1 AND 2 AT 900°C, 3000 PPM SO₂ AND 5% O₂ FOR 20 MINUTES.

Figure 4 compares the sulfation of limestone 1, DFB and hydrated DFB samples which are also from the same limestone, against the number of cycles. The DFB sample shows the lowest sulfation while the hydrated DFB is the highest. The fresh limestone 1 lies in-between. The lowest sulfation of the DFB sample could have been caused by the loss of surface area due to the repetitive carbonations and calcinations, rapid heating and attrition experienced by the particles at the DFB test facility. However the hydrated DFB achieved the highest suflation. Hydration seems to enhance the CaO availability by causing cracks on the granulers. A detailed description of the hydration process and the effect of hydration on carbonation has been reported in previous work of the authors [12].



FIGURE 4. CaO TO CaSO₄-MOL% CONVERSION OF LIMESTONE 1, DFB SAMPLE AND HYDRATED DFB SAMPLE AT 900°C, 3000 PPM SO₂ AND 5% O₂ FOR 20 MINUTES.

Figure 5 plots the carbonation of limestone 1 and hydrated DBF with number of cycles. In order to compare the effect of sulfation on carbonation, one test run was conducted without sulfation. It is a well-reported fact that the carbonation conversion decreases with increasing number of cycles due to the loss of surface area. In addition to this, the sulfation offers an added adverse effect on carbonation conversion of limestone particles as can be seen in figure 5. The difference between the carbonation only line and the sulfation & carbonation lines are considerably large. It can be attributed to the fact that the CaSO₄ produced by 'sulfation 1' reaction remained in the particle during the carbonation too. This not only reduces the available CaO for the carbonation but also effectively blocks the pore structures of the CaO. The effect of pore blockage by the CaSO₄ product layer can be realized by the comparison of CaO to CaCO₃ (X_{CO2}) and CaO to CaSO₄ ($X_{SO2@calc}$) - mol% conversions between carbonation with and without sulfation. The sum of X_{CO2} and $X_{SO2@calc}$ in the former case is much less than X_{CO2} in the latter. Thus the sulfation significantly hindered the carbonation.

 X_{CO2} shows the decreasing trend in all three cases. However the gap between the cases of limestone 1 with and without sulfation increases with number of cycles. This seemed to suggest the accumulation of CaSO₄ in the particles. The hydrated DFB took over the X_{CO2} of the sulfated limestone 1 at the 2nd cycle and this trend retained for the 4 cycles. It can also be noted that the deactivation of the hydrated sample occurs at a slower rate than limestone 1. This means that the hydrated samples performed well in achieving higher sulfation as well as carbonation.



FIGURE 5. CaO TO CaCO₃-MOL% CONVERSION OF THE LIMESTONE 1 AND THE HYDRATED DFB SAMPLE AT 650°C, 15%CO₂ FOR 20 MINUTES. SULFATION AT 900°C 3000ppm SO₂ FOR 20 MINUTES. ONE CASE SHOWN WITHOUT ANY SULFATION.

2. INFLUENCE OF SULFATION AT CARBONATOR CONDITIONS

As discussed in earlier case the sulfation at calciner conditions reduces the CO_2 capture capacity of the sorbent due to the formation of $CaSO_4$ which remains very stable within the sample, at CaL process conditions. When it comes to the carbonator, the sulfation and carbonation will take place simultaneously. Sulfation 2 reactions concerning the CaCO₃ will also occur in addition to the CaO sulfation. This part of experiments is to quantify the extent of sulfation and carbonator during the simultaneous reactions at the carbonator temperatures of 650°C and 700°C. The trend in the ratio of carbonation to sulfation as a function of residence time has also been determined by varying the number of cycles.

The samples were calcined at 850°C and subjected to simultaneous carbonation and sulfation at 700°C and 650°C at 2700ppm SO₂ and 10%CO₂ (100 000 ppm). Since the CO₂ concentration is more than 30 times higher than the SO₂, a higher rate of carbonation could be expected. However, a higher free energy change of sulfation reaction thermodynamically favors it over carbonation. In order to shed light on these reactions kinetics, the residence time of the simultaneous carbonation and sulfation was varied as 5, 10, 30 and 50 minutes

Figures 6 and 7 respectively show the limestone 1's conversion of CaO to $CaSO_4$ -mol% and CaO to $CaCO_3$ -mol%, occurred simultaneously, against the residence times of 5, 10, 30 and 50 minutes in 10%CO₂ and 2700ppm SO₂ gas mixture for four calcination and carbonation cycles. Altogether there were four experiments conducted in each of the four residence times. The rate and the value of X_{SO2} for the first two cycles steadily increase with the increasing residence time. In the third cycle the X_{SO2} rate slightly falls at 50 minutes while it gets even slower in the 4th cycle, reaching a lower value than at 30 minutes. This could have been caused by the combined effect

of sorbent sintering and the thickening of $CaSO_4$ product layer due to the prolonged residence time of 50 minutes for four consecutive cycles. Sintering leads to loss of specific surface area which cause reactivity loss.



FIGURE 6. CaO TO CaSO₄ - MOL% COVERSION DURING THE SIMULTANIOUS CARBONATION AND SULFATION AT 650°C, 10%CO₂, 2700 PPM SO₂, 4.5%O₂ FOR 5,10,30 &50 MINUTES RESIDENCE TIME FOR FOUR CYCLES.CALCINATION WAS AT 850°C IN N₂.

In the case of X_{CO2} in figure 7, the rate and the values do not change significantly up to 10 minutes residence time. This would correspond to the initial kinetically controlled fast reaction phase. After 10 minutes the reaction rate reduces due to the internal pore diffusion controlled reaction phase [12]. It can be seen that the reaction rate also reduces with increasing number of cycles. X_{CO2} remains the same at 30 and 50 minutes for the first two cycles. However the corresponding X_{SO2} keeps increasing (refer figure 6). This observation suggests that the sulfation 2 reaction occurs and converts the CaCO₃ into CaSO₄.



FIGURE 7. CaO TO CaCO₃ - MOL% COVERSION DURING THE SIMULTANIOUS CARBONATION AND SULFATION AT 650°C, 10%CO₂, 2700 PPM SO₂&4.5%O₂ FOR 5,10,30 &50 MINUTES RESIDENCE TIME FOR FOUR CYCLES.

Figure 8 plots the ratio of X_{CO2}/X_{SO2} against the residence time for all the four cycles. The aim of the CaL process is to capture as much CO₂ as possible from the flue gas with a minimum amount of sorbent circulating between the reactors. The amount of sorbent circulation required for CaL process depends on the ratio of active sorbent material present in the circulating stream. However it has been noted that the accumulation of CaSO₄, the product of sulfation, deactivates the sorbents. Hence, finding an optimum residence time which maximizes the X_{CO2} and minimizing the X_{SO2@carb} is very important. Moreover, the average residence time of sorbent particles in a CFB carbonator will be in the range of a couple of minutes. The figure 8 plot apparently shows that the lower residence time favours the carbonation than its competing sulfation. That means, when comparing 5 and 10 minutes residence time, the former will fit the criteria for a CFB carbonator. Apart from that the number of cycles also has a significant effect on X_{CO2} and X_{SO2@carb} according to figures 6 and 7. In a real CaL plant the sorbent particles will undergo several dozens of cycles, thus to calculate the optimum residence time, one has to consider the average characteristics of the sorbent population. It is necessary to analyze tens of cycles in the same manner to find out the residence time suitable for a real CaL plant. These experiments can serve as a template for further investigations in this regard.





Carbonation temperature is also to be optimized in order to get the maximum CO₂ separation in the presence of SO₂. Table 1 lists the ratio of $X_{CO2}/X_{SO2@carb.}$ for the carbonation temperatures of 650°C and 700°C and for 5 minutes residence time. It is apparent that the ratio is much higher at 650°C throughout all the cycles. The absolute values have also been found to be higher at this temperature. Hence, comparing 700°C and 650°C, the latter can be suggested as the optimum carbonator temperature to maximize the CO₂ separation in the presence of SO₂.

TABLE 1. RATIO OF X _{CO2} /X _{SO2@carb.} FOR THE
TEMPERATURES OF 650°C AND 700°C CARBONATION.
THE RATIO WAS OBTAINED WITH THE 5 MINUTES
DESIDENCE TIME

	X_{CO2} / X_{SO2} @carb.					
carb. temp	cycle 1	cycle 2	cycle 3	cycle 4		
650°C	24.9	22.2	19.3	18.9		
700°C	10.0	8.1	7.0	6.6		

3. SULFATION RATE ANALYSIS

It was witnessed that the sulfation occurred much slower than the carbonation at CaL reactor operating conditions. It can be attributed to the lower SO_2 concentration than the CO_2 in the carbonator. It has also been observed that the sulfation adversely affected the carbonation capacity of the sorbents. A set of experiments were conducted to analyze the rate of sulfation at typical calciner and carbonator temperatures without the presence of CO2. Figure 9 shows the rate of sulfation of calcined limestone 1 at 900°C and 650°C for more than 2 hours. The rates are almost the same up to 80 minutes and then the 900°C sulfation begins to slow down. The reason could have been the sintering of particles exposed to high temperatures for a long time. Sintering reduces the specific surface area which is proportional to the reactivity. However at 650°C, sulfation seems to occur at a consistent rate as it is not significantly affected by the sintering.



FIGURE 9. SULFATION OF CALCINED LIMESTONE 1 AT 650°C AND 900°C. SO₂ CONCENTRATION IS 3000PPM & $5\%O_2$.

Sulfation 2 reaction occurs mostly in the carbonator due to availability of $CaCO_3$, while the sulfation 1 reaction with CaO takes place in both the reactors. Figure 10 shows a comparison of sulfation rates of limestone 1, calcined limestone (lime) and once carbonated limestone 1. The sulfation rate of the calcined limestone 1 (CaO) and once carbonated limestone are comparable at the beginning and then fall apart. That means, at the beginning the sulfation 1 and the sulfation 2 reactions occurred at comparable rates. The limestone 1's sulfation rate appears to be the lowest. Therefore it can be stated that the newly formed $CaCO_3$ is more reactive to SO_2 than the one in the original limestone.



FIGURE 10. RATE OF SULFATION OF LIMESTONE 1 WITH VARIOUS FORMS AT 650°C AND 2700 PPM 4.5% O_2 FOR AN HOUR DURATION.

CONCLUSION

Sulfation and carbonation experiments were conducted in a thermo-gravimetric analyzer in a typical calciner and carbonator operating conditions of calcium looping based post combustion CO₂ separation process. It was witnessed that the CaSO₄ formed as a result of sulfation got accumulated in the sample over the number of cycles and hence effectively undermined its CO₂ capture potential in case of both the reactor operating conditions. After subjected to hydration, the DFB (dual fluidized bed) sample was found to be highly reactive as almost equal as a fresh limestone towards both SO_2 and CO_2 . Analysis of carbonation to sulfation ratio against the residence time revealed that the smaller the residence time better the CO_2 capture efficiency as the formation of pore blocking CaSO₄ reduced. Out of the two tested carbonation temperature of 650°C and 700°C, the former one was found to be more favorable for CO₂ separation. No significant rate difference was observed in sulfation-only tests at both reactor operating temperatures. However the sulfation rate of once carbonated limestone (subjected to one cycle) was faster than the original limestone. The calcined limestone 1 (CaO) sulfation was the fastest.

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REFERENCES

- 1. R. Quadrelli and S. Peterson, 2007, *The energy climate change: Recent trends in CO*₂ *emissions from fuel combustion.* Energy Policy, **35**: p. 5938-5952.
- S. Sivalingam, S. Gleis, H. Spliethoff, C. Hawthorne, A. Charitos, and G. Scheffknecht, 2009, Cyclic carbonation and calcination studies of limestone and dolomite for CO₂ separation from combustion flue gases J. Eng. for Gas turbine and Power, 131: p. 0118011-0118018.
- C. Abanades., E. Anthony., J. Wang., and Johneoakey, 2005, *Fluidized Bed Combustion* Systems Integrating CO₂ Capture with CaO. Environ. Sci. Technol., **39**: p. 2861-2866.
- C. Abanades, G. Gemma, N. Alonso, N. Rodriguez, E. Anthony, and L. M. Romeo, 2007, *Cost Structure of a Postcombustion CO₂ Capture System Using CaO.* Environ. Sci. Technol., **41**(15): p. 5523 - 5527.
- A. Charitos, C. Hawthorne, A. R. Bidwe, S. Sivalingam, A. Schuster, H. Spliethoff, and G. Scheffknecht, 2010, *Parametric investigation of the Calcium Looping process for CO₂ capture in a 10 kWth Dual Fluidized Bed.* Int. J. of Greenhouse Gas Control, 4(5): p. 776 784.
- 6. G.S. Grasa and J.C. Abanades, 2006, CO₂ capture capacity of CaO in long series of carbonation/calcination cycles. Industrial and Engineering Chemistry Research, **45**(26): p. 8846-8851.
- M. V. Iyer, H. Gupta, B. B. Sakadjian and L.-S. Fan, 2004, *Multicyclic Study on the Simultaneous Carbonation and Sulfation of High-Reactivity CaO*. Ind. Eng. Chem. Res., 23: p. 3939-3947.
- 8. Abanades, J.C., 2002, *The maximum capture efficiency* of CO₂ using a carbonation/calcination cycle of CaO/CaCO₃, Chemical Engineering Journal, **90**: p. 303-306.
- 9. Y. Li, S. Buchi, J. Grace and J. Lim.C., 2005, SO₂ Removal and CO₂ Capture by Limestone Resulting from Calcination/Sulfation/Carbonation Cycles. Energy & Fuels, **19**: p. 1927-1934.
- G.Grasa, M. Alonso and C. Abanades, 2008, Sulfation of CaO Particles in a Carbonation/Calcination Loop to Capture CO₂, Ind. Eng. Chem. Res., 47(5): p. 1630– 1635.
- P.Sun, J.R. Grace, C.J. Lim and E.J.Anthony, 2007, Removal of CO₂ by Calcium-Based Sorbents in the Presence of SO₂. Energy & Fuels, 21: p. 163-170.
- S. Sivalingam, S. Gleis, H. Spliethoff, C. Hawthorne, A. Charitos, and G. Scheffknecht, Analysis and comparison of reactivity and CO₂ capture capacity of fresh calcium-based sorbents and samples from a lab scale dual fluidizedbed calcium looping facility. J. Eng. for Gas Turbine and Power, (accepted for publication).