Removal of Sulphur Dioxide by Calcium-Based Materials from Different Sources in South Africa.

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Abstract
The sulphation reactions of two limestone and two dolomite materials from quarries in South Africa were investigated in an isothermal fixed bed reactor under conditions similar to those encountered in fabric bag filters of the dry flue gas desulphurization system. The raw materials used in this study were calcined at 900 ºC and the produced quicklime slaked. The fixed bed reactor was operated batchwise with a single charge (0.1g of the sorbent material dispersed in 3g of inert silica sand) of particles for obtaining the SO_2 breakthrough curves. Experiments were carried out at different temperatures ($60 \leq T \leq 100$ºC), varying SO_2 feedstock concentration ($1000 \leq C \leq 3000$ ppm), and relative humidity ($0\% \leq RH \leq 40\%$). Both the limestone and dolomite samples showed appreciable desulphurization activity at the conditions tested. The SO_2 concentration was found not to have any significant effect on the final sorbent conversion although the initial conversion rate was seen to increase with an increase in the SO_2 concentration in the flue gas. There was no temperature dependence of the sorbent activity in the temperature range investigated. The sorbent activity increased with an increase in the relative humidity and this was concluded to be the most influential factor in the sorbent conversion.

Keywords: Sorbents, Dolomite, Limestone, Flue Gas Desulphurisation

1.0 INTRODUCTION
South Africa is an energy intensive country, with a high reliance on electricity and primary energy resources such as coal and imported oil. Coal presently provides about 75% of South Africa's primary energy needs, and over 90% of electricity in the country is coal-derived [1]. Conventional combustion technology for fossil fuels results in most of the sulphur in the fuel being oxidized and released into the atmosphere as sulphur dioxide (SO_2). Coal combustion is the single largest manmade source of SO_2 accounting for 50% of the annual global emissions [2]. In coal-fired power plants, the main methods that have been used for SO_2 reduction are fuel switching or blending, coal preparation, boiler modernization, technology change, and flue gas desulphurisation (FGD). Most of the nonregenerable FGD methods utilize calcium-based sorbents (limestone or lime) because they produce a relatively safe and stable end product, *viz.* calcium sulphate. These processes can be divided, depending on the reactive phase where sulphur dioxide is removed, into wet, semi-dry or dry processes. In this paper, we will discuss the dry FGD process.
For the removal of SO_2 from flue gas, dry processes using calcium based sorbents injected into the duct offer an attractive alternative with a simple technology as a retrofit for existing coal-fired power plants. In this process the sorbent particles are normally introduced into humidified and temperature controlled flue gas in the duct between the air pre-heater and particulate control device. The sorbent used widely in the humidified duct injection processes is hydrated lime ($Ca(OH)_2$) [3]. The residence time of the gas and solid phases in the duct is very short, in terms of seconds, and the desulphurization reaction also takes place in the particulate collection device (fabric filter or electrostatic precipitator). The total SO_2 dioxide removed is the sum of both capture places; the duct section and the subsequent capture in the particulate collection device [4].

In the current work, experimental data on the sulphation of 2 limestone and 2 dolomite samples in an isothermal fixed bed reactor under conditions similar to those in fabric filters of the spray-drying flue gas desulphurization system are reported. The main objective of the work presented was to obtain some sort of ranking of the sorbents

tested and relate this to the chemical properties of the sorbents. Further, it is the intention of this work to try and explain the differences in the conversion of chemically similar limestones and dolomites. The effects of the various operating parameters (inlet SO_2 concentration, relative humidity, and reaction temperature) on the sulphation process are also reported in this work.

2.0 MATERIALS AND METHODS

2.1 Materials
To carry out this investigation, four samples of commercial calcareous material (quarried in South Africa and herein named A, B, C, and D) were selected. The samples have varying amounts of calcium and magnesium carbonates. Table 1 shows their composition as obtained by a chemical analysis. For comparison, a 99.8% pure commercial $Ca(OH)_2$ sample (LC) was used. The raw samples were heated at 900°C for 3 hours obtaining the relevant calcines, which were cooled and slowly hydrated to obtain the required test material. Hydration was achieved by weighing 10 g of the calcinated sample and mixing, while stirring, with 20 mL of water. The resulting slurry was dried off in an oven maintained at 105 ^{o}C to produce a dry solid. All samples were then milled and sieved to a particle size below 200 μm before being used in the tests.

Table 1: Chemical Analysis of Raw Sorbent Materials

Element	A	B	C	*D*	LC
SiO_2 (%)	5.95	13.33	-	4.48	-
Al_2O_3 (%)	1.53	1.67	-	0.36	-
Fe_2O_3 (%)	1.83	0.67	-	1.61	≤0.05
CaO (%)	88.39	81.67	44	53.54	≥99.8
MgO (%)	1.26	1.67	39.0	36.52	-
Combustible matter (%)	38.3	40	-	45.60	-

2.2 Sulpation
The experiments for the SO_2 absorption of the samples were carried out in a laboratory – scale fixed bed reactor (Fig. 1). The reaction zone is contained in a 0.008m inner diameter stainless steel tube fitted in a furnace for isothermal operation. 0.1 g of the sorbent material is dispersed in 3 g of inert silica sand, packed in the centre of the reactor and is supported by glass wool. The inert silica sand helps to ensure isothermal operation, improve gas solid contact and avoid channeling of the flue gas. A N_2 stream is passed through a humidification system
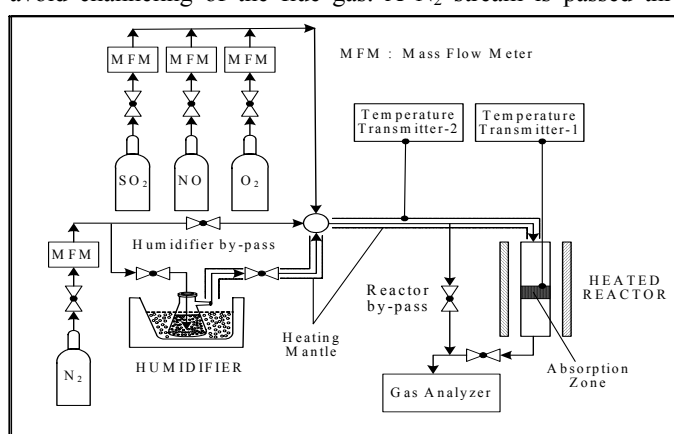

Figure 1. Schematic diagram of the experimental rig
for fixed bed desulfurization

consisting of two 250 mL conical flasks immersed in a water bath maintained at constant temperature. After

humidification, the N_2 stream is mixed with a gas stream consisting of SO_2, NO, and O_2. The simulated flue gas then flows through the reactor at a flow rate of 150 ml/min. The SO_2 concentration of the effluent gas is continuously monitored by an IMR 2800P flue gas analyzer. The desulphurization activity is monitored in three ways:

- Maximum utilization of the sorbent (mol SO_2/mol sorbent) when it is completely exhausted (i.e. percentage removal of SO_2 reaches zero).
- Duration the sorbent could maintain above 100% removal of SO_2 per g of CaO (min/g)
- SO_2 capture efficiency.

The total sorbent utilization removed is evaluated from the area between the blank and reaction breakthrough curves. The amount of SO_2 retained per mole of sorbent is given by [5]:

$$mol\ SO_2\ retained/\ mol\ sorbent\ =\ (A_{bl} - A_{exp})C_0 10^{-6}\ \frac{\phi_v}{22400}\frac{M_{sorbent}}{m_{sorbent}} \qquad (1)$$

where, A_{bl} is the area under the blank run, A_{exp} is the area under the reaction curve, C_0 is the inlet SO_2 concentration, ϕ_v is the volumetric flow rate ($mL min^{-1}$), $M_{sorbent}$ is the molar mass of the sorbent, and $m_{sorbent}$ is the mass of the sorbent used in the experiment. This method of estimating the sorbent activity has also been used by J.F. Izquierdo et al. [6] with good results.

3.0 RESULTS AND DISCUSSION

3.1 Effect of Sorbent Type and Source
The sulphation of two dolomite and two limestone samples have been investigated to ascertain whether the source and type of material plays any significant role in the sulphur capture capacity. Fig. 2 gives a comparison of the breakthrough curves for the four samples and a commercial calcium hydroxide sample (LC) at 10% relative humidity.
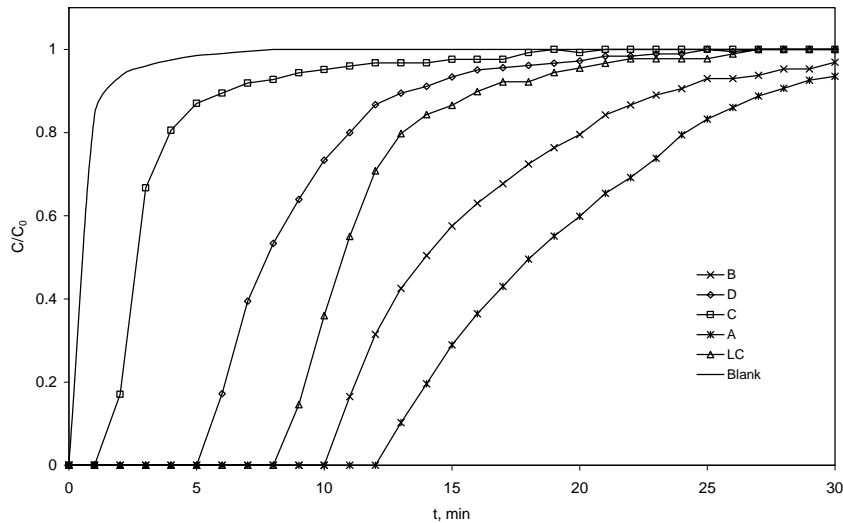

Figure 2. Comparison of SO_2 Breakthrough Curves for Four South African Calcium-Based Samples and Commercial Calcium Hydroxide. (C_0=2000ppm, T_R=80°C, RH=10%)

From Fig. 2, it can be seen that the capacity of the slaked samples to maintain 100% SO_2 removal vary from one material to the other. Applying equation (1) to the results, the amount of SO_2 retained by A, B, C, D and LC are 0.1823, 0.1478, 0.0274, 0.0798 and 0.1081 mol SO_2 per mol of sorbent respectively for the 30 minute duration considered. The limestone samples (A and B) thus have a better capture capacity than the commercial calcium hydroxide while the capacity of the dolomite samples (C and D) is lower than that of the commercial sample. The sulphation capacity of the raw samples can be related to their CaO contents. The higher CaO content samples show a higher sulphation capacity while the lower CaO content samples display a lower capacity. The sulphation of the commercial calcium hydroxide, however, does not fall into this neat generalization. Despite having the highest CaO content of the tested samples, its capacity falls in between those of the dolomites and those of the

limestones. A possible explanation for this anomaly could be in the iron oxide content of the samples. The calcium hydroxide sample has less than 0.05% Fe_2O_3, while samples A and B have 1.83 and 0.67% Fe_2O_3 respectively. Iron oxide plays an important role in the $CaSO_4$ formation, probably related to the catalytic activity that the iron itself can have in the oxidation process of SO_2 to SO_3, which when reacting with solid CaO particles, favours $CaSO_4$ formation. Using three marble by-products and a commercial limestone material, P. Davini [7] showed that the maximum conversion of the sulphation reaction of the calcium oxides has an increasing relationship with the percent content of the iron oxide in the original carbonaceous material.

3.2 Effect of SO_2 Concentration

Ch'un-Sung Ho and Shin-Min Shih [8] have reported a low influence of SO_2 concentration on the reaction rate at 30% relative humidity but reported an increased reaction rate and final conversion with increasing SO_2 concentration at 70% relative humidity. C-F. Liu et al [9] reported a very weak influence of the SO_2 concentration on the total conversion and the reaction when testing $Ca(OH)_2$/fly ash sorbents at 30-80% relative humidity and 1000-5000 ppm SO_2 concentration. At a reactor temperature of 71.5°C and 38% relative humidity, J.F. Izquierdo et al. [6] concluded that the reaction rate between sulphur dioxide and calcium hydroxide does not depend on the sulphur dioxide partial pressure for sulphur dioxide concentration of less than 3000 ppm. Fig. 3 gives the results of the amount of SO_2 retained per mole of sample A for flue gas concentrations 1000, 1500, 2000 and 2500 ppm. Although the total amount of SO_2 retained for the different concentrations is approximately
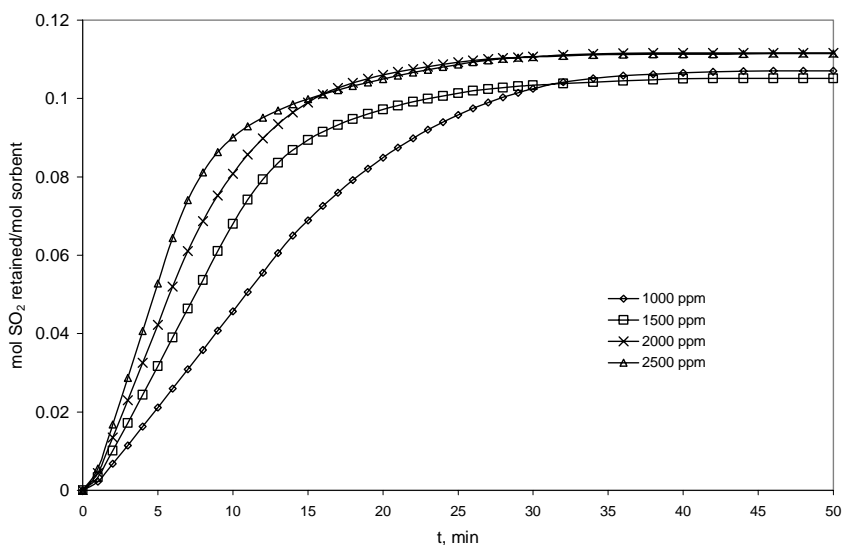

Figure 3. Influence of SO_2 Concentration on the Amount of SO_2 Retained/mol of sample A. T_R=80°C, RH = 0%

the same (0.1071, 0.1051, 0.1116 and 0.1115 for 1000, 1500, 2000 and 2500 ppm respectively) the time taken to reach maximum conversion seems to be dependent on the concentration. The higher the concentration, the faster the conversion proceeds. This result agrees with that obtained by K.T. Lee et al [10] who observed a linear correlation between the concentration and the time the sorbent can maintain 100% SO_2 removal.

3.3 Effect of Relative Humidity

The water adsorbed on the sorbent surface plays an important role in the reaction. Adsorption isotherms on a sorbent at 60-80°C obtained by C.F. Liu et.al. [9] showed that the amount of water adsorbed increased with increasing relative humidity and decreased with increasing temperature. They hypothesized that the fundamental processes taking place at the water adsorption surface could include: (a) Adsorption of SO_2 on the outer surface of water layer, (b) Hydration of SO_2 to form $SO_2.H_2O$ (c) Diffusion of $SO_2.H_2O$ inward (d) Dissolution of $Ca(OH)_2$ to form Ca^{2+} and OH^- (e) Diffusion of Ca^{2+} and OH^- outward (f) Reaction of OH^- and $SO_2.H_2O$ to form HSO_3^- and SO_3^{2-} (g) Reaction of Ca^{2+} and SO_3^{2-} to form calcium sulphite precipitate. They further hypothesized that since the overall reaction rate of the sorbent decreases with conversion and is slightly affected by SO_2

concentration, the rate controlling step may be that involving OH⁻ or Ca^{2+} ions, which are generated by the dissolution of the sorbent surface i.e. process (f) or (g). The rate of either process (f) or (g) will increase with increasing relative humidity because the higher amount of adsorbed water can produce higher amounts of reactant to react. Similar results have been reported by Ch'un-Sung and Shin-Min [8]. C.Y Chu and S.J.Hwang [12] have observed a SO_2 removal efficiency (RE) of over 100% at a relative humidity (RH) of 80% for up to 140 minutes. They attributed this to the fact that the reaction rate was very high at such a high RH and therefore all of the inlet SO_2 was absorbed and reacted at the surface of the calcium sorbent. RE decreased dramatically after that because a low porosity product layer ($CaSO_3 . \frac{1}{2} H_2O$) began to form at the surface of the sorbent. Consequently, the diffusion resistance of SO_2 from the gas phase to the inner unreacted calcium sorbent increased, which results in a decrease in RE. At last, RE was quite low due to the formation of a thick product layer on the sorbent surface. Fig. 4 shows the amount of SO_2 retained/mol of sample D as a function of relative humidity. From the
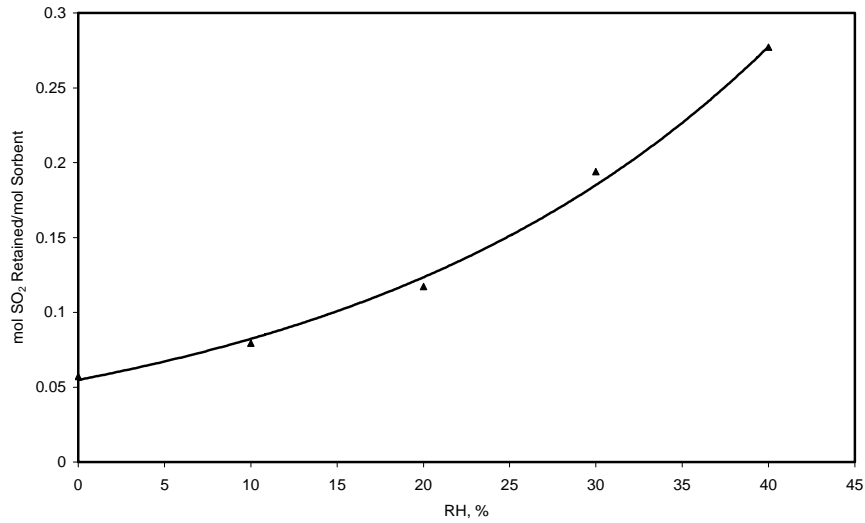

Figure 4. Influence of Relative Humidity on the Amount of SO_2 Retained/mol of Sample D. T_R=80ºC, C_0=2000ppm

results, the relative humidity is a major factor in the ability of the sorbent to capture SO_2. Regression analysis of the results shows the amount of SO_2 retained in one hour to be related to the percentage relative humidity by an exponential expression of the form:

$$mol \ SO_2 \ retained \ / \ mol \ of \ SampleD = 0.0549 e^{0.0405 \, RH} \tag{2}$$

where, RH is the relative humidity. The regression coefficient for the curve fitting was high at R = 0.998.

3.4 Effect of Reaction Temperature
Several researchers have studied influence of reaction temperature on the sorbent conversion. C.F. Liu et al. [9] observed a weak dependence of sorbent conversion on reaction temperature. They postulated that though increasing temperature could raise the chemical reaction rate constant, it could simultaneously reduce the adsorption amounts of water vapor and reaction gas. Ch'un-Sung and Shin-Min [8] have also reported a mild influence of the reaction temperature on the conversion as the temperature was increased from 60 to 90ºC. E.H. Raymond-Ooi et al. [11] observed a modest increase in the SO_2 capture capacity when they increased the reaction temperature from 60 to 80ºC. Similar observations have been reported by C.Y. Chu et al. [12]. Using a bubbling fluidized bed reactor, they found out that the sulphur dioxide removal efficiency was not significantly affected by the bed temperature ranging from 40 to 65ºC. Table 2 shows the amount of SO_2 retained per mol of Sample A as a function of temperature and relative humidity. From the results, temperature does not appear to significantly influence the sorbent conversion. As can be confirmed from the table, the conversion (area between experimental and blank curve) depends on the relative humidity but is independent of the reaction temperature.

Table 2. SO$_2$ Retained/mol of SA9 at 60 and 80°C (0 and 20% RH)

Temperature, ^{o}C	Relative Humidity, %	Mol SO$_2$ retained/mol SA9
80	0	0.111
	20	0.213
60	0	0.100
	20	0.210

4.0 CONCLUSIONS

The sulphation reaction of two calcitic and two dolomitic limestones have been studied at 60-80°C in an isothermal fixed bed reactor. The origin of the sorbent material seems to have an influence on its desulphurization capacity as was noted in figure 2. The limestone samples (A and B) showed a better capture capacity than the commercial calcium hydroxide used while the capacity of the dolomite samples (C and D) was seen to be lower than that of the commercial sample. Although the initial sorbent activity increases as the concentration of SO$_2$ increases, the maximum conversion of the sorbent is independent of the concentration. The results obtained show that the relative humidity is the most important parameter that influences the degree of conversion achieved by the sorbent. The reaction temperature on the other hand was seen to have a minimal effect on the sorbent activity.

5.0 References

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