

Comparative Analysis of H₂S Removal Ability for Different Calcium-Based Absorbents Under Coal Gasification Conditions

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Calcium-based sorbents, such as limestone and dolomite are viable candidates for capturing pollutants in an in-situ coal gasification/desulphurisation process. Recently, scallop shell is also used as a Ca-based sorbent. However, the ability in capturing pollutants varies from one type to another and it also depends on the process involved. In this study, two types of limestone, scallop shell and dolomite were characterized and studied for H₂S absorption ability under the coal gasification conditions. The characterizations were done using Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Thermal analysis and Surface Area analysis. All of the samples showed a porous structure, and in addition, the column structure was found in the scallop shell sample. The calcination temperature for all the sorbents was found to be in the range of between 783-803°C. The surface area of the scallop shell was slightly higher than the two limestone samples and dolomite showed the lowest surface area. H₂S absorption ability was studied by using a tubular flow reactor. The H₂S absorption ability for the two limestones was found to be almost the same at 900°C and about 1800 ppm of H₂S. Their absorption ability was also higher than the scallop shell and dolomite. Studies were also conducted under different reaction temperatures and H₂S concentration. The temperature was found to have a very small effect on H₂S absorption ability. On the other hand, the ability increased with H₂S concentration. Furthermore, the complete H₂S absorption time was found to be longer at low H₂S concentration.

Keywords: H₂S removal, Coal gasification, Ca-based sorbents

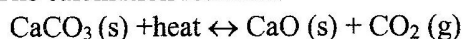
INTRODUCTION

Coal gasification is a promising way to counter a possible decrease in natural gas supply in the near future. However, the gas derived from coal contains some pollutants including sulphur, which are harmful to our environment. Therefore, ways to ensure a clean utilization of the gas through desulphurisation must be developed and perfected. Despite the fact that the first large scale effort to develop flue gas desulphurisation technology for electric power plants was in the 1960s[1], to date the same technology is still being studied and improved in different aspects.

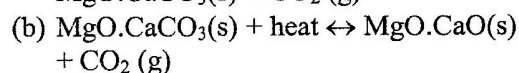
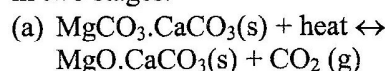
In coal combustion, sulphur is present in SO₂ form while under coal gasification conditions; sulphur is present in the form of H₂S. In this case, desulphurisation can be accomplished by the addition of a calcium compound as an H₂S

absorbent[2]. The reaction between hydrogen sulphide and limestone, scallop shell or dolomite is assumed to occur in two steps[3].

1) The calcination reaction:

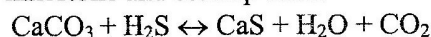


However, the calcination of dolomite occurs in two stages.

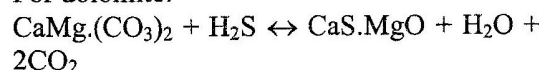


2) The sulphidation reactions:

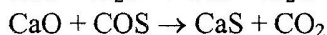
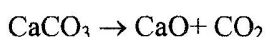
For limestone and scallop shell:



For dolomite:



Reactions taking place in the bulk of the gasifier with limestone or scallop shell are as follows.



The CaS formed is thermodynamically more stable at higher temperatures than the CaSO₄ formed under oxidizing conditions, and faster reaction rates may thus be possible. CaS would also be less limited by intraparticle resistance caused by product accumulation because it has a smaller molar volume than CaSO₄ [1].

Limestone and dolomite have been extensively studied and comparisons of their respective performances have been presented [1-8]. On the other hand, the use of scallop shell is relatively newer and fewer studies are available. It is therefore worthwhile to know how it compares with the traditionally used sorbents and also its suitability in the gasification process.

This work is being carried out using two types of limestone, scallop shell and dolomite as sorbents for the removal of H₂S resulting from the gasification of high-sulphur coal. The major focus is on studying their comparative abilities on H₂S removal based on their structural differences. Also, the effects of reaction temperature as well as H₂S concentration on absorption ability are investigated.

EXPERIMENTAL

Before the sulfidation experiments, the adsorbents to be used in this work were characterized in order to study their physical properties. The characterization of the sorbents included studying of the micrographs of the sorbents using the Scanning Electron Microscope analysis (SEM), studying the composition by the X-ray diffraction, undertaking the thermal analysis to determine the decomposition (calcination) temperatures and the analysis of the surface area.

Following the characterization of the samples, experimental work on sulfidation reaction was

undertaken. Three sets of experiment were conducted. In the first set, the temperature of the reactor was fixed at 900 °C and H₂S was supplied at about 1800 ppm and the best sorbent was determined. The second set of experiments was done by using the best sorbent selected from the results of the first set of experiments. In this case, the temperature of the reactor was held at 850, 900, 950 and 1000°C. The reaction temperatures were selected in such a way that they were above the decomposition temperature (783-803°C) obtained from the thermal gravimetric analysis (TGA) and a differential thermal analysis (DTA). The last set of experiments also used the same sorbent but this time at various H₂S concentration (ca. 850, 1800 and 3920 ppm).

Apparatus

A tubular quartz reactor was used for sulfidation experiment under atmospheric pressure and its schematic diagram is shown in Fig.1. The equipment is fitted with a sintered quartz plate to support the sample. The reactor space below the quartz plate is filled with quartz rings in order to establish a stable gas up flow. The sorbents (limestone, scallop shell or dolomite) were diluted with inert aluminium oxide (ratio 1/19 w/w) to increase the bed height. Our investigation found that for laboratory scale experiments, limestone dilution by inert quartz material or aluminium oxide does not disturb the chemical reaction and the 1/19 limestone/quartz ratio showed excellent conditions to reduce intraparticle diffusional effects. Further, the sorbent's particle sizes of between 105-210 microns showed a better performance for H₂S removal and the same size was used in this study.

The reactor was heated by an electrical resistance heater, which was controlled by the basic reactor temperature. During the experiment, the H₂S concentration was continuously monitored by an Ultraviolet/Visible Infrared (UV/VIS) spectrometer at 196.2 nm. The gas flows were measured by gas flow meter. There were three kinds of gases used in these experiments,

namely H₂S, Ar, and H₂. H₂ was added to the reaction in order to avoid H₂S decomposition,

which may form solid sulphur at high temperature.

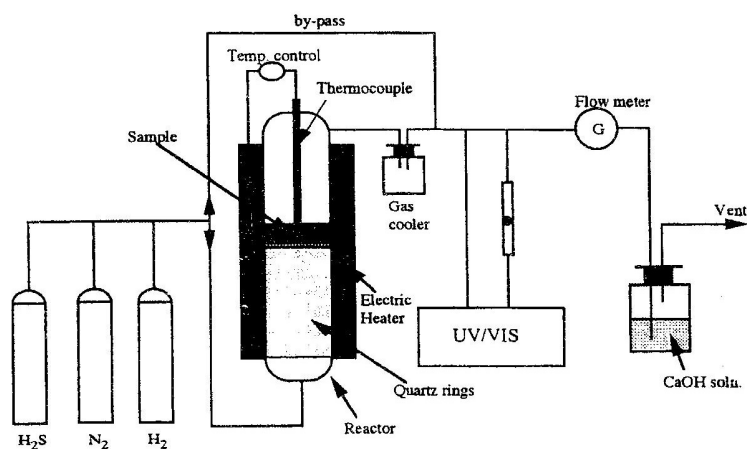


Figure 1 A Schematic diagram of the tube reactor

Procedure

The mixture of sorbent and the inert aluminium oxide was introduced into the tubular reactor. An argon gas flow (about 550 ml/min) was passed through the reactor while the reactor was being heated until it reached the desired reaction temperature. The Ar was then replaced with a mixture of Ar, H₂S and H₂. The experiment was run until no absorbance change was detected in the UV/VIS equipment (i.e. the sorbents were saturated). The representative change of absorbance with time is shown in Fig. 2.

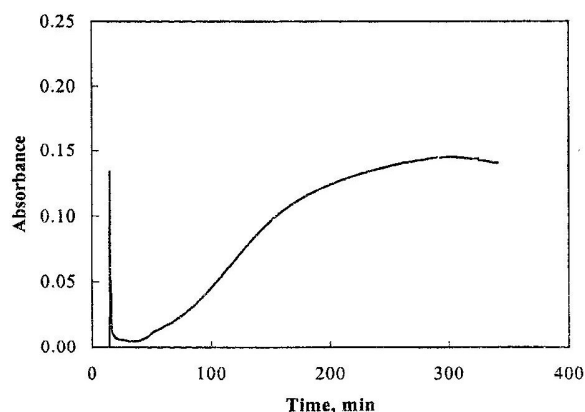


Figure 2 Sample of results output from UV/VIS for sulfidation reaction

Calculations

Some calculations were needed in order to convert the absorbance obtained from the UV/VIS equipment into volume and subsequent weight of the H₂S. First the UV absorbance results were converted into H₂S concentration in ppm by using a calibration curve, which was developed using known H₂S concentrations. This produced another curve similar to the one in Fig. 2, but this time showing the variation of H₂S concentration with time t . Then an equation, $f(t)$, was fitted to this curve so as to enable the calculation of the area under the curve, A_u . The area under the curve represents the H₂S that was not absorbed by the sorbents and is given by:

$$A_u = \int_b^a f(t) dt \quad (1)$$

where a and b represents the time interval during which absorption took place.

The area A_u , which now represents the product of concentration and time, was then multiplied by the gas flow rate in order to obtain the H₂S volume, V_u . The product of the input H₂S concentration and time gave a total area, A_{tot} ,

which represents the total amount of H₂S passed into the reactor. This was also multiplied by the flow rate in order to obtain the total H₂S volume passed, V_{tot} . The volume of the H₂S absorbed, V_a , was then determined by the difference, i.e.:

$$V_a = V_{tot} - V_u \quad (2)$$

This could then be changed to number of moles by using the Ideal Gas Law equation:

$$n = \frac{PV}{RT} \quad (3)$$

where the gas constant, $R = 0.0820567$ liter.atm/Kelvin.mole.

From the number of moles, the weight of H₂S could then be calculated (molecular weight=34). The absorption ability was then calculated as:

$$\text{Absorption ability} = \frac{\text{weight of H}_2\text{S absorbed}}{\text{weight of adsorbent}} \quad (4)$$

Note that this can also be expressed in molar ratios.

RESULTS AND DISCUSSION

From the characterization, SEM results showed that all the sorbents had a rough and porous surface. However, as opposed to the limestone, the scallop shell exhibited also a column structure being caused by the presence of aragonite, which was also detected in the XRD analysis. Figure 3 shows the SEM micrographs for limestone and scallop shell. In the scallop shell, the vertical columns are clearly seen which represents the aragonite. Other samples exhibited a pure calcite in their XRD results. From the thermal analysis, the decomposition temperature of sorbents was found to occur in the temperature range between 783-803 °C as shown in Table 1.

From the surface area analysis, results indicate that the surface area of the scallop shell sample is slightly higher than the two limestone samples (Table 2). At the same time, dolomite sample shows the lowest surface area.



Limestone



scallop shell

aragonite

Figure 3. The SEM micrograph for limestone (above) and scallop shell (below). Aragonite is clearly seen in the scallop shell on the right hand side. (Magnification x3500)

Table 1. Thermal analysis results

Sample name	TGA Peak Temp. (°C)	DTA Peak Temp. (°C)	Wt. loss (%)
Limestone A	803	803	40.57
Limestone B	783	783	37.52
Scallop shell	803	803	43.03
Dolomite	793	793	53.70

Table 2. Surface area analysis

Sample name	Sample Weight (g)	Surface Area (m ² /g)
Limestone A	1.0594	6.3
Limestone B	1.1724	6.1
Scallop shell	1.1188	7.1
Dolomite	1.117	5.2

To ensure that there were no errors arising from the experimental apparatus, reproducibility tests were undertaken. Results for this are given in Fig.4 and it can be seen that the weight of H₂S absorbed per weight of sorbent is nearly equal for the same type of sorbents. For example, results from limestone A are almost the same as those from limestone B, also results from scallop shell sample 1 are similar to scallop shell sample 2 and dolomite sample 1 is same as dolomite sample 2. This indicates that reproducibility of results is very good. Furthermore, Fig. 4 shows the comparison of H₂S absorption ability among various sorbents under atmospheric condition. From the figure, limestone shows the highest overall absorption ability and on the other hand, dolomite shows the lowest absorption ability. Since limestone and scallop shell showed higher absorption ability, they were selected to be sorbents in the second and the third sets of experiment. It should be noted that in this case, limestone A and limestone B are two different samples whereas scallop shell 1 and scallop shell 2 and dolomite 1 and dolomite 2 are the same samples.

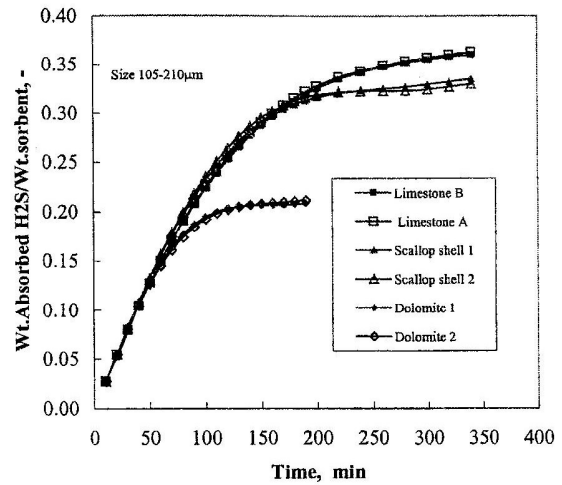


Figure 4 Variation of H₂S absorption ability with time for different absorbents.

As an absorbent absorbs H₂S, the absorption ability continues to decrease with time. In order to compare absorption ability for different sorbents, normalization was done by dividing the volume of H₂S absorbed at a given time, *t*, to the total volume of H₂S passed through the reactor during the entire experimental duration. This value is designated as *X*, which can also be referred to, as the sorbent's conversion. Figure 5 therefore presents the sorbent's conversion (1-*X*) as a function of time. For example, the figure shows that at 100 minutes, 90% of dolomite has already converted whereas only 55% of limestone and 60% of scallop shell has converted to form sulphides. As for the rate of reaction, it can be said that dolomite reacts faster than the other two sorbents.

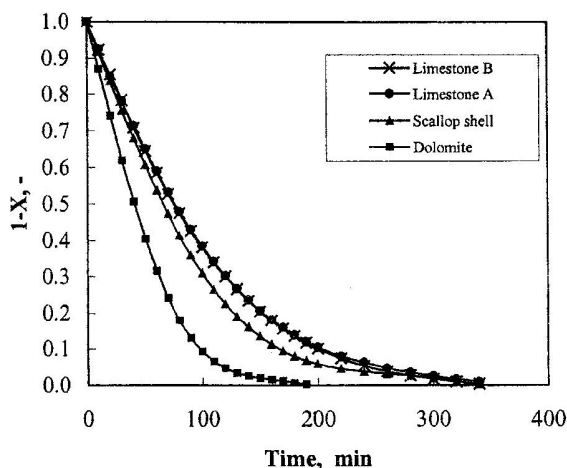


Figure 5 Sorbent's conversion as a function of time

The effect of temperature on absorption ability was also investigated. The total weight of H₂S absorbed until a sorbent reached saturation was determined for each sorbent at different reactor temperatures, in this case at 850, 900, 950 and 1000°C. Figure 6 shows the H₂S absorption ability at different temperatures using limestone A and scallop shell as sorbents. The H₂S absorption ability for both the scallop shell and limestone seems to increase slightly with increasing reaction temperature. This suggests that the reaction temperature does not have a strong influence on the absorption ability, at least in the range investigated. The finding is further supported by results from Fig. 7, which presents the variation of the reaction rate constant, *k*, with temperature in the form of an Arrhenius plot. It can be seen that slope of the curve is very small, with a value of the activation energy, Δ*E*, of about 0.27J/mole. This shows that, the reaction in this range is not temperature controlled but rather the diffusion of H₂S into the sorbent's pore matrix is the one controlling the reaction. Similar findings were also reported by Abbasian et. al [3] who also showed that temperature had a much more pronounced effect on the reaction rate constant at temperatures lower than 900K.

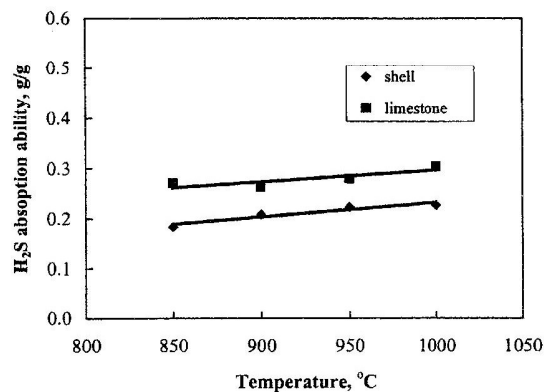


Figure 6 Effect of reaction temperature on H₂S absorption ability

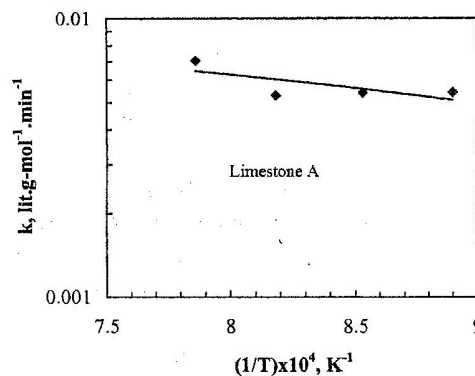
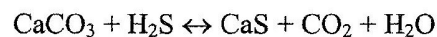


Figure 7 The first order rate constant for sulfidation reaction

An investigation was also done to determine the extent of the sorbent's saturation. Theoretically, based on the chemical reaction:



It is clear that 1g-mole of CaCO₃ (mw = 100) reacts with 1 g-mole of H₂S (mw = 34) to form 1 g-mole of CaS and other products. This being the case, if the sorbent reacts with H₂S with a 100% conversion to CaS, then the molar ratio of H₂S to CaCO₃ would be 1 mole/mole, but the weight ratio would be 34/100 or 0.34 g/g. However, the absorption abilities obtained experimentally are less than the above value, which means that some of the CaCO₃/CaO was left unreacted. This could be attributed to the blockage of pores on the sorbents surface caused by the formation of a CaS layer, and

hence leaving the inner part of a sorbent unreacted. Table 3 shows the percentage of reacted CaCO_3 , which was determined by analysing the sulphur contents in the spent sorbents. It can be seen that, despite the fact that the sorbents show saturation during

Temperature. (°C)	Reacted CaCO_3 (%)	
	Scallop Shell	Limestone
850	54.12	79.76
900	61.56	77.26
950	65.59	82.15
1000	66.76	89.39

Given the fact that different flue gases may consist of different H_2S concentrations, the effect of input H_2S concentration on sorbent's absorption ability was also investigated. Figure 8 shows the variation of H_2S absorption ability for limestone and scallop shell under different H_2S concentrations. It can be seen that with an increase in H_2S concentrations, the absorption ability also increases for both sorbents. This can be explained by the fact that when the H_2S concentration is low, the reaction time becomes longer. This, therefore, may lead to a decrease in CaO reactivity at higher temperatures, thus resulting in less H_2S absorption. On the other hand, an increase in H_2S concentration may make the diffusion effect (mentioned above) much stronger resulting into an increased H_2S absorption.

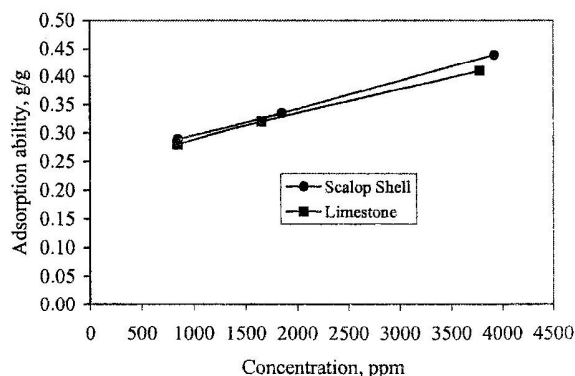


Figure 8 Sorbent's absorption ability at different H_2S concentrations.

absorption, but the inner pore matrix remains unreacted. Further, it can be seen that the percentage of CaCO_3 reacted is higher in limestone than scallop shell. The presence of aragonite in scallop shell might be a reason for less percentage of CaCO_3 reacting.

At the start of the absorption reaction, all the H_2S passed into the reactor is absorbed; i.e. complete absorption takes place. The duration under which there is a complete absorption depends on the concentration of H_2S . Figure 9 shows the duration for complete absorption under different H_2S concentrations while using limestone A as a sorbent. It can be seen that the duration for complete absorption increases with a decrease in H_2S concentration. Such information is useful in determining the amount of sorbent as well as the residence time required for a complete H_2S removal in different types of coal if their sulphur contents are known.

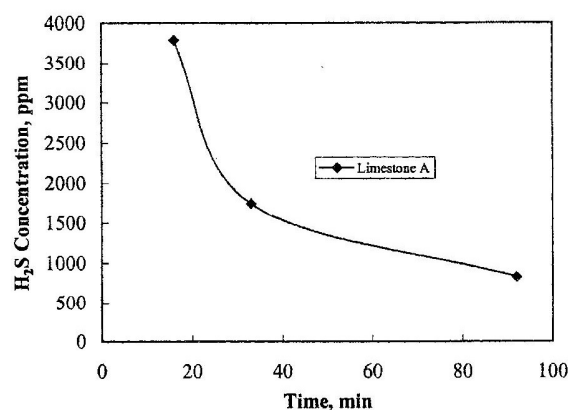


Figure 9 Time required for H_2S complete absorption under different H_2S concentrations

Generally, it has become clear that scallop shell can be used as a sorbent in coal gasification processes just like limestone or dolomite. Its absorption ability is almost as good as that of limestone. In this work, dolomite's absorption ability was found to be lower than that of other sorbents but its reaction rate is much faster. This means, in cases where short residence times are involved, dolomite would be a better sorbent than limestone or scallop shell.

CONCLUSION

From the characterization analysis results and the sulfidation reaction, the following can be concluded:

- (i) All sorbents investigated in this study showed porous structure as observed from the SEM. The column structure was found in the scallop shell sample and this was due to the presence of aragonite as shown in the XRD analysis.
- (ii) Scallop shell had the largest surface area followed by limestone as exhibited from the surface area analysis. Dolomite had the smallest surface area. As far as H₂S absorption is concerned, scallop shell and limestone performed better than dolomite, showing a relationship between surface area and absorption ability. This shows that scallop shell can be used as a sorbent in gasification processes just as well as limestone
- (iii) From the comparison of H₂S absorption ability among different sorbents, the two limestones showed better overall absorption ability. This could be due to the fact that the percentage of CaCO₃ reacted was higher because of the absence of aragonite.
- (iv) Temperature was found to have only a slight effect on H₂S absorption ability as evidenced by results obtained at 850, 900, 950 and 1000°C.
- (v) Different input of H₂S concentration into the reactor affected the absorption ability of sorbents. The sorbents could absorb larger amount of H₂S at higher concentration.
- (vi) The time needed for complete H₂S absorption depends on the input H₂S concentration and it is longer at low concentrations.

NOMENCLATURE

a, b	Time interval, s
A _{tot}	Total area, m ²
A _u	Area under the curve, m ²
DTA	Differential Thermal Analysis
mw	Molecular weight, kg/kmol
n	Number of moles
p	Pressure, Pa
R	Universal gas constant, litre.atm/mol.K
SEM	Scanning Electron Microscope
T	Temperature, K
t	Time, s
TGA	Thermal Gravimetric Analysis
UV/VIS	Ultra Violet/
V _a	Volume of H ₂ S absorbed, m ³
V _{tot}	Total volume of H ₂ S passed, m ³
V _u	Volume of H ₂ S not absorbed by sorbent, m ³
X	Sorbent conversion
XRD	X-Ray Diffraction

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