Activity Study of Absorbent Prepared from CaO/CaSO$_4$/Coal Fly Ash for SO$_2$ Removal at Low Temperatures

E. H. Raymond-Ooi, K.T. Lee and A.R. Mohamed*
School of Chemical Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, SPS, Pulau Pinang, Malaysia,
Email : chrahman@eng.usm.my

ABSTRACT
This study presents findings from an experimental investigation of the influences of several factors on the desulfurization capacity of absorbent prepared from coal fly ash, CaO, and CaSO$_4$. The absorbent was synthesized using hydrothermal reaction while the sulfation experiments were performed in a fixed-bed reactor under isothermal conditions at low temperature. Specifically, the effects of reaction temperature ($60 < T < 80$ºC), SO$_2$ inlet concentration ($500 < C_o < 2000$ ppm), relative humidity ($50 < RH < 70\%$) and absorbent particle size ($200 \leq PS \leq 600$ μm) on the desulfurization capacity of the absorbent were investigated. In general, the desulfurization capacity of the absorbent was found to increase with higher relative humidity but with decreasing SO$_2$ inlet concentration and absorbent particle size. The reaction temperature was found to have negligible effect on the desulfurization activity. The chemical composition of the absorbent before and after SO$_2$ capture was characterized using X-ray diffraction (XRD). The diffraction spectrum showed that calcium aluminum silicate hydrate and calcium carbonate were formed during the hydration process. However, after reacting with sulfur dioxide, aluminum silicate hydrate and calcium sulfate were the prominent phases detected in the spent absorbent.

Keywords: Absorbent; Coal combustion; Coal fly ash; Flue gas; SO$_2$ removal process.

1   INTRODUCTION

Coal, being the most abundant energy resource and also the cheapest will have an important role to meet the increasing demand of electricity in the world. For instance, in Malaysia, coal is expected to play a leading role in meeting the increasing demand of energy in the coming years, at least up to the year 2010. This is partly to ensure that Malaysia has a diversified source of fuel for the energy sector. With a balanced energy mix, the economy and particularly the power sector is less vulnerable to shocks in the fuel supply [1].Although coal has an important role as a source of energy in Malaysia and the world, the combustion of coal faces some challenges. One of the most crucial challenge faced by coal-fired power plants is the emissions of pollutants particularly sulfur dioxide (SO$_2$) into the environment. SO$_2$ is formed when the sulfur in the coal reacts with air during the combustion process. For example, a coal-fired power plant of 600 MW capacity burning coals containing 1.2% sulfur releases 1,785 m^3 h^{-1} (NTP) of SO$_2$ with a concentration of 500 ppm. In order to reduce the emission of SO$_2$ to the environment, appropriate flue gas desulfurization (FGD) technologies must be utilized. Apart from releasing pollutants such as SO$_2$, coal combustion also produce another type of combustion waste, coal fly ash. A 1,400 MW power station burning on coal produce 1.3 million tonnes of coal ash per year, which must be disposed off or utilized in other areas. At the moment, most of the ash produced has to be disposed off, either in landfills or ash ponds, requiring a lot of land areas.

In order to overcome these challenges, flue gas desulfurization process utilizing absorbent synthesized from mixtures of coal fly ash/Ca(OH)$_2$/CaO/CaSO$_4$ has been widely studied. For instance, many studies have shown that when coal fly ash is mixed with Ca(OH)$_2$ or CaO in a hydration process, absorbents with SO$_2$ capture capacity higher than that of hydrated lime can be attained [2-11]. Furthermore, addition of CaSO$_4$ to the preparation mixture has a positive or negative effect on the absorbent desulfurization activity, depending on the preparation conditions [12-14].The extent of SO$_2$ capture by the absorbent derived from coal fly ash/CaO/Ca(OH)$_2$/CaSO$_4$ varies significantly under different desulfurization reaction conditions. Although there have been several reports on the effect of desulfurization conditions on the reactivity of absorbent prepared from coal fly ash, however, the results were not in agreement. Apart from the effect of relative humidity on the reactivity of the absorbent [15-17], the effect of other desulfurization conditions such as reaction temperature and SO$_2$ inlet concentration has led to divergent conclusions, possibility due to the complex composition of the hydrated products/coal fly ash. Garea et al., [15] reported that the influence of SO$_2$ concentration on the reactivity of the absorbent can be describe by a partial reaction order equal to 1, however, Liu et al., [17]

reported that the SO_2 concentration had only slight effects on the initial rate of the desulfurization reaction and negligible effects on the maximum conversion of the absorbent. On the other hand, Chu and Rochelle [18] reported that the temperature dependences of SO_2 removal using hydrated coal fly ash absorbent were not the normally observed for chemical reactions. In their study, they found a threshold temperature for the desulfurization reaction, whereby, when the reaction temperature was below 70°C, the removal activities for the absorbent were not appreciable but above the that temperature, the activities jumped up and stayed constant at higher temperatures. On the other hand, based on the observation by Davini [19], increasing the reaction temperature from 60 to 95°C favors the reactivity of the absorbent in almost a linear way. Liu et al. [17] studied the reactivity of the absorbent within the same range of temperature and they reported only a weak effect of reaction temperature.

These previous results suggest that further study on the effect of different reaction conditions on the desulfurization activity of absorbent prepared from $CaO/Ca(OH)_2/CaSO_4$/coal fly ash is warranted. In this work, we report an experimental investigation of the SO_2 removal by $CaO/CaSO_4$/coal fly ash absorbent under different reactor operating conditions such as different reaction temperature, relative humidity, absorbent particle size and feed concentrations of SO_2. The absorbent was also characterized using X-ray diffraction (XRD) to detect the various phases present in the absorbent before and after the desulfurization reaction.

2   Experimental Section

2.1   Absorbent Preparation and Analysis
The starting materials used to prepare the absorbents were coal fly ash, calcium oxide (CaO) and calcium sulfate ($CaSO_4$). The coal fly ash used in this study was supplied by Kapar Power Plant, Malaysia of Tenaga Nasional Berhad. Its chemical composition was analyzed using Rigaku X-Ray Spectrometer RIX 3000 and was found to consist of 60% SiO_2, 20% Al_2O_3, 4.7% Fe_2O_3, 3.0% CaO, 1.1% K_2O, 1.0% MgO, 7.5% C, 2.4% others and 0.3 % ignition loss. The CaO and $CaSO_4$ used were of laboratory grade supplied from BDH Laboratory Supplies, England.

For the preparation of the absorbent, 5g of CaO was added to 100 ml of distilled water at 90°C. 13.1g of coal fly ash and 7.4g of $CaSO_4$ were then added to the slurry simultaneously. The slurry was heated up to 95°C and maintained at that temperature using a heating thermal mantle for 10 hr for the hydration process to occur. The resulting slurry was then filtered and dried at 200 °C for 2 hr producing dry powder type absorbents. The powder type absorbents were then palletized, crushed and sieved to produce the required particle size range. This preparation conditions was obtained based on the optimization of the absorbent preparation conditions reported elsewhere [20]. In order to detect the various phases present in the absorbents before and after the desulfurization reaction, the absorbents were analyzed using X-ray diffraction (XRD). The XRD analysis was carried out using a Philips PW 1820 X-ray diffractometer with Cu-Kα radiation in the diffraction angle (2θ) range of 5-90° at a sweep rate of 3°/min. The specific surface area the absorbents were determined using the BET method, on an Autosorb 1C Quantachrome analyzer.

2.2   Desulfurization Activity Study
Desulfurization experiments were performed using a fixed bed test rig, as shown in Fig. 1. The reaction zone was contained in a 0.01 m inner diameter stainless steel tube fitted in a furnace for isothermal operation. The absorbent (0.7 g) was packed in the center of the reactor supported by glass wool. A stream of feed gaseous mixture containing 500 to 2000 ppm of SO_2, 500 ppm of NO, 12% of CO_2, 5% of O_2 and balance nitrogen at a reaction temperature of 60 to 80°C was passed through the absorbent. Prior to that, the N_2 gas stream was humidified using a humidification system, which consists of two 250 ml conical flask immersed in a water bath at constant temperature. The total flow rate of the gas stream was controlled at 150 ml/min using mass flow controller. The concentration of SO_2 in the flue gas was measured using a Portable Flue Gas Analyzer IMR2800P before and after the absorption process. The concentration of SO_2 was recorded continuously until 60 min. Two or three replicate measurements were made for each activity test. For clarity, only the averages are presented in this paper. The activity/capacity of the absorbent is reported in terms of percent removal of SO_2 as shown in Equation (1).

$$\text{Percent removal of } SO_2 \, (\%) = \frac{\{[SO_2]_{inlet} - [SO_2]_{outlet}\}}{[SO_2]_{inlet}} \times 100\% \tag{1}$$
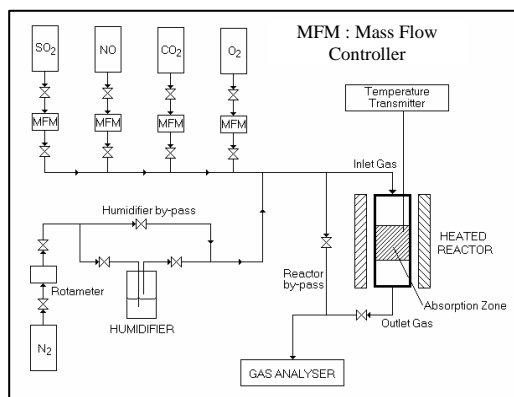
Figure 1: Schematic Diagram of the Experimental Set-up for Fixed Bed Desulfurization

3 RESULTS AND DISCUSSION

3.1 Absorbent Particle Size

Flue gas desulfurization utilizing absorbent synthesized from coal fly ash/CaO/CaSO$_4$ involved a solid-gas reaction between the absorbent and SO$_2$. In a solid-gas reaction, absorbent particle size plays an important role in determining the overall reactivity of the absorbent. In order to study the effect of absorbent particle size on the desulfurization capacity of the absorbent, absorbent with different particle size range were tested for its desulfurization activity. Fig. 2 shows the desulfurization activity of the absorbent at different range of absorbent particle size. The range of the particle size tested were 200 to 250 µm, 250 to 300 µm, 300 to 355 µm, 355 to 425 µm and 500 to 600µm. Absorbent particle size smaller than the 200 to 250 µm range was not studied as it was found to have external mass transfer resistance that block the flow rate of the synthetic flue gas.

From Fig. 2, it was observed that the absorbent with particle size range of 200 to 250 µm and 250 to 300 µm exhibited the highest desulfurization capacity whereby 100% of the feed SO$_2$ was removed for the first 22 min. When the range of the particle size used was increased from the 250 to 300 µm range to the 500 to 600 µm range, the desulfurization capacity of the absorbent dropped. This was reflected by the dropped in the time the absorbent can maintain 100% removal of the feed SO$_2$ (a drop from 22 min to 9 min).
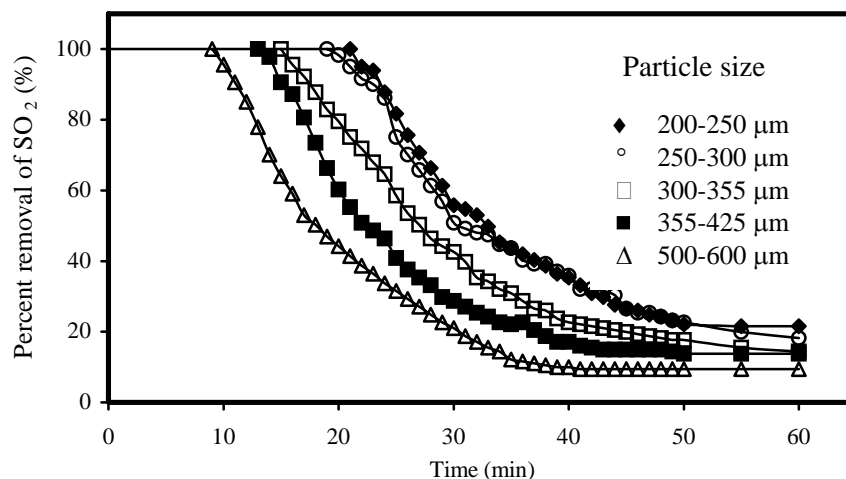

Figure 2: Percent Removal of SO$_2$ vs. Reaction Time at various range of Absorbent Particle Size. Feed Gas Composition at 70 °C and 40% RH: 1000 ppm SO$_2$, 500 ppm NO, 5% O$_2$, 12% CO$_2$, and the balance N$_2$

The drop in the desulfurization capacity at larger absorbent particle size range could be attributed to two reasons; longer interior diffusion path and smaller external specific surface area. When the particle size increases, the interior diffusion path increases as well (longer path within the absorbent molecule for the absorbate (SO$_2$) molecules to penetrate), resulting in slower mass transfer between SO$_2$ and the active sites in the absorbent [21]. Therefore the absorption rate of SO$_2$ decreased causing the absorbent to yield a shorter time for 100% removal of SO$_2$.

It was reported in the literature that the desulfurization activity of hydrated coal fly ash absorbent increases with higher surface area [5,7]. The total specific surface area of the absorbent measured is the sum of the internal surface area and the external surface area. Absorbent with smaller particle size (such as 200 to 250 μm) will have higher external surface area because smaller particles have a greater ratio of surface area to volume. Therefore, higher external surface area will increase the total specific surface area of the absorbent and as a direct consequences, the absorbent will have a higher desulfurization capacity as shown in the result in Fig. 2. In contrast to this, absorbents with bigger particle size (such as 500 to 600 μm) will have smaller external surface area. Therefore, the desulfurization capacity of absorbent with bigger particle size will be lower due to lower total surface area. However, since the desulfurization capacity of the absorbent are almost identical when the range of the particle size is 200 to 250 μm and 250 to 300 μm range, therefore it can be concluded that the effect of external surface area is only significant when the absorbent particle size is greater than 300 μm.

In order to verify further, all the absorbents with the various range of particle sizes were tested for its specific BET surface area. Table 1 shows the results of the surface area measured. The surface area of the particles size ranging from 200 to 250 μm and 250 to 300 μm were found to be almost similar. However, the range of the particles above 300 μm shows that the surface area of the absorbent decreased as the particles size increases. Based on this result, it can be concluded that external surface area contributed significantly to the total surface area of absorbent synthesized from coal fly ash/CaO/CaSO₄. Apart from that, this result also shows that the lower desulfurization capacity of absorbent with bigger particle size is due to the lower surface area (external surface area). It was then decided that the range of the particle size between 200 to 250 μm will be used in the rest of this study.

Table 1: BET Surface Area of the Absorbent at various Particle Size Range

Particle size range (μm)	BET surface area (m^2/g)
200 to 250	64.5
250 to 300	64.1
300 to 355	60.9
355 to 425	56.8
500 to 600	52.2

3.2 Reaction Temperature

Fig. 3 shows the effect of reaction temperature (60-80°C) on the percent removal of SO_2 at a relative humidity of 60% and SO_2 inlet concentration of 2000 ppm. When the temperature was raised by 20 °C from 60 to 80 °C, a rather modest increase in the absorbent's ability to maintain 100% SO_2 removal was observed. This results suggests that chemical reaction is not the rate limiting step for the reaction between SO_2 and the absorbent. This observation corroborates the finding of Liu et al. [17] and Chu and Rochelle [18].
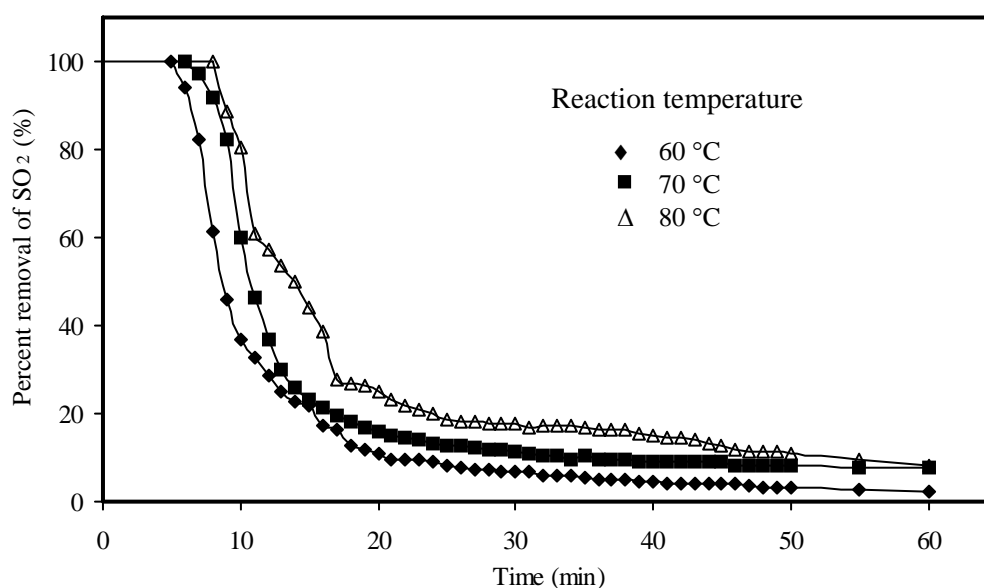

Figure 3: Percent Removal of SO_2 vs. Reaction Time at various Reaction Temperature. Feed Gas Composition at 60 to 80°C and 60% RH: 2000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2

3.3   Relative humidity

The effect of relative humidity (50-70%) on the percent removal of SO_2 at a reaction temperature of 80 °C and SO_2 inlet concentration of 2000 ppm is shown in Fig. 4. It is evident that a higher relative humidity resulted in a longer period of 100% SO_2 removal. For instance, when the relative humidity was increased from 50 to 70%, the period of 100% SO_2 removal increased almost two-fold from 6 to 14 min. The positive effect of relative humidity is believed to be due to water sorption on the absorbent surface which plays an important role in the reaction between the absorbent and SO_2. Fig. 5 shows a schematic diagram of several fundamental processes taking place in a layer of water adsorbed on the absorbent surface proposed by Liu et al. [17]. The amount of water in the monolayer increases with increasing relative humidity in the feed gas which in turn enhances the formation of active species such as Ca^{2+}, OH^-, and SO_3^{2-} ions. The presence of these ions promotes the reaction between the absorbent and SO_2, leading to higher SO_2 removal.
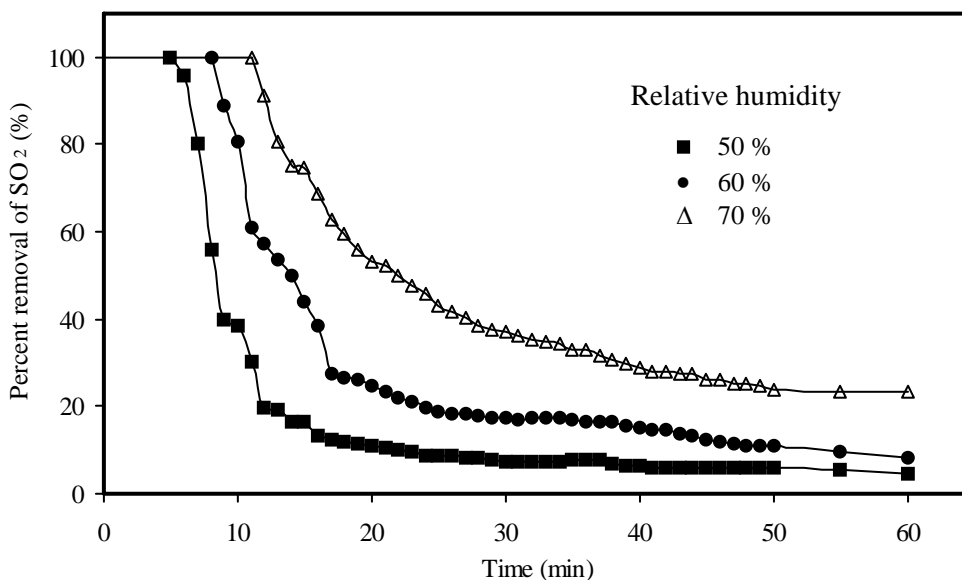

Figure 4: Percent Removal of SO_2 vs. Reaction Time at various Relative Humidity. Feed Gas Composition at 80 °C and 60 to 80% RH: 2000 ppm SO_2, 500 ppm NO, 5% O_2, 12% CO_2, and the balance N_2
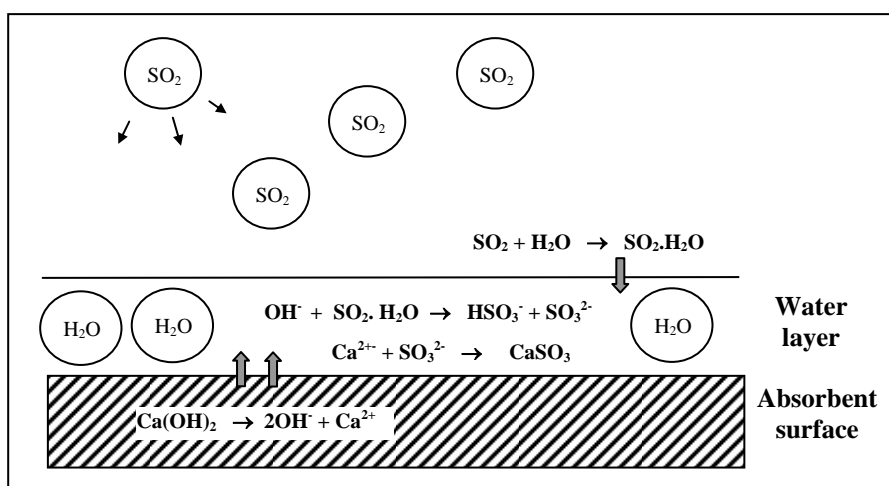

Figure 5: Schematic Representation of the Possible Sulfation Reactions taking place in a Layer of Water Formed on Absorbent Surface

3.4   Feed Concentration of SO$_2$

From the percent removal of SO$_2$ curves obtained for different feed concentration of SO$_2$ ranging from 500 to 2000 ppm at constant reaction temperature and relative humidity, it was observed that the absorbent capacity in absorbing SO$_2$ decreased with increasing feed concentration of SO$_2$. The decrease in the desulfurization capacity of the absorbent was a direct consequence of exposing a fixed amount of absorbent to increasing SO$_2$ concentration in the feed gas. At a higher feed concentration of SO$_2$, the number of SO$_2$ molecules available for surface absorption of SO$_2$ will also be high, as compared with lower feed concentration of SO$_2$. As a result, more active sites available for absorption on the absorbent surface were occupied, thus causing a limitation of the total active sites capable of absorbing SO$_2$. Therefore only limited number of molecules were absorbed and the remaining SO$_2$ molecules were passed through the reactor un-reacted. This caused the percent removal of SO$_2$ to remain at minimum values when the feed concentration of SO$_2$ was high. Whereas, when the feed concentration of SO$_2$ in the flue gas was lower, the active sites on the surface of the absorbent were sufficient to sustain the lower number of SO$_2$ molecules available for reaction. Therefore, the desulfurization reaction would be at optimum level as less active sites would be occupied by the SO$_2$ molecules and deactivation rate was kept at minimum level.
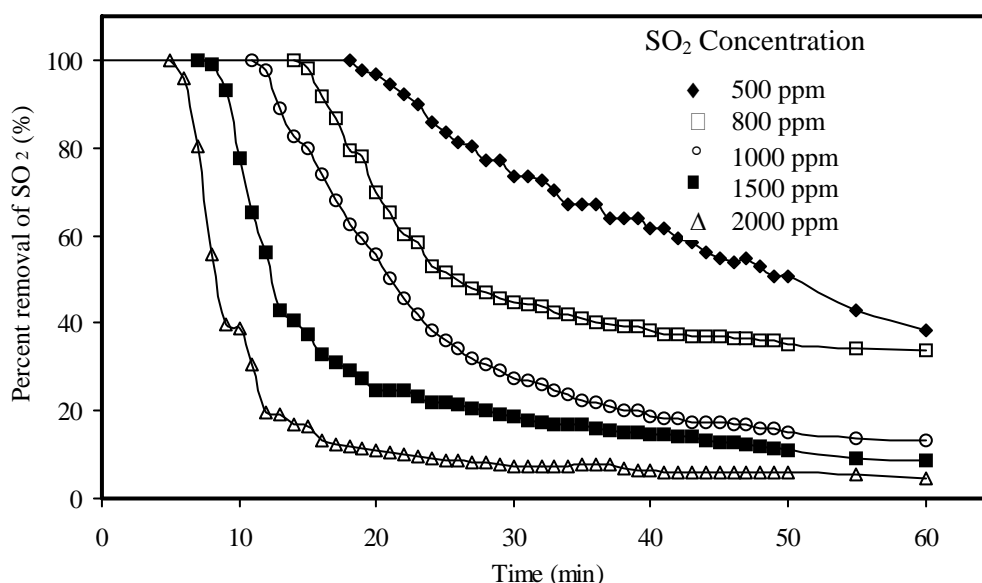

Figure 6: Percent Removal of SO$_2$ vs. Reaction Time at various Reaction Temperature. Feed Gas Composition at 80°C and 50% RH: 500 to 2000 ppm SO$_2$, 500 ppm NO, 5% O$_2$, 12% CO$_2$, and the balance N$_2$

3.5   XRD Analysis

The chemical composition of the absorbent before and after desulfurization reaction was studied through X-Ray Diffraction (XRD) analysis. The XRD spectrum are shown in Fig. 7a and b respectively. The peaks of the various phases detected in the absorbent were assigned as follows: peaks a (calcium aluminate silicate hydrate compound, $Ca_2(Si_9Al_3)O_{24} \bullet 8H_2O$), peaks b (calcium carbonate, $CaCO_3$), peaks d (calcium sulfate, $CaSO_4$) peaks j (aluminate silicate hydrate, $Al_4Si_2O_{10}.H_2O$). Fig. 7a shows that the phases detected in the fresh absorbent were $Ca_2(Si_9Al_3)O_{24} \bullet 8H_2O$, $CaCO_3$ and $CaSO_4$. The absence of SiO_2, the main component in the coal fly ash, suggests that they have reacted completely to form $Ca_2(Si_9Al_3)O_{24} \bullet 8H_2O$. After desulfurization, Fig. 7b shows noticeable changes in the spectrum of the absorbent. It can be seen that peaks a became weaker, indicating that $Ca_2(Si_9Al_3)O_{24} \bullet 8H_2O$ was converted to other chemical form. Since the intensity of peaks d for $CaSO_4$ increased and there was a presence of a new phase, $Al_4Si_2O_{10}.H_2O$ detected, it may be concluded that $Ca_2(Si_9Al_3)O_{24} \bullet 8H_2O$ reacted with SO$_2$ to produce $Al_4Si_2O_{10}.H_2O$ and $CaSO_4$.
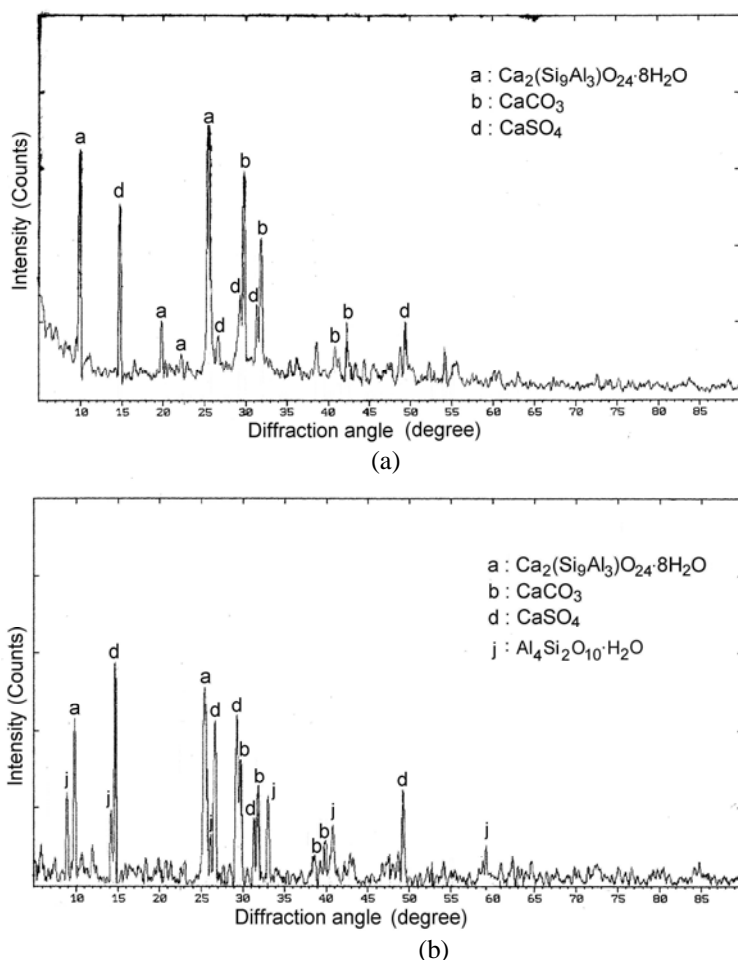
Figure 7: XRD Spectrum of the Absorbent (a) Before and (b) After Desulfurization Reaction

4   CONCLUSION

The desulfurization activity/capacity of absorbents synthesized from coal fly ash/CaO/CaSO$_4$ was evaluated using a fixed bed reactor. The desulfurization activity/capacity of the fly ash/CaO/CaSO$_4$ absorbent was found to increase with higher relative humidity but with lower SO$_2$ inlet concentration and absorbent particle size. The reaction temperature was found to have negligible effect on the desulfurization activity. XRD analysis confirmed that SO$_2$ was absorbed into the absorbent in the form of sulfate salts.

REFERENCES

1. Thaddeus J., Complementary roles of natural gas and coal in Malaysia, Proceedings of The 8th APEC Coal Flow Seminar/9th APEC Clean Fossil Energy Technical Seminar/4th APEC Coal Trade, Investment, Liberalization and Facilitation Workshop, Kuala Lumpur, Malaysia, March, 2002.
2. Fernandez F, Renedo MJ, Garea A, Viguri J and Irabien JA, Preparation and characterization of fly ash/hydrated lime sorbents for SO$_2$ removal, *Powder Technology*, Vol. 94, pp133-139, 1997.
3. Garea A, Fernandez I, Viguri JR, Ortiz MI, Fernandez J, Renedo MJ and Irabien JA, Fly-ash/calcium hydroxide mixtures for SO$_2$ removal: structural properties and maximum yield, *Chemical Engineering Journal*, Vol. 66, pp171-179, 1997.
4. Ishizuka T, Tsuchiai H, Murayama T, Tanaka T and Hattori H, Preparation of active absorbent for dry-type flue gas desulfurization from calcium oxide, coal fly ash and gypsum, *Industrial Engineering Chemistry Research*, Vol. 39, pp1390-1396, 2000.
5. Lin BL, Shih SM and Liu CF, Structural properties and reactivities of Ca(OH)$_2$/fly ash sorbents for flue gas desulfurization, *Industrial Engineering Chemistry Research*, Vol. 42, pp1350-1356, 2003.

6. Karatepe N, Mericboyu AE and Kucukbayrak S, Effect of hydration conditions on the physical properties of fly ash/Ca(OH)$_2$ sorbents, *Energy Sources*, Vol. 20, pp505-511, 1997.
7. Karatepe N, Ersoy-Maricboyu A, Demirler U and Kucukbayrak S, Determination of the reactivity of Ca(OH)$_2$ fly ash sorbents for SO$_2$ removal from flue gases, *Thermochima Acta*, Vol. 319, pp171-176, 1998.
8. Karatepe N, Ersoy-Maricboyu A and Kucukbayrak S, Activation of Ca(OH)$_2$ using different siliceous materials, *Environment Technology*, Vol. 20, pp377-385, 1999.
9. Renedo MJ, Fernandez J, Garea A, Ayerbe A and Irabien JA, Microstructural changes in the desulfurization reaction at low temperature, *Industrial Engineering Chemistry Research*, Vol. 38, pp1384-1390, 1999.
10. Renedo MJ and Fernandez J, Preparation, characterization and calcium utilization of fly ash/Ca(OH)$_2$ sorbents for dry desulfurization at low temperature, *Industrial Engineering Chemistry Research*, Vol. 41 pp2412-2417, 2002.
11. Tsuchiai H, Ishizuka T, Ueno T, Hattori H and Kita H, Highly active absorbent for SO$_2$ removal prepared from coal fly ash, *Industrial Engineering Chemistry Research*, Vol. 34, pp1404-1411, 1995.
12. Fernandez J, Renedo MJ, Pesquera A and Irabien JA, Effect of CaSO$_4$ on the structure and use of Ca(OH)$_2$/fly ash sorbents for SO$_2$ removal, *Powder Technology*, Vol. 119, pp201-205, 2001.
13. Fernandez J and Renedo MJ, Study of the influence of calcium sulfate on fly ash/Ca(OH)$_2$ sorbents for flue gas desulfurization, *Energy Fuels*, Vol. 17, pp1330-1337, 2003.
14. Ishizuka T, Yamamoto T, Murayama T, Tanaka T and Hattori H, Effect of calcium sulfate addition on the activity of the absorbent for dry flue gas desulfurization, *Energy Fuels*, Vol. 15, pp438-443, 2001.
15. Garea A, Viguri JR and Irabien A, Kinetics of flue gas desulfurization at low temperatures: fly ash/calcium (3/1) sorbent behavior, *Chemical Engineering Science*, Vol. 52, pp715-732, 1997.
16. Karatepe N, Ersoy-Mericboyu A, Yavuz R and Kucukbayrak S, Kinetic model for desulfurization at low temperatures using hydrated sorbent, *Thermochima Acta*, Vol. 335, pp127-134, 1999.
17. Liu CF, Shih SM and Lin RB, Kinetics of the reaction of Ca(OH)$_2$/fly ash sorbent with SO$_2$ at low temperatures, *Chemical Engineering Science*, Vol. 57, pp93-104, 2002.
18. Chu P and Rochelle G, Removal of SO$_2$ and NO$_x$ from stack gas by reaction with calcium hydroxide solids, *Journal of Air Pollution Control Association,* Vol. 39, pp175, 1989.
19. Davini P, Investigation of the SO$_2$ adsorption properties of Ca(OH)$_2$-fly ash systems, *Fuel,* Vol. 75, pp713-716, 1996.
20. Lee KT, Flue gas desulfurization studies using absorbent prepared from coal fly ash. *PhD thesis*, School of Chemical Engineering, Universiti Sains Malaysia, Penang, Malaysia, 2004.
21. Guo J and Lua AC, Adsorption of sulphur dioxide onto activated carbon prepared from oil-palm shells with and without pre-impregnation, *Separation and Purification Technology*, Vol. 30, pp265-273, 2003.