Preparation and characterization of absorbent prepared from coal fly ash for sulfur dioxide (SO$_2$) removal

Lee Keat Teong, Subhash Bhatia and Abdul Rahman Mohamed

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, Seberang Perai Selatan, Penang, Malaysia.

Abstract

Active absorbent for flue gas desulfurization was prepared from coal fly ash, calcium oxide and calcium sulfate by steam hydration. The absorbent was examined for its macro and micro-structural properties. The effect of various absorbent preparation variables ; hydration period, ratio of CaO to fly ash, amount of CaSO$_4$ used and drying temperature towards the BET (Brunauer-Emmett-Teller) specific surface area of the absorbent were studied. The BET surface area obtained ranges from 18.9 – 86.4 m^2/g. Based on the results, it was concluded that absorbents prepared from steam hydration has a higher sulfur dioxide (SO$_2$) adsorption activity as compared to absorbents prepared using the more common water hydration method. X-ray diffraction showed that calcium aluminum silicate hydrate and calcium carbonate formed during the hydration process are converted into aluminum silicate hydrate and calcium sulfate after reacting with SO$_2$. SEM analysis showed the macro-structural property of coal fly ash, hydrated absorbent and the absorbent after reacting with SO$_2$.

Keywords

Absorbent; Characterization; Coal fly ash; Design of experiment; Desulfurization.

Introduction

In the effort to protect the environment, industrial operations are required to reduce its emission of sulfur dioxide (SO$_2$). SO$_2$, with an acidic and toxic characteristic, is the primary cause of acid rain and can cause harmful effect towards vegetation and human health. The primary source of SO$_2$ comes from boilers running on solid and liquid fuels. This is due to the nature of the fuel, where the sulfur compound present in the fuel will react with air to form SO$_2$ during combustion process in the boiler. Presently, different types of flue gas desulfurization (FGD) units are being operated. At the moment, a wet-type FGD unit based on a limestone-gypsum method is most widely used and suitable for large-scale boilers such as those installed in coal-or oil-fired power stations. However, this process has its disadvantages which include the large space needed for installation, the large volume of water required and the high capital and operating expenses.

On the other hand, utilization of coal fly ash in the preparation of absorbents for dry FDG systems presents advantages both economically and environmentally. Coal fly ash, a waste product from coal power plants, has no commercial value

5-012 (O)

Proceedings of the
2ⁿᵈ Regional Conference on Energy Technology Towards a Clean Environment
12-14 February 2003, Phuket, Thailand

except for making building materials. At the moment, most of the ash produced has to be disposed off, either in landfills or ash ponds. This method of ash disposal requires a lot of land area, which is not easily available in urban areas. However, when it is used to synthesized the absorbent, it will be converted into gypsum, a raw material used in the manufacturing of building materials, deodorant, coagulating agent and fertilizer upon absorbing SO_2. The active absorbent is due to the pozzolanic reaction that takes place between fly ash and calcium oxide/calcium hydroxide which yield compounds with higher surface area such as calcium silicates and calcium aluminates [1-7]. At the moment, in the literature, the most common method used in the preparation of the absorbent is by using water hydration, where the raw materials are mixed in excess water. However, reports on other preparation method such as steam and pressurized hydration are still limited.

In the present study, absorbents prepared from coal fly ash using steam hydration was investigated. The effect of various absorbent preparation variables such as hydration period (x_1), ratio of calcium oxide (CaO) to fly ash (x_2), amount of calcium sulfate ($CaSO_4$) used (x_3) and drying temperature (x_4) towards the BET surface area of the absorbent were studied. Design of Experiments (DOE) based on full factorial design of 2^4 will be used in the present study to establish the significance of each independent variables and interaction between variables on the BET surface area of the absorbent. XRD (X-Ray Diffraction) was used to identify the various phases present in the absorbent before and after reacting with SO_2 while SEM (Scanning Electron Micrograph) analysis was used to observe the macro-structural properties of the absorbent. The activity of the absorbent was compared with those reported in literature.

Materials and Methods

The absorbents were prepared from calcium sulfate, calcium oxide and coal fly ash. The calcium sulfate used was of reagent grade, whereas the calcium oxide used was of laboratory grade (BDH Laboratory Supplies, England). The coal fly ash was supplied by Kapar Power Plant, Malaysia of Tenaga Nasional Berhad. The fly ash used was thoroughly sieved, to obtain average sizes smaller than 75 μm. The fly ash has the following composition: SiO_2 42.0%, Al_2O_3 19.0%, CaO 4.6%, Fe_2O_3 9.6%, MgO 2.1%, NaO 1.6% and ignition loss 21.1%. Standard procedure to prepare the absorbent is as follow. To prepare 20 g of the absorbent (dry weight), a mixture of coal fly ash (50 % of the total used) and calcium oxide was mix with 28 – 35 % of water at 70 °C for 5 minutes. Then calcium sulfate and the rest of the coal fly ash were added into the slurry and kneading was continued for 10 minutes. The kneaded materials were then extruded to form pellets and were subjected to hydrothermal treatment with steam for a specific period of time followed by drying for 2 hours at a specific temperature. The amount of chemicals used and experimental parameters are given in Table 1.

The activity test was carried out in a fixed bed reactor made of 13 cm (outer diameter) stainless steel tube fitted in a furnace under isothermal condition (100 °C). The absorbent (1 g) was packed in the center of the reactor supported by

5-012 (O)

Proceedings of the
2nd Regional Conference on Energy Technology Towards a Clean Environment
12-14 February 2003, Phuket, Thailand

glass wool. The particle size distribution of the absorbent was in the range of 180 – 250 μm. A gas stream of 4000 ppm of SO_2 and N_2 as the balance was passed through the absorbent until the reading of SO_2 concentration in the Portable Flue Gas Analyzer Enerac 2000E is constant. The absorbents were analyzed for its BET specific surface area using Autosorb 1C Quantachrome. XRD patterns were recorded on a Philips PW 1820 system for the powdered samples with Cu-Kα radiation in the range of diffraction angle (2θ) 5°-90° at a sweep rate of 3 deg/min. SEM image were taken with Leica Cambridge S360 with 15 kV of accelerating voltage.

Table 1. Experimental design matrix and results

Solid code	Experimental variables				Surface area (m²/g)	Solid code	Experimental variables				Surface area (m²/g)
	x_1	x_2	x_3	x_4			x_1	x_2	x_3	x_4	
S1	4	2:1	3	200	30.1	S11	4	1:2	3	500	42.0
S2	10	2:1	3	200	46.5	S12	10	1:2	3	500	54.8
S3	4	1:2	3	200	58.9	S13	4	2:1	6	500	19.7
S4	*10*	*1:2*	*3*	*200*	*86.4*	S14	10	2:1	6	500	21.2
S5	4	2:1	6	200	21.6	S15	4	1:2	6	500	33.4
S6	10	2:1	6	200	24.0	S16	10	1:2	6	500	58.4
S7	4	1:2	6	200	54.1	S17-I	7	1 : 1	4.5	350	55.5
S8	10	1:2	6	200	59.7	S17-II	7	1 : 1	4.5	350	57.0
S9	4	2:1	3	500	18.9	S17-III	7	1 : 1	4.5	350	51.7
S10	10	2:1	3	500	42.0	S17-IV	7	1 : 1	4.5	350	56.2

Results and Discussion

Table 1 presents the 2^4 full factorial design matrix of 16 experiments, covering full design of two level factors used in this study. All the experiments were performed in a random manner to minimize personal bias. Experiment 17-I to 17-IV at the center point of the experimental design were performed in order to determine the experimental error. As the results of these 4 runs are quite consistence, single replicate experiment are essential for this study.

In relation to the results of BET specific surface area tabulated in Table 1, it was found that the values obtained ranges from 18.9 m²/g to 86.4 m²/g, with the highest value of 86.4 m²/g corresponding to the experiment S4 performed at hydration period of 10 hrs., CaO to fly ash ratio of 1:2, 3g of $CaSO_4$ used and drying temperature of 200°C. Comparing the range of absorbent surface area obtained in this work with those reported in the literature [7], where the absorbents are prepared from water hydration (9.8 m²/g to 44.5 m²/g), it was found that absorbents prepared from steam hydration method yield absorbents with higher surface area. Apart from that, it was observed that higher hydration period and higher fly ash ratio resulted in absorbents with higher BET surface area, while increasing the drying temperature had a negative effect. However, the amount of calcium sulfate ($CaSO_4$) used in the preparation of the absorbent have mix effect on the BET surface area. These results are similar to those reported in our previous paper [5].

Figure 1 shows the breakthrough curves (the ratio of SO_2 concentration to the initial SO_2 concentration, C/C_o) for absorbent (J-1) prepared by coal fly ash and calcium hydroxide as reported by Garea et. al. [2], inert silica sand and prepared absorbent (S4). For comparison purposes, the activity study carried out in this work is in accordance to those reported by Garea et. al. [2]. From the figure, it is clear that the absorbent prepared in this work gives a higher SO_2 removal activity as compared to the absorbent reported. For absorbent S4, SO_2 was completed remove from the flue gas in the first 7 minutes. From that point, the concentration of SO_2 gradually increases until there was no more SO_2 adsorption activity (when the outlet SO_2 concentration in the outlet flue gas is the same as the inlet concentration).
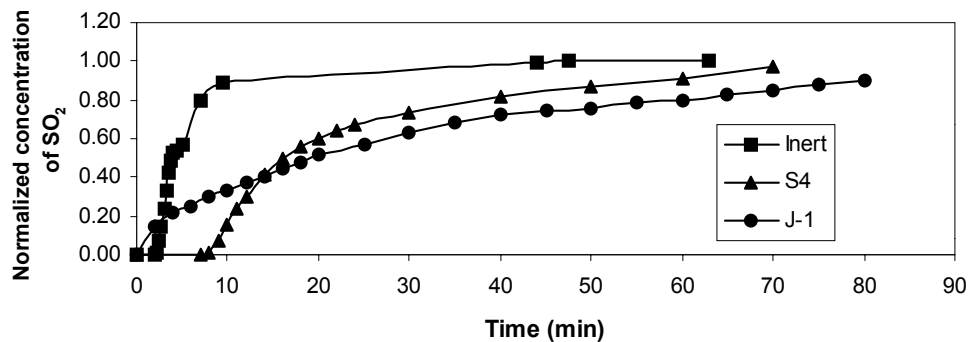

Figure 1. Breakthrough curves for inert, S4 and reported absorbent (J-1)

To study the significance of each independent variables and interaction between variables on the BET surface area, the data of the factorial design was fitted to a multiple linear equation as in Equation (1) :

$$S = \beta_o + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_i \sum_j^i \beta_{ij} x_i x_j + \varepsilon \qquad (1)$$

where S is the specific surface area in m^2/g (the dependent variable), and x_i (x_1, x_2, x_3 and x_4) are the experimental variables studied (the independent variables). The values of the unknown coefficients were determined based on the "YATES' algorithm, while the significance of the independent variables and interaction between variables on the BET surface area of the absorbent is determined using analysis of variance (confidence level of 99%). The calculations were carried out using Design-Expert 6.0.4 software [8]. Comparing the experimental F values with the theoretical F values for the independent variables, it was deduced that all the independent variables ; hydration period (x_1), ratio of CaO to fly ash (x_2), amount of $CaSO_4$ added into the absorbent (x_3) and drying temperature (x_4) were the significant independent variables. On top of that, the following interaction between variables ; hydration period and amount of $CaSO_4$ added into the absorbent ($x_1 x_3$) and ratio of CaO to fly ash and drying temperature ($x_2 x_4$) were also significant. It was found that there is no high order interaction between factors that effects the BET surface area of the absorbent.

5-012 (O)

Proceedings of the
2nd Regional Conference on Energy Technology Towards a Clean Environment
12-14 February 2003, Phuket, Thailand

Figure 2 (a) and (b) shows the XRD pattern for the prepared absorbent (S4) and the same absorbent after subjected to SO_2 in the activity test, respectively. From the diffraction spectrum, it can be deduced that there are 4 main phases present in the absorbent (S4) which are, calcium aluminum silicate hydrate $(Ca_2(Si_9Al_3)O_{24} \cdot 8H_2O)$, calcium carbonate $(CaCO_3)$, calcium oxide (CaO) and calcium sulfate $(CaSO_4)$. The formation of calcium aluminum silicate hydrate and calcium carbonate are from the hydration process while calcium oxide and calcium sulfate are the un-reacted raw materials. Calcium aluminum silicate hydrate compound is believed to be the main component in absorbing SO_2. The absence of silica (SiO_2) and alumina (Al_2O_3) (the main component in coal fly ash) in S4 shows that it reacts completely with calcium oxide to form calcium aluminum silicate hydrate. On the other hand, from the spectrum shown in Figure 2 (b), there were only 2 main phases present in absorbent after reacting with SO_2, which are aluminum silicate hydrate $(Al_4Si_2O_{10} \cdot H_2O)$ and calcium sulfate $(CaSO_4)$. This shows that all the calcium species present in the absorbent reacted with sulfur dioxide to form calcium sulfate. Aluminum silicate hydrate is the remains of calcium aluminum silicate hydrate after reacting with sulfur dioxide. From the XRD results, it can be concluded that the products from the hydrothermal reaction of calcium oxide and coal fly ash $(Ca_2(Si_9Al_3)O_{24} \cdot 8H_2O)$ does not take part in the sulfur dioxide adsorption reaction, but it merely exposed more Ca ions to sulfur dioxide (for the adsorption reaction to occur) as it has a higher surface area.
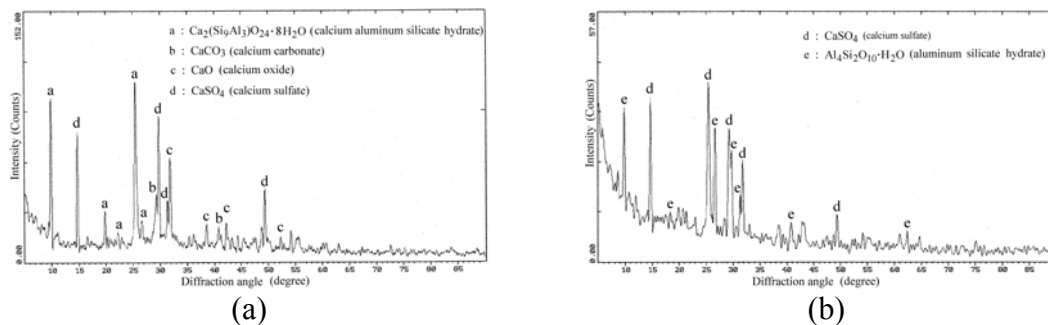

(a)   (b)

Figure 2. XRD pattern for (a) prepared absorbent and (b) after activity test

SEM micrographs of coal fly ash, absorbent S4 (5000X & 10000X magnification) and absorbent S4 after subjected to sulfur dioxide in the activity test are shown in Figure 3 (a), (b), (c) and (d) respectively. SEM micrographs of coal fly ash shows that it consists mostly of spherical particles of different sizes with smooth surface. However, from Figure 3 (b), it was observed that in the hydrated coal fly ash with calcium oxide and calcium sulfate, the spherical particles were no longer seen in the SEM micrographs. Instead, particles with irregular shapes were observed. Higher magnification of the irregular shapes particles, as shown in Figure 3 (c), revealed that the hydration process resulted in absorbent with higher structural porosity. This suggests that the spherical coal fly ash reacted so extensively with calcium oxide that not only the surface layers of the spherical particles but also the inside of the particles could not retain their original shapes [3]. On the other hand, after reacting with SO_2 (Figure 3 (d)), the porous structure of the absorbent

5-012 (O)

Proceedings of the
2nd Regional Conference on Energy Technology Towards a Clean Environment
12-14 February 2003, Phuket, Thailand

is no longer observed as it is covered by a layer of product, believed to be calcium sulfate.

Conclusions

Based on the results, it was concluded that absorbents prepared from steam hydration has a higher surface area (leading to higher SO_2 adsorption activity) as compared to absorbents prepared using water hydration. Apart from that, it was concluded that there is a strong influence of all the factors studied on the absorbent surface area. However, there were no high order interaction between factors that effect the absorbent surface area except for interaction between factor x_1x_3 and x_2x_4. XRD pattern confirmed the formation of calcium sulfate from the reaction between the absorbent and SO_2 while SEM micrographs confirmed the formation of absorbent with high structural porosity (calcium aluminum silicate hydrate).
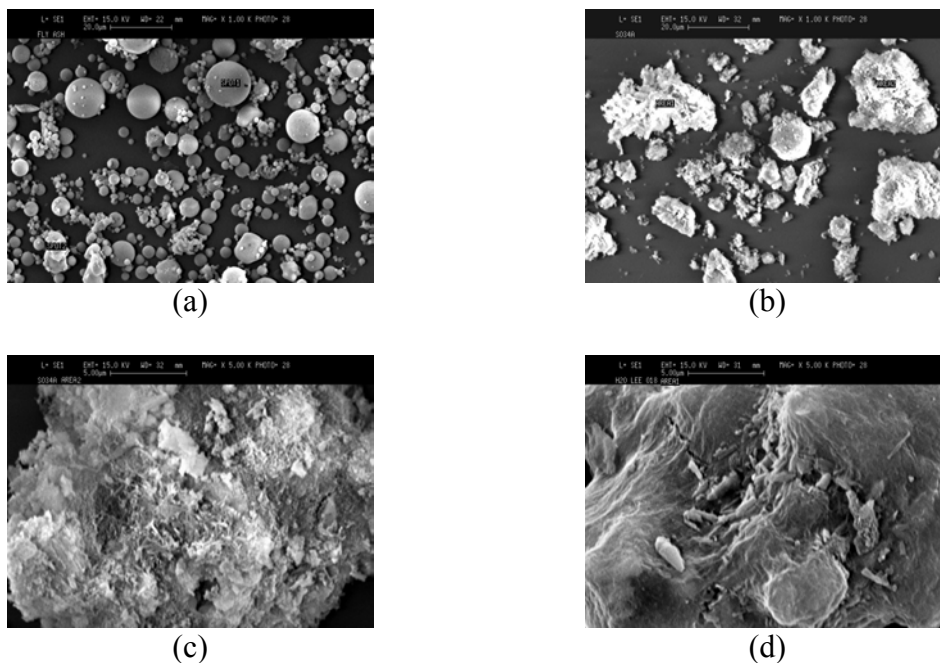

(a)

(b)

(c)

(d)

Figure 3. SEM micrographs of (a) coal fly ash, (b) absorbent S4 (5000X magnification), (c) absorbent S4 (10000X magnification) and (d) after activity test

Acknowledgement

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