Philippine Engineering Journal (1999) XIX (2): 43-62

HIGHLY ACTIVE ABSORBENT FOR SO2 REMOVAL PREPARED FROM COAL ASH (PART 2)

C.G. Magpantay, H.H. Bion, T.A. Quilao, W.A. Balais,
A.B. Herrera, E.M. Alcoba, F.I. Abarquez, D.L. Pugal, and T. Ogata
Fuels and Energy Division
Industrial Technology Development Institute
Bicutan, Taguig, Metro Manila

and

K. Yamada
Hokkaido National Industrial Research Institute
Hokkaido, Sapporo, Japan

ABSTRACT

This paper is a sequel of previous study (Part I) on the preparation of highly active absorbents for SO_2 *removal from coal ash and limestone. The prepared absorbent from coal fly ash was tested for its desulfurization activity at varying conditions using the experimental* SO_2 *absorption analyzer. Simulated flue gas moisture used was composed of* SO_2*,, NO,* CO_2 *,* O_2 *and* H_2O*. The activity of the produced absorbent closely depends on the method of preparation taking into account the effect of time and temperature for curing and drying. The effects of particle size, surface area and % glass content were correlated with the* SO_2 *removal efficiency. The produced absorbent exhibited high efficiency not only for* SO_2 *but also for NO removal at temperatures ranging from 100-165*^{0}*C of the gas mixture. NO serves as catalyst in the oxidation of* SO_2 *to* SO_2 *forming ettringite [*$Ca_6Al_2(SO_4)_3(OH)_{12}25H_2O$ *or* $6CaOAl_2O_33SO_331H_2O$*) and* $CaSO_4$ *in the spent absorbent.*

I. Introduction

Coal is a principal indigenous energy resource in the Philippines. Coal production and consumption have steadily increased during the last five years as a result of the government's strong coal conversion and coal development program. As projected in the Energy Plan (1994-2010), coal generating capacity is expected to reach 18,000 MW by the end of 2010.

At present, the Philippines has four (4) existing coal fired thermal power plants located in Calaca, Batangas; Cebu and Pagbilao, Quezon with a total rated capacity of 1441 MW, generating about 1 million metric tons.

Ash from the combustion of coal in electric utility boilers is one of the major wastes produced by the industry. Disposal of these materials is a major problem, however they can be potentially useful. Lately, there has been numerous research on coal ash conversion and utilization not only to protect the environment but also to produce value added products. The Industrial Technology Development Institute (ITDI) of the Department of Science and Technology through the Fuels and Energy Division (FED) had entered into a joint collaboration with Hokkaido National Industrial Research Institute (HNIRI) to conduct a research project on the production of highly active absorbent for SO_2 removal from coal ash. This project is being implemented within the framework of the Institute for Transfer of Industrial Technology (ITIT) Program organized by the International Research and Development Cooperation Division, Agency of Industrial Science and Technology (AIST), Ministry of International Trade and Industry.

Based on the results in Part I, it was concluded that among the coal ashes, fly ash is the most appropriate raw material for the preparation of highly active absorbent for SO_2 removal. [6] This paper aims to evaluate the produced absorbent from fly ash based on its SO_2 removal efficiency at varying conditions namely:

- Effect of curing time on surface area
- Effect of curing temperature
- Effect of particle size
- Effect of drying temperature
- Effect of mixed gas temperature
- Effect of glass content
- Effect of SO_2 concentration on SO_2 absorption rate

II. Experimental Procedure

2.1 Preparation of Absorbent

The preparation of absorbent was carried out by mixing fly ash (80 wt.%) and $CaCO_3$ (CaO:20 wt.%) with water and CO_2. The resulting slurry was kept overnight and cured with constant stirring at 80°C and 120°C for 5 to 20 hours. The absorbent was dried at 100 ~ 400°C for 2 hours. The dried absorbent was crushed and screened according to sizes (0.5 ~ 5 mm). Table 1 and Figure 1 show the basic conditions and schematic diagram on the preparation of SO_2 absorbent respectively.

2.1 Characterization of the SO_2 Absorbent

The testing of the prepared absorbent was carried out by using the experimental SO_2 Absorption Analyzer shown in Figure 2. Five (5) - gram sample of absorbent was placed in a sample holder enclosed in a temperature-controlled reactor at 165°C using the thermocouple. Simulated flue gas mixture whose composition is given in Table 2, is composed of SO_2, NO, CO_2, O_2, H_2O and N_2 as the balance gas. The gas after being mixed in a gas mixer flows from the reactor at $SV=162h^{-1}$. The tested gas passed through a special type of moisture remover and analyzed simultaneously in SO_2, NO_x, CO_2 and O_2 analyzers. Gas leaks are being monitored through a pressure drop in the manometer.

Table 1

Preparation Conditions of SO_2 Absorbent

Combination of raw materials	Coal ash: 80 wt% CaO ($CaCO_3$): 20 wt%
Curing condition	Reaction temperature: 80 ~ 120°C Reaction time 5 ~ 20 hours
Drying temperature 100 ~ 400°C	Drying time: 2 hours

Table 2

SO_2 Absorption Condition

SO_2	150 ~ 900 ppm
NO	450 ppm
CO_2	13%
O_2	6%
H_2O	10%
Weight of absorbent 5 g	

III. Discussion of Results

3.1 SO_2 and NO Absorption Characteristics of Absorbent

The SO_2 and NO_x absorption characteristics of the absorbent are shown in Figure 3 indicate that the produced absorbent exhibits higher activity not only for SO_2 but also for NO removal. The aforecited absorbent had very strong affinity to NO that its activity was of short duration. For SO_2, 98% removal efficiency and longer activity at about 4.5 hours was observed. The reaction of SO_2 with absorbent results in the formation of ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12}25H_2O$ *or* $6CaOAl_2O_33SO_331H_2O$ and $CaSO_4$ as shown in the X-ray diffraction. [6]

3.2 Effect of Curing Time on the Surface Area of Absorbent

The surface area of absorbent represents the area of the surface in square meter per gram of sample (m^2/g). As shown in Figure 4, at curing time of 5 hours, both samples cured at 120°C and 80°C showed gradual increase in surface area up to 10 hours and had the same activity up to 18 hours. However, absorbent cured at 120°C had more surface area of about 55 m^2/g than those cured at 80°C of about 38 m^2/g. (Ueno, [8]) found out that absorbent cured at higher temperature have more surface area due to the formation of micro porous structures in the absorbent.

3.3 Effect of Curing Temperature on the SO_2 Removal Efficiency of Absorbent

The same trend in Figure 4 can be observed in Figure 5. At higher curing temperature, higher SO_2 removal efficiency can be obtained. Samples cured for 5 hours at 70°C had SO_2 removal efficiency of 15% which gradually increased up to 45% at 120°C. Absorbent cured for 10 hours had 45% SO_2 removal efficiency at 70°C and had its maximum activity of 98% at 120°C curing temperature. Figure 5 shows that the optimum curing temperature for absorbent should be at 120°C for 10 hours.

3.4 Effect of Particle Size on the SO_2 Removal Efficiency of Absorbent

Generally, absorbent of smaller particle sizes shows higher SO_2 removal efficiency than absorbent of bigger particle sizes. Small particles exhibit more surface area and higher efficiency. Figure 6 shows the comparative effects of particle size on the SO_2 removal efficiency of absorbent, cured and dried at varying temperatures. Absorbent with particle sizes ranging from 0.5 ~ 5 mm, cured at 120°C and dried at 200°C had the highest SO_2 removal efficiency followed by absorbent cured at 120°C but dried at 150°C. By projecting the trend in Figure 6, the particle size could be used as a basis for the targeted SO_2 removal requirement for certain applications. It can also be mentioned that for large scale production of absorbent such as in pilot/commercialization, bigger particles can be considered due to ease in handling and operation since low space velocity (SV) requirement will be needed.

The same trend was also observed with absorbent cured at 80°C with drying temperature of 200°C and 150°C. It can be observed that absorbent cured at 80°C and dried at 200°C exhibited higher SO_2 removal efficiency than those dried at 150°C.

3.5 Effect of Drying Temperature and Surface Area on SO_2 Removal Efficiency

The drying temperature affects much the activity of the absorbent. The variation of the activity of the SO_2 absorbent as a function of the drying temperature is shown in Figure 7. The activity of the absorbent, both cured at 120°C and 80°C markedly increased with an increase in drying temperatures ranging from 100 ~ 200°C. Beyond 220°C, SO_2 removal efficiency gradually decreases. Absorbents cured at 120°C showed a maximum efficiency of 98% at 250°C drying temperature but absorbent cured at 80°C had lower SO_2 removal efficiency.

During the drying period, hydration reaction proceeds. The surface area of the absorbent increased gradually and reached a maximum when the absorbent was dried at 200 ~ 220°C. Beyond 250°C dehydration occurs resulting in the removal of OH molecules and H_2O crystallization. It has been proven that after dehydration, shrinkage follows and surface area decreases.

Similar results were observed for related materials and explained by sintering a process caused by coalescence of CaO micro grains that comprise the porous particles. [1] Absorbent cured for 10 hours with drying temperatures of 120°C had more surface area than those dried at 80°C. This observation is clearly shown in Figure 8. If surface area is high, the SO_2 removal efficiency follows the same trend.

3.6 Effect of Mixed Gas Temperature on SO_2 Removal Efficiency

The temperature of the mixed gas affects the activity of the absorbent (Figure 9). At low temperature of mixed gas, absorbent cured at 80°C had SO_2 removal efficiency of about 9% which markedly increase up to 63% at 100 ~ 165°C. At higher curing temperature of 120°C, the activity increases almost 3 times initially and almost 1.5 times higher at temperature ranging from 100 ~ 150°C of the mixed gas. This can be explained by diffusion coefficient of gases, that at high temperature diffusion rates increase.

3.7 SO_2 Absorption Characteristics of Absorbent at Different Gas Mixture

The activity for SO_2 removal efficiency was strongly influenced by coexistence of NO in the reaction mixture. In the absence of NO, the absorbent showed small activity for SO_2 absorption which was only 40% for the reaction time of 3 hours as shown in the first curve of Figure 10. The reaction of SO_2 was enhanced by the presence of NO which took more than 4 hours with SO_2 removal efficiency of 68% as shown in the second curve of the same figure. However, with the presence of H_2O in the form of steam and NO in the gas mixture, the SO_2 removal efficiency of absorbent is significantly effective with an efficiency of 98%. The existence of NO in the flue gas is necessary because NO plays an important catalytic role in the absorption of SO_2. As shown in Scheme 1, NO and NO_2 do not react with SO_2 in the gas phase but on the surface of the absorbent.

Considering that NO_2 is a strong oxidant, it is plausible that the oxidation of SO_2 to SO_3 proceeds by the action of NO_2 that is formed by oxidation of NO. The oxidation of NO to NO_2 was reported to be thermodynamically feasible. The oxidized SO_2 reacts with $Ca(OH)_2$ components to form ettringite and $CaSO_4$ in the spent absorbent.

3.8 Effect of Glass content on the SO_2 Removal Efficiency of Absorbent

The percent crystallinity of partly devitrified glass was determined by X-ray Diffraction Method. Results on % glass content of different coal ashes from the Philippines, Japan and Thailand are given in Table 3 and correlated with SO_2 removal efficiency as shown in Figure 11. Fly ash with the highest glass content of 80 ~ 83% exhibited the highest SO_2 removal efficiency followed by bottom ash and slag as the lowest.

The glass content of fly ash corresponds to the non-crystalline components of fly ash which is more soluble in H_2O than the crystalline components resulting in the formation of calcium aluminum-silicate-hydrate making the absorbent more porous and reactive. It is therefore necessary to consider the glass content of fly ash above 80% in order to have a highly active absorbent.

Table 3
Chemical Composition and Glass Content of Coal Ash

Coal Ash No.	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	K_2O (%)	Glass (%)
1	47.07	30.01	4.87	4.50	1.37	0.79	80-83
2	48.66	24.83	7.89	5.89	1.81	0.77	53-56
3	48.07	26.12	7.92	6.47	1.60	0.63	40-45
4	48.60	25.90	10.30	4.21	1.70	2.26	70-73
5	46.50	27.00	10.50	4.01	2.63	1.04	47-53
6	40.78	22.50	10.10	7.43	3.79	2.06	68-70
7	54.01	25.38	6.01	4.63	1.00	0.60	80-85
8	47.90	22.00	12.15	2.14	0.81	0.15	60-65

1: Fly ash (Philippine), 2: Bottom ash (Philippine),
2: Slag (Philippine), 4, 5, 6 : Fly ash (Thailand)
7, 8: Fly ash (Japan)

3.9 Effect of SO_2 Concentration on SO_2 Absorption Rate

The prepared absorbent was tested with SO_2 at varying concentrations ranging from 150 ~ 900 ppm and with SO_2 absorption conditions given in Table 2. It can be drawn from Figure 12 that the SO_2 absorption rate of the absorbent follows a linear relationship proportional to SO_2 concentration. By plotting, a slope of 0.93 corresponds to absorption rate constant of the tested absorbent.

IV. Conclusions

Based on the results of Part 1 on the detailed chemical and mineralogical study and preliminary evaluation of the absorbent, a more intensive characterization of the prepared absorbent from coal fly ash was conducted. The following conclusions could be drawn:

1. The prepared absorbent is not only effective for SO_2 but also for NO_x.
2. Absorbent of smaller particle sizes, cured and dried at 120°C and 190 ~ 220°C respectively exhibited high SO_2 removal efficiency.
3. High surface area and glass content of absorbent increases the SO_2 removal efficiency.
4. Mixed gas temperatures of 100 ~ 165°C is effective for obtaining high SO_2 absorption activity.
5. The coexistence of NO and H_2O will greatly enhance the activity of the absorbent for SO_2 removal.
6. The absorption rate constant of the produced SO_2 absorbent is 0.93.

References

1. Borgwardt, R.H.; Rochelle, G.T. (1990). Sintering and Sulfation of Silicate Calcium Aluminate. Industrial Engineering Chemical Research, vol. 29, pp. 2118-2123.
2. Chu, P.; Rochelle G.T. (1989). Removal of SO_2 and NO_x from Stack Gas by Reaction with Calcium Hydroxide Solids. JAPCA, vol. 39, pp.175-179.
3. Jozewics, W.; Rochelle, G.T. (1986). Fly Ash Recycle in Dry Scrubbing Environmental Program, vol. 5, pp. 219-223.
4. MacCarthy, G.J. Glasser, F.P., Roy, D.M., Diamond, S. (1984). Fly Ash and Coal Conversion By-Products; Characterization, Utilization and Disposal I and III, Symposia Proceedings, Materials Research Society, Boston, Massachusetts, U.S.A.
5. Ohlberg, S.M.; Strickler, D.W. (1962). Determination of Per Cent Crystallinity of Partly Devitrified Glass by X-ray Diffraction. Journal of American Ceramics Society, vol 45, pp. 170-171.
6. Part 1, Highly Active Absorbent for SO_2 Removal Prepared from Coal Ash (ITDI-HNIRI) October 1996.
7. Pugal, D.L.; Herrera, A.B., et.al. (1995). "Studies on the Fusibility of Coal Ash", Philippine Engineering Journal, vol. VXI, no.1, June 1995, pp. 85 -102.
8. Ueno, T. (1996). Process for Preparing Desulfurizing and Denitrating Agents, U.S. Patent No. 4629721, December 16, 1996.

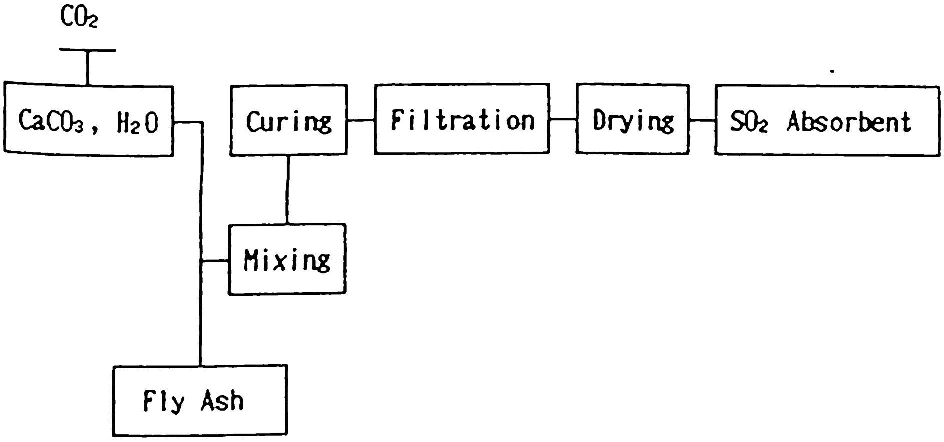


Figure 1. Preparation process of SO_2 absorbent

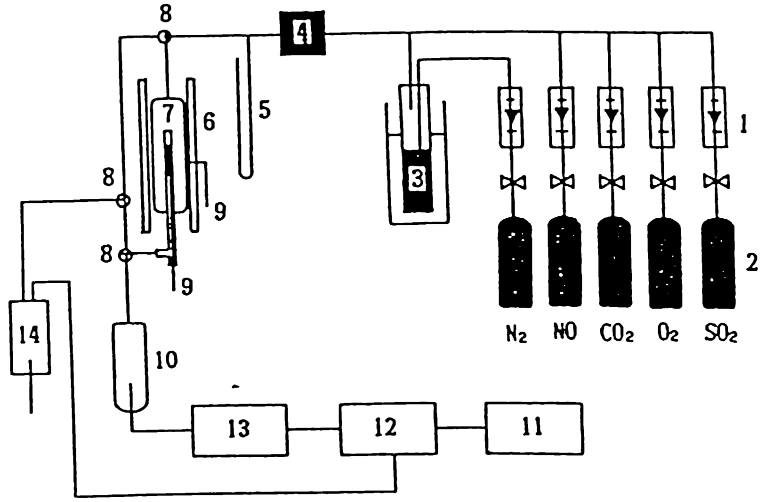


Figure 2. SO_2 absorption analyzer

1: Flowmeter
2: Gas cylinder
3: Steamer
4: Gas mixer
5: Manometer
6: Furnace
7: Sample Holder
8: Cock
9: Thermocouple
10: Moisture remover
11: Gas sampling unit
12: Analyzer (SO_2, NO, CO_2, O_2)
13: Recorder
14: Scrubber

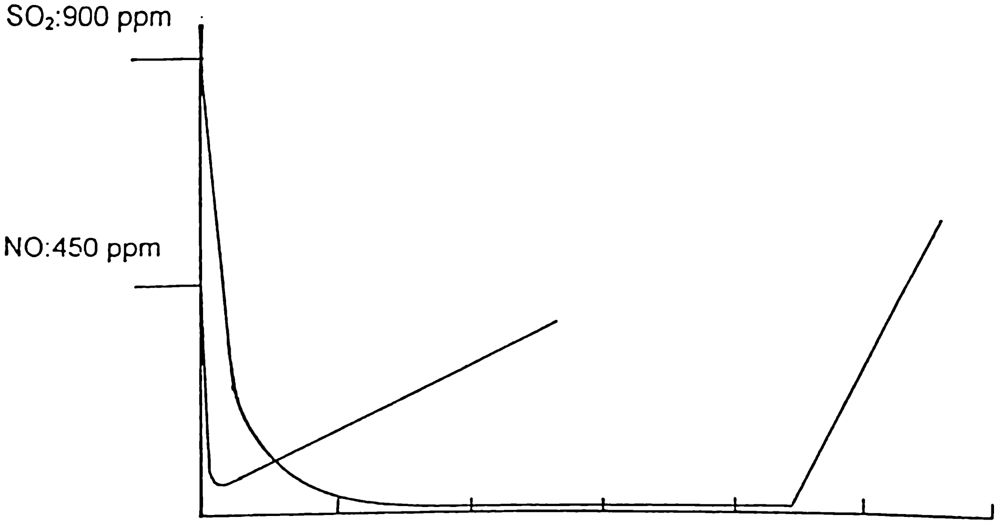


Figure 3. SO$_2$ and NO absorption characteristics of SO$_2$ absorbent

Absorption condition

SO$_2$: 900 ppm, NO: 450 ppm, CO$_2$: 13%, O$_2$: 6%, H$_2$O: 10%

Reaction temperature 165°c

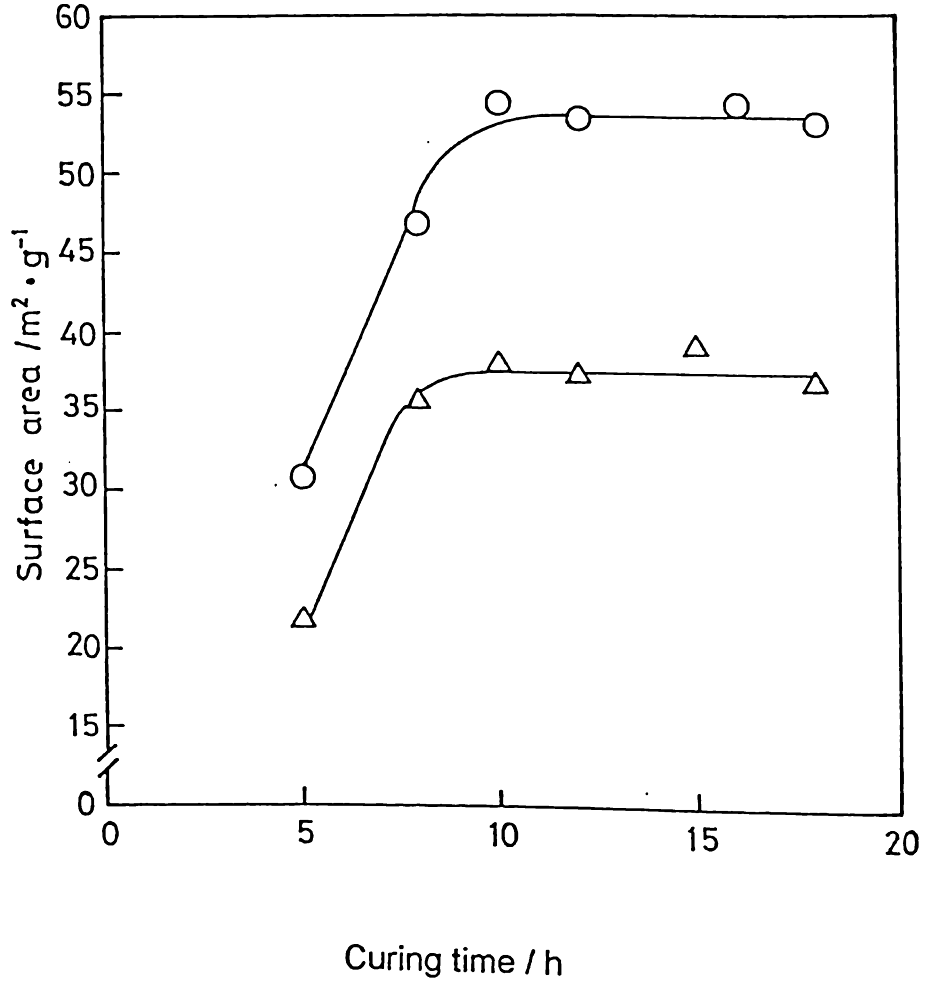


Figure 4. Correlation between curing time and surface area

Absorption condition

SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C

Curing temperature

O: 120°C,∇:80°C

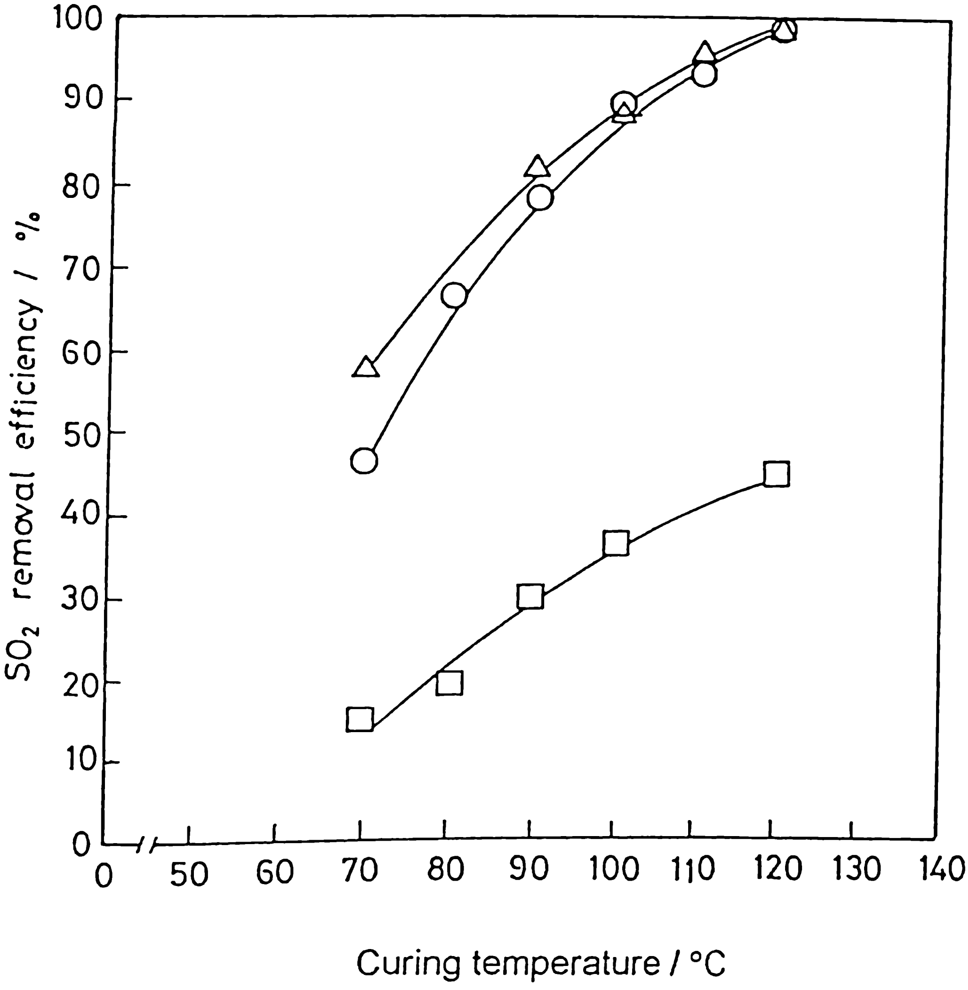


Figure 5. Correlation between curing temperature and SO_2 removal efficiency

Absorption condition

SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%

Reaction temperature 165°C

Curing time

Δ 15 hrs O:10 hrs , □: 5 hrs

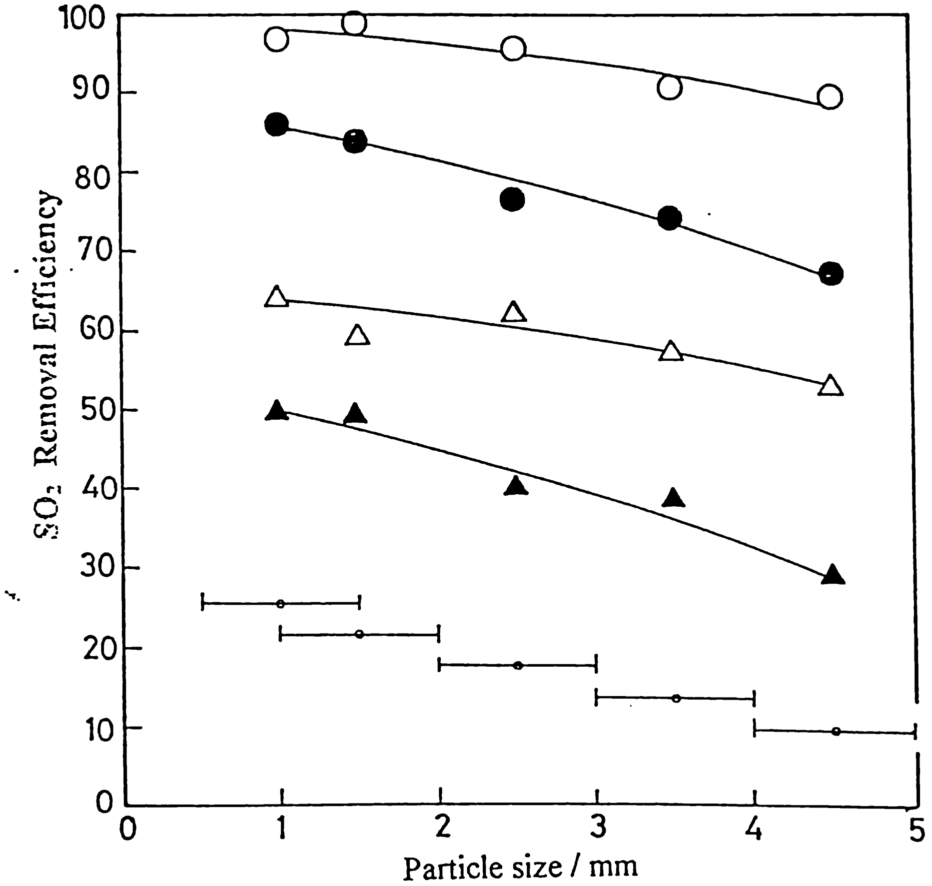


Figure 6. Correlation between particle size and SO_2 removal efficiency

Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C
Curing time: 10 hrs
Curing temperature
O, **O**: 120°C, Δ, Δ: 80°C
Drying temperature
O, Δ: 200°C, **O**, Δ:150°C

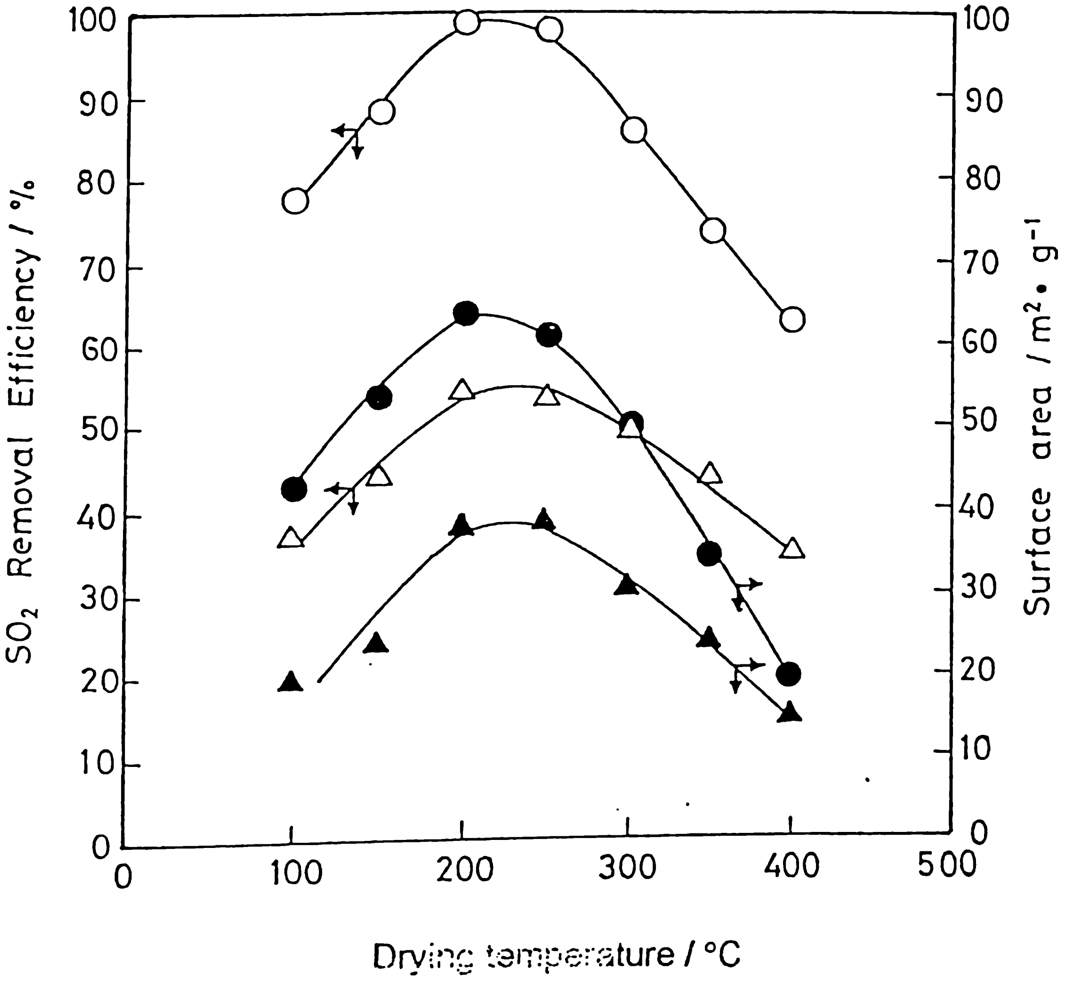


Figure 7. Correlation of drying temperature, SO₂ removal efficiency and surface area

Absorption condition

SO$_2$: 900 ppm, NO: 450 ppm, CO$_2$: 13%, O$_2$: 6%, H$_2$O: 10%

Reaction temperature 165°C

Curing time: 10 hrs

Curing temperature

O, Δ: 120°C, **O** Δ: 80°C

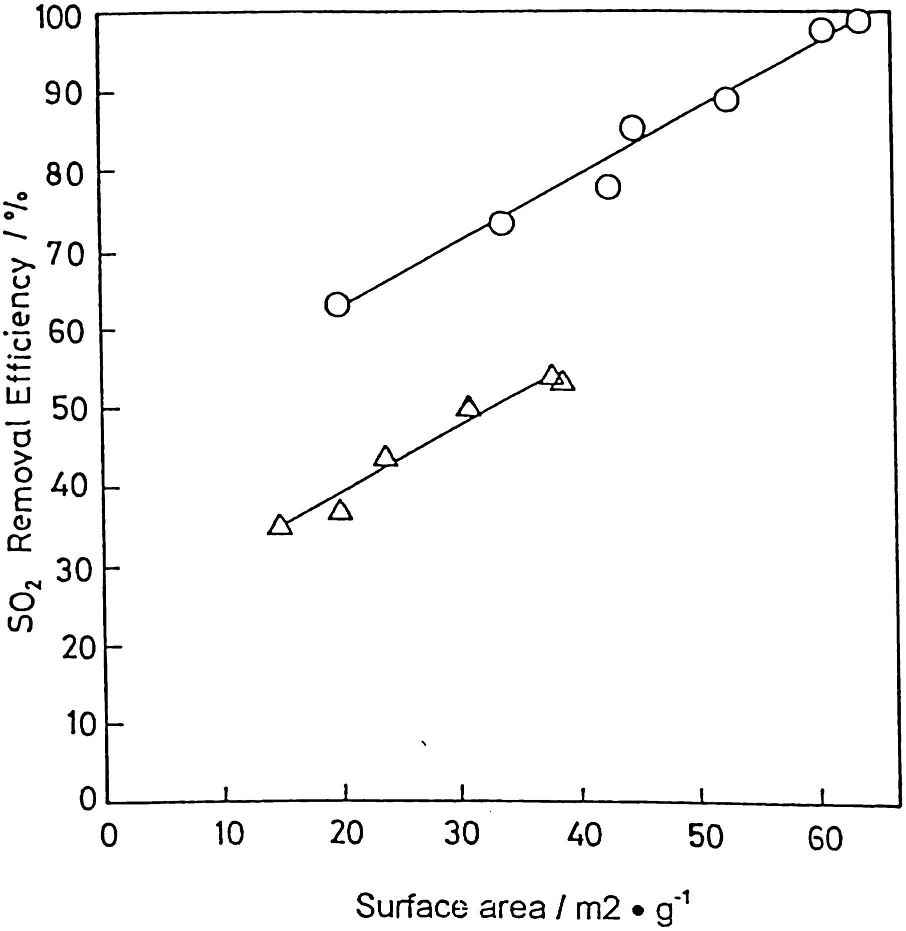


Figure 8. Correlation between surface area and SO_2 removal efficiency

Curing time: 10 hrs
Curing temperature
O: 120°C, Δ: 80°C
Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C

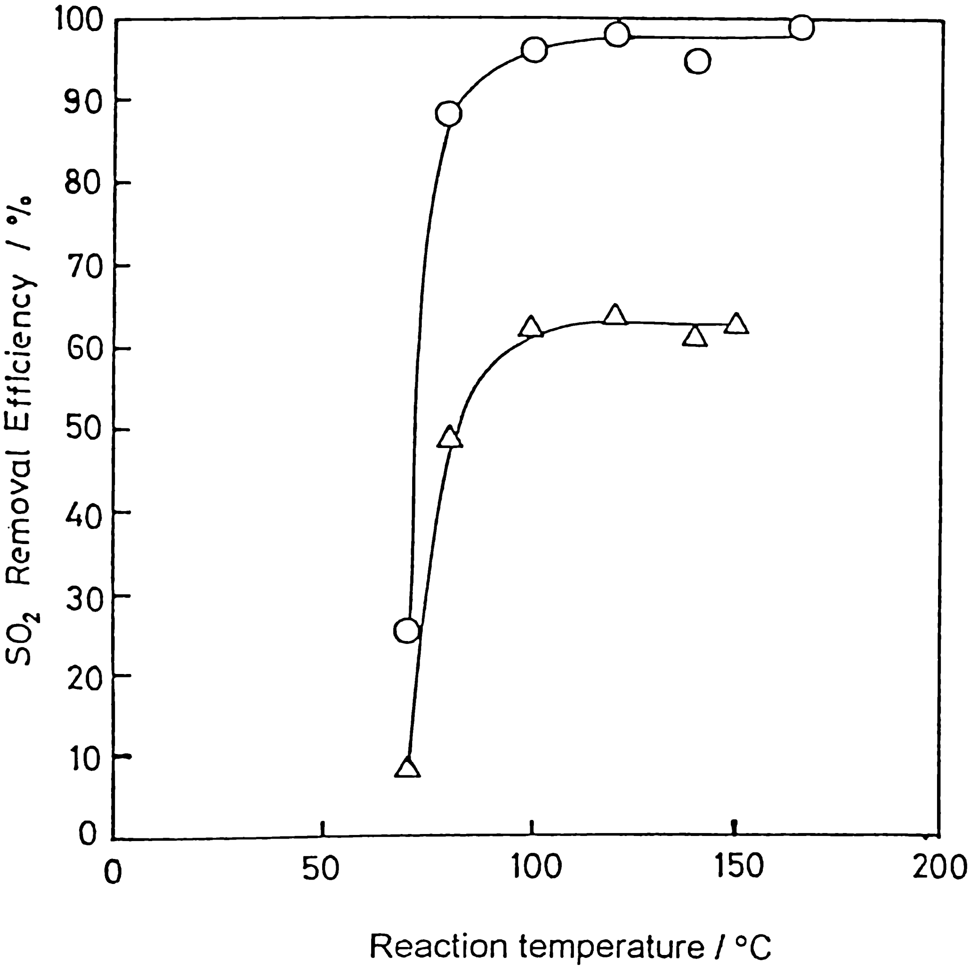


Figure 9. Correlation between gas temperature and SO_2 removal efficiency

Curing time: 10 hrs
Curing temperature
O: 120°C, Δ: 80°C
Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%

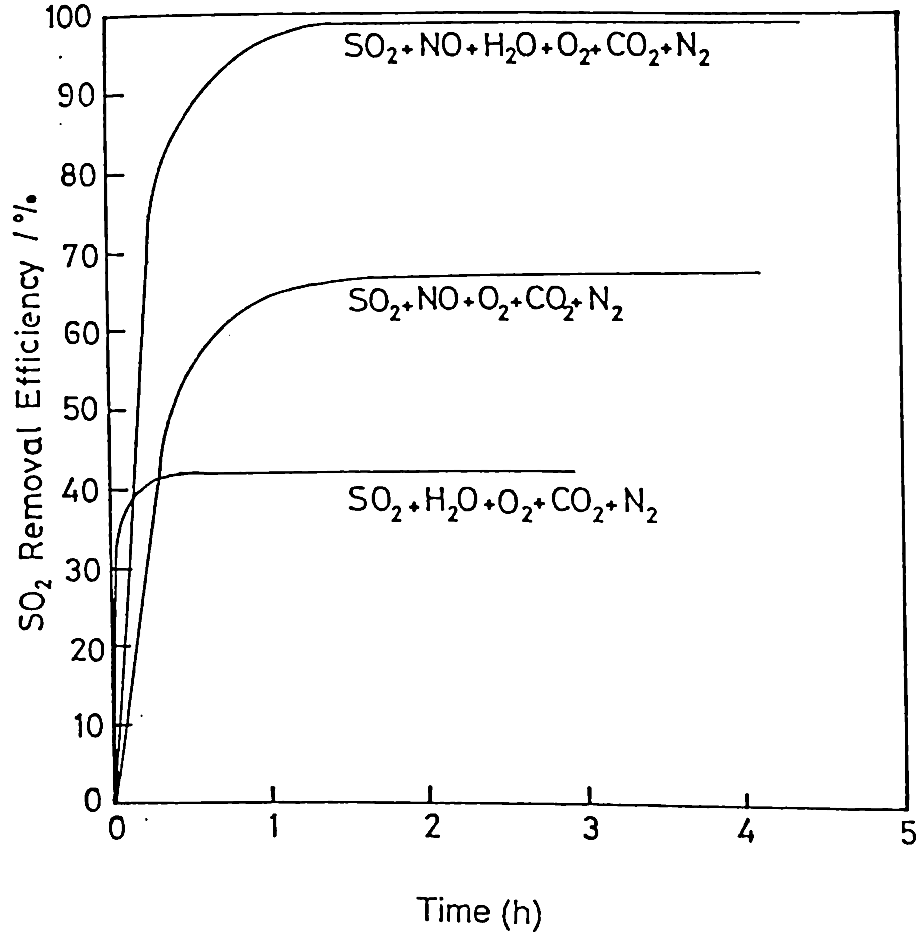
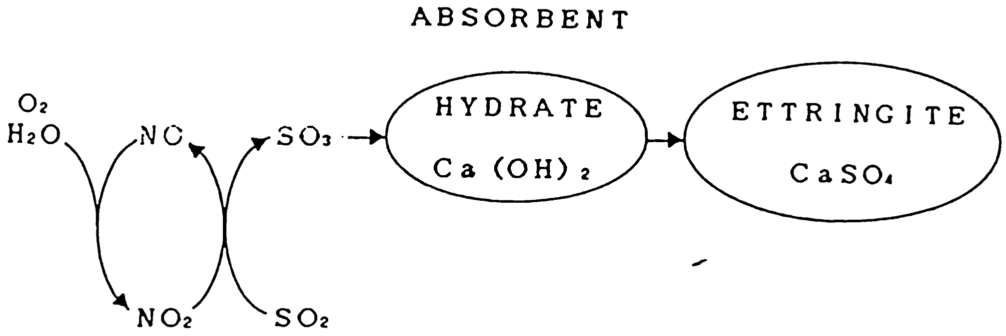


Figure 10. Correlation between reaction time and SO_2 removal efficiency at varying gas composition

Curing time: 10 hrs, Curing temperature: 120°C
Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C



Hydrate : Calcium • Aluminum • Silicate • Hydrate
Ettringite : $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 25H_2O$ or $6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 31H_2O$

Scheme 1. Desulfurization reaction of SO_2 absorbent

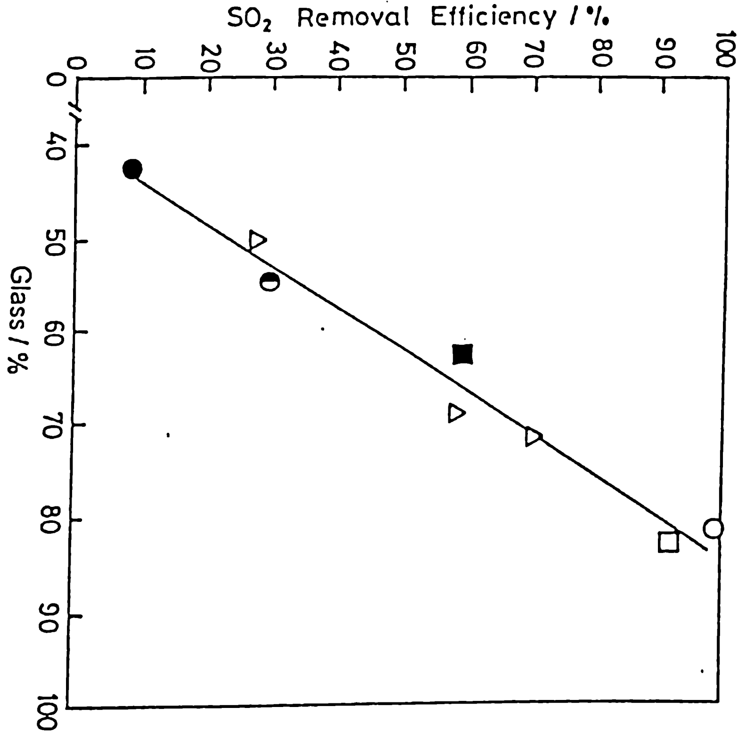


Figure 11. Correlation between glass content and SO_2 removal efficiency

Curing time: 10 hrs, Curing temperature: 120°C
Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C
O, Δ, □, □: Fly ash, O: Bottom ash, O: Slag

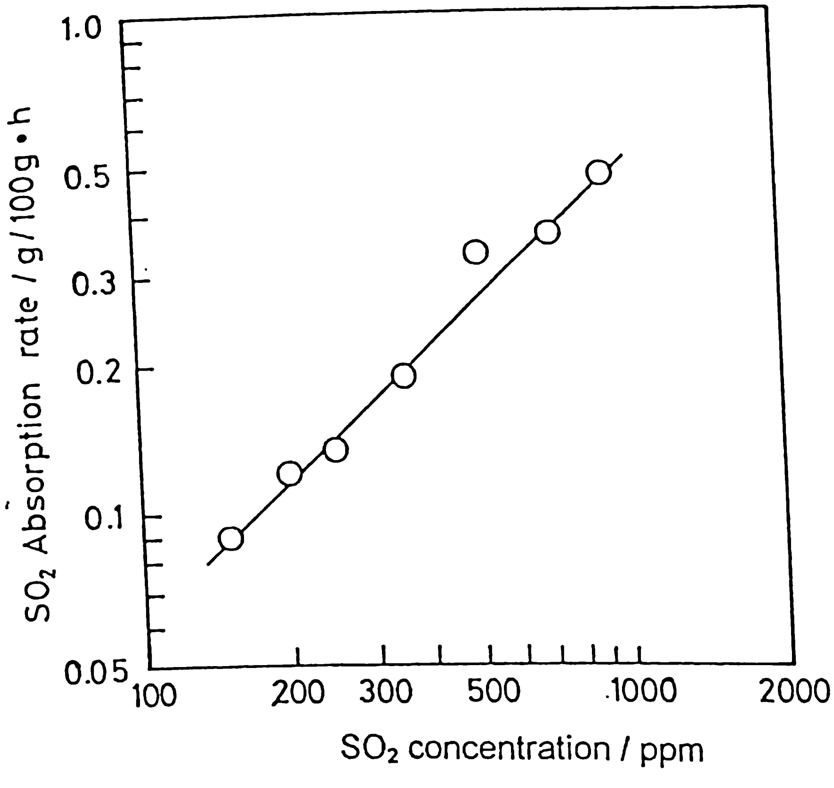


Figure 12. Correlation between SO_2 concentration and SO_2 absorption rate

Curing time: 10 hrs, Curing temperature: 120°C
Absorption condition
SO_2: 900 ppm, NO: 450 ppm, CO_2: 13%, O_2: 6%, H_2O: 10%
Reaction temperature 165°C