

# Development of an active sorbent from fly ash for dry desulphurization of simulated flue gas in a fluidized-bed reactor

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## Abstract

In this work, dry desulphurization of simulated flue gas was investigated in a batchwise operated laboratory-scale stainless steel fluidized-bed reactor (46 mm × 500 mm) by using an active sorbent composed of a mixture of fly ash, FGD-gypsum and calcium-containing local Turkish limestone (Mengen/Bolu) which was calcined at 900 °C with 5% H<sub>2</sub>O vapour. The sulphation reaction was carried out in a range of SO<sub>2</sub> feedstock concentration (1000 ppm SO<sub>2</sub> ≤ C ≤ 5000 ppm SO<sub>2</sub>) and at a temperature range of 300 °C ≤ T ≤ 500 °C. The experimental sulphation conversion data of active sorbent were compared with those of literature. Results obtained with the sorbent of this study indicated an increased sulphation conversion according to the conventional calcium-containing sorbent.

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**Keywords:** Desulphurization; Fly ash; Fluidized bed

## 1. Introduction

Dry flue gas desulphurization by direct injection of calcium-based absorbents into the flue gas duct offers an attractive alternative to semidry or wet methods for controlling SO<sub>2</sub> emission at low temperature with a simple technology as a retrofit option for existing coal-fired power plants. Since the residence time of the solids in the duct injection of absorbents is short, a highly active absorbent must be used to achieve acceptable levels of SO<sub>2</sub> removal [1]. One method of obtaining that absorbent under medium temperatures is by using a mixture prepared from coal fly ash, calcium oxide and gypsum [2–5]. It was considered that the high activity of the mixture resulted according to the literature on one hand from the presence of calcium silicate hydrate material formed by the hydration reaction between calcium and alumina silicate in the fly ash, and the difference in reactivity was caused by the structure of calcium silicate hydrate material formed [6]. In this case, the surface area from the formation of hydrated calcium silicates is effective in the desulphurization process. On the other hand, the significant increase of calcium utilization rate was mainly attributed to the Ca(OH)<sub>2</sub> covering the surface of fly ash particles, and the hydration reactions did not

play an important role under the absorbent preparation condition at ambient temperature [7]. On the contrary of these findings in literature, the desulphurization activity of the absorbent depends on which step calcium sulphate is added in the preparation of absorbents. Recently Ishizuka et al. [8] found that the addition of calcium sulphate in the step of slaking calcium oxide with fly ash brings about a negative effect while the addition of that in the step of hydrothermal treatment following slaking brings about a positive effect.

With this state of knowledge given above, the purpose of this work is to develop highly active desulphurization sorbent by exploring the reaction of this sorbent composed of a mixture of lignite fired power plant waste (a disposed mix of FGD-gypsum and fly ash of Çayırhan/Ankara power plant) and calcined Turkish limestone (Mengen/Bolu) at the simulated conditions of real flue gases of that power plants for regenerative calcium utilization.

## 2. Experimental

### 2.1. Apparatus

The experimental setup consisted of mainly a fluidized-bed reactor (FBR) surrounded by an electrically heated tubular ceramic furnace, and auxiliary equipment for fluidizing gas

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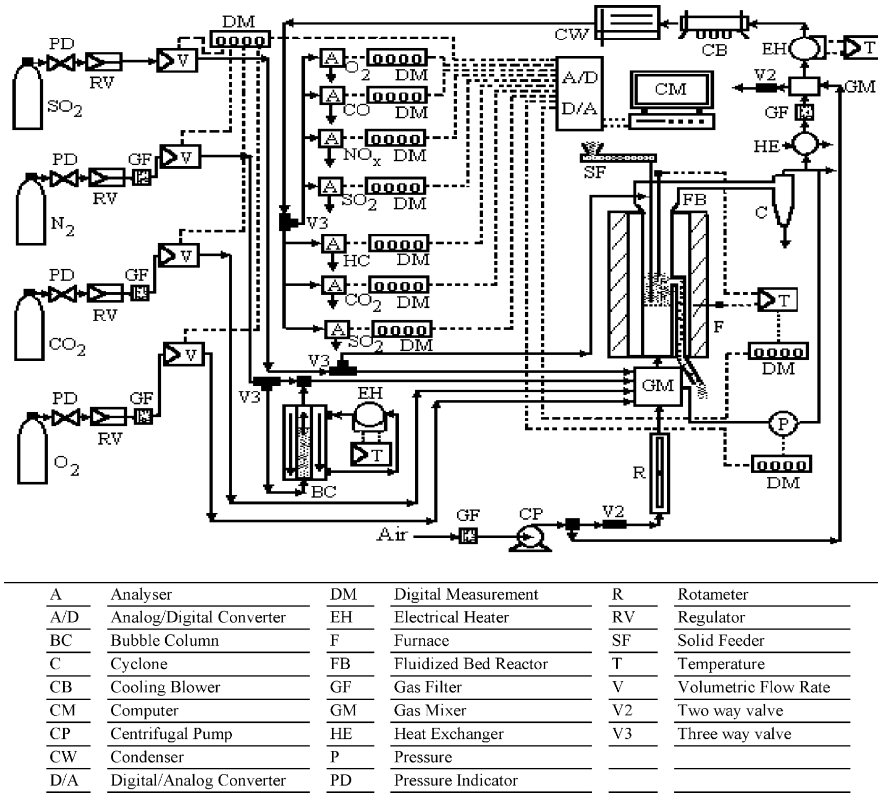


Fig. 1. Schematic diagram of the experimental setup.

preparation, gas analysis and on-line data logging system. The FBR is a stainless steel tube of 46 mm inside diameter and 500 mm length. It is fitted with a stainless steel sieve (325 mesh) gas distributor. The reactor is heated by Kanthal-A1 heating wire and the bed temperature is measured by a NiCr/Ni thermocouple, and controlled by a feedback PID loop using the heating power supplied to the furnace as manipulated variable. A preheater is connected to the FBR for heating the incoming fluidizing air before it is introduced to the reactor. The experimental setup is shown schematically in Fig. 1 and the details of that were given elsewhere [9,10].

## 2.2. Materials

Calcium based raw material (RS) was provided by Bolu/Mengen limestone deposits of Turkey. Calcined sorbent (CS) to the preparation of the mixture for the active sorbent

(AS) was obtained by fluidized-bed calcination with humid air containing 5% H<sub>2</sub>O vapor as fluidizing medium at 900 °C [11]. Lignite fly ash (LFA) and FGD-Gypsum (FGDG) to the preparation of the mixture for the active sorbent (AS) were supplied by Park Termik Çayırhan Power Plant of Turkey. The chemical analyses of the RS, CS, LFA and FGDG are given in Table 1 together with the sulphated sorbents of the CS (SCS) and that of AS (SAS) for comparison. The surface characteristics of these materials are given in Table 2, respectively.

## 2.3. Preparation of the active sorbent

The active sorbent (AS) was prepared from the materials of CS, LFA and FGDG given above by using the addition of calcium sulphate (FGDG) in the step of hydrothermal treatment following slaking step [3,8]. For the preparation of 60 g of the AS, CS (13.6 g) was added to 300 mL of water at a tempera-

Table 1  
Complete chemical analyses of materials (% w/w)

Materials	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	Ignition loss
RS	0.57		0.51	55.28		0.02	0.10	0.06			0.20 (Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> )	43.42
CS	0.67	0.30	2.30	64.61	3.16	0.22	0.00	0.04	0.04	0.26	1.57 (Cr <sub>2</sub> O <sub>3</sub> + Mn <sub>2</sub> O <sub>3</sub> )	24.58
LFA	1.97	13.66	51.48	14.00	8.18	2.68	1.74	2.38	0.27	0.84	0.30 (Cr <sub>2</sub> O <sub>3</sub> + Mn <sub>2</sub> O <sub>3</sub> )	0.81
FGDG	0.42	0.53	0.49	33.73	0.01	45.57	0.003	0.01	0.00	–	–	19.21
AS	1.79	5.59	19.07	33.04	3.02	12.94	0.67	0.83	0.12	0.46	0.32	20.98
SCS <sup>a</sup>	0.59	0.19	1.15	57.87	0.75	5.62	0.00	0.04	0.03	0.00	0.48 (Cr <sub>2</sub> O <sub>3</sub> + Mn <sub>2</sub> O <sub>3</sub> )	32.33
SAS <sup>a</sup>	1.92	5.40	20.40	37.90	3.03	13.46	0.60	0.78	0.11	0.31	0.43 (Cr <sub>2</sub> O <sub>3</sub> + Mn <sub>2</sub> O <sub>3</sub> )	13.24

<sup>a</sup> Sulphated at  $T=500$  °C,  $C_{SO_2} = 3000$  ppm.

Table 2  
Surface characteristics of the RS, CS, SCS, SAS

Material	Mean particle diameter ( $\mu\text{m}$ )	BET surface area <sup>a</sup> ( $\text{m}^2/\text{g}$ )	Cumulative pore volume <sup>a</sup> ( $\text{cm}^3/\text{g}$ )	Average pore diameter <sup>b</sup> (4 V/A, $\mu\text{m}$ )	Total pore area <sup>b</sup> ( $\text{m}^2/\text{g}$ )	Total intrusion volume <sup>b</sup> ( $\text{cm}^3/\text{g}$ )
RS	260	0.9860	0.00360	0.4487	2.1491	0.2411
CS		8.2954	0.05509	0.2070	12.5743	0.6508
AS	255	11.8668	0.06425	0.2258	21.1550	1.1942
SCS <sup>c</sup>		7.0968	0.03332	0.2081	15.2614	0.7939
SAS <sup>c</sup>		10.9989	0.04436	0.1503	18.3796	0.6905

Characterization test: Sieve analysis ASTM E 11.87.

<sup>a</sup> Adsorption–desorption of  $\text{N}_2$ .

<sup>b</sup> Intrusion of Hg (Micromeritics Pore Sizer 9310).

<sup>c</sup> Sulphated at  $T=500^\circ\text{C}$ ,  $C_{\text{SO}_2} = 3000$  ppm.

ture of  $50^\circ\text{C}$ . The temperature of the slurry increased to about  $56^\circ\text{C}$  upon addition of the CS. To the slurry, FGDG (19.2 g) and LFA (24 g) were added with stirring. The resulting slurry was evaporated at  $66^\circ\text{C}$  normally for 8 h with stirring. After hydration, the sorbent slurry was dried normally at  $150^\circ\text{C}$  for 2 h. The resulting sorbent was pelletized by adding white cement in a proportion of 2% (w/w) as binder and used for sulphation with a mean particle diameter of  $255\ \mu\text{m}$ .

#### 2.4. Procedure

The fluidized-bed reactor was operated batchwise with a single charge of (0.5 g) particles for 15 min sorbent residence time in a differential mode by providing gas phase  $\text{SO}_2$  conversion smaller than 5–10% [12]. The fractional sulphation conversion values of CS and AS were obtained from experimentally measured total sulphate (sum of sulphite and sulphate) and sulphate concentrations by using ORION 960 Autochemistry System (ATI ORION, Boston, MA/USA) according to a method given in the literature [13]. Sulphite fraction was then determined by difference. Reactor operating parameter ranges are given in Table 3.

The flow rate of simulated flue gas was set to the corresponding value so that a constant ratio of  $U_0/U_{\text{mf}} = 6$  was maintained, and when steady-state temperature was reached, the CS and AS prepared were introduced into the reactor.

### 3. Results and discussion

#### 3.1. Comparison of experimental sulphation conversion values of CS and AS

Experimental sulphation conversion values ( $X_{\text{s,exp}}$ ) obtained in 15 min reaction time are given in Figs. 2 and 3 as a func-

Table 3  
Ranges of experimental conditions

Parameters	Ranges
Reactor operating pressure	101.3 kPa
$\text{SO}_2$ -feedstock concentration	$1000\ \text{ppm} \leq C_{\text{SO}_2} \leq 5000\ \text{ppm}$
Reactor operating temperature	$300^\circ\text{C} \leq T \leq 500^\circ\text{C}$
Low temperature	
Reactor operating mode	500 mg CS and AS
Differential	

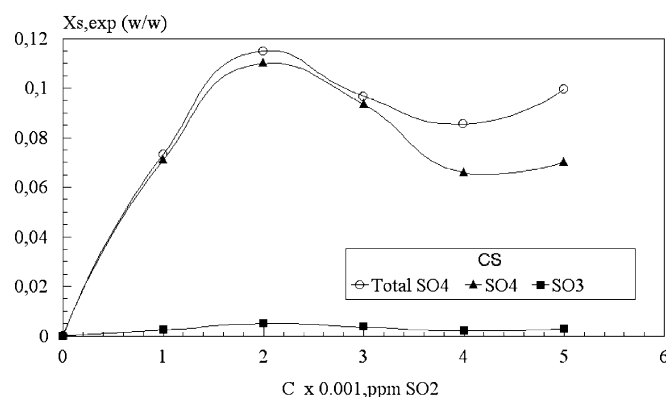


Fig. 2. The effect of  $\text{SO}_2$  feedstock concentration on sulphation conversion of CS at  $500^\circ\text{C}$  (gas composition: 10%  $\text{CO}_2$ , 6%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ).

tion of  $\text{SO}_2$ -feedstock concentration at  $500^\circ\text{C}$  according to the sulphite, sulphate and total sulphate conversion of the CS and AS at  $500^\circ\text{C}$ , respectively. As can be discerned from Figs. 2 and 3, the sulphation conversion of the AS was greater than that of the CS at the operating conditions of this study given in Table 3. Therefore, it was concluded that the AS prepared as given in Section 2.3 significantly increased the desulphurization ability of CS obtained from the calcination of limestone.

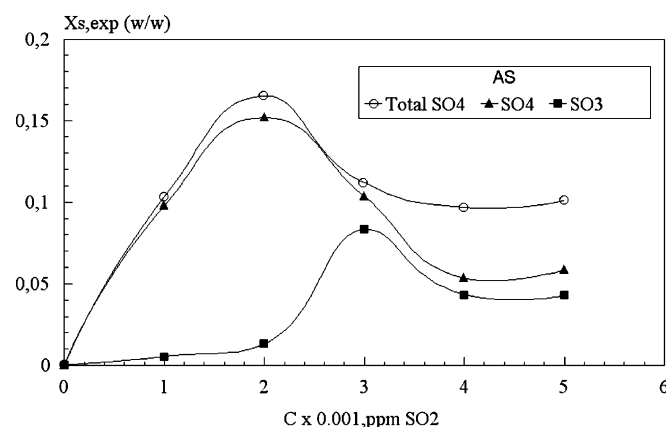


Fig. 3. The effect of  $\text{SO}_2$  feedstock concentration on sulphation conversion of AS at  $500^\circ\text{C}$  (gas composition: 10%  $\text{CO}_2$ , 6%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ , balance  $\text{N}_2$ ).

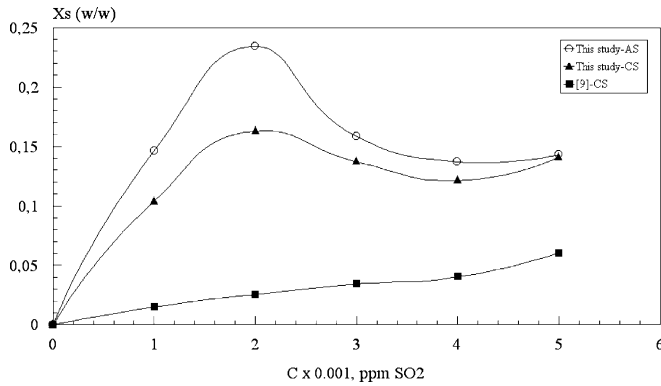


Fig. 4. Comparison of the fractional sulphation conversion values of the CS and AS with the previous study at 500 °C (gas composition: 10% CO<sub>2</sub>, 6% O<sub>2</sub>, 5% H<sub>2</sub>O, balance N<sub>2</sub>).

### 3.2. Comparison of experimental sulphation conversion values of CS and AS with previous studies

The fractional conversion values based on total sulphate measured were converted to the corresponding values ( $X_s$ ) based on CaSO<sub>4</sub> by multiplying the ratio of molecular weights of CaSO<sub>4</sub> to SO<sub>4</sub> to compare with the sulphation values of previous studies as a function of SO<sub>2</sub>-feedstock concentration at 500 °C and temperature in Figs. 4 and 5, respectively. As can be seen from Figs. 4 and 5, the values of this study were significantly higher than that of the previous studies. In the study of Shi and Xu [14], the AS was a mixture of equal amounts of fly ash and lime and for comparison, second sulphated sorbent of that study was considered. The authors of that study used conversion rate to compare the desulphurization ability of the sorbents as the ratio of the mass of the sorbent reacted with SO<sub>2</sub> under a certain time

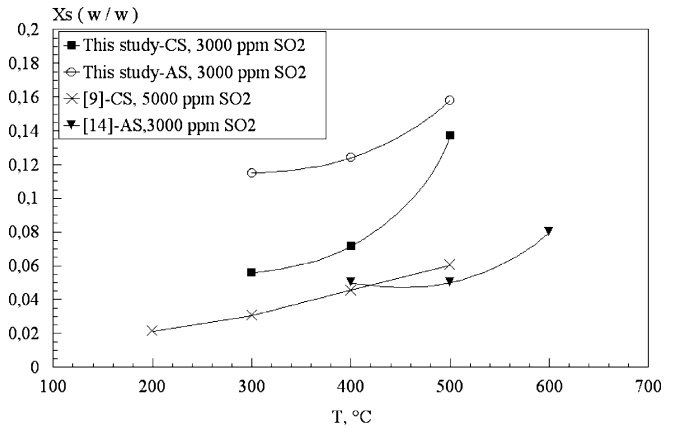


Fig. 5. Comparison of the fractional sulphation conversion values of the CS and AS with the previous studies as a function of temperature.

period over the initial mass of the sorbent and the product was assumed to be CaSO<sub>4</sub> only by that authors. The fractional sulphation conversion ( $X_s$ ) of the present study is the same except that the sulphation product measured as total sulphate was converted to the mass of CaSO<sub>4</sub> over the initial mass of the sorbent. The properties of the previous studies for CS and AS were tabulated in Table 4 for comparison.

### 3.3. Low temperature sulphation kinetics

From the fractional sulphation conversion values obtained,  $\ln(dX_s/dt) - \ln C_{SO_2}$  pairs at constant temperature were formed to evaluate the effect of SO<sub>2</sub>-feedstock concentration and temperature on the observed reaction rate for the CS and AS in Figs. 6 and 7, respectively. The data give slight dependency of reaction rate ( $dX_s/dt$ ) to the inlet concentration of SO<sub>2</sub> ( $C_{SO_2}$ ) as

Table 4  
Material properties and operating conditions of selected studies to compare conversions of this study

Reference	Material properties/operating conditions		
	Material	Gas composition	Experimental conditions
[9]	Calcined limestone of Karaağaçlı/Muş; total intrusion volume: 0.357 mL/g; total pore area: 21.684 m <sup>2</sup> /g; mean particle radius: 93 μm	Concentrations: C <sub>SO<sub>2</sub></sub> = 5000 ppm, C <sub>O<sub>2</sub></sub> = 6% (v/v), C <sub>CO<sub>2</sub></sub> = 10% (v/v), C <sub>H<sub>2</sub>O</sub> = 5% (v/v), balance N <sub>2</sub>	Fluidized-bed reactor; pressure: 101.3 kPa; U <sub>0</sub> /U <sub>mf</sub> : 6; temperature: 200–500 °C
This study-CS	Calcined limestone of Mengen/Bolu; see Table 2	Concentrations: C <sub>SO<sub>2</sub></sub> = 5000 ppm, C <sub>O<sub>2</sub></sub> = 6% (v/v), C <sub>CO<sub>2</sub></sub> = 10% (v/v), C <sub>H<sub>2</sub>O</sub> = 5% (v/v), balance N <sub>2</sub>	Fluidized-bed reactor; pressure: 101.3 kPa; U <sub>0</sub> /U <sub>mf</sub> : 6; temperature: 300–500 °C
[14]	Fly ash-lime mixture (1:1); SiO <sub>2</sub> (%): 30.50; Al <sub>2</sub> O <sub>3</sub> (%): 12.70; Fe <sub>2</sub> O <sub>3</sub> (%): 4.95; CaO (%): 38.50	C <sub>SO<sub>2</sub></sub> = 3000 ppm; balance: primary air (0.07 m <sup>3</sup> /h); secondary air + SO <sub>2</sub> : 1.2 m <sup>3</sup> /h + 60 cm <sup>3</sup> /min	Drop tube reactor; pressure: 101.3 kPa; temperature: 400–800 °C; retention time: less than 1 s
This study-AS	See Table 1	Concentration: C <sub>SO<sub>2</sub></sub> = 3000 ppm, C <sub>O<sub>2</sub></sub> = 6% (v/v), C <sub>CO<sub>2</sub></sub> = 10% (v/v), C <sub>H<sub>2</sub>O</sub> = 5% (v/v), balance N <sub>2</sub>	Fluidized-bed reactor; pressure: 101.3 kPa; U <sub>0</sub> /U <sub>mf</sub> : 6; temperature: 300–500 °C

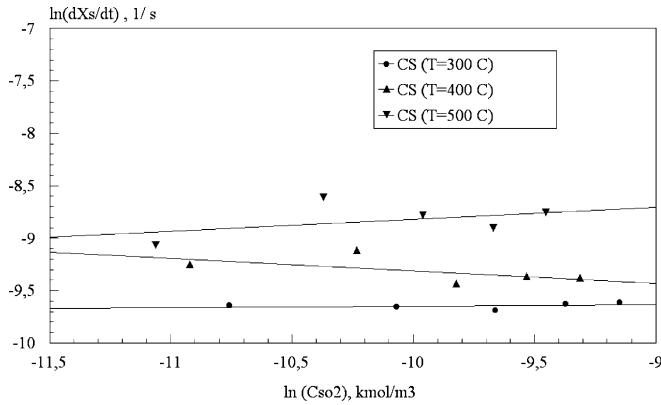


Fig. 6. Dependency of the observed reaction rate ( $dX_s/dt$ ) to the inlet concentration of  $SO_2$  for the CS at the temperature range worked.

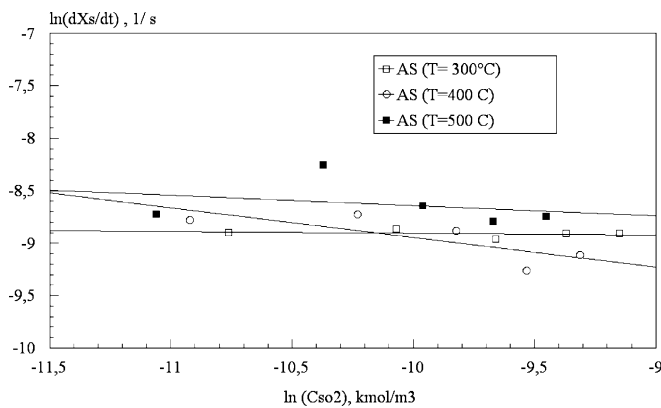


Fig. 7. Dependency of the observed reaction rate ( $dX_s/dt$ ) to the inlet concentration of  $SO_2$  for the AS at the temperature range worked.

can be discerned also from Figs. 6 and 7. The Arrhenius dependency of the observed reaction rate constants to the temperature gives an activation energy ( $E_a$ ) of 12.6 and 7.5 kJ/mol for CS and AS, respectively as given in Fig. 8. The corresponding pre-exponential factor ( $k_0$ ) are  $2.035 \times 10^{-4}$  and  $2.75 \times 10^{-4} \text{ s}^{-1}$  for CS and AS, respectively. In the majority of the kinetic studies, the sulphation reaction was considered as first order with respect to  $SO_2$  concentration [15]. Borgwardt and Bruce [16] recom-

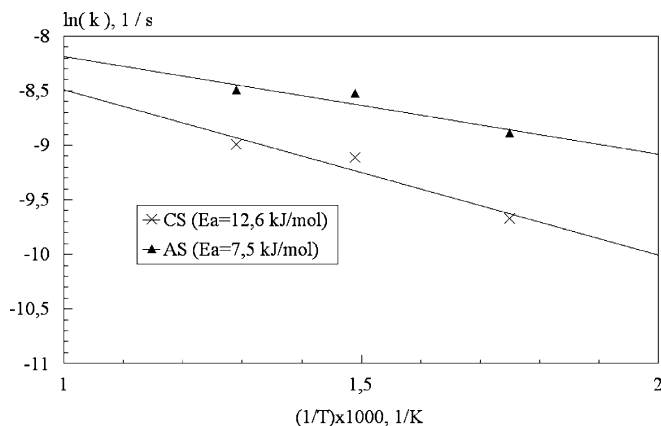


Fig. 8. Arrhenius plots of observed rate constant at the temperature range worked for CS and AS.

mended the value of 0.62 as reaction order with respect to  $SO_2$  concentration based on their experimental studies. The apparent activation energy,  $E_a$  was found to be dependent upon the type of stone, with values in the range of 34–76 kJ/mol [17]. On the other hand, an apparent activation energy of 25.5 and 21.5 kJ/mol were reported for the sulphation of calcined dolomite in the presence of water vapor (4.7–7.5%) by Stein [18], and for the sulphation of  $Ca(OH)_2$  pellets in the presence of  $NO_x$ ,  $CO_2$ ,  $H_2O$  vapor (5%) by Schmitt [19], respectively. The previous study of the author [9] gave a reaction order of 0.7 according to  $SO_2$  concentration and an activation energy of 10.8 kJ/mol for the low temperature sulphation conditions of the calcined limestone of Karaağaçlı/Muş as given in Table 4 coinciding with the values of 12.6 and 7.5 kJ/mol of the present study for the CS and AS, respectively but nearly zero reaction order according to  $SO_2$  concentration. These lower activation energies of the present and the previous study of the author [9] compared with that of the former studies reported above [17–19] indicated that both the sulphation reaction of CS and AS prepared by calcination of limestone in the presence of water vapor and mixing of that with FA and FGD-gypsum, respectively is diffusion controlled reaction giving an order of magnitude of activation energy for diffusion [20].

#### 4. Conclusions

The highly active sorbent for dry desulphurization of simulated flue gas was developed from the LFA, CS and FGDG. For the preparation of this highly active sorbent (AS), FGDG was added in the hydrothermal treatment step after the slaking step of CS and fly ash giving a positive effect reported also in literature. The sulphation conversion of the AS obtained was found to be greater than that of the CS of this study and the previous studies. The lower activation energy values of the sulphation reaction of CS and AS as compared with the corresponding literature indicated a more pronounced diffusion controlled reaction by giving an order of magnitude of activation energy for diffusion. The results of the present study can give on one hand the real possibility of recycling large amounts of the power plant wastes disposed usually as a mixture of fly ash and FGD-gypsum. On the other hand, the results of the present study can make the dry flue gas desulphurization by direct injection of these calcium and Class F fly ash based absorbents into the flue gas duct an attractive alternative to semidry or wet methods for controlling  $SO_2$  emission at low temperature with a simple technology as a retrofit option for existing lignite-fired power plants.

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