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Determination of the reactivity of $Ca(OH)_2$–fly ash sorbents for SO_2 removal from flue gases

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Abstract

$Ca(OH)_2$ was activated towards SO_2 by hydrating it with various fly ashes collected from three different coal-fired power plants in Turkey. Reactive $Ca(OH)_2$–fly ash sorbents were prepared using both atmospheric and pressure hydration techniques. The hydrated sorbents were analyzed using mercury porosimeter, thermogravimetric analyzer and X-ray diffractometer. The relative surface area increments of sorbents are influenced by the hydration conditions and the source of the fly ash. The reactive species formed during hydration as detected with X-ray diffraction measurements, were found to be responsible for these surface area increments. Thermogravimetric measurements showed that decreasing the $Ca(OH)_2$ content of the hydrated sorbent which was presumably converted to Ca-containing reactive species caused an increase in the surface area of the sorbent. It was concluded that the reactivity of hydrated sorbents towards SO_2 closely related to the sorbent surface area and the presence of the reactive species in the sorbent. © 1998 Elsevier Science B.V.

Keywords: Sorbent; Hydration; Reactivity

1. Introduction

The emission of sulfur oxides resulting from the combustion of fossil fuels is one of the greatest problem that leads to undesirable changes in our environment. Injection of a suitable sorbent directly into a flue gas duct to control SO_2 emissions is attractive for many reasons relating to the non-requirement of costly atomizers or solids dewatering equipment needed for wet processes which are commonly adopted in commercial plants. In the process, sorbent particles are normally introduced into humidified and temperature controlled flue gas in the duct between the air pre-heater and particulate control device. The total SO_2 removal achieved is the sum of the removal in the duct section and in the particulate control device. The major advantages of this process over conventional wet methods are that a dry solid waste is produced and equipment can be easily set up in an existing power plant.

The sorbent material which used widely in the humidified duct injection processes is hydrated lime ($Ca(OH)_2$). It was shown that when $Ca(OH)_2$ is used as a sorbent material, the majority of the SO_2 removal takes place in the fabric filter [1]. For the efficient reaction of $Ca(OH)_2$ with SO_2 long sorbent/gas contact time as provided by the fabric filter is needed. Electrostatic precipitators have a shorter sorbent/gas contact time than fabric filters but most existing power plants are already equipped with this device. In order to increase desulfurization efficiency of these systems,

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hydrated lime is activated towards SO_2 by reacting with different additives such as siliceous materials and inorganic deliquescent salts.

Using fly ash as a reagent material for the production of reactive SO_2 sorbents, is very attractive both economically and environmentally because fly ash is a waste product of coal-fired power plants. The production of the reactive sorbents can be achieved by hydration of fly ash samples with $Ca(OH)_2$ slurry. The reaction between the fly ash and $Ca(OH)_2$ is called as the pozzolanic reaction and it gives a reactive product with a large surface area. In the reaction, activation starts with the digestion of vitreous-phase silica and/or alumina by alkaline water and this stage is considered to be rate limiting. Digestion of vitreous phase in the presence of $Ca(OH)_2$ yields hydrated calcium silico-aluminates which are fibrous gels, which can enhance the surface area of the reaction product [2,3]. Previous studies [3,4] have shown that the reactivity of $Ca(OH)_2$–fly ash sorbents depends strongly on their surface areas.

The aim of this work is to investigate the relation between the surface areas $Ca(OH)_2$–fly ash sorbents and the amount of reacted $Ca(OH)_2$ during hydration. In order to calculate the amount of reacted $Ca(OH)_2$, the $Ca(OH)_2$ content of sorbents is determined from their non-isothermal thermogravimetric curves.

2. Experimental

Fly ash samples collected from three different coal-fired power plants in Turkey were used in this study. The chemical composition of the ashes were determined according to the ASTM standards [5]. Fly ashes were hydrated with a natural hydrated lime which has a CaO content of 49.91% by weight.

Atmospheric hydration experiments were carried out in a polyethylene bottle which has been immersed in a thermostated water bath. The hydration variables were temperature (T) (333 and 363 K) and time (t) (4 and 8 h). Pressure hydration experiments were carried out in a 1000 ml Parr stirred autoclave. Hydration conditions were determined considering the following variables: time (1 and 2 h), temperature, and pressure (p) (383 K and 0.143 Mpa; 448 K and 0.892 MPa). Hydration pressures correspond to the vapor pressure of water at the experimental temperature. In hydration experiments fly ash/$Ca(OH)_2$ weight ratio (R) was kept constant and selected as 5/1 for atmospheric hydration and 1/1 for pressure hydration.

The $Ca(OH)_2$–fly ash mixtures were stirred well throughout the hydration. After hydration, the sample was vacuum-filtered and the filter cake was dried overnight in an atmospheric oven at 378 K. Physical properties of the hydrated fly ashes were then determined using an Autoscan-33 mercury porosimeter. The composition of the crystalline phases was detected with a X-ray diffractometer. The sorbents were X-rayed from 0° to 80° (2θ) using a Philips PW 3710 X-ray diffractometer with nicel filtered copper radiation.

A Shimadzu TG 41 thermal analyzer is used to obtain the thermal decomposition curves of hydrated sorbents. The experiments were performed at linear heating rate of 10 K min^{-1} from room temperature to 1073 K. Thermal decomposition of sorbents was carried out under nitrogen atmosphere with a flow rate of 40 cc min^{-1}.

3. Results and discussion

The production of reactive sorbents for flue gas desulfurization is achieved by hydration of $Ca(OH)_2$ with various fly ashes. The chemical composition and the mean particle size of fly ashes used in this study was given in Table 1. It is obvious from Table 1 that

Table 1
Chemical composition and mean particle size of the fly ash samples

Sample code	SiO_2 (%)	CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	Na_2O (%)	K_2O (%)	SO_3 (%)	Mean particle size (mm)
F1	32.83	30.35	4.51	5.61	13.34	2.15	1.37	7.36	0.021
F2	48.45	16.56	2.95	5.60	17.80	2.57	2.90	1.77	0.035
F3	21.04	51.02	3.09	3.01	7.31	1.48	0.85	9.84	0.049

each fly ash has a different chemical composition and mean particle size.

Hydration of fly ash–$Ca(OH)_2$ mixtures under favorable time and temperature conditions can enhance the utilization of $Ca(OH)_2$ during sulfation as compared to the utilization of pure $Ca(OH)_2$ [6]. The main reason of this phenomena is the pozzolanic reaction in the SiO_2–$Ca(OH)_2$–H_2O system with fly ash being the source of silica. It was reported that the reactivity of fly ash and its ability to react with $Ca(OH)_2$ to form highly reactive species (calcium aluminate silicate hydrates, calcium silicate hydrates, calcium aluminate hydrates, etc.) changes depending on hydration conditions and its chemical composition [7]. By taking into account these findings, hydration of fly ash–$Ca(OH)_2$ mixtures were conducted at different conditions using three different fly ashes. Measured surface areas and $Ca(OH)_2$ contents of hydrated sorbents were summarized in Tables 2 and 3.

It has been indicated that the reactivity of $Ca(OH)_2$–fly ash sorbents toward SO_2 depends strongly on their physical properties. The sorbent reactivity especially correlated well with its surface area and greater the surface area leads to, greater the amount of sulfur dioxide captured [3,4,6,9]. The effect of hydration conditions and the chemical composition of fly ashes on the surface area of hydrated fly ash–$Ca(OH)_2$ sorbents used in this study were discussed in detail elsewhere [6,9]. The aim of this study is to investigate the relation between sorbent surface area and reacted $Ca(OH)_2$ (the amount of $Ca(OH)_2$ that took part in pozzolanic reaction) during hydration. Reacted $Ca(OH)_2$ is equal to the difference between the amount of $Ca(OH)_2$ added to hydration mixture and $Ca(OH)_2$ content of the hydrated sorbent. The $Ca(OH)_2$ content of hydrated sorbents were determined from their non-isothermal thermogravimetric curves. The weight loss occurred between 623–823 K that corresponds to the thermal decomposition of $Ca(OH)_2$ to CaO and H_2O is used to calculate the $Ca(OH)_2$ contents of the hydrated sorbents (Tables 2 and 3).

Table 2
$Ca(OH)_2$ content and the total surface area of the sorbents prepared by atmospheric hydration technique

Sample code	Hydration conditions *T*/*R*/*t*	Added $Ca(OH)_2$ (mg)	$Ca(OH)_2$ content of sorbent (mg)	Total surface area ($m^2\ g^{-1}$)
F1	333/5:1/4	6.45	5.34	13.88
	333/5:1/8	6.45	4.72	14.50
	363/5:1/4	6.45	3.37	21.43
	363/5:1/6	6.45	2.55	28.71
	363/5:1/8	6.45	1.43	42.13
	363/–/8	–	–	22.49
F2	333//5:1/4	6.45	3.28	15.00
	363/5:1/4	6.45	2.88	21.73
	363/5:1/6	6.45	1.64	27.85
	363/5:1/8	6.45	0.82	28.62
	363/–/8	–	–	13.58
F3	333/5:1/4	6.45	7.21	13.97
	363/5:1/4	6.45	8.83	16.11
	363/5:1/6	6.45	8.55	18.62
	363/5:1/8	6.45	7.61	21.49
	363/–/8	–	3.70	14.34

Table 3
$Ca(OH)_2$ content and the total surface area of the sorbents prepared by pressure hydration technique

Sample code	Hydration conditions *T*/*p*/*R*/*t*	Added $Ca(OH)_2$ (mg)	$Ca(OH)_2$ content of sorbent (mg)	Total surface area ($m^2\ g^{-1}$)
F1	383/0.143/1:1/1	16.16	12.33	41.16
	448/0.892/1:1/2	16.16	16.03	8.82
	383/0.143/–/2	–	–	19.60
F2	383/0.143/1:1/1	16.16	13.89	30.95
	448/0.892/1:1/2	16.16	14.39	8.95
	383/0.143/–/2	–	–	10.22
F3	398/0.232/1:1/1	16.16	14.59	31.10
	448/0.892/1:1/2	16.16	16.03	17.21
	383/0.143/–/2	–	4.93	14.42

In order to determine the reactive species formed during the hydration reactive sorbents were examined by X-ray diffraction analysis (Table 4). It is possible to deduce from Table 4 that all sorbents contain the reactive hydrated species. The structure of these species changed depending on the chemical composition of the fly ash and hydration conditions. It was observed that $Ca_5SiO_{3.5}{\cdot}xH_2O$, $Ca_2SiO_4{\cdot}H_2O$, $Ca_2Al_4Si_{14}O_{36}{\cdot}14H_2O$ species existed in most of the hydrated sorbents. However the species which contain less molecular water such as $Ca_2SiO_4{\cdot}0.35H_2O$, $Ca_2SiO_4{\cdot}0.30H_2O$ are especially present in the sorbents produced through pressure hydration. Beside the sorbents prepared under pressure (at 448 K) contain

Table 4
The X-ray diffraction results of the $Ca(OH)_2$–fly ash sorbents prepared at different hydration conditions

Component		F1					F2				F3			
	T	363 K	333 K	363 K	383 K	448 K	363 K	363 K	383 K	448 K	363 K	363 K	398 K	448 K
	R		5/1	5/1	1/1	1/1		5/1	1/1	1/1		5/1	1/1	1/1
	t	8 h	4 h	8 h	1 h	2 h	8 h	8 h	1 h	2 h	8 h	8 h	1 h	2 h
$Ca(OH)_2$ Portlandite			▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
$Ca_5SiO_{3.5} \cdot xH_2O$ Calcium Silicate Hydrate		▨	▨	▨	▨	▨		▨	▨	▨	▨	▨	▨	▨
$Ca_2Al_4Si_{14}O_{36} \cdot 14\ H_2O$ Stellerite		▨	▨	▨	▨			▨	▨		▨	▨	▨	
$Ca_2SiO_4 \cdot 0.35\ H_2O$ Calcium Silicate Hydrate					▨	▨			▨	▨			▨	▨
$CaAl_2Si_2O_8 \cdot 4\ H_2O$ Gismondine			▨	▨	▨	▨		▨	▨					
$Ca_2SiO_4 \cdot 0.30\ H_2O$ Calcium Silicate Hydrate				▨	▨	▨			▨	▨		▨	▨	▨
$Ca_2SiO_4 \cdot H_2O$ Calcium Silicate Hydrate		▨	▨	▨	▨				▨		▨	▨	▨	
$CaSO_4$ Calcium Sulfate		▨	▨	▨	▨	▨	▨				▨	▨	▨	▨
$Ca_2Al_2SiO_7$ Gehlenite		▨	▨	▨	▨	▨								
SiO_2 Quartz		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
C Graphite		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
$CaSiO_3$ Wollastonite				▨	▨	▨	▨	▨	▨		▨	▨	▨	
$CaAl_2Si_2O_8$ Anorthite							▨	▨	▨	▨				
Fe_2O_3 Hematite		▨	▨	▨	▨	▨	▨	▨	▨	▨				
CaO Calcium Oxide											▨	▨	▨	▨
SiO_2 Silicon Oxide									▨	▨				
$CaCO_3$ Calcite		▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨
$Ca_4Al_2O_6(SO_4) \cdot 14H_2O$ Calcium Alumina Sulfate Hydrate			▨	▨	▨	▨					▨	▨	▨	▨
$CaAl_2Si_3O_{10} \cdot (OH)_2$ Prehnite					▨	▨			▨	▨	▨	▨	▨	▨

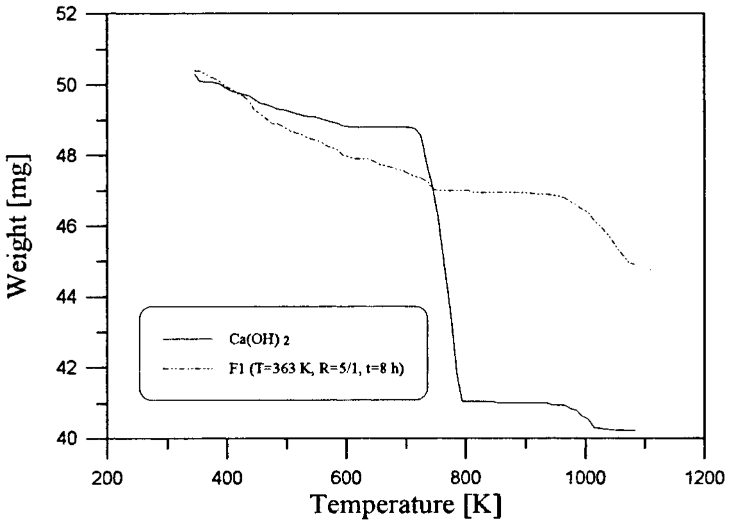

Fig. 1. Non-isothermal thermal decomposition curves of $Ca(OH)_2$ and selected $Ca(OH)_2$–F1 sorbent in N_2 atmosphere.

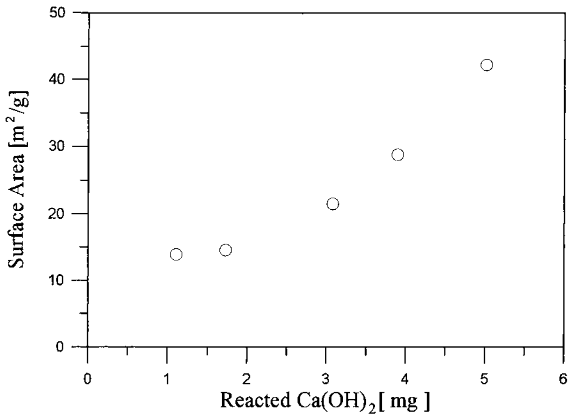

Fig. 2. The relation between the reacted $Ca(OH)_2$ and the total surface area of the $Ca(OH)_2$–F1 sorbents prepared by atmospheric hydration technique.

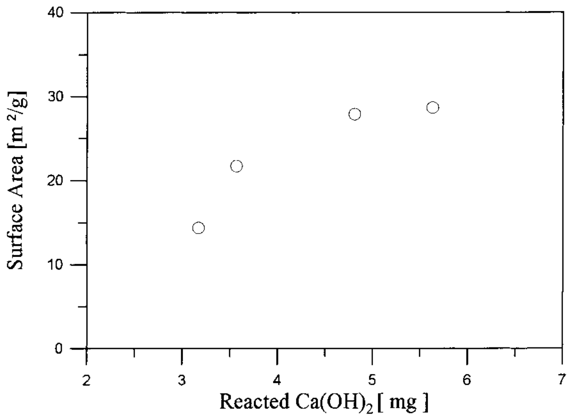

Fig. 3. The relation between the reacted $Ca(OH)_2$ and the total surface area of the $Ca(OH)_2$–F2 sorbents prepared by atmospheric hydration technique.

some ionic hydroxyl and also peak intensity of prehnite ($Ca_2Al_2Si_3O_{10}(OH)_2$) was found to be stronger in these sorbents. These results are in agreement with results reported by Jozewicz et al. [3]. The formation of calcium alumina sulfate hydrate ($Ca_4Al_2O_6(SO_4)\cdot 14H_2O$) was also observed for the sorbents produced from F1 and F3 fly ashes due to their high SO_3 content.

The typical thermograms for pure $Ca(OH)_2$ and fly ash (F1)–$Ca(OH)_2$ sorbent were shown in Fig. 1. Literature data indicated [10] that the surface area of the hydrated sorbents increases with the increasing amount of reactive species formed during hydration. The dissolution of $Ca(OH)_2$ and SiO_2 in the slurry and the ability of these components to combine each other determines the amount of these reactive species. Therefore, the amount of reacted $Ca(OH)_2$ is a decisive parameter for reactivity which can be calculated from the $Ca(OH)_2$ content of the sorbent. Figs. 2 and Fig. 3 clearly show that the surface area and hence reactivity of the sorbent increases with the increasing amount of reacted $Ca(OH)_2$ during pozzolanic reaction. It has also been concluded that the relation between the reacted $Ca(OH)_2$ and sorbent surface area changes with respect to the particle size, form of the SiO_2 present in fly ash (quartz or silicon oxide) and CaO contents of the fly ashes (Tables 1 and 4). As mentioned earlier, these properties strongly effect the ability of fly ash to react with $Ca(OH)_2$ during hydration. Since the CaO content of F3 fly ash is high, the $Ca(OH)_2$ contents of sorbents produced from the ash were found to be higher than the added $Ca(OH)_2$. Besides the sorbent produced without the addition of $Ca(OH)_2$ contains $Ca(OH)_2$ (Table 2). Thus, it is possible to obtain reactive SO_2 sorbents through hydration of fly ashes with high CaO content alone (no $Ca(OH)_2$ added to the slurry). These sorbents can be as reactive towards SO_2 as those produced by slurrying low calcium fly ash with $Ca(OH)_2$ [8]. It was also detected by X-ray diffraction that although the sorbents prepared by the hydration of F1 and F2 fly ashes alone contains no $Ca(OH)_2$ peak, this peak is present in the sorbents those prepared from F3 fly ash alone. These results are compatible with the results obtained from thermogravimetric analysis.

In Table 3, the results obtained for the sorbents produced through pressure hydration were given. These results clearly showed that pressure hydration fosters the formation of a sorbent reactive with SO_2 from fly ash and $Ca(OH)_2$ in a much shorter time than does atmospheric hydration. Although the solubility of SiO_2 present in fly ash increased with increasing temperature and pressure (448 K and 0.891 MPa); the solubility of $Ca(OH)_2$ decreases and as a result the amount of hydrated species obtained through pozzolanic reactions is being reduced. Besides, since aluminium containing reactive species (CaAlSi) are decomposed at high temperature (446–473 K), according to the reaction given below this also caused a significant decrease in the surface area of the sorbents obtained at 448 K. The X-ray diffraction results also showed that the peak intensity of these species (gismondine and stellerite) decreased (even disappeared) in the sorbents hydrated at 448 K.

$$\mathrm{CaAlSi} \rightarrow \mathrm{CaSi} + \mathrm{Al_2O_3} \qquad (1)$$

While the added $Ca(OH)_2$ do not react with SiO_2 during the atmospheric hydration of F3 fly ash, a certain amount of it reacts with SiO_2 during the pressure hydration of the same fly ash. The reason of this phenomena is probably due to the fact that almost all SiO_2 available for the reaction with lime is used. As a result the surface area of the sorbent obtained through pressure hydration ($31.09\ m^2\ g^{-1}$) is found higher than that obtained at atmospheric hydration ($21.49\ m^2\ g^{-1}$).

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