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Fly Ash Reactivation for the Desulfurization of Coal-Fired Utility Station's Fluc Gas

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Abstract

Fly ash hydration in the liquid phase has been studied by employing temperature, hydration time, and water/fly ash weight ratio as variables. The results show that temperature and hydration time have a large positive effect in surface area development of the hydrated ashes (due to the formation of hydrated tetracalcium aluminate) whereas the water/fly ash weight ratio effect seems to be negative but its influence is very small. Desulfurization tests have been carried out with some of these hydrated fly ashes. Tests consisted of exposing the solid for 1 h to an N_2/SO_2 gas stream containing 500 ppm SO_2. The variables employed were temperature and relative humidity. The results show that SO_2 capture rises with temperature and, particularly, with an increase in relative humidity. A correlation between surface area and SO_2 capture was found. The greater the surface area, the greater the amount of SO_2 captured. This fact shows that hydrated tetracalcium aluminate is a highly reactive substance against SO_2.

INTRODUCTION

Coal-fired utility stations remove large amounts of waste powder called fly ash. This removal is necessary to prevent pollution of the environment. At the present time, economical analyses about the modification of old power plants show that postfurnace injection of calcium hydroxide and humidification in the ductwork downstream of the air preheater and upstream of the particulate collection system (baghouse or ESP) are the best processes (*1–9*). This zone provides the necessary reaction space for SO_2 capture. Therefore, this process offers the potential for low capital cost retrofitable technologies.

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Fly ashes with a small amount of calcium can be used as additives in cement production. High calcium fly ashes could be employed for SO_2 removal, and afterward reactivated in utility stations which do not warrant great investment and whose remaining boiler time is limited.

From a mineralogic point of view, fly ashes mainly consist of vitreous silicoaluminates, mullite, quartz, hematites, magnetite, and no combusted materials (*10*). Mullite ($3Al_2O_3 \cdot 2SiO_2$) is generally present in low calcium fly ashes but rarely found in fly ashes of high calcium content. Anhydrite ($CaSO_4$), hydrated tricalcium aluminate ($3CaO \cdot AL_2O_3 \cdot xH_2O$), and, sometimes, calcium oxide (CaO) can be present into high calcium fly ashes as well (*10*).

Fly ashes contain a large amount of vitreous material because their solidification process is very fast when the magma goes out of the boiler. Its temperature decreases very quickly. So fly ashes have a large vitreous phase/crystalline phase weight ratio, which is decisive for the pozzolanic power of fly ashes. Previous workers have reported that 70/30 is the best ratio (*11*). The fly ashes used in this work have a ratio of 72/28.

Fly ash reactivation is based on the pozzolanic reaction (*7, 12, 13*) which consists of the production of both a large surface area and reactive compounds.

Fly ash hydration leads to digestion of the vitreous phase and, in the presence of calcium hydroxide, yields hydrated silicoaluminates that reprecipitate on the fly ash surface. It is possible that hydrated monocalcium silicate, dicalcium silicate, and/or hydrated tetracalcium aluminate, which are fibrous gels, can enhance the surface area. The controlling step of this reaction seems to be the dissolution rate of alumina or/and silica from the vitreous phase into the aqueous phase. The dissolution can be enhanced by increasing the temperature, the reaction time, or/and by adding $(NH_4)_2HPO_4$ or NaOH that aid in alumina and silica digestion (*12, 14–19*).

Reactivated fly ashes can be employed as reactive solids for SO_2 capture because the silicates and/or aluminates obtained have great reactivity. According to the experimental conditions used, the reactive solid can have a higher desulfurization power than calcium hydroxide. SO_2 capture capacity improves when the temperature and/or the relative humidity increases (*12, 15, 18–20*). Surface area and alkalinity are also very important factors in SO_2 removal. On the other hand, the addition of inorganic deliquescent salts ($CaCl_2$, NaOH, NaCl, $FeCl_3$, etc.) can increase the SO_2 desulfurization power as well (*8, 16, 21–24*).

The present paper deals with the reactivation of a fly ash that contains a large amount of free calcium. Temperature, time, and water/fly ash weight ratio effects were tested. Desulfurization tests were performed under bag-filter conditions, with temperature and relative humidity as the assayed variables.

EXPERIMENTAL

Apparatus

Figure 1 shows the experimental apparatus used in our desulfurization experiments. The glass reactor (12 mm in diameter, 450 mm in height) was packed with 2 g hydrated fly ash mixed with stainless steel coils (2 mm in diameter) to prevent channeling and an excessive pressure drop. The reactor was thermostated by pumping on oil from an external bath. Further details on the experimental setup are described elsewhere (*25*).

The procedure starts with conditioning the fixed bed for 15 min with a N_2/steam mixture at a flow rate of 27 mL/s (measured at the reactor temperature and with the pressure slightly higher than atmospheric). Then, SO_2 (proceeding from an N_2/SO_2 cylinder with 1870 ppm of SO_2) was added to this stream with an initial concentration of 500 ppm to keep the same global flow as reported above. The desulfurization test lasted 1 h, and the SO_2 concentration was measured continuously by a nondispersive infrared photometer (UNOR 6N) which yielded a curve of SO_2 (ppm) versus time.

The experiment was repeated using inert silica as the solid to determine the model flow of the system. The amount of SO_2 removal was calculated from the area enclosed by the two curves.

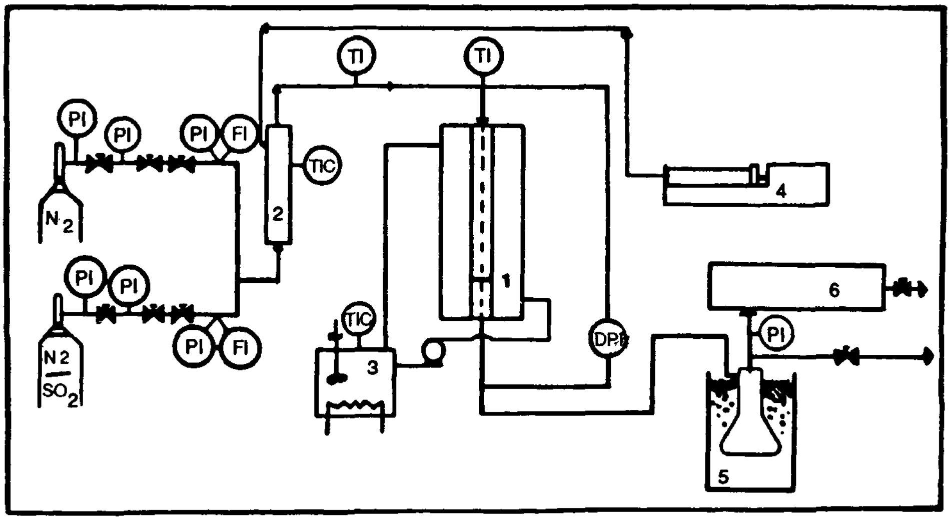

FIG. 1. Apparatus for desulfurization test: (1) reactor; (2) vaporizer; (3) thermostatic bath; (4) syringe pump; (5) ice trap; (6) SO_2 analyzer.

Reactivation of Fly Ash

Reactivation of fly ash was carried out by hydration at atmospheric pressure. Fly ash came from the Cercs (Barcelona) Power Station which belongs to the electric company F.E.C.S.A. Table 1 shows its chemical and mineralogical analysis and surface area.

Experimental tests were made by using a 2^3 factorial design with the following variables: temperature T (55–85°C), hydration time t (2–7 h), and water/fly ash weight ratio R (10–20). The objective function was the surface area (S_w) of the reactivated fly ash. Table 2 shows the experimental values of the surface areas obtained.

Another set of hydration experiments was performed but with the hydration time reduced to 1–2 min. We called them "zero time" experiments. Table 3 shows these experimental conditions and results. As can be seen, in all cases we obtained a significant increase in the surface area, especially in Samples A-2 and A-8, which were prepared at the highest temperatures and the longest hydration times. The surface area development of "zero time" samples was lower than the values obtained at long times.

The Yates' algorithm application (*26*) to the factorial design of hydrated solids at long times (see Table 4) showed a positive influence of the average of the overall hydration treatment on the surface area increment. However,

TABLE 1
Analysis of Cercs Fly Ash[a]

1. Mineralogic Analysis:	
Vitreous phase	72
Crystalline phases:	
Anhydrite	8
Calcium oxide	7
Iron oxide	8
Quartz	5
2. Chemical Analysis:	
SiO_2	37.05
Al_2O_3	13.45
Fe_2O_3	7.12
MgO	1.57
CaO	34.21
Na_2O	0.35
K_2O	1.21
TiO_2	0.68
P_2O_5	0.14
SO_3	4.70
3. Surface Area	0.42 m^2/g

[a] All values are percentages by weight.

TABLE 2
Experimental Conditions and Surface Area Values of Hydrated Fly Ash at Long Times

Sample	T (°C)	t (h)	R (g water/g fly ash)	S_w (m^2/g)
A-1	70	4.5	15	5.5
A-2	85	7	10	30.8
A-3	70	4.5	15	5.0
A-4	85	2	10	2.8
A-5	55	7	20	2.8
A-6	70	4.5	15	2.3
A-7	55	2	20	4.1
A-8	85	7	20	24.0
A-9	55	2	10	1.5
A-10	85	2	20	3.2
A-11	55	7	10	3.9
A-12	70	4.5	15	3.5

the individual effect of the three tested variables showed that temperature and reaction time do have a positive effect on the surface area increment whereas the water/fly ash weight ratio has a slightly negative effect but is very close to zero. As expected, crossed terms have a lower incidence. The influence of each has been evaluated by fitting a linear first-order empirical model (*26*) whose normalized variables were

$$x_1 = \frac{T - 70}{15}; \qquad x_2 = \frac{t - 4.5}{2.5}; \qquad x_3 = \frac{R - 15}{5} \tag{1}$$

where x_1 is the normalized temperature, x_2 is the normalized time, and x_3 is the normalized water/fly ash weight ratio.

TABLE 3
Experimental Conditions and Surface Area Values of Hydrated Fly Ash at "Zero Time"

Sample	T (°C)	R (g water/ g fly ash)	S_w (m^2/g)
A-13	70	23	2.0
A-14	70	7	1.8
A-15	95	15	2.1
A-16	45	15	1.7

TABLE 4
Yates' Algorithm Application to Long-Time Hydrated Samples

Sample	S_w	(1)	(2)	(3)	Divisor	Estimate	Variable
A-9	1.5	4.3	39	73	8	9.1	Mean
A-4	2.8	34.6	35	48	4	12.1	T
A-11	3.9	7.3	28	50	4	12.4	t
A-2	30.8	26	20	48	4	11.9	$T \times t$
A-7	4.1	1.3	30	−4.9	4	−1.2	R
A-10	3.2	27	19	−8.0	4	−2.0	$T \times R$
A-5	2.8	−0.8	26	−10	4	−2.7	$t \times R$
A-8	24	21	22	−3.6	4	−0.9	$T \times t \times R$

Variance analysis involving the experimental error calculated from the three replies of the center point showed that at a probability level of 95%:

$$F_{\text{exp}} = 17.8 < F_{\text{theor}} = 18.5 \tag{2}$$

Therefore, the model is statistically significant. However, the proximity of the experimental and theoretical F values indicates that a nonlinear model could be better.

A variance test of the parameters showed that the variables x_3, $x_1 \cdot x_3$, $x_2 \cdot x_3$, and $x_1 \cdot x_2 \cdot x_3$ are not statistically significant. Therefore, their respective terms can be rejected in the proposed model. Thus, the linear model that relates the hydrated fly ash surface area to the temperature and hydration time is

$$S_w = 7.8 + 6.1 * x_1 + 6.2 * x_2 + 6.0 * x_1 x_2 \quad (\text{m}^2/\text{g}) \tag{3}$$

On the other hand, x-ray diffractometries have been performed for a large number of the samples to detect the presence of complex compounds which were not detected in the original fly ash. Results (see Table 5) showed the formation of hydrated tetracalcium aluminate ($4CaO \cdot Al_2O_3 \cdot 13H_2O$) in almost all the samples. The formation of this hydrated complex compound correlated well with the surface area increment of the solid. According to this, Sample A-2 presented the highest surface area because it contained the largest amount of hydrated tetracalcium aluminate.

This sample had been prepared at 85°C over 7 h. A conclusion can be drawn from the last result: Surface area development is due to the formation of complex hydrated compounds according to the previously reported values.

A SEM study was made to confirm the surface area increment of some

TABLE 5
Intensity of Tetracalcium Aluminate Peaks in X-Ray Analyses

Sample	S_w (m^2/g)	Counts
A-1	5.5	—
A-2	30.8	112
A-3	5.0	—
A-4	2.8	25
A-5	2.8	13
A-6	2.3	—
A-7	4.1	11
A-8	24	44
A-9	1.5	0
A-10	3.2	28
A-11	3.9	17

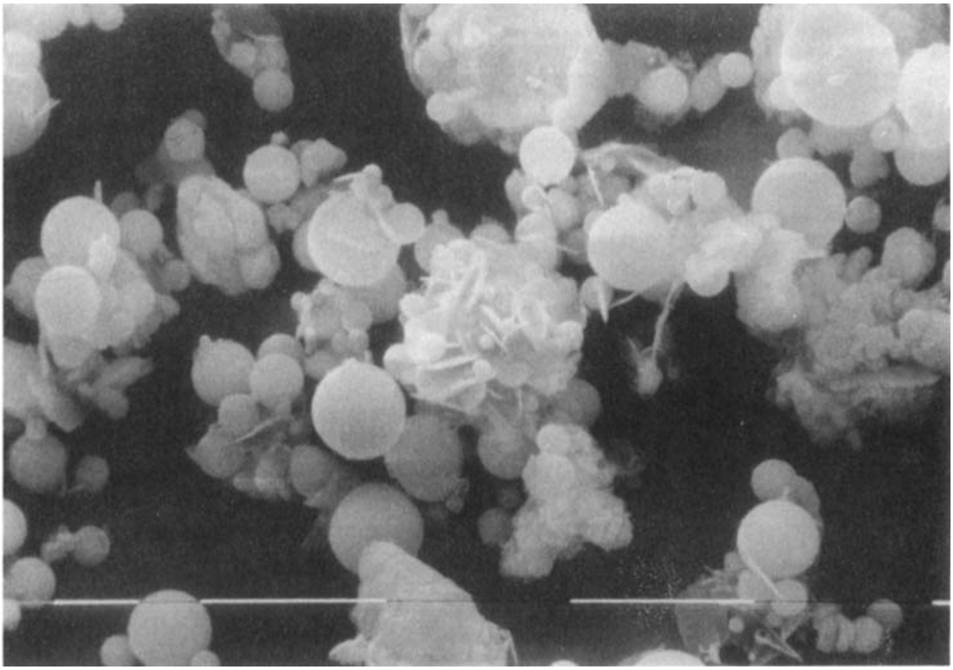

FIG. 2. SEM microphotograph of Sample A-9 after 2 h of hydration at 55°C.

of the prepared samples. Figure 2 shows a microphotograph (2500×) of Sample A-9 (hydrated at 55°C for 2 h). As can be seen, a more irregular structure (due the formation of portlandite) has been formed compared with the spherical forms and even environs of the original fly ash (see Fig. 3). The SEM microphotograph of Sample A-2 (hydrated at 85°C for 7 h) is shown in Fig. 4. In this case the structure was less irregular but more porous, which is due to the formation of hydrated tetracalcium aluminate.

Desulfurization Test Using Hydrated Fly Ashes

A number of runs have been performed to determine the desulfurization power of some of the solids obtained, and to establish the influence of both the temperature and relative humidity (RH) on SO_2 removal by using the hydrated fly ash as well. The ranges of variation of the variables were: RH (30–60%) and T (60–80°C).

By taking into account that the water/fly ash weight ratio does not affect the hydration process, four of the eight samples of the factorial design were chosen for these tests. These samples correspond to the side of the factorial design in which the water/fly ash weight ratio is 10. In order to obtain data close to the operation conditions of the power plant, three

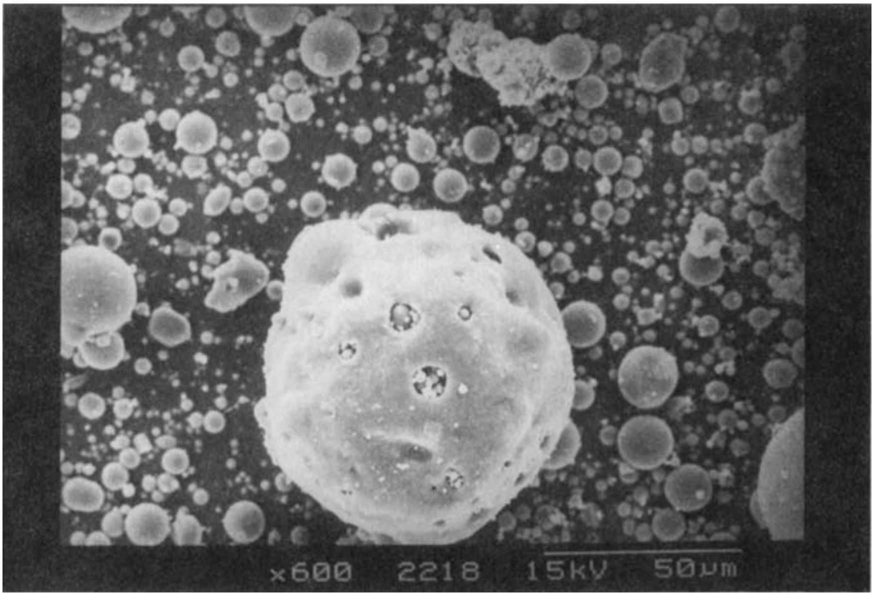

FIG. 3. SEM microphotograph of untreated fly ash sample.

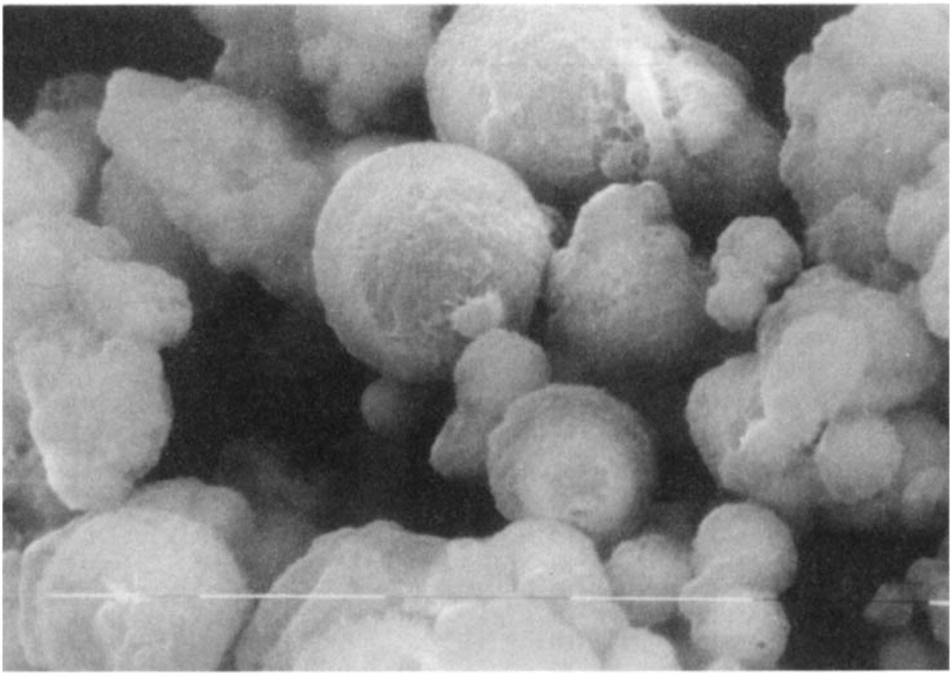

FIG. 4. SEM microphotograph of Sample A-2 after 7 h of hydration at 85°C.

hydrated fly ashes at "zero time" were also assayed (A-14, A-15, and A-16).

Table 6 shows the experimental conditions of the desulfurization runs, the percentages of SO_2 removal, and the surface area decrease ($-\Delta S_w$) of each sample. By studying this result it can be deduced that, for a given sample, SO_2 capture increases when the temperature and, especially, the relative humidity increases. It seems that the activation energy of the reaction increases with temperature. When the relative humidity increases, the adsorption of water on the fly ash surface is greater. Thus, the amount of water is larger and SO_2 removal increases.

Data show that there is a direct relationship between hydrated fly ashes surface area and the amount of captured SO_2. So_2 removal increased with increasing surface area (as can be seen in Table 6 for Sample A-2), and the subsequent decrease in the percentage of surface area was greater. It follows from these facts that hydrated tetracalcium aluminate is a very reactive compound with respect to SO_2.

Samples A-2, A-4, and A-11 were subsequently analyzed by x-ray dif-

TABLE 6
Desulfurization Tests: Conditions and Results

Sample	Experiment	T (°C)	Relative humidity	% SO_2 removal	$-\Delta S_w$
A-14	AD-13	60	30	5	1.2
	AD-14	60	60	25	—
	AD-15	80	30	13	0.9
	AD-16	80	60	35	0.9
A-15	AD-5	60	30	7	0.8
	AD-6	60	60	23	0.9
	AD-7	80	30	8	0.7
	AD-8	80	60	24	0.7
A-16	AD-9	60	30	8	1.1
	AD-10	60	60	17	0.9
	AD-11	80	30	10	—
	AD-12	80	60	32	1.0
A-9	AD-1	60	30	6	0.9
	AD-2	60	60	19	0.6
	AD-3	80	30	8	0.8
	AD-4	80	60	37	0.9
A-4	AD-17	60	30	18	1.9
	AD-18	60	60	37	1.7
	AD-19	80	30	19	1.8
	AD-20	80	60	65	1.8
A-2	AD-21	60	30	64	—
	AD-22	60	60	100	22.8
	AD-23	80	30	72	20.0
	AD-24	80	60	100	22.9
A-11	AD-25	60	30	14	2.4
	AD-26	60	60	43	2.6
	AD-27	80	30	22	2.3
	AD-28	80	60	74	2.7

fractometry. Before the desulfurization tests, the solids had a significant amount of hydrated tetracalcium aluminate. After the runs were made (exposure time of 1 h to a stream with 500 ppm of SO_2, at 80°C, relative humidity of 60%), the three samples experienced a very large decrease in the x-ray peak intensity corresponding to hydrated tetracalcium aluminate. To sum up, in Samples A-2 and A-4, hydrated tetracalcium aluminate was not detected. This confirms the following conclusion: Hydrated tetracalcium aluminate is a very reactive substance with respect to SO_2 (*12, 13, 15, 18, 19*).

CONCLUSIONS

Laboratory studies indicate that hydrated fly ashes can be used as reactive solids in the desulfurization dry-wet process of fumes. In a practical situation it would be necessary to separate (partly or totally, by using a baghouse or ESP) the fly ashes before the ductwork is reached. After the fly ashes have been captured, they have to be hydrated at high temperatures (85°C) and for reaction times as long as possible (7 h). Then the solid obtained has to be injected into the ductwork close to the injection point of humidification water. Hydration of fly ashes is more effective as the temperature and reaction time are increased. Hydrated tetracalcium aluminate with a large surface area is formed in the hydration process.

Desulfurization of a stream of flue gas through the use of different reactivated fly ashes shows that increases in the temperature and/or, particularly, in the relative humidity promote higher SO_2 removal. On the other hand, hydrated fly ashes that initially had a large surface area (due to the formation of portlandite and/or hydrated tetracalcium aluminate) lead to greater SO_2 removal.

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