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Desulfurization yield of calcium hydroxide/fly-ash mixtures. Thermogravimetric determination

A. Garea, M.I. Ortiz, J.R. Viguri, M.J. Renedo, J. Fernandez, J.A. Irabien*

Departamento de Química. E.T.S.I.I. y T., Universidad de Cantabria, Avda. Los Castros s/n. 39005 Santander, Santander, Spain

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Abstract

This work reports the thermogravimetric characterization of the solid products resulting from the low temperature reaction between SO_2 and mixed solids containing hydrated mixtures of calcium hydroxide and fly-ashes. The latter sorbents were obtained after a pressurized hydration procedure of coal fly-ashes and commercial calcium hydroxide following a factorial design of the experiments. The analysis of the TG curves performed in a high temperature thermobalance allowed calculation of yield of the desulfurization reaction expressed as mol SO_2/mol Ca, a parameter needed for the design and optimization of desulfurization processes.

Keywords: $Ca(OH)_2$/fly-ash sorbents; Desulfurization yield; Thermogravimetric characterization

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1. Introduction

Control of sulfur-dioxide emissions in large coal-fired plants is performed by three categories of post-combustion techniques: dry sorbent injection, semi-dry systems and wet systems. The direct injection of dry into flue gas duct offers a useful alternative for controlling sulfur dioxide emissions at low temperature, and is relatively simple compared to semi-dry or wet methods with a potential for retrofit applications [1–3].

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* Corresponding author.

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In-duct injection systems work with a dry powdered sorbent introduced into the humidified flue gas duct, downstream of the air preheater and ahead of the particulate collector. Due to the short residence time of the solids in the injection process (1–3s), a reactive sorbent must be used in order to achieve acceptable levels of SO_2 removal.

A great deal of effort has been devoted to improving sorbent reactivity by substituting conventional high calcium content hydrated lime with other sorbents with a high specific surface. Alternatives investigated have included sodium-based sorbents such as sodium bicarbonate and sodium sesquicarbonate, or naturally occuring sodium bicarbonate minerals [4,5]. But the main problem is the cost of these reagents (except where these are locally available in the naturally occurring form).

Reactivation and reuse of different spent solids such as lime and recycled spent sorbent [6], boiler limestone or $Ca(OH)_2$ injection solids [7], hydrated lime with silica fume and aluminum hydroxide [8], and ψ–alumina/Ca sorbents containing metal oxides, have also been investigated [9].

The addition of inorganic hygroscopic or deliquescent sodium-based salts, NaCl, $NaNO_3$, Na_2CO_3/MgO, $Mg(OH)_2$, Na_2HPO_4, NaOH, $CaSO_3$, and $CaCl_2$ [10–12], as potential performance additives to conventional high calcium hydrate, can increase the desulfurization rate and yield.

Sorbents obtained by mixing lime or $Ca(OH)_2$ with different sources of silica such as diatomaceous earth, montmorillonitic/bentonitic clays and fly-ash [13,14], have been demonstrated to provide significantly higher conversion of calcium compared to the conversion obtained using hydrated lime. The use of fly-ashes [15] in dry FGD systems is attractive both economically and environmentally, because fly-ash is the most voluminous by-product from all coal-fired power plants.

Several studies [16–23] have shown that hydration products with different reactivities can be prepared from $Ca(OH)_2$ and fly-ash. The solid reactivities after 1 h of exposure to different SO_2 concentrations in packed bed reactors, increased with the specific surface in the tests carried out at low temperatures ($< 100°C$) and relative humidities ranging from 10% to 70%. The pozzolanic reaction of silica in the fly-ash with $Ca(OH)_2$ in the slurry to form highly hydrated solids has been considered to be the reason for the improvement in solid reactivity [16,18,22,23].

Although the reactivity of $Ca(OH)_2$/fly-ash hydrates was generally reported to be higher than the reactivity of $Ca(OH)_2$, there are some exceptions in solids containing silica [18]. However, the hydrated solids produced at temperatures higher than 150°C and at high pressure were less reactive towards SO_2 than those obtained at lower hydration temperatures [7,14]. At reaction times less than 10s Rochelle et al. [21] showed that lime hydrates were not more reactive than the reference hydrate.

The study of the desulfurization yield of different sorbents prepared with commercial $Ca(OH)_2$ and fly-ash has been the main interest of this work in order to establish the maximum conversion with reference to calcium and compared to the previous value of 0.62 mol SO_2/mol Ca given for $Ca(OH)_2$ in the literature [24,25] for dry processes. Thermogravimetric analysis at high temperature has been used to characterize the sorbents and to obtain the desulfurization yield of the products.

2. Experimental

The sorbents were prepared using commercial $Ca(OH)_2$ obtained from Calcinor S.A. and ASTM Class F coal fly-ash collected in an electrostatic precipitator at Pasajes (Guipuzcoa-Spain), a bituminous coal-fired power plant. The chemical composition and physical properties of these materials are shown in Table 1. Sample preparation consisted of the batch pressure hydration of the fly-ash/$Ca(OH)_2$/H_2O mixture in a Parr 4562 stirred stainless steel reactor of 325 cm^3 volume as a pressure hydrator. The solid materials were kept at a constant value of 15 g with a fly-ash/$Ca(OH)_2$ (FA/CH) weight ratio of 3/1 and 1/3 ($g\,g^{-1}$). The total solid and water, in water/solid (W/S) weight ratios of 20/1 and 10/1 ($g\,g^{-1}$), were loaded into the reactor at room temperature. The reactor was sealed and then the sampling cylinder was pressurized with nitrogen. The amount of nitrogen was calculated, taking into account the vapour pressure of water at the experimental temperature, to reach the selected pressure (p) ranging from 0.843 MPa to 1.26 MPa. Temperature (T) was maintained at 170 and 110°C for a given period of time (t) of 1 and 4h by a Parr 4841 controller. After reaction, the reactor and its content were cooled to 35°C; then the N_2 was released, the reactor disassembled, and the mixture was filtered with a 0.45 μm mesh filter; the filter cake was dried in a oven at 105°C to constant weight, ground and sieved through a 60 μm mesh, and the filtrate was analyzed for dissolved calcium by atomic absorption spectrophotometry in a Perkin-Elmer 1100B Atomic Absorption Spectrometer.

The reaction between the sorbents and SO_2 was performed in a glass-jacketed fixed bed reactor, under isothermal conditions, where the sorbent was dispersed in an inert

Table 1
Physical properties and chemical composition of $Ca(OH)_2$ and fly-ash

Physical properties	Calcium hydroxide	Fly-ash
BET specific surface/$m^2\,g^{-1}$	16.2	2.9
Pore volume/$cm^3\,g^{-1}$	1.395	0.686
Porosity	0.719	0.564
Particle diameter/μm	< 60	< 60
Pore diameter (mean vol.)/μm	1.322	4.344
Skeletal density/$g\,cm^{-3}$	1.830	1.889

Chemical composition/%	Calcium hydroxide	Fly-ash
SiO_2 + Insolubles	0.50	87.00
Al_2O_3	0.20	0.90
Fe_2O_3	0.11	2.67
MgO	0.40	0.24
CaO	2.00	0.84
$Ca(OH)_2$	93.10	—
CO_2	3.90	—
MnO_2	0.01	—
S	0.01	0.16
C + volatiles	—	8.17

silica sand. The entire bed was supported on a 3.6 cm diameter fritted glass plate contained in the glass cylinder.

100% SO_2 flue gas was passed through the humidification system where the gas in contact with water vapour was produced at a steady rate in two absorbers of 250 cm^3 each. Both flasks contained small glass spheres in order to improve the contact between gas and liquid phases and were submerged in a water bath at a maintained constant temperature by means of a controller. After water saturation, the humidified SO_2 flowed to the reactor through a system of preheated pipes. The reactor was maintained at the reaction temperature by means of hot water passing through the jacket. A schematic diagram of the experimental set-up is shown in Fig. 1.

The wet bulb temperature was measured just downstream of the reactor using a wetted wick thermometer. The difference between dry and wet bulb temperatures was the "approach to saturation", which together with the pressure measurement (U-tube manometer) established the relative humidity under the test conditions.

After the reaction time was completed, the entire bed was brought out from the reactor. The reaction product was sieved to separate the spent sorbent ($d_p < 60\,\mu m$) from the inert silica sand ($d_p < 150\,\mu m$) using a Retsch Vibro type sieving unit. The reaction products without inert sand were analyzed using two analytical methods:

(i) The thermogravimetric analysis was carried out in a Perkin-Elmer TGA-7 unit, with a high-temperature furnace (50–1500°C), a PE 7500 microprocessor and a TAC-7 thermal analysis controller. Synthetic air was used as carrier gas (30 ml min^{-1}) in order to oxidize the $CaSO_3$ formed in the desulfurization reaction to $CaSO_4$. In all TG analysis, the sample mass was between 10 and 20 mg. The temperature program was:

$$\begin{tikzcd}
50\,^{\circ}\mathrm{C} \arrow[r, "20\,^{\circ}\mathrm{C\,min^{-1}}"] & 600\,^{\circ}\mathrm{C}\ (20\,\mathrm{min}) \arrow[r, "20\,^{\circ}\mathrm{C\,min^{-1}}"] & 1200\,^{\circ}\mathrm{C}\ (0\text{-}60\,\mathrm{min}) \arrow[dl, "20\,^{\circ}\mathrm{C\,min^{-1}}"] \\
50\,^{\circ}\mathrm{C} & 1300\,^{\circ}\mathrm{C}\ (0\text{-}60\,\mathrm{min}) \arrow[l] &
\end{tikzcd}$$

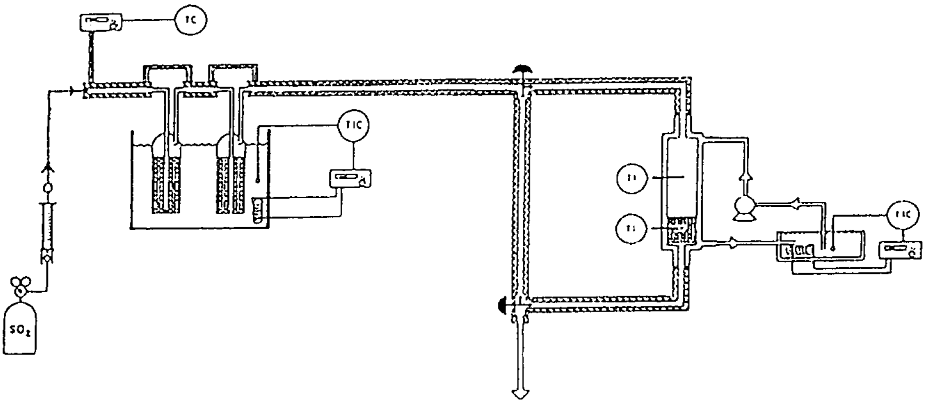

Fig. 1. Experimental set-up for the desulfurization tests.

(ii) Ion chromatography was utilized in order to calculate the desulfurization yield of the products after acidic digestion and solubilization of the reacted solids [26]. The resulting solution was analyzed with a Waters 746 Ion Chromatograph, with a conductivity detector, model 430, and IC-Pack A anionic column, yielding the SO_4^{-2} concentration in the sample.

3. Results and discussion

3.1. Characterization of the sorbents

Table 2 presents the factorial design of the experiments (2^3). Five replicate experiments (S17) carried out on the mid-range of the experimental variables were used to determine the experimental error.

First, a TG characterization of the initial $Ca(OH)_2$, fly-ash and hydrated solids S1–S17 was carried out by heating from 50 to 1300°C in synthetic air for the $Ca(OH)_2$. Analysis and comparison of the TG curves led to the following observations: (i) the first mass loss, between 50 to 225°C, attributed to the humidity of the solids; (ii) the second, which was only present in the hydrated solids between 225 and 450°C, attributed to dehydration of the hydrated sorbents; (iii) the next, between 450 and 850°C, due to the decomposition of $CaCO_3$ [25]; (iv) the sorbents obtained from low fly-ash/$Ca(OH)_2$ hydration ratios of 5/3 and 1/3, showed a mass increase between 450 and 550°C, probably due to the oxidation reaction of highly hydrated products originating from pozzolanic reactions of $Ca(OH)_2$ with fly-ash; and (v) the final mass loss between 850 and 1300°C attributed to sulfate decomposition (SO_3(g)) as will be explained. Fig. 2 gives representative thermoanalytical curves of the initial reagents and the sorbents S14, S17 and S8, corresponding to the three different fly-ash/$Ca(OH)_2$ hydration weight ratios of 3/1, 5/3 and 1/3. Similar weight–time profiles were obtained with the remaining solids. The sorbent mass losses at different temperatures are shown in Table 3, the mass loss between 850 and 1300°C in all the tested sorbents being negligible ($< 1.1\%$).

3.2. Desulfurization yield

The desulfurization yield of fly-ash/calcium hydroxide mixtures has been studied under the reaction conditions given in Table 4.

The reaction products were characterized using thermogravimetric analysis. Due to the complexity of the reacted solids, the work has focused on the determination of the yield of the desulfurization reaction, trying at the same time to give an explanation of the thermoanalytical behavior of the studied solids according to a previous work reported in the literature by the authors [25].

Fig. 3 presents the thermoanalytical curves of the S14 reacted solid, i.e., S14p. Six differentiated weight changes can be observed in the DTG curve: (i) the mass loss between 50 and 225°C due to the humidity of the solid; (ii) the mass loss between 225 and 375°C attributed to dehydration of the reaction of the product; (iii) the next,

Table 2
Experimental design, temperature (T), time (t), fly-ash/$Ca(OH)_2$ weight ratio (FA/CH), pressure (p) and water/solid weight ratio (W/S) in the hydration runs S1–S17

Sample code	T/ °C	t/ (h)	FA/CH/ ($g\,g^{-1}$)	p/ MPa	W/S ($g\,g^{-1}$)	Sample code	T/ °C	t/ h	FA/CH ($g\,g^{-1}$)	p/ MPa	W/S ($g\,g^{-1}$)
S1	170	1	3/1	1.26	20/1	S10	170	1	1/3	1.26	10/1
S2	170	4	3/1	0.84	20/1	S11	110	1	1/3	1.26	20/1
S3	110	4	3/1	1.26	20/1	S12	110	1	3/1	1.26	10/1
S4	170	4	3/1	1.26	10/1	S13	170	1	1/3	0.84	20/1
S5	170	4	1/3	1.26	20/1	S14	170	1	3/1	0.84	10/1
S6	110	4	1/3	1.26	10/1	S15	110	1	3/1	0.84	20/1
S7	170	4	1/3	0.84	10/1	S16	110	1	1/3	0.84	10/1
S8	110	4	1/3	0.84	20/1	S17	140	2.5	5/3	1.05	15/1
S9	110	4	3/1	0.84	10/1						

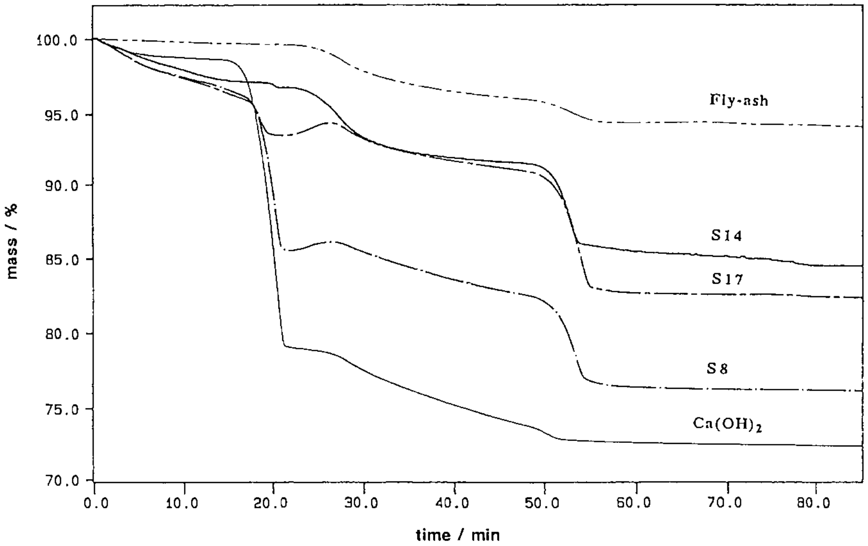

Fig. 2. Thermoanalytical curves of $Ca(OH)_2$, fly-ash and selected sorbents S8, S14 and S17 between 50 and 1300°C in air.

Table 3
TG mass loss of fly-ash, calcium hydroxide and sorbents S1–S17

Sorbent	Mass loss % at different intervals of T/° C				
	50–225	225–450	450–550	550–850	850–1300
Fly-ash	0.21	0.17	←5.29→		0.26
$Ca(OH)_2$	0.86	19.72	←6.38→		0.28
S1	1.39	2.11	–	9.02	0.35
S2	2.53	1.88	–	8.77	0.77
S3	1.12	1.81	+0.72	8.52	0.09
S4	1.98	2.57	–	17.47	0.14
S5	0.43	11.42	+0.40	10.95	0.62
S6	1.96	10.81	+0.75	12.21	0.18
S7	0.33	11.43	+0.45	10.01	0.42
S8	1.89	11.87	+0.57	9.83	0.54
S9	2.47	3.04	–	9.38	0.44
S10	0.63	8.76	+1.49	14.81	0.49
S11	0.99	12.93	+0.71	9.58	0.05
S12	0.99	2.15	+2.40	13.76	0.89
S13	0.52	11.35	+1.05	11.04	0.37
S14	1.67	1.19	–	11.29	1.08
S15	0.79	2.22	+2.44	12.24	0.40
S16	1.06	9.87	+0.43	14.78	0.11
S17	2.18	3.89	+0.87	11.65	0.31

Key: +, mass increase (%).

Table 4
Experimental conditions of the desulfurization test

SO_2	100%
Reaction temperature	57°C
Relative humidity	90%
Solid reagent	S1–S17 sorbents
Sorbent size	< 60 μm
Sorbent weight	2 g
Inert	Silica
Inert size	> 150 μm
Sorbent/Inert ratio	1/25
Gas flowrate	$30\,cm^3\,min^{-1}$
Reaction time	1,4 and 8 h

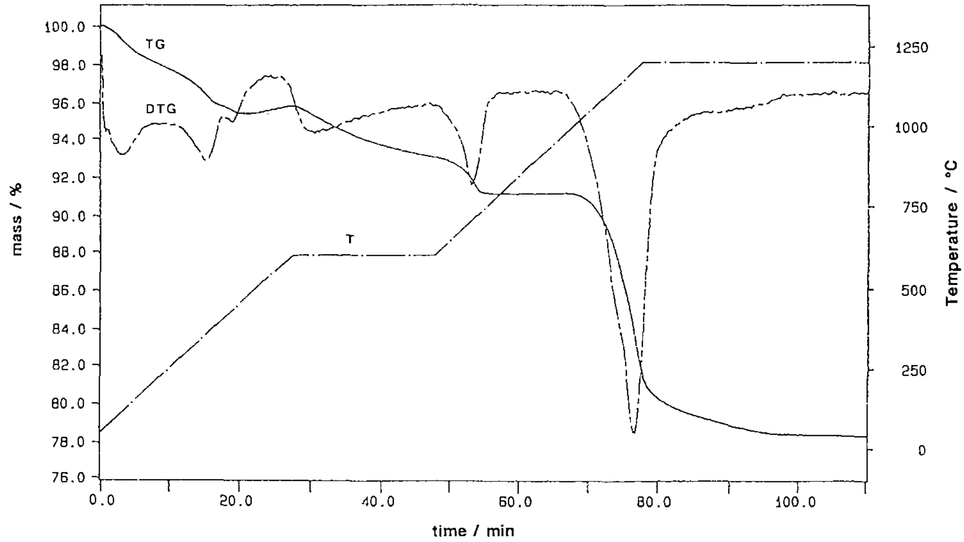

Fig. 3. Thermoanalytical curve of the S14p desulfurization product between 50 and 1300°C in air. TG, DTG and *T* evolution.

between 375 and 450°C, due to the dehydration of unreacted calcium hydroxide to give CaO; (iv) the mass increase between 450 and 575°C attributed to the oxidation reaction of the desulfurization product [25]; (v) the mass loss between 600 and 850°C due to the decomposition of calcium carbonate to CaO; and (vi) the final mass loss, between 850 and 1300°C, attributed to the sulfate decomposition (SO_3) allowing the determination SO_2 capture during the desulfurization reaction as mol SO_3/mg product.

A similar reaction procedure was followed using calcium hydroxide as solid sorbent and the reaction products were characterized accordingly, see Fig. 4. Analysis of the TG

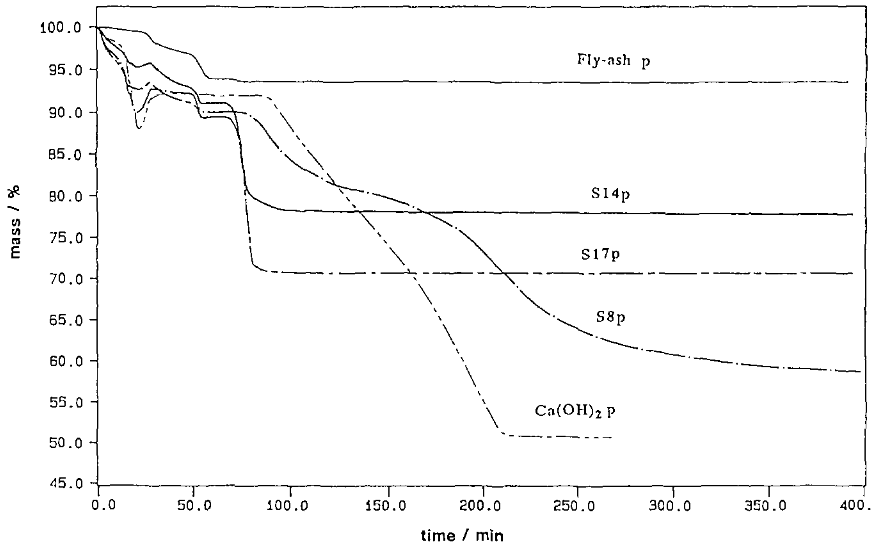

Fig. 4. Thermoanalytical curves of desulfurization products $Ca(OH)_2$p, fly-ash p and S8p, S14p and S17p between 50 and 1300°C in air.

curves of the reacted calcium hydroxide revealed that the mass loss occurring between 850 and 1300°C was due to sulfate decomposition following the reaction

$$CaSO_4(s) \xrightarrow{850\text{–}1300^\circ C} CaO(s) + SO_3(g) \tag{1}$$

This analysis allows the calculation of the amount of SO_2 that has reacted in the bed as SO_4^{-2}. Therefore, knowing the number of moles of calcium in the bed (by means of TG analysis of the sorbent before the reaction), the solid conversion is presented as mol SO_2/mol Ca, and with the mass balance in the bed, the composition of the latter can be obtained as mol of each component per mol of calcium. The sulfate content of the solids was also determined by ion chromatography after an acidic digestion procedure described in the literature [26].

Fig. 4 also includes the TG curves of the desulfurization products, fly-ash p, and S8p, S14p, S17p obtained from the reaction of SO_2 with fly ash, and S8, S14 and S17 sorbents respectively. A similar weight–time profile was found for S14p and S17p sorbents (3/1 and 5/3 fly-ash/$Ca(OH)_2$ weight ratio hydration respectively). Table 5 summarizes the mass losses identified in the reacted analyzed solids.

The reactivity of the sorbents towards SO_2 is expressed as the total number of moles of SO_2 removed after reaction divided by the initial moles of Ca in the sorbent. The reactivity was defined by the following expression

$$\frac{\text{mol } SO_2}{\text{mol Ca}} = \frac{\text{mol } SO_2}{\text{g product}} \times \frac{\text{g product}}{\text{g sorbent}} \times \frac{\text{g sorbent}}{\text{mol Ca}} \tag{2}$$

Table 5
TG mass loss of the desulfurization products fly-ash p, $Ca(OH)_2$ p and S1p–S17p

Product	Mass loss/% at different intervals of T/° C					
	50–225	225–375	375–450	450–550	550–850	850–1300
Fly-ash p	0.21	←0.31→		←5.54→		0.335
$Ca(OH)_2$ p	1.88	4.39	5.64	+4.15	–	41.15
S1p	1.94	1.88	0.73	–	4.59	10.85
S2p	3.56	1.88	0.41	–	6.10	9.27
S3p	1.97	1.81	1.14	+1.15	3.51	12.83
S4p	4.62	2.19	0.31	+0.08	4.23	13.25
S5p	1.28	2.48	8.28	–	4.85	11.76
S6p	4.70	4.17	1.31	+2.16	2.76	27.07
S7p	1.09	2.66	8.77	–	5.45	10.01
S8p	2.61	4.27	2.26	+2.74	2.72	31.31
S9p	3.23	2.43	0.56	+0.02	5.91	11.23
S10p	2.36	4.74	1.75	+2.38	1.78	33.26
S11p	1.39	3.68	3.85	+3.06	3.45	27.66
S12p	1.22	1.82	1.21	+1.06	6.01	12.11
S13p	1.79	4.12	2.77	+2.47	3.97	27.97
S14p	1.98	1.81	0.47	+0.41	4.64	12.97
S15p	1.20	1.62	0.93	+0.76	5.88	11.11
S16p	1.39	3.74	4.48	+2.61	3.04	27.14
S17p	3.21	2.98	0.31	+0.75	4.00	18.73

Key: +, mass increase (%).

The first term of Eq. (2), the amount of SO_2 referred to the final product (mol SO_2/g product) has been calculated as previously mentioned by means of TG analysis, taking into the mass loss in the range of temperatures 850–1300°C, which can be considered to be due to sulfate decomposition (SO_3). The stability of the reagents at these temperatures was checked previously. Ion chromatography analysis which provides the amount of SO_4^{-2} in the digested solution of the final product was also carried out.

After the desulfurization experiment was concluded, the final product was weighed to measure the weight increase and the product to sorbent ratio (g product/g sorbent) which is the second term of Eq. (2). The third term in Eq. (2), moles Ca/g sorbent, is known from the difference between the theoretical moles of Ca in the reactor and the solubilized Ca in the filtrate as a consequence of the hydration process. After calculating the amount of SO_2 referred to the final product (by TGA and ion chromatography (IC)), the desulfurization product to sorbent ratio, and the moles of calcium to sorbent weight by calcium balance in the reactor, the desulfurization yield can be determined.

The desulfurization yield data obtained from the analysis of the products S1p–S17p are shown in Table 6. The comparison shows that IC data were systematically lower than TG yield data, a fact that was attributed to the experimental error inherent in the considerably longer preparation procedure for the solid digestion required before ion chromatography analysis, compared to thermoanalytical characterization. For this reason, the TG analysis was selected as a direct and relatively simple method to obtain

Table 6
Products (S1p–S17p) desulfurization yield (%) obtained by TG analysis (TGA) and Ion chromatography (IC)

Product	IC	TGA	Product	IC	TGA	Product	IC	TGA
S1p	44.10	48.71	S7p	13.15	13.86	S13p	36.24	48.40
S2p	30.50	37.50	S8p	37.40	50.14	S14p	47.32	59.16
S3p	55.10	56.90	S9p	43.62	49.70	S15p	50.61	51.50
S4p	46.23	51.10	S10p	47.21	56.18	S16p	34.60	42.00
S5p	16.00	16.60	S11p	43.80	46.10	S17p	47.50	58.37
S6p	39.60	40.71	S12p	40.81	53.80			

the desulfurization yield of complex solids containing fly-ash/calcium hydroxide hydrated mixtures.

The desulfurization yield of sorbents obtained after one hour of reaction did not reveal a significant influence of fly-ash/$Ca(OH)_2$ weight ratio, 0.53 ± 0.08 mol SO_2/mol Ca being the average value. Previously it was reported [24,25] that the maximum conversion attainable by commercial $Ca(OH)_2$ with SO_2 under the same experimental conditions reaches the value of 0.62 mol SO_2/mol Ca; therefore long-term experiments (4 and 8 h) were needed to analyze a possible increase in the maximum yield of the sorbents.

TG characterization of the reaction products and determination of the desulfurization yield in the way previously mentioned gave the data shown in Fig. 5, where it can be confirmed that the sorbent maximum yield was 0.56 ± 0.07 mol SO_2/mol Ca, very similar to the $Ca(OH)_2$ yield.

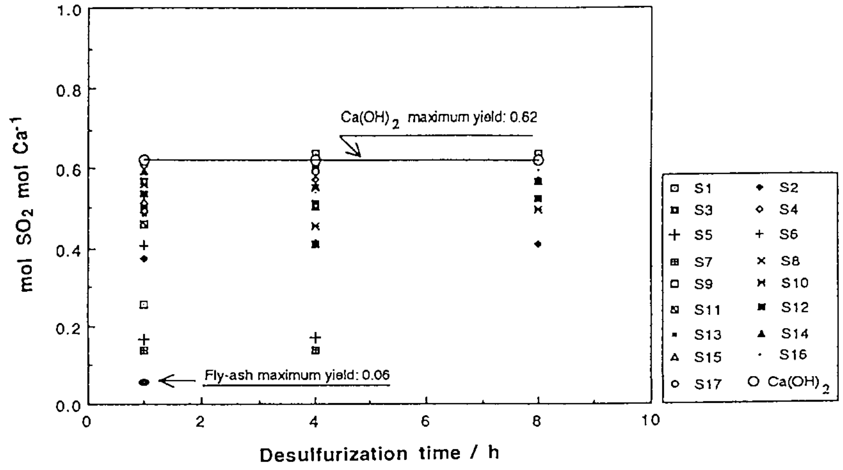

Fig. 5. Yield evolution of S1–S17 sorbents at desulfurization times of 1,4 and 8 h.

4. Conclusions

In this work the thermogravimetric characterization of the solid sorbents obtained after a pressurized hydration of commercial calcium hydroxide and coal combustion fly-ashes at different values of the hydration variables, and of the solid products obtained from the reaction of SO_2 with the previous solid sorbents at low temperature, has been carried out.

Taking into account previous results, the experiments were designed in the range of temperature from 170 to 110°C, time from 1 to 4 h, fly-ash/$Ca(OH)_2$ weight ratio from 3/1 to 1/3, pressure from 1.26 MPa to 0.843 MPa, and water/solid from 20/1 to 10/1. Their reactivity to SO_2 was tested in a packed bed reactor at 57°C and 90% relative humidity.

By means of the interpretation of the thermoanalytical curves of the sorbents of the interpretation of the thermoanalytical curves of the sorbents and products of desulfurization, the degree of solid conversion was calculated. The results obtained after 1 h of reaction time showed a maximum conversion of 0.53 ± 0.08 mol SO_2/mol Ca. Long-time desulfurization tests at 4 to 8 h showed a maximum conversion of 0.56 ± 0.07 mol SO_2/mol Ca, similar to the commercial $Ca(OH)_2$ maximum conversion.

Thermogravimetric analysis at high temperature of these complex solids appears to be an accurate method to determine the yield of the SO_2 removal reaction, a parameter necessary for the design and optimization of low-temperature desulfurization processes.

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