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Development of Sorbents for SO₂ Capture Prepared by Hydration of Fly Ash and Hydrated Lime in Seawater

Josefa Fernández,* José Luis Rico, Hipólito García, and M. Josefina Renedo

Departamento de Ingeniería Química y Química Inorgánica, ETSIIyT, Universidad de Cantabria, Avenida Los Castros s/n, 39005, Santander, Spain

The influence of seawater salts on the physicochemical properties and desulfurization behavior of mixtures of fly ash and $Ca(OH)_2$ hydrated in seawater at different initial ratios and hydration times was investigated. The $Ca(OH)_2$ conversion as a measure of the pozzolanic reaction extent was determined. The properties characterized in the sorbents include BET surface area and porosity distribution, X-ray diffraction pattern, and SEM image. The composition of the silicates synthesized in the reaction between fly ash and hydrated lime was obtained by atomic absorption spectrometry. The sorbents were tested in a flue gas desulfurization reaction at 57 °C. The seawater salts do not increase the formation of calcium silicates, but the sorbents obtained in the presence of these salts exhibit higher specific surface areas and better desulfurization behavior than sorbents hydrated in distillate water. The ability of the sea salts, present in the sorbent, to capture moisture from the flue gas, promoted by the higher specific surface area of the sorbents prepared in seawater, can explain the increase in SO₂ retention. The use of seawater as a hydration medium to prepare desulfurant sorbents is an inexpensive means of supplying these types of additives for coastal power stations.

Introduction

Dry processes for the removal of SO₂ from flue gas using calcium-based sorbents injected directly into the duct are not as common as wet processes, but they offer an attractive alternative with a simple technology as a retrofit option for existing coal-fired power plants. These are also complementary processes for increasing SO₂ capture when a previous process of desulfurization at high temperature is used in newly installed power plants. Some of these combined processes are LIMB/COOLSIDE or LIMB/ADVACATE.[1,2] Such processes can also be used in industrial boilers and waste incinerators to treat the flue gas under conditions of low sulfur emissions. In-duct injection systems work with a dry powdered sorbent, typically calcium hydroxide, that reacts with the humidified flue gas.

Sorbents obtained by the hydration of lime or hydrated lime with different sources of silica lead to significantly higher calcium utilization (moles of SO₂ per mole of Ca in the sorbent) compared to the values obtained using hydrated lime.[3–14] When fly ash is used as a silica source, the products of the pozzolanic reaction of silica with $Ca(OH)_2$ are considered to be responsible for the improvement of the solid behavior,[3,14–19] but low sorbent utilization is still a disadvantage of these desulfurization processes with respect to the wet processes. To increase the utilization of calcium in calcium hydroxide or in sorbents obtained from fly ash and lime or hydrated lime, different additives have been tried. In the reaction between fly ash and $Ca(OH)_2$, the effect of additives has been related to the calcium concentration in the slurry[20–22] or to the variations in the specific surface area of the sorbents. In a previous work,[23] the effect of $CaSO_4$ used as an additive was found to depend on the starting fly ash/$Ca(OH)_2$ ratio, the amount of $CaSO_4$, and the hydration time. Among the additives studied, hygroscopic or deliquescent substances such as ethylene glycol, triethylene glycol, NaCl, and $NaNO_3$ have been added to hydrated lime,[24,25] and the increase in reactivity toward SO₂ of the modified calcium

hydroxides was found to depend on the relative humidity and additive amount and was related to the modifications in the specific surface areas of the sorbents. This type of additives has also been added to slurries of $Ca(OH)_2$ and fly ash[20] or other silica sources.[26] Under optimal conditions, the sorbents prepared with hygroscopic additives increased the SO₂ capture.

Taking into account that seawater is easy to use in coastal power stations and that it is an inexhaustible source of hygroscopic salts, seawater has been tested as a hydration medium to prepare desulfurant sorbents from fly ash and calcium hydroxide. The influence of sea salts on the physicochemical properties and desulfurization behavior of the obtained sorbents was studied. As a reference, distillate and synthetic water were also used as hydration media.

Experimental Section

Preparation of Sorbents. Sorbents were prepared using commercial calcium hydroxide supplied by Calcinor S.A. and ASTM class F coal fly ash from a pulverized coal boiler that was collected in an electrostatic precipitator of Pasajes (Guipuzcoa, Spain), a coastal power station. NaCl for the preparation of the synthetic water was supplied by Merck with a purity of 99.5%, with small amounts of K, Ca, and Mg as the principal impurities. The chemical composition and physical properties of $Ca(OH)_2$ and fly ash are reported in Table 1.

Solids were prepared by slurrying fly ash and calcium hydroxide mixtures at a constant temperature of 90 °C and a stirring rate of 1400 rpm in a 2-L discontinuous stirred-tank reactor, equipped with three connections to a reflux refrigerator to maintain a constant liquid/solid ratio of 10/1. As hydration media, distillate water and filtered seawater from the beach of Santander (Spain), with a total solids content of 3.6% (w/w) or a water solution (synthetic water) containing the same amount of NaCl as is present in the seawater (2.88%) were used. The fly ash/$Ca(OH)_2$ weight ratios tested were 5/3 and 9/3 (w/w), as it was shown in previous work[13] that these ratios produce the best desulfurization sorbents. The amount of liquid was 1.5 L, and the amount of total solid was 150 g, with the amounts

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* To whom correspondence should be addressed. E-mail: fernandj@unican.es. Tel.: 34-42-202026. Fax: 34-42-201591.

Table 1. Physical Properties and Chemical Compositions of Ca(OH)₂ and Fly Ash

Physical Properties		
	hydrated lime	fly ash
Adsorption−Desorption of N_2		
BET specific surface area (m^2/g)	16.2	3.0
Intrusion−Extrusion of Hg:		
pore volume (cm^3/g)	1.395	0.680
macropore volume (>50 nm) (cm^3/g)	1.319	0.658
mesopore volume (6.7−50 nm) (cm^3/g)	0.076	0.022
skeletal density (g/cm^3)	1.830	1.889
Laser Diffraction:		
mean volume diameter (D 4.3)	6.59	27.64
Chemical Composition (wt %)		
	hydrated lime	fly ash
SiO_2	−	49.26
Al_2O_3	−	30.04
Fe_2O_3	−	6.92
MgO	−	0.85
CaO	−	1.91
$Ca(OH)_2$	89.45	−
$CaCO_3$	7.716	−
Na_2O		0.64
K_2O	−	2.44
insoluble	−	0.17
loss by Heat	−	6.31
impurities	2.84	−

of fly ash and calcium hydroxide varying depending on the fly ash/Ca(OH)₂ ratio. Samples of the reaction mixture were withdrawn at different reaction times, from 3 to 38 h. Samples were filtered with a 0.45-μm mesh filter, dried in an oven at 105 °C for 1 h, and ground.

Sulfation Test. The reaction between the solid sorbents and SO₂ was performed in a glass-made jacketed fixed-bed reactor, under isothermal conditions at 57 °C and a relative humidity of 52%. Approximately 1 g of the sorbent was weighed and dispersed manually in 30 g of an inert silica sand bed (particle size range = 250−300 μm) to avoid channeling of the gas and to ensure isothermal conditions. The whole bed was supported on a 3.6-cm-diameter fritted glass plate contained in the glass cylinder.

The volume composition of the gas stream was 5000 ppm SO₂, 12% CO₂, 2% O₂, and the balance N₂, and the flow rate was 1000 cm^3/min. This gas passed through the humidification system, where it was brought into contact with water in an absorber flask (250 cm^3) that contained glass spheres used to improve the contact between the gas and liquid phases. The absorber flask was submerged in a water bath at a constant temperature of 50 °C. After humidification, the gas mixture flowed to the reactor. The water content in the gas stream was obtained by cooling the stream with cool water in a reflux refrigerator for 3 h and measuring the condensed water. From these data, the experimental vapor pressure at the reaction temperature (57 °C) was obtained. The quotient between the experimental vapor pressure and the saturation vapor pressure at the reaction temperature gave the relative humidity. When the reaction time (1 h) was over, the reactor content was sieved to separate the sorbent from the sand, and the sorbent was analyzed by the thermogravimetric technique. From the weights of the sorbent before and after the SO₂ capture, the ratio of the number of grams of sorbent reacted to the initial number of grams of sorbent was determined to calculate the calcium utilization value.

Physical and Chemical Analysis of the Sorbents. The pore size distribution and specific surface area of the sorbents were measured using a Micromeritis ASAP-2000 apparatus. The specific surface area was determined following the BET standard method. The experimental error was evaluated using three replicates of some data, and a relative standard deviation of less than 10% was found. The pore size distribution was calculated by applying the Barret−Joyner−Halenda (BJH) method from nitrogen desorption data. The porosity ranges studied were microporosity (<2 nm) and mesoporosity (2−50 nm) according to IUPAC rules. Small macropores (ca. 50−200 nm) calculated from this method were also included as a comparative value among sorbents.

The amount of unreacted Ca(OH)₂ in the solid was measured by dissolving a small sample of the sorbent in a sugar solution at ambient temperature and titrating the dissolved Ca(OH)₂ with HCl following the procedure given by Peterson and Rochelle.[16] This amount is a measure of the hydration extent. The Ca(OH)₂ conversion in the hydration process, obtained from this value, is a quantitative expression of the pozzolanic reaction

$$\frac{\begin{array}{c}Ca(OH)_2 \text{ used in the preparation of solid} - \\ Ca(OH)_2 \text{ after hydration}\end{array}}{Ca(OH)_2 \text{ used in the preparation of solid}} \times 100 \quad (1)$$

The amount of Ca(OH)₂ used in the preparation of the solid was calculated by considering the composition of commercial Ca(OH)₂ (Table 1) and subtracting its solubility in water at the reaction temperature. Three replicates of the amount of unreacted Ca(OH)₂ for each sample were determined, and a relative standard deviation of less than 1% was found.

The evolution of the starting materials and the synthesis of calcium silicates were followed by X-ray diffraction (XRD) performed in a Phillips PW 1729 X-ray diffractometer for powdered samples of less than 0.150 mm with Cu radiation. To obtain the diffraction pattern of the sea salts, a filtered seawater sample was evaporated, and the milled and sieved solid was kept in an oven at 90 °C to constant weight to eliminate the water content. Considering the complexity of the diffraction pattern of these solids, because of the presence of the unreacted starting materials and the variety of possible products obtained in the reaction, only the peaks of the starting materials are marked in the figures.

Scanning electron microscopy (SEM) was used to observe the surface morphology of the sorbents and was performed with a JEOL JSM 5800-LW apparatus.

Determination of the Composition of the Products of the Pozzolanic Reaction. The amount of Ca (in grams) in the products of the hydration reaction per gram of sorbent was obtained from the values of Ca(OH)₂ conversion as follows

$$Ca(OH)_2 \text{ conversion} \times$$
$$\frac{g \text{ of } Ca(OH)_2 \text{ used in the preparation of the solid}}{\begin{array}{c}[g \text{ of } Ca(OH)_2 + g \text{ of fly ash}) \text{ used in the} \\ \text{preparation of the solid}\end{array}} \times$$
$$0.8945 \times \frac{40}{74} \quad (2)$$

with 40 and 74 being the molecular weights of Ca and Ca(OH)₂, respectively, and 0.8945 being the Ca(OH)₂ content in the commercial hydrated lime.

According to the procedure stated by Peterson and Rochelle,[27] the products formed by the reaction of Ca(OH)₂ and fly ash were dissolved by adding 200 mg of the prepared solid to 100 mL of 0.1 M HCl and stirring for 5 min. After filtration, the filtrate containing the dissolved products of the reaction, was

analyzed by atomic absorption spectrometry (AAS) for Al and Si and by atomic emission spectrometry (AES) for Na. Atomic absorption and atomic emission spectrometry measurements were made using a Perkin-Elmer 560 apparatus. A N_2O acetylene flame was used. Instrument, flame, and hollow cathode lamp conditions were those recommended by Perkin-Elmer. Three replicates of some data were obtained, giving a relative standard deviation of less than 10%.

The same dissolution process was used with the fly ash to probe its dissolution behavior at the same experimental conditions.

From data on the Al, Si, and Na concentrations in the filtrate, the numbers of grams of these elements in the products of the hydration reaction per gram of sorbent were calculated.

Values for Al and Si found in the experiment on selective dissolution performed with fly ash indicate that the dissolution of the unreacted fly ash in dilute hydrochloric acid is negligible and that all of the Al and Si found in the filtrate comes from the synthesized calcium aluminum silicates. The Na evaluated could arise from the new silicates and from the NaCl retained in the porous structure of the sorbent.

Determination of the Calcium Utilization in the Desulfurization Reaction. The sorbents after the sulfation test (reacted sorbents), with the captured SO_2 forming mainly calcium sulfite, were analyzed by the thermogravimetric technique as in previous works[13] in a Perkin-Elmer TGA unit with a temperature furnace program between 50 and 1250 °C, a PE 7500 microprocessor, and a TAC-7 thermal analysis controller. Synthetic air was used as the carrier gas (30 cm³/min). The temperature program was

$$50\ ^{\circ}C \xrightarrow{20\ ^{\circ}C\ min^{-1}} 600\ ^{\circ}C\ (20\ min) \xrightarrow{20\ ^{\circ}C\ min^{-1}}$$
$$1200\ ^{\circ}C\ (30\ min) \xrightarrow{1\ ^{\circ}C\ min^{-1}} 1250\ ^{\circ}C\ (15\ min)$$

TG curves of the reacted sorbent presented a mass loss occurring between 850 and 1250 °C that was attributed to SO_3 formed from the sulfate decomposition in CaO(s) and SO_3(g). This analysis allowed the calculation of the calcium utilization. The calcium utilization expressed as number of moles of captured SO_2 per mole of Ca from fly ash and $Ca(OH)_2$ was obtained as follows

$$\frac{\dfrac{\text{moles of } SO_2 \text{ captured}}{\text{grams of sorbent}}}{\dfrac{\text{moles of calcium [in fly ash and } Ca(OH)_2]}{\text{grams of sorbent}}} =$$

$$\frac{\dfrac{\%\ SO_3\ (TG)}{100 \times 80} \times \dfrac{\text{grams of reacted sorbent}}{\text{grams of sorbent}}}{\left(\dfrac{89.45}{100 \times 74} + \dfrac{7.716}{100 \times 100}\right) \times \dfrac{\text{grams of } Ca(OH)_2}{\text{grams of sorbent}} + \dfrac{\%\ CaO\ \text{in fly ash}}{100 \times 56} \times \dfrac{\text{grams of fly ash}}{\text{grams of sorbent}}} \quad (3)$$

where 89.45 is the percentage of $Ca(OH)_2$ and 7.716 the percentage of $CaCO_3$ in the commercial hydrated lime (Table 1). The relative standard deviation evaluated with three replicates of some data was less than 5%.

Results and Discussion

Table 2 shows the results of the calcium hydroxide reacted with fly ash [expressed as percent $Ca(OH)_2$ conversion], the BET specific surface areas of all of the sorbents prepared, and the porosity values evaluated in selected samples.

Table 2. $Ca(OH)_2$ Conversion, BET Surface Area, and Porosity Values of the Sorbents

	slurry time (h)				
	3	7	15	24	38
$Ca(OH)_2$ Conversion (%)					
5/3 dist water	29	54	83	93	96
5/3 seawater	28	58	80	93	95
5/3 synth water	30	56	83	87	89
9/3 dist water	35	79	95	96	97
9/3 seawater	30	64	82	90	95
9/3 synth water	30	76	85	88	90
BET Surface Area (m²/g)					
5/3 dist water	16	26	33	37	83
5/3 seawater	19	67	126	143	160
5/3 synth water	16	37	49	88	110
9/3 dist water	14	22	32	65	76
9/3 seawater	14	29	98	107	100
9/3 synth water	13	28	70	68	78
Macropore Volume (cm³/g)					
5/3 dist water	0.03	0.04	0.04		0.04
5/3 seawater					
9/3 dist water	0.04	0.06	0.04		0.05
9/3 seawater		0.04	0.1		0.086
Mesopore Volume (cm³/g)					
5/3 dist water	0.05	0.07	0.18		0.31
5/3 seawater					
9/3 dist water	0.06	0.10	0.23		0.30
9/3 seawater		0.06	0.35		0.45
Micropore Volume (cm³/g)					
5/3 dist water	0.24	0.8	3.31		7.8
5/3 seawater					
9/3 dist water	0.64	2.34	4.37		5.6
9/3 seawater		0.0002	0.0022		0.0035

The influence of the sea salts on the $Ca(OH)_2$ conversion values is not clear for 5/3 sorbents, as similar values of conversion were found regardless of the hydration medium. For 9/3 sorbents, these values are clearly higher for sorbents prepared with distillate water at any hydration time, suggesting that the seawater salts can diminish the reaction rate between the hydrated lime and the fly ash. Conversion results for samples prepared with synthetic water also corroborate this conclusion.

A great increase in the specific surface area values was found for sorbents prepared principally in seawater compared to the sorbents prepared in distillate water. The values of the BET surface areas for the sorbents hydrated in the synthetic water lie between those obtained in sea and distillate water.

Porosity distribution values show an increase in the porosity, mainly in the micropore region, with hydration time for sorbents prepared in distillate water; the most relevant influence of the sea salts on the porosity is the plugging of the micropores and an increase in the macropore and mesopore regions at high hydration time.

The X-ray diffraction patterns of the seawater salts, obtained by drying the water to constant weight, were very similar to that of NaCl with the most intense peaks at $2\theta = 31.75°$, $45.6°$, and $56.45°$; the peaks of the rest of the salts are not detectable because of the intensity of these peaks. The diffraction pattern of the fly ash presents a mild hump with peaks at $2\theta = 24°$ characterizing amorphous SiO_2, peaks of quartz at $26.64°$ and $20.8°$, and typical peaks of mullite at $2\theta = 26.3°$, $26°$, and $40.8°$. The peaks of the commercial $Ca(OH)_2$ were found at $34°$, $18.1°$, $47.1°$, $50.4°$, $53.9°$, and $28.7°$. The order of the angles of peaks is written following their intensities. These figures are omitted as the information obtained from them is obvious.

XRD patterns of the adsorbents obtained at 3 or 38 h of hydration in distillate or seawater are shown in Figure 1. In the
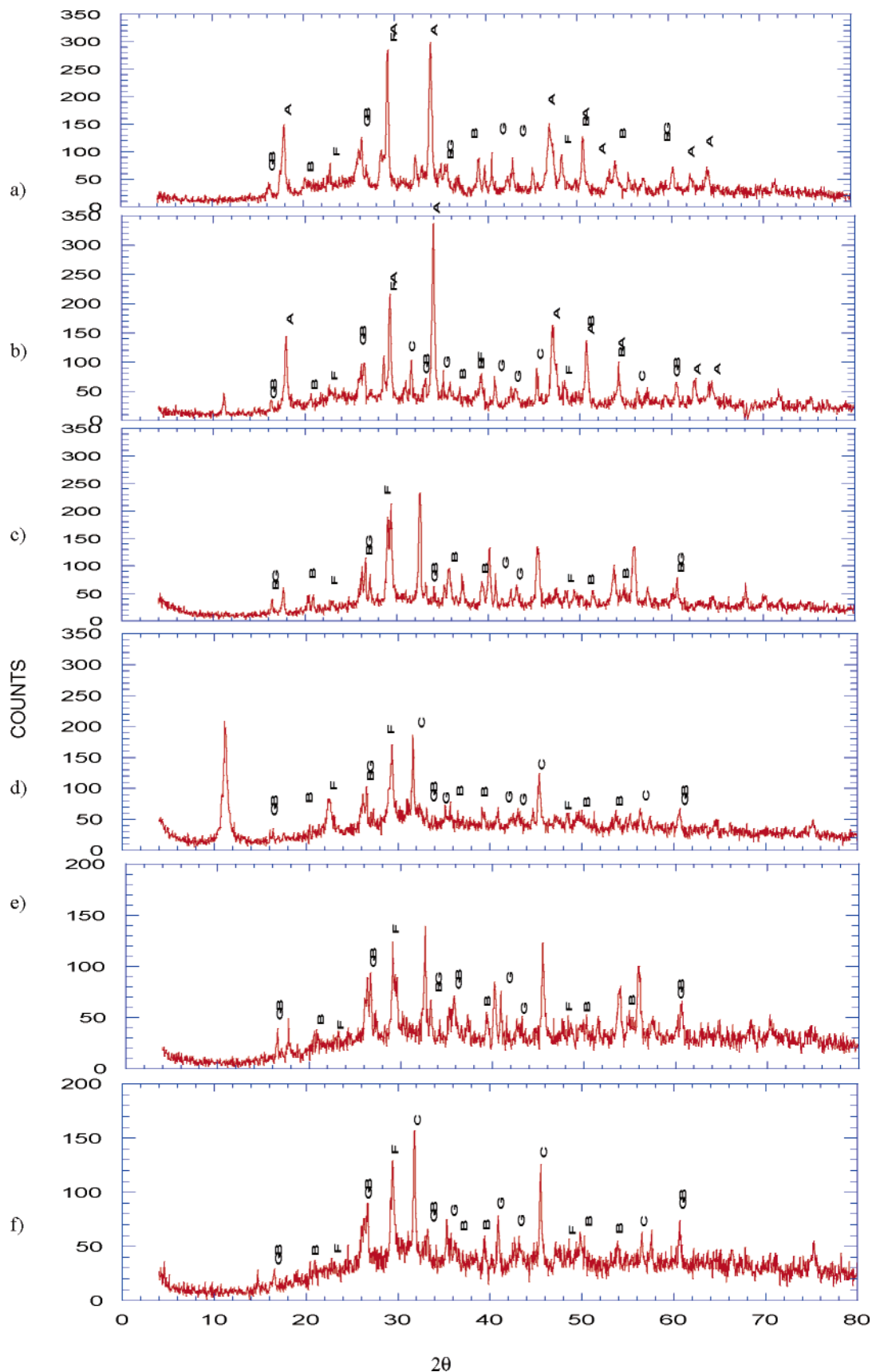
Figure 1. XRD diffraction patterns for sorbents prepared in distillate and seawater. A, Ca(OH)$_2$; B, fly ash; C, NaCl; F, CaCO$_3$; G, mullite. a) 5/3, 3h, distillate water; b) 5/3, 3h, sea water; c) 5/3, 38h, distillate water; d) 5/3 38h, sea water; e) 9/3 38h, distillate water; f) 9/3, 38h, sea water.

figure, only the peaks of the starting materials, Ca(OH)$_2$, fly ash, and NaCl, are marked. For the fly ash, the peaks of mullite are marked separately as G, and the rest of the peaks as B.

CaCO$_3$ ($2\theta = 29.45°$, 48.7°, and 23.1°) is considered as a starting material, as 7.716% of the commercial Ca(OH)$_2$ is CaCO$_3$ (see Table 1), although this compound is also synthe-

sized during the sample preparation by reaction between CO_2 and $Ca(OH)_2$.

A significant reduction of the amount of $Ca(OH)_2$ is found with hydration time for all of the sorbents, whereas the intensity of the peaks of the fly ash does not vary substantially, meaning that most of the fly ash does not react in the pozzolanic reaction.

Comparing parts a (5/3, 3 h, distillate water) and b (5/3, 3 h, seawater) and parts c and d of Figure 1, the peaks of the sea salts and a peak at 11° in samples b and d are the main differences. It is also significant that the peaks of $Ca(OH)_2$ seem more intense in sample b prepared in seawater. No reflections of $Ca(OH)_2$ appear in the patterns of samples prepared at 38 h of hydration, as all of the hydrated lime had reacted to produce silicates. The diffraction patterns of the 9/3 sorbents, 3 h, prepared in distillate and in seawater do not differ significantly from those of the 5/3 sorbents prepared under the same conditions, except in the intensity of the peaks of the starting materials, and these figures are omitted. NaCl is present in all of the sorbents prepared in sea or synthetic water, and its amount is higher at higher hydration times. Although the main application of the X-ray diffraction technique in these sorbents is to follow the evolution of the raw materials, product D (not marked in Figure 1), calcium silicate hydrate, $Ca_2SiO_4 \cdot H_2O$ ($2\theta = 29.4°$, $33.2°$, and $47.8°$), seems to be present in all of the samples, although its peaks overlap with peaks of $CaCO_3$ and $Ca(OH)_2$. Product E (not marked in Figure 1), calcium aluminum silicate hydroxide, $3CaO \cdot SiO_2 \cdot Al_2O_3 \cdot 4H_2O$ ($2\theta = 32.5°$, $29°$, and $40°$), is easier to identify and has been detected only in samples prepared in distillate water. Parts e and f of Figure 1 correspond to 9/3 sorbents, 38 h, prepared with distillate and seawater, respectively. Comparing samples c and e, prepared for 38 h in distillate water, a higher amount of product E was detected in sample c prepared at an initial ratio of 5/3. This result shows that, at the 5/3 initial ratio, the hydration rate is higher than it is at the 9/3 ratio, and this result is confirmed with the data from atomic absorption spectrometry. The diffraction figures of the sorbents hydrated in synthetic water do not differ significantly from those obtained in seawater at any hydration time. The NaCl amounts are similar for sorbents prepared with seawater and with synthetic water. An unidentified peak at $2\theta = 11°$ appears with sea or synthetic water at 3 h of hydration, presents a maximum in intensity at 15 h, and decreases or disappears at 38 h of hydration time.

X-ray diffraction results show that NaCl is present in all of the sorbents prepared in synthetic or seawater in similar amounts, increasing slightly with hydration time. Considering the amounts of unreacted hydrated lime in the sorbents found by XRD, it seems that the sea salts do not enhance the pozolanic reaction, as can also be deduced from the $Ca(OH)_2$ conversion values and from the atomic absorption results. The synthesized products of the pozzolanic reaction are not exactly the same with or without sea salts.

The SEM micrograph of the starting materials (omitted) shows spherical particles for the fly ash and particles of irregular shape for $Ca(OH)_2$. The seawater salts micrograph shows an agglomerate of crystalline particles because of the hygroscopicity of the sea salts. The SEM images of selected sorbents are shown in Figure 2. Figure 2a,b shows 9/3 samples prepared at 3 and 38 h in distillate water; in both micrographs, spherical particles of fly ash are observed, but in Figure 2b, these spheres are covered with the products of hydration; the images in parts c and d show the same sorbents prepared in seawater. No appreciable differences exist between images a and c (9/3, 3 h prepared with sea and distillate water), but a particle size
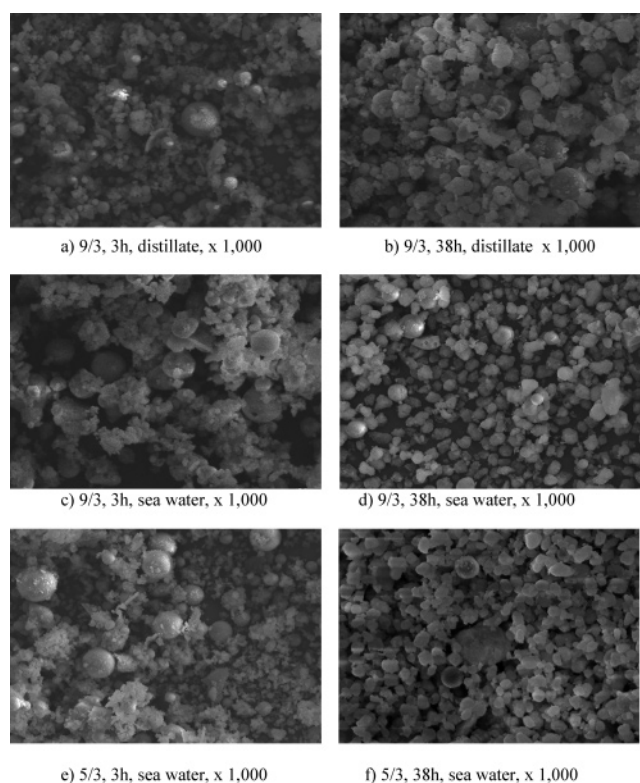

a) 9/3, 3h, distillate, x 1,000   b) 9/3, 38h, distillate x 1,000

c) 9/3, 3h, sea water, x 1,000   d) 9/3, 38h, sea water, x 1,000

e) 5/3, 3h, sea water, x 1,000   f) 5/3, 38h, sea water, x 1,000

Figure 2. SEM photomicrographs for sorbents prepared in distillate and seawater.
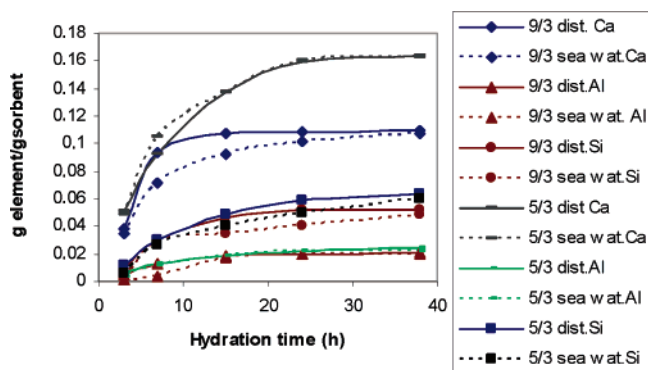

Figure 3. Ca, Al, and Si contents in the products of the pozzolanic reaction for sorbents prepared in distillate and seawater.

reduction is clearly found in the sorbent prepared with seawater at 38 h of hydration with respect to that of sample b, prepared in distillate water. This size reduction can contribute to an increase in the surface area of the sorbents obtained in seawater. Figure 2e,f shows the 5/3 sorbent prepared with seawater at 3 and 38 h of hydration, respectively. The size reduction is also clear in sorbent f. Although XRD analysis confirms the presence of NaCl at any hydration time in sorbents prepared in sea or synthetic water, this salt is not clearly detected in the microphotographs of 9/3 sorbents, but in the middle of Figure 2f, an agglomeration of crystals of NaCl can be observed, similar to those obtained in the SEM micrograph of seawater salts (not shown), confirming its presence.

Figure 3 shows the numbers of grams of Si, Al, and Ca per gram of sorbent, obtained according to the experimental procedure previously stated for the sorbents prepared at 5/3 and 9/3 initial ratios hydrated in distillate or seawater. The values obtained with sorbents prepared in synthetic water are always intermediate between the values found for sorbents prepared in distillate and in seawater and have therefore been omitted. As

the Si, Al, and Ca obtained come from the new silicates, a higher amount of these elements means a higher hydration rate. Comparing 5/3 and 9/3 sorbents prepared in distillate water, values of Ca, Si, and Al are always higher for 5/3 sorbents, as was previously found.[28] The results show that the amounts of these three elements in the synthesized silicates are lower for sorbents prepared in sea or synthetic water than the values found when the hydration occurs in distillate water. These results suggest that the sea salts, mainly NaCl, do not increase the rate of the pozzolanic reaction and confirm the results found by XRD and $Ca(OH)_2$ conversion. The saline effect produced by the high concentration of inorganic ions in the seawater can increase the solubility of the calcium silicates [calcium silicates $\rightarrow Ca^{2+} +$ $Si(OH)^-_5$] and reduce the amount of solid silicates in the sorbent. These results do not agree with those obtained by Yaniv et al.[29] working with fly ash under deep sea conditions. These authors found that the solubility of the fly ash was higher in the presence of seawater with class A fly ash. Differences in the time, pressure, and class of fly ash make it difficult to compare results. As Figure 3 shows, the amount of Al and Si in the silicates synthesized does not almost increase after 15 h of hydration regardless of the hydration medium, meaning that the synthesis of silicates has finished at this time. The sorbents prepared at higher hydration times exhibit higher surface areas, but the amounts of calcium silicates are not higher.

The range of variation of Na, in grams of Na per gram of sorbent, was from 0.0186 at 3 h of hydration to 0.0255 at 38 h of hydration for the 3/1 sorbents prepared in seawater and from 0.0140 to 0.0268 for the 5/3 sorbents; these values were similar for sorbents prepared in synthetic water and confirm the increase in the NaCl content in the sorbent with hydration time found by X-ray diffraction.

Considering that the presence of sea salts does not increase the reaction rate between fly ash and $Ca(OH)_2$ and that NaCl is present in all of the sorbents regardless of the initial ratio, increasing in amount with hydration time, it can be concluded that Na evaluated by AES comes mainly from the NaCl that precipitates as water evaporates in the drying step, in the porous structure of the sorbent. The high values of the specific surface areas of the sorbents prepared in sea or synthetic water must be principally due to the effect of the presence of salts. The particle size reduction observed principally at high hydration time when seawater or synthetic water was used can also contribute to this increase. In the experimental determination of the BET surface area by N_2 adsorption, in the degasification step, it was found that the mass loss of sorbents prepared in sea or synthetic water was generally higher than that obtained with sorbents prepared in distillate water. This mass loss is principally due to the water previously captured in higher amounts when the hygroscopic salts are present. The release of this water in the degasification step will produce a higher N_2 adsorption and an increase in the surface area values. The special ability of the minority sea salts to retain water could explain the higher surface areas of the sorbents prepared in seawater with respect to those prepared in synthetic water. Kind et al.[20] working with fly ash/$Ca(OH)_2$ sorbents, also found that, when $CaCl_2$ or NaCl was added to the slurry, the effect of the $CaCl_2$ was due to the presence of the salts and was not an effect of calcium silicate formation.

In Figure 4, the calcium utilization values (as moles of SO_2 per mole of Ca in percent) obtained in the desulfurization reaction with all of the sorbents prepared are shown. Comparing results of sorbents prepared in distillate water, higher values were found for 9/3 with respect to 5/3 sorbents, as in a previous
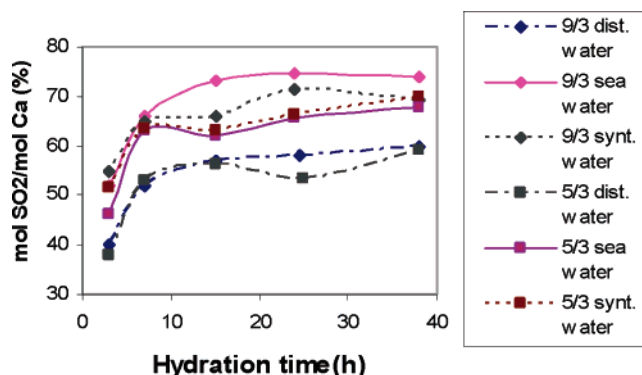

Figure 4. Desulfurization behavior for all of the studied sorbents.

work.[13] The figure shows that, for 9/3 sorbents, the numbers of moles of SO_2 per mole of Ca were clearly higher when the sorbents were prepared in seawater, being lower for sorbents prepared in synthetic water and lowest for sorbents prepared in distillate water. For the 5/3 sorbents, no great difference was found between sea or synthetic water, but the SO_2 capture was again clearly lower when distillate water was used as the hydration medium.

From the study of the physicochemical properties of the sorbents, it has been found that, when NaCl or sea salts are present in the hydration medium, the sorbents contain NaCl in amounts increasing with hydration time and probably small amounts of the minority sea salts. These sorbents exhibit much higher values of specific surface area although the salts reduce the rate of synthesis of silicates. On the other hand, regardless of the hydration medium, the synthesis of silicates finishes within about 15 h of hydration. Consequently, the amount or the composition of the silicates detected in the sorbents should not be the key to explain the better desulfurization behavior of the sorbents prepared in seawater at any hydration time. This behavior must be mainly related to the very presence of the salts and their ability to retain water from the flue gas; this ability increases with the amount of salts and with the specific surface area, both of which increase with hydration time.

As Figure 4 shows, the capture of SO_2 does not increase continuously with hydration time. Rather, a maximum in the SO_2 capture is observed for all of the sorbents, regardless the hydration medium; this maximum is obtained with the sorbents prepared at about 15 h, even though the surface area values increase continuously with hydration time. At higher hydration times, the sorbents obtained in any hydration medium do not show a great enhancement in SO_2 capture with respect to the sorbents prepared at about 15 h. The positive effect of the salts, retaining moisture and therefore increasing the SO_2 capture, is observed at all hydration times, making this maximum higher for the sorbents prepared in sea or synthetic water. Differences in the composition, surface area, and ability to retain moisture that can explain the different desulfurization behaviors of the sorbents prepared in sea or synthetic water with respect to the sorbents prepared in distillate water cannot explain the limit in the capture of SO_2 found for all of the sorbents. This limit must be related to the process of the synthesis of silicates that finishes in about 15 h. If there are no more basic silicates in the sorbents prepared at higher hydration times, no more SO_2 can be neutralized, and the SO_2 capture will not increase. The amount of silicates limits the capture of SO_2. As was previously stated,[13] the specific surface area is effective in the desulfurization process when it is the result of the formation of hydrated calcium silicates. The beneficial effect of the presence of sea salts in sorbents in the desulfurization process is maintained after 15 h

of hydration but does not increase, as no calcium silicates are synthesized after this time.

Conclusions

The use of seawater and, to a lesser extent, the use of dissolved NaCl as hydration medium in the preparation of desulfurant sorbents renders sorbents with smaller particle size, with not exactly the same composition, and with higher specific surface areas than those sorbents prepared in distillate water. All of these sorbents contain NaCl in their composition. The sea salts or NaCl do not increase the pozzolanic reaction between fly ash and $Ca(OH)_2$.

These sorbents show higher values of calcium utilization in a gas desulfurization process principally because of the ability of the sorbents to retain moisture from the flue gas.

The capture of SO_2 in a flue gas desulfurization process, at the conditions tested, is limited by the amount of calcium silicates contained in the sorbent.

The most efficient sorbents for capturing SO_2, within the studied conditions, is that prepared at a 9/3 fly ash/$Ca(OH)_2$ initial ratio, using seawater as the hydration medium for about 15 h of hydration time.

The use of seawater as a hydration medium is a good way to take advantage of the properties of sea salts for coastal power stations.

Acknowledgment

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