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USE OF WASTES OF THE SUGAR INDUSTRY AS POZZOLANA IN LIME-POZZOLANA BINDERS: STUDY OF THE REACTION

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PAPERS

ABSTRACT

Mineralogical studies of different wastes of the sugar industry, mainly sugar cane bagasse ash and sugar cane straw ash, have shown that such by-products are likely to be pozzolanic. Their use in lime-pozzolana binders could become an interesting alternative for developing countries. This paper presents a study that was aimed at monitoring the reaction between lime and wastes of the sugar industry having pozzolanic properties by evaluating 1) content of calcium hydroxide, dependent on time; 2) development of the pore structure, dependent on time; 3) study of the reaction products at different stages; and 4) mechanical properties of hardened pastes. The presence of calcium hydroxide was confirmed by x-ray diffraction analysis and thermogravimetic analysis of powder from samples of hydrated lime-pozzolana pastes. The reaction products in hydrated pastes were observed in a scanning electron microscope, and the pore structure was assessed using a mercury intrusion porosimeter. The results of the study show that sugar cane bagasse ash does not act like a reactive pozzolana, mainly due to the presence of unburned material and carbon, whereas sugar cane straw ash shows good pozzolanic activity comparable to that of rice husk ash. *© 1998 Elsevier Science Ltd*

Introduction

Lime-pozzolana binders recently have become an interesting alternative for social construction in developing countries. Natural pozzolanas, such as diatomaceous earth and volcanic ashes, and by-products of industry and agriculture, such as pulverized fly ash from power plants and rice husk ash (RHA), are the most frequently used pozzolanas (1,2). Recent studies have shown that the wastes of the sugar industry, mainly sugar cane bagasse ash (SCBA) and sugar cane straw ash (SCSA), have pozzolanic activity due to the high content of amorphous silica found in these materials (3,4). This paper presents a study of the reaction between calcium hydroxide (CH) and SCBA/SCSA acting as pozzolana.

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TABLE 1
Chemical composition determined by x-ray fluorescence.

	Mass percent		
Compound	RHA	SCBA	SCSA
SiO_2	71.74	72.74	59.06
Al_2O_3	5.61	5.26	4.75
Fe_2O_3	3.47	3.92	3.18
TiO_2	0.38	0.32	0.34
CaO	10.42	7.99	19.59
MgO	1.98	2.78	2.25
SO_3	0.50	0.13	1.37
K_2O	3.62	3.47	4.75
Na_2O	0.40	0.84	0.73
P_2O_5	0.89	1.59	1.67
Ignition loss	0.78	0.77	2.05
Total	99.79	99.81	99.74

Experimental Methods

Wastes of the Sugar Industry

The SCBA was extracted directly from the boilers of the sugar factory, 10 de Octubre, in the province of Villa Clara, Cuba. SCSA was sampled from the heaps of open-air burnt straw in the vicinity of the sugar factory, Mexico, in the province of Matanzas, Cuba. In both cases, the samples were selected carefully to avoid the presence of clay, unburned material, soil, and other matter.

A third group of pozzolana also was evaluated (RHA). The sample was taken from a heap of rice husks burnt in the open air. This pozzolana was used as a control series, because its pozzolanic activity has been assessed thoroughly (1,5–7).

The chemical composition of the ashes was determined using the x-ray fluorescence method. Loss on ignition was measured in accordance with ASTM C 114 method. Table 1 shows the results. The samples used for determination of the chemical composition were

TABLE 2
Inorganic and organic carbon.

	Mass percent	
Material	Inorganic carbon	Organic carbon
RHA	1.87	0.79
SCBA	8.32	7.83
SCSA	3.12	1.45

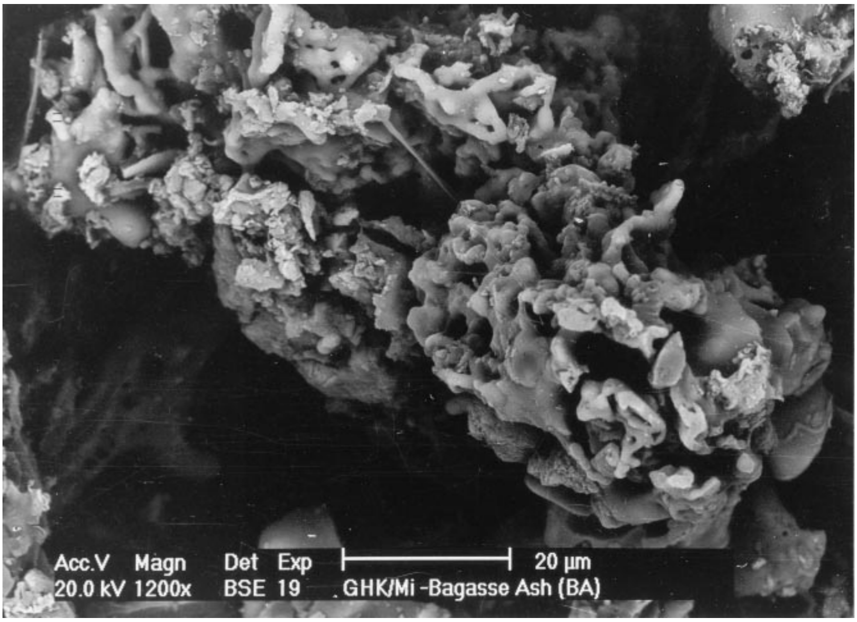

FIG. 1.
SEM photograph of SCBA sample.

burnt further to remove undesirable substances, such as carbon. Table 2 shows the amount of inorganic and organic carbon (according German standard method DIN 38 409, part 3) found in each sample in its natural state.

X-ray diffraction (XRD) analyses were performed on the samples to determine the crystalline phases of silica. A significant presence of quartz and cristobalite was confirmed for both samples studied, indicating that the temperature of combustion was higher than 800°C in some cases. However, the XRD diagram indicates the presence of amorphous substances, probably silica phases.

Thermogravimetic analysis was conducted to detect probable phase changes at temperatures below 800°C. The studies were complemented by scanning electron microscope (SEM) observation of the morphology of the ashes.

Figure 1 shows an SEM photograph of an SCBA sample in which the porous structure of the ash can be observed clearly.

Lime

Pure CH was used to prepare the lime-pozzolana mixtures.

Lime-Pozzolana Mixtures

Three series of pastes were prepared for experimental purposes. A control series was cast with a mixture of lime-RHA. The two other series cast were lime-SCBA and lime-SCSA. The lime to ash ratio was fixed for all mixtures at 30%/70% by weight.

TABLE 3
Manufactured pastes.

Binder	Lime/pozzolana ratio	Water/binder ratio
Lime-RHA	1/2.33	0.47
Lime-SCBA	1/2.33	0.47
Lime-SCSA	1/2.33	0.62

The powder resulting from dry mixing lime and ash was homogenized carefully in all cases. The powder then was ground to a fineness similar or greater than that of Portland cement (0% retained in the 0.063-mm opening sieve).

Water was added to the dry mixture to reach normal consistency in accordance with Cuban Standard NC 54-207:80. The differences in water to binder ratio is due to the different internal porosity of the studied materials, that is, the ashes. The fresh paste was cast in cylindrical molds (diameter 30 mm, height 50 mm) that were closed tightly to ensure that the material was isolated from room air, thus avoiding carbonation. Another group of specimens was prepared, in which the paste was cast in a 40 × 40 × 160-mm prismatic mold to accomplish compressive strength tests in hardened pastes. The pastes were kept in a climatic chamber at constant temperature and humidity (20°C, 65% relative humidity). The hardened pastes were removed from the mold only at the time of performance of the tests. Table 3 lists the compositions of the pastes made for the experiments. When needed, the reaction was stopped by using acetone.

Experimental Program

The experimental program was aimed at evaluating the properties of hardened lime-pozzolana pastes as a means to monitor the development of the hydrating reaction in the pastes. The following techniques were used:

1. XRD of powdered samples of hydrated pastes at 3, 7, 28, 45, and 60 days. The tests were conducted in a Philips diffractometer using Cu Kα radiation at 40 kV, 30 mA. Crystalline phases were identified using the JCPDS database (PDF-1).
2. Thermogravimetric (TG) analysis of powdered samples of hydrated pastes at 7, 28, and 45 days.
3. Mercury intrusion porosimetric studies of the pore structure of hardened pastes at 28 days.
4. SEM observation of samples of hardened pastes at 28 days, conducted using a model XL 30 DX4i Philips SEM.

Several parameters were used to establish the degree of maturity of the reaction. Among them were the following:

1. Content of CH, which was assessed with the aid of TG tests and the interpretation of XRD diagrams.

TABLE 4
Results of XRD measurements.

No.	Sample	Age	Detected phases
Sugar cane bagasse ash (SCBA)			
1	Original ash	—	Quartz, cristobalite, calcite
2	Hydrated pastes	7 days	Quartz, cristobalite, calcite, CSH, portlandite
3	Hydrated pastes	28 days	Quartz, cristobalite, calcite, CSH, portlandite
4	Hydrated pastes	43 days	Quartz, cristobalite, calcite, CSH, portlandite
Sugar cane straw ash (SCSA)			
5	Original ash	—	Quartz, cristobalite, calcite
6	Hydrated pastes	7 days	Quartz, cristobalite, calcite, CSH, portlandite
7	Hydrated pastes	28 days	Quartz, cristobalite, calcite, CSH
8	Hydrated pastes	43 days	Quartz, cristobalite, calcite, CSH

2. Evolution of the pore structure, which was evaluated from mercury intrusion porosimetric measurements.
3. Study of new products formed during the reaction, which were detected mainly during direct observations from the SEM and using the XRD method (i.e., CSH [calcium-silicate-hydrate] phase, reference pattern 33-0306).
4. Compressive strength of pastes, dependent on time.

Results and Discussion

Content of CH

The presence of CH in cured samples clearly indicates that the reaction between reactive silica and CH was not yet finished. It can be traced with the aid of XRD and TG analyses (5,8–11). There are two possibilities for the CH to react. The first is with the reactive silica in the pozzolana to form CSH phases. The second is with CO_2 from the air to form $CaCO_3$. The study of the XRD diagrams (Table 4) indicates the presence of CH in the hydrated pastes. In the lime-SCBA pastes, the CH remains present even at late ages, whereas in the lime-SCSA pastes, the CH appears to be totally consumed before 7 days. In both cases, the intensity of the peak for portlandite (CH) tends to decrease dependent on time, thus indicating that the CH is being consumed. Only major phases are listed in Table 4.

The TG analyses permitted estimation of the content of CH present in the hardened pastes from the weight losses in the range of temperatures from 425°C to 550°C measured directly in the thermograms (5,8,10). It can be seen in Figures 2 and 3 that a sudden step is produced in both thermograms at temperatures beyond 400°C, which appears to be due to the dehydroxylization of CH. Another step takes place at temperatures close to 700°C, probably caused by the release of CO_2 in the decomposition of $CaCO_3$ that was formed by carbonation (10).

In the lime-SCBA pastes, the thermogram does not substantially change during the first 28 days. After 43 days, a slight change can be noticed, but even at this age there is a significant

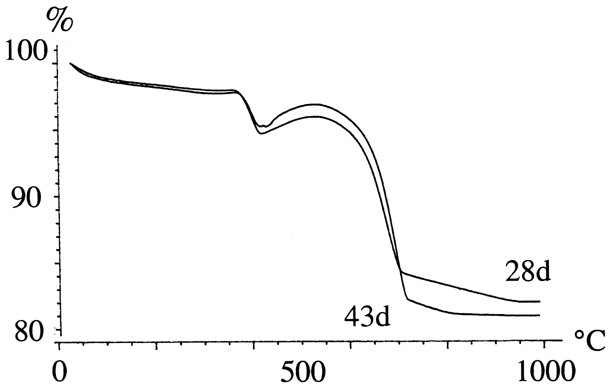

FIG. 2.
TG diagram of SCBA paste.

amount of CH present in the hydrated paste. However, the lime-SCSA pastes showed a different performance. After 28 days, the presence of CH is almost negligible, indicating that the reaction is nearly completed.

Both diagrams show significant weight losses at temperatures close to 700°C, indicating the release of CO_2.

Pore Structure

The change in pore structure in hardened pastes is associated strongly with the formation of new products. The precipitation of the new reaction products densifies the intricate net created by air voids and capillary and gel pores (9,10,12–15).

Table 5 presents the results of a comparative study of the pore structure of different groups

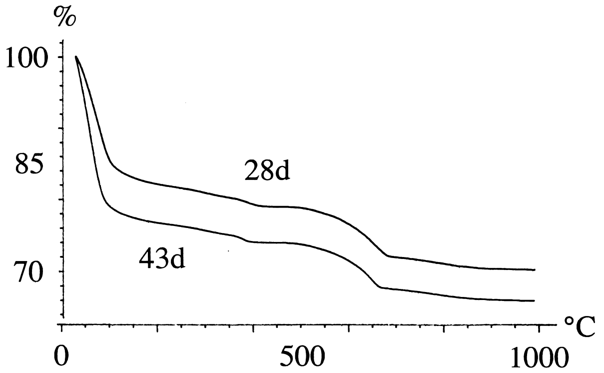

FIG. 3.
TG diagram of SCSA paste.

TABLE 5
Pore structure of hardened pastes.

No.	Sample	Air voids (%)	Capillary pores (%)	Gel pores (%)	Total porosity (%)
1	Lime-pozzolana SCBA	4.1	38.0	3.8	45.9
	Lime-pozzolana SCSA	3.9	28.5	19.2	51.6
	Lime-pozzolana RHA	3.4	17.1	25.2	45.7
2	OPC (70%) + SCBA (30%)	4.6	15.5	19.8	39.9
	OPC (70%) + SCSA (30%)	4.6	17.2	20.6	42.4
	OPC (70%) + RHA (30%) (control)	3.5	19.7	10.6	33.8
3	Control group (100% OPC)	3.6	24.2	10.4	38.2

of pastes. The groups contain pastes manufactured with both SCSA and SCBA. A new group was introduced, which consisted of ordinary Portland cement (OPC) blended with SCBA or SCSA. Three control groups were designated; the first two were related with the use of RHA in lime-pozzolana and blended cement pastes. The third group included pastes manufactured with pure OPC. The aim was to compare the different degrees of maturity of the reaction at 28 days in connection with the properties of the pore structure.

Three categories of pores were evaluated: 1) air voids (radius $>10^4$ nm); 2) capillary pores (10^4–30 nm); and 3) gel pores (<30 nm) (10). The total porosity also was considered for comparative studies.

As expected, the highest total porosity was found in lime-pozzolana pastes. The pore size distribution in lime-SCSA pastes was similar to that of the control series (lime-RHA). However, the lime-SCBA pastes had a different performance. The content of gel pores was insignificant, whereas the percentage of capillary pores was much higher than in the rest of the samples. The average pore size for lime-SCSA was smaller compared to that of the lime-SCBA. It then can be inferred that a denser net of reaction products occurs in lime-SCSA pastes than in lime-SCBA pastes.

Comparison of the pore size distribution of lime-SCSA pastes with that of the blended and pure cement pastes allows us to detect differences in the degree of maturity of the reaction. This can be explained by the fact that the greater the number of reaction products formed, the denser the net of capillary and gel pores, and the lower the total porosity and average pore size. In lime-SCBA, the comparison does not make sense, because there is no evidence of formation of new reaction products.

Reaction Products

The main product in the lime-pozzolana reaction is CSH, which is formed when silica, in an amorphous state, reacts with CH. There is not much information available on the nature of this reaction (5,6,16).

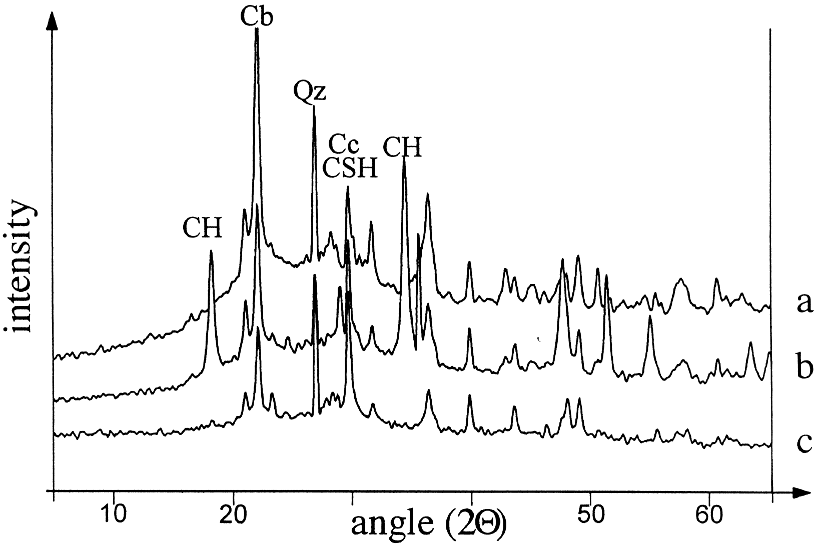

FIG. 4.
XRD diagrams of lime-SCBA pastes. (*a*) ash; (*b*) 7-day-old pastes; (*c*) 28-day-old pastes. Cb, cristobalite; Cc, calcite; CH, portlandite; CSH, calcium-silicate-hydrate; Qz, quartz.

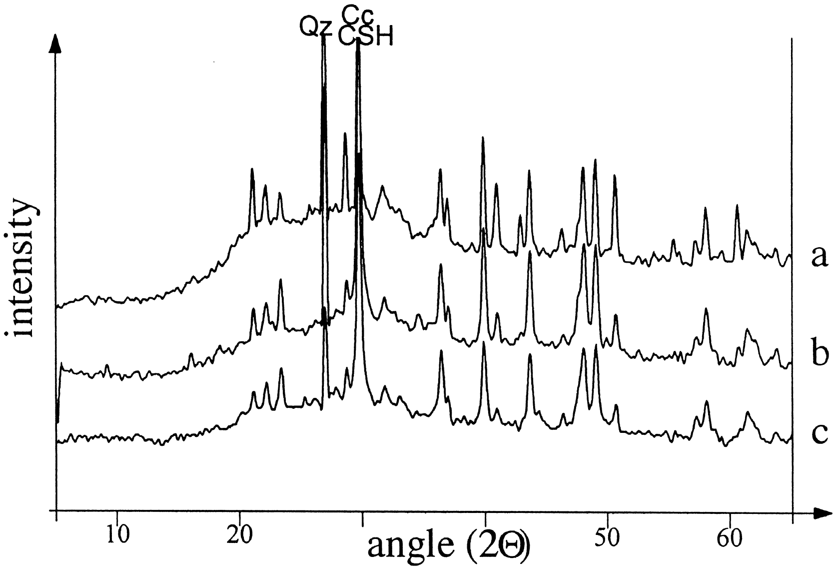

FIG. 5.
XRD diagrams of lime-SCBA pastes. (*a*) ash; (*b*) 7-day-old pastes; (*c*) 28-day-old pastes.

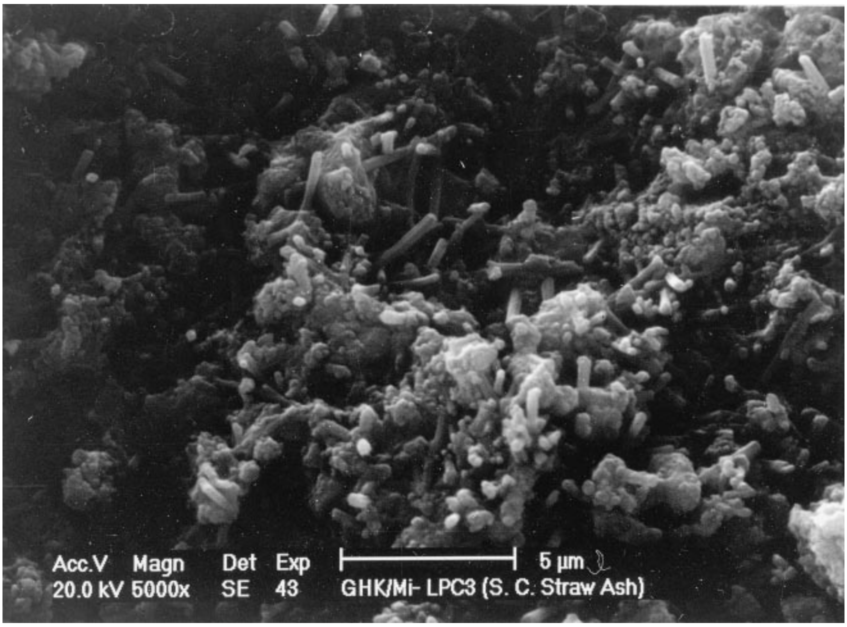

FIG. 6.
SEM observation of a sample of lime-SCBA paste.

The XRD diagrams of lime-SCBA and lime-SCSA pastes confirm the formation of new products with properties that match well with those of CSH. The products are detected during the first 7 days after hydration of the pastes. In the beginning, the vicinity of the calcite peak caused some confusion, but as the reaction evolved, the intensity of the main and secondary peaks of CSH increased, thus leaving no doubts about the nature of the products. Figures 4 and 5 show the XRD diagrams, starting from the ash and continuing with the pastes at different ages.

Observation by SEM of the lime-SCBA and lime-SCSA pastes at 28 days confirmed the presence of CSH phases, shaped as dense needles radiating in a procubine fashion from the grains rich in silica. A similar structure was observed in lime-RHA paste (5,6). Although the CSH needles were found in both observed samples (SCBA, SCSA), the greater amount was found in the lime-SCSA pastes, as can be seen in Figure 6.

Figure 7 shows an SEM photograph of a sample of lime-SCBA hydrated paste. Large quantities of carbon and organic material can be found together with the products of reaction and unreacted material. It is assumed that these substances slow down the process of formation of the reaction products, because they interfere with the contact of CH with the grains rich in silica. The shape, intensity, and contrast of the CSH needles in lime-SCSA and lime-SCBA, as seen using the SEM, are similar to those of the products of the same nature found in the lime-RHA samples. It also was confirmed that morphological similarities can be found between such products and the reaction products formed in the hydration of OPC (10).

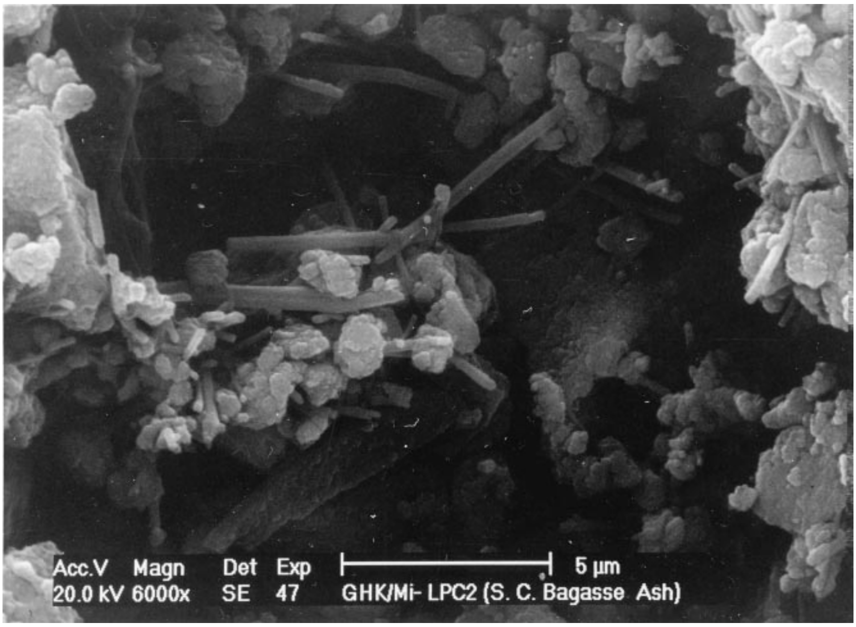

FIG. 7.
SEM observation of a sample of lime-SCSA paste.

Mechanical Properties

The change in the microstructure of a material necessarily affects its mechanical properties. The compressive strength is a reliable indicator of the evolution of the reaction, because the formation of reaction products makes the structure of the material denser and tougher to fracture.

The lime-SCBA and lime-SCSA pastes cast in prismatic molds were submitted to compressive loads at 7 and 28 days. The specimens were kept in definite climatic conditions (20°C, 65% relative humidity). This analysis confirmed the results of the other experiments:

TABLE 6
Compressive strength results.

Sample	Age (days)	Compressive strength (MPa)
Lime-pozzolana SCBA	7	2.7
Lime-pozzolana SCBA	28	7.7
Lime-pozzolana SCSA	7	7.2
Lime-pozzolana SCSA	28	13.7

Values of compressive strength are given as the mean of six measurements.

lime-SCSA pastes have a higher compressive strength than lime-SCBA pastes. At 28 days, the lime-SCSA paste attained nearly twice the compressive strength of the lime-SCBA pastes (Table 6). This result demonstrates that the degree of maturity of the reaction in lime-SCSA pastes is greater than in lime-SCBA pastes due to the higher reactivity of the SCSA. The measured values of the compressive strength of lime-SCBA and lime-SCSA pastes at 7 and 28 days are listed in Table 6.

Conclusion

1. SCBA produced in boilers of the sugar industry can be classified as a probable pozzolanic material. However, the high temperatures and incomplete combustion that take place in the boilers influence its reactivity, which in some cases could be negligible. The main factors that affect the reactivity are the degree of crystallinity of the silica present in the ash and the presence of impurities, such as carbon and unburned material. Such impurities could limit the contact between CH and reactive silica to form stable compounds.
2. SCSA produced from burning husks in the open air proved to be a very reactive pozzolana that fulfills the principal requirements for pozzolanic materials. This probably is due to the lower temperatures occurring in the combustion, mainly providing an amorphous structure for the silica present in the ash.
3. Lime-SCSA pastes consumed most of the CH added to the mixture in <7 days, whereas the lime-SCBA pastes seemed to have significant amounts of CH even after 28 days of hydration. This result shows the high reactivity of the SCSA, which is comparable to that of RHA.
4. SEM observations of the lime-SCBA and lime-SCSA pastes, together with the interpretation of the XRD diagrams, confirm the formation of stable compounds. The compounds are mainly CSH resulting from the reaction between lime and pozzolana. The CSH phases form a dense net of needles that radiate from the grains rich in silica.
5. Studies of the pore structure of lime-SCSA pastes demonstrate that the distribution of pores of such pastes at 28 days is similar to that of OPC pastes, although in an earlier stage of maturity. However, the pore-size distribution in the lime-SCBA pastes does not evidence the formation of reaction products.

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