Paper

Title: Pozzolans out of wastes from the sugar industry

Authors: J. Fernando Martirena H., Universidad Central Las Villas, Santa Clara, Cuba
Bernhard Middendorf, Universitaet Dortmund, Dortmund, Germany
Robert L. Day, University of Calgary, Calgary, Canada

Abstract

Pozzolans can be successfully used as cement replacement materials in regular concrete applications. Industrial and agricultural wastes such as sugar cane bagasse and straw can be an attractive source of pozzolans for developing countries. The paper presents an assessment of the different possibilities to produce reactive pozzolans through recycling wastes of the sugar industry. Three alternatives have been assessed: a) collecting the ashes produced during firing agricultural wastes in boilers, b) Producing ashes through firing sugar cane straw under controlled conditions in an specially designed incinerator, and c) Producing a reactive ash, which consists of thermally activated clay resulting from firing a solid fuel block (SFB), a mixture of clay and sugar cane straw. The three pozzolans are compared based on reactivity. The pozzolanic reaction was monitored in lime-pozzolan pastes by measuring the lime consumption with time with XRD, TG and SEM observations. Compressive strength of pastes was also measured. The ashes from wastes burnt in the boilers did not prove reactive. Sugar-cane straw ash, both burnt in heaps in the open or in special incinerators produced a highly reactive pozzolan. The ash resulting from the SFB was the most reactive.

Introduction

Pozzolans have drawn the attention of cement manufacturers for their good performance as cement replacement materials. Many wastes of industrial processes, such as fly ash, produced in energy generation, are suitable to be used as pozzolans. There is, however, a great potential to produce pozzolanic materials from wastes in the agriculture and food industries. Recycling these wastes could open new perspectives for cement manufacturers in the developing world and further contribute to improve sustainability of cement manufacture[1,3].

Extensive research has been done in processing and using Rice Husk Ash (RHA) to produce a highly reactive pozzolan[2]. Recent studies have shown that the wastes of the sugar industry, mainly Sugar Cane Bagasse Ash (SCBA) and Sugar Cane Straw Ash (SCSA) are high in silica content and the ashes from firing these materials can have pozzolanic properties when fired and cooled under conditions that produce amorphous silica[3,4,11]. Both rice husks and sugar cane bagasse and straw are waste materials that show a great potential for recycling in the building materials industry.

This paper presents the results of an assessment of the different possibilities to produce reactive pozzolans through recycling processes that involve burning wastes of the sugar industry.

Scope of the work

Sugar cane production is responsible for the generation of huge amounts of organic wastes, which are commonly burnt in the fields, as there are no commercial applications available where they can be recycled. The main wastes are the crushed sugar-cane stalks (bagasse) and sugar cane straw. In Cuba, for example, the estimated amount of bio-wastes from the sugar industry is 300,000 tonnes per year [3].

Sugar cane has the ability of fixing silica in its organic structure. When burnt, the organic volatiles disappear and the remaining ash is rich in micro-crystalline silica. Depending on the burning and cooling régimes, the ash can occur in an amorphous, reactive, state or in less-reactive crystalline forms. To produce a reactive pozzolan out of sugar cane, it must be fired and the temperature must be kept within 400 -800 degrees Celsius, in order to prevent the transition to crystalline phases during heating. [5,6,7,11].

Burning is the most frequent way to recycle these wastes. Different procedures have been developed to burn the organic wastes under controlled conditions. Some of them, like the Fluidized Bed Boiler (FBB)[5] require complicated operational systems, and others, like rudimentary incinerators simply burn under very simple conditions[8]. It appears that burning temperature, residence time and cooling regime are the most influencing factors.

The authors have studied different approaches to produce pozzolans through recycling processes that involve burning bio-wastes of the sugar industry:

1. Collecting the ashes produced during firing agricultural wastes in boilers.
2. Producing ashes through firing sugar cane straw under controlled conditions in an specially designed incinerator
3. Producing a reactive ash, which consists of thermally activated clay resulting from firing a solid fuel block (SFB), a briquette made of clay and finely shredded sugar cane straw.

The three different pozzolans produced as a result of the recycling process were evaluated in the laboratory. As part of the testing procedure, the likely pozzolanic ashes were ground and mixed with Calcium Hydroxide (CH), and normal consistency pastes were prepared with this lime-pozzolan binder. The following tests were performed:

a) XRD of powdered samples of oven dried hydrated pastes at 3, 7, 28, and 60 days. The tests were conducted in a Philips diffractometer by using Cu Kα radiation at 40 KV, 30 mA.
b) TG analysis of powdered samples of hydrated pastes at 7 and 28 days.
c) MIP studies of the pore structure of hardened pastes at an age of 28 days
d) SEM observation of samples of hardened pastes at an age of 28 days, conducted in a Philips SEM, model XL 30 DX4i.
e) Compressive strength tests of the hardened pastes at the age of 7 and 28 days.

The comparison of the results obtained assist in determining the best way to produce reactive pozzolans through recycling sugar cane wastes.

Reactivity of ashes without special treatment

The easiest procedure is to collect the ashes just as they are produce in the industry, without any further treatment. Two types of ash were examined. The SCBA ash was extracted directly from boilers of the sugar factory “10 de Octubre” in the province of Villa Clara, Cuba. The SCSA ash was sampled from the heaps of open air-burnt straw in the fields surrounding the sugar factory. The ash was collected as a representative sample from the entire heap – e.g. by taking several grab samples at different heap depths and then blending them together. In both cases the samples were carefully selected to avoid the presence of clay, unburned material, soil, etc. Reagent-grade Calcium Hydroxide (CH) was used to prepare the lime-pozzolana mixtures.

The chemical composition of both ashes was determined by X-Ray-Fluorescence (Table 1)[9]. XRD analyses were carried out in order to identify crystalline phases of silica. A significant presence of quartz and cristobalite was confirmed for both samples the SCBA and the SCSA ashes, thus indicating that the temperature of combustion was in some cases higher than 800 ^{o}C. However, the hump at the XRD diagram also indicated the presence of amorphous substances (see Fig. 3).

Two series of pastes were prepared. Lime-SCBA and lime-SCSA pastes were cast in 4 x 4 x 16 cm prisms and sealed to avoid carbonation. The lime/ash ratio was fixed for all mixtures to 30/70 % by mass. The water demand was established in accordance with Cuban standard NC 54-207:80 – this standard is similar to ISO/R 679:68 and embodies similar methods found in ASTM C191, C451 and C109.

Table 1: Chemical Composition determined by X-ray fluorescence

Compound	SCBA	SCSA
	mass percentage	
SiO_2	72.74	59.06
Al_2O_3	5.26	4.75
Fe_2O_3	3.92	3.18
TiO_2	0.32	0.34
CaO	7.99	19.59
MgO	2.78	2.25
SO_3	0.13	1.37
K_2O	3.47	4.75
Na_2O	0.84	0.73
P_2O_5	1.59	1.67
Ignition Loss	0.77	2.05
Total	*99.81*	*99.74*

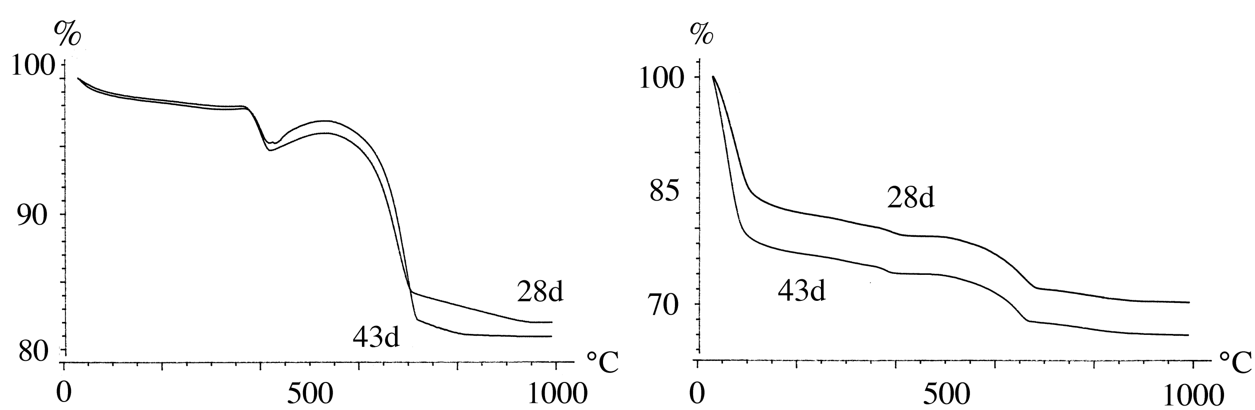

Fig. 1: TG diagrams for lime-pozzolan pastes: (right) lime-SCSA paste, (left) lime-SCBA paste

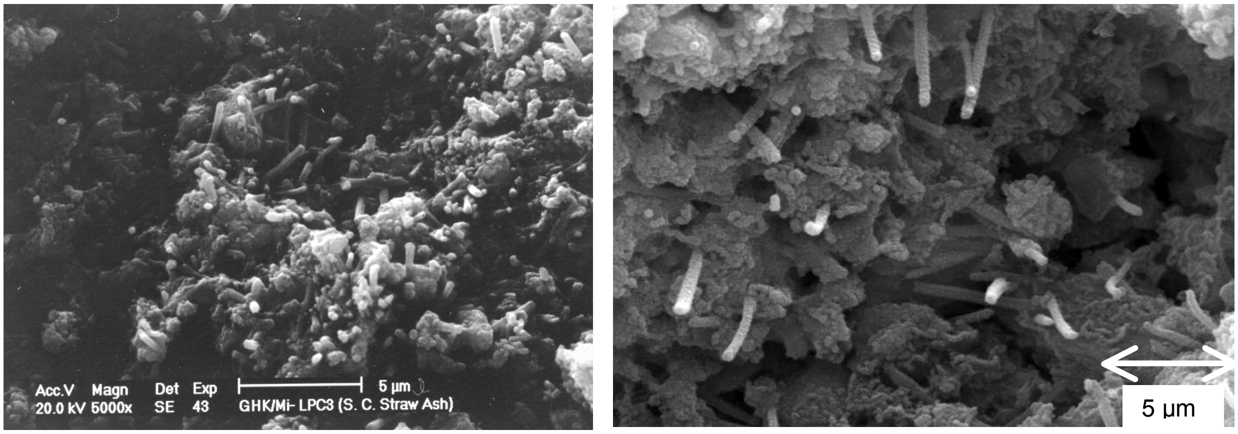

Fig. 2: SEM pictures of lime-pozzolan pastes (fracture surfaces): (right) lime-SCSA paste, (left) lime-SCBA paste

The pastes made with SCBA showed poor reactivity. There was a significant amount of CH remaining at 28 days, as shown by both the XRD and TG analysis (see Fig 1, left). MIP results showed a very coarse porosity, a large component between 0.1-100 microns, and an insignificant amount of the smaller pore-fraction The SEM micrographs showed very few likely CSH phases, scattered around large particles of unreacted material and quartz. The prisms had a 28 days compressive strength of 7 MPa.

The pastes made with SCSA ash that was fired in the field showed a reasonably good reactivity. At 28 days the CH peaks in the XRD diagram reduced in intensity, and the weight loss associated with dehydroxylation of CH during TG analysis was lower, thus indicating that CH consumption was significantly higher than that in the SCBA pastes (see Fig. 1, right). The pastes showed a lower coarse porosity, with a concomitant higher proportion of smaller pores. The SEM micrographs showed a denser network of needle-like CSH phases, and a generally denser structure. The prisms had a 28 days compressive strength of 13 MPa.

The main results of this study may be summarized as:

1. SCBA-ash that is produced in boilers of the sugar industry shows a poor pozzolanic activity. The high firing temperatures, incomplete non-uniform combustion and slow cooling that take place in the boilers are likely reasons for the low reactivity. The main factors that affect the reactivity are the resultant degree of crystallinity of the silica present in the ash and the presence of impurities like carbon and unburnt material.
2. SCSA that is produced from burning sugar cane straw in the open air has proved to be a reactive pozzolan that fulfills the principal requirements for pozzolanic materials. Probably, this is due to the lower temperatures occurring in the combustion, mainly providing an amorphous structure for the silica present in the ash.

Reactivity of ash treated in rudimentary incinerators

If one expects a higher reactivity from the pozzolan, the thermal treatment of the biomass during firing must be strictly controlled. With this purpose, a rudimentary incinerator was conceived and built with the aim of firing the bio-wastes at temperature under 700 ^{o}C, and the residence time under 2 hours, in order to create optimal conditions to produce a reactive ash. The incinerator was designed to process raw sugar cane straw. The target output of the incinerator is 25 kg of ash per hour. [10]

The incinerator was built so as to guarantee that the airflow in the combustion chamber travels through meshes in the external walls. After the start of combustion, the incoming air drags heat from the burning mass to the chimney outlet, and cools down the burning chamber. The input of cool air can be regulated in order to attain the target burning temperature and residence time. A faster airflow lowers the temperature inside the burning chamber and lowers the residence time, as the biomass burns faster with an ample supply of oxygen.

Thermocouples were set in various places of the burning chamber in order to monitor temperatures during firing. The highest temperature, measured with thermocouples in different places within the burning chamber did not exceed 600 ^{o}C. The residence time in the chamber varied between one and three hours. There was a strong relationship between the intensity of the airflow and the temperature occurring in various parts of the incinerator.

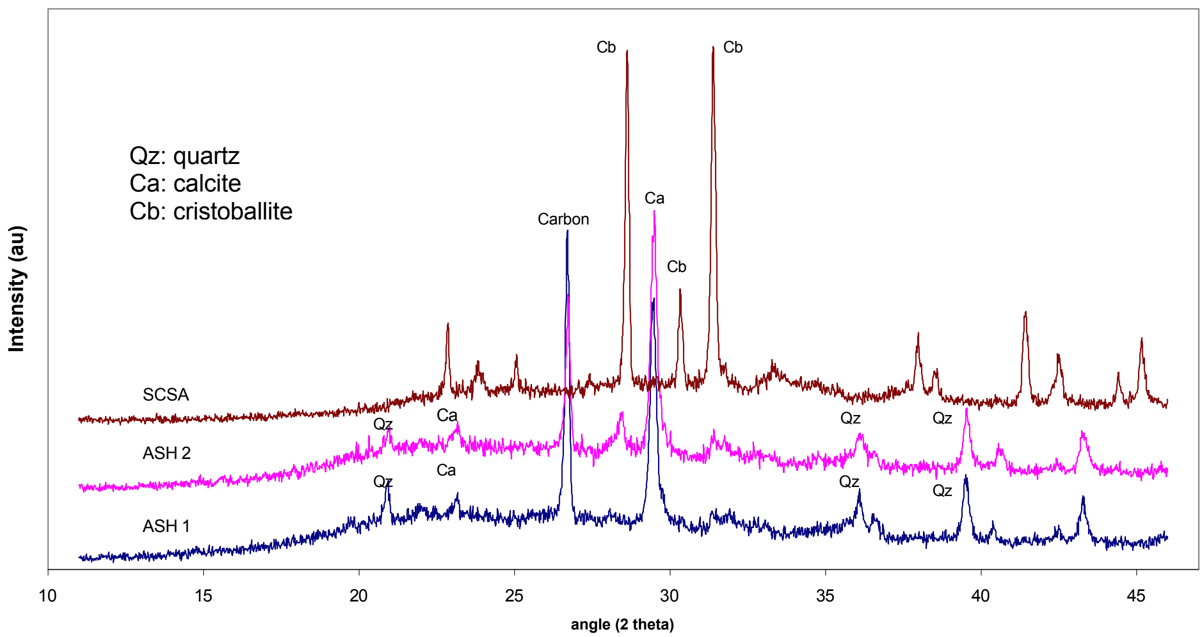

Fig. 3: XRD of the ashes resulting from firing sugar cane straw in the open field (SCSA) and in a special incinerator (ASH1 and ASH2)

The ash resulting from the burning trials was evaluated and compared with the results from SCSA ash burnt in the open field presented above. This ash was burnt at temperatures under 600 ^{o}C, and was allowed to cool slowly within the incinerator for approximately 2 hours. Two different ashes were sampled for the evaluation: ASH 1 was collected at the upper part of the incinerator, directly in the burning chamber, and ASH 2 was collected from the bottom of the incinerator. Table 2 shows the chemical composition of the ashes. Both have a high CaO content; and according to ASTM 618-78 can be classified as High Calcium Ashes.

Table 2: Chemical composition of the incinerator-fired ashes [7]

Description	ASH 1)(%)	(ASH 2) (%)
CaO	10.35	11.40
MgO	3.60	3.62
SiO_2	61.73	57.36
Fe_2O_3	3.55	1.54
Al_2O_3	3.29	1.79
K_2O	2.72	4.20
BaO	0.03	0.03
SrO	0.03	0.04
Mn_2O_3	0.34	0.45
Na_2O	0.37	0.50
SO_3	1.19	1.49
CO_2	7.08	8.36
Carbon	1.17	1.55
Bonded H_2O	4.03	5.33
Moisture		
TOTAL	**99.47**	**97.66**

Fig. 3 presents the results of XRD performed on SCSA, ASH1 and ASH2. Both ASH 1 and ASH2 show the “hump” or “halo” that corresponds to the presence of amorphous substances. This “halo” appears to be wider and larger than that of the ash used for comparison (SCSA, ash burnt in the open field). The XRD diagram shows fewer crystalline compounds than SCSA ash burnt in the open field; cristobalite has disappeared and quartz is evident. This tends to confirm that combustion of Ashes 1 and 2 occurred at a lower temperature where crystalline phases cannot occur.

Lime-pozzolan pastes were prepared with ASH 1 and ASH 2, ground to powder (under 125 microns) and mixed with CH. For chemical and porosity testing, fresh pastes were cast into 35mm cylindrical film containers and tightly capped until testing to prevent carbonation. For mechanical testing 40 x 40 x 160 mm paste prisms were cast. The prisms were covered with a plastic sheet to prevent carbonation of the un-reacted lime due to contact with air, and were cured at room temperature. Specimens were demoulded just prior to testing. The lime / ash mix proportions were: 30% / 70% by mass. The water demand was established in accordance with Cuban standard NC 54-207:80 – this standard is similar to ISO/R 679:68 and embodies similar methods found in ASTM C191, C451 and C109.

No major differences in the performance of the ashes burnt under more-controlled conditions in the incinerator were found in comparison with those burnt in the open field. XRD and TG testing showed that the major part of the pozzolanic reaction is complete after 28 days because most of the CH present in the fresh paste at 3 days had disappeared at 28 days, apparently consumed in the pozzolanic reaction (see Fig. 4).

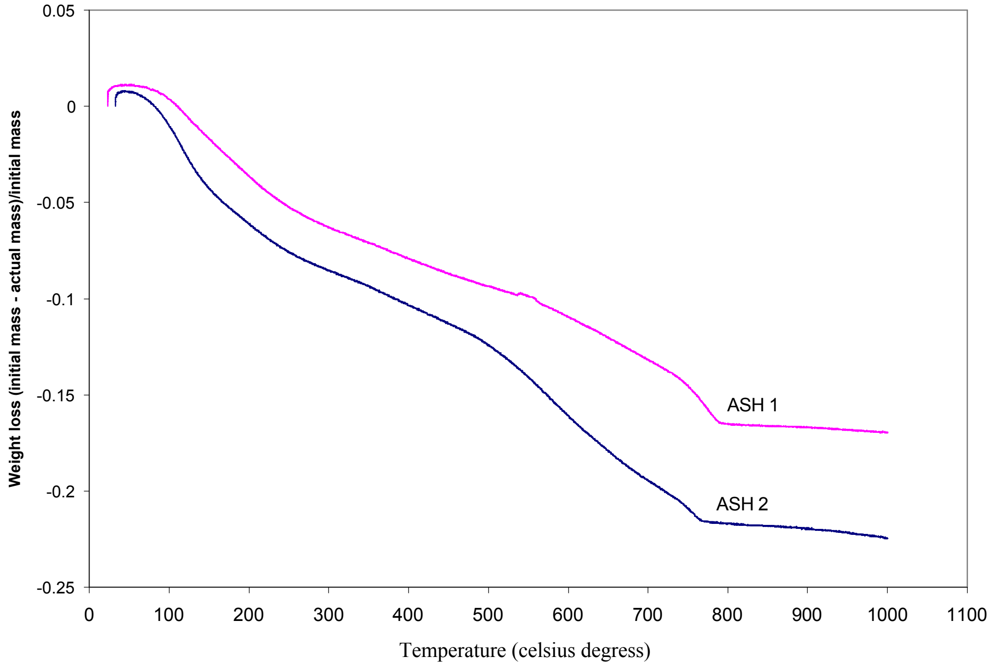

Fig. 4: TG results of 28 days lime-pozzolan pastes made with ASH1 and ASH2

SEM observations of the hydrated pastes at age 28 days, presented in Fig. 5, confirm the presence of C-S-H needle-like phases.

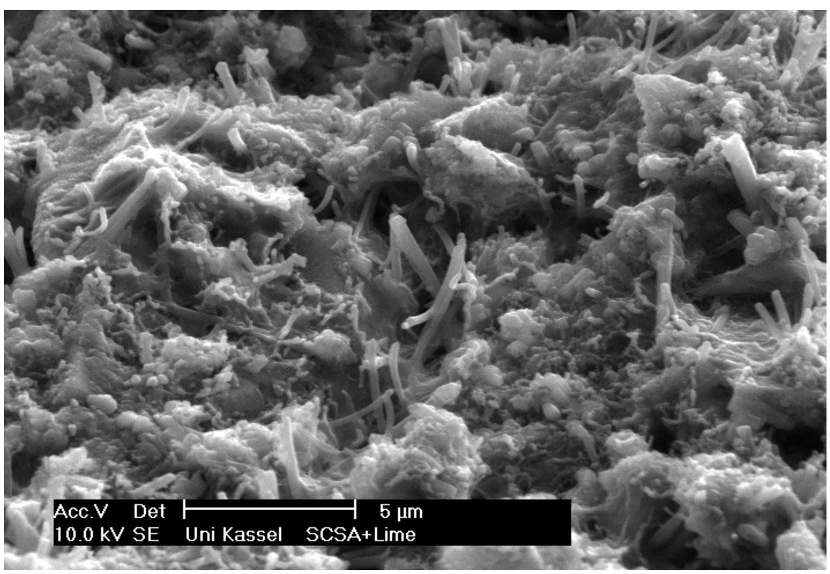

Fig. 5: SEM picture of a fracture surface of a paste made with lime-pozzolan; sugar cane straw ash burnt under controlled conditions.

The compressive strength tests performed in pastes made with ASH 2 and ASH 1 show a 28 d strength of 13 MPa, which is similar to that of pastes made with ash burnt in the open field, presented above.

Based upon the strength results, there appears to be no significant benefit in firing sugar-cane wastes in semi-controlled conditions, when compared to firing in open-air heaps. Although the mineralogical study shows that the ashes resulting from incinerator firing have less crystalline phases and more glass phase, this difference is not reflected in strength gain.

The reason for this could be the relatively long residence time of the ash in the burning chamber of the incinerator, and the slow cooling process afterward, which would not promote the retention of the more-reactive glass phase. This, combined with the low output shown by the incinerators during their use, confirms that from a practical/economic viewpoint transition from open-field firing to rudimentary incinerator firing is not warranted. A more sophisticated, higher output, version of incinerator with better and more uniform temperature control coupled with controlled cooling might prove to be a worthwhile future endeavour.

Ash from Solid Fuel Blocks made out of clay and waste biomass

Previous testing has indicated that if firing-temperature is kept below 750 ^oC, a reactive ash can be obtained by burning bio-wastes, but the practical applications of this solution are limited because at this low temperature heat recovery devices are difficult to implement.

When firing above 750 ^oC, the ashes resulting from burning bio-wastes become highly crystalline and thus non reactive[11]. At this range of temperature the only chance to produce reactive pozzolans through thermal treatment is by calcining clay. This is a well-known procedure, which involves a relatively large energy consumption, but yields a highly reactive pozzolan. If the energy needed to calcine clay could come from firing bio-wastes, the whole process would be more economically viable, and less dependant on external energy.

To contribute to this, the authors have developed the Solid Fueld Block (SFB) [12]. In this block, the bio-waste is mixed with clay before burning and pressed into briquettes; its high calorific value can be used at its maximum potential and the resulting ash – a mixture of the non-reactive ashes from the biomass (approx. 20-30%) and the likely reactive activated clay (approx 70-80%)- can likely be used as a pozzolan. The SFB can be burnt at temperatures around 800-950°C. The higher firing temperature increases the options for use of the resulting energy -- for instance, to fire clay or fly ash-clay bricks. Various techniques for energy utilization from this process are currently under investigation.

The Solid Fuel Block (SFB) is an attractive alternative to recycle waste biomass for the production of reactive pozzolan. Waste biomass, such as agri-wastes, sawdust or waste paper is shredded to fine particles, wet mixed with a suitable clay and pressed into solid fuel blocks. The clay that is used should be high in silica content because the activated clay becomes the main source of pozzolanic material, as the ashes resulting from firing the bio-wastes at temperature above 750 ^oC are likely non-reactive. The optimum proportion of clay has been found by experiment to be in the range 20-30% by mass. The SFB typically has a dry density of 800 to 1100 kg/m^3. The average calorific value is 15 kJ/kg, which makes the SFB acceptable for use a sole source of fuel in an ordinary furnace.

The ash that results from SFB firing needs to be cooled fairly rapidly in order to form a primarily amorphous reactive silica. Slower cooling results in a higher proportion of non-reactive crystalline compounds. Sophisticated techniques for rapid cooling produce optimum pozzolanic activity of the ash but are not practicable for implementation within an agricultural community. It has been found in experimental trials that a simple process of periodically removing the ash from the furnace and spreading it on a metal surface cools the ash rapidly enough to produce a highly reactive pozzolan, which can be used in the manufacture of lime-pozzolan cements or as a supplementary cementing material.

Table 3 shows the average composition of the ash resulting from burning a SFB made with sugar cane straw and clay. The biomass has a higher loss on ignition and thus becomes a minor part of the resulting ash. The clay only losses the combined water (10-15% of the total weight), and becomes the major component of the resulting ash. If burning temperatures is held around 900 °C, approximately 70% the ash should be reactive.

Table 3: Composition of the SFB and the ash resulting from burning it

Material	**Ratio before burning**	**Loss on ignition**	**Ratio after burning**
Clay	18 %	15 %	68 %
Sugar cane straw	75 %	93 %	32 %
Water	7 %	100 %	0 %

To simulate the ash resulting from burning a SFB in the laboratory, clay and the bio-wastes were fired separately in a lab oven and later mixed in accordance with the proportions given in Table 3. The source of bio-waste used was sugar cane straw, which came from the same source as that used in the other tests described above. The clay selected was rich in montmorillonite. Both the clay and the biomass were fired at two different temperatures, 900 °C and 1000 °C The ashes were cooled with two different cooling regimes -- some series were left in the oven for cooling down, while others were cooled rapidly by spreading the ash on a large metal sheet.

Lime-pozzolan pastes were prepared and cast in 4 x 4 x 16 cm prisms. The prisms were moist cured and preserved against carbonation. The pastes made with ash burnt at 1000 °C did not set at any time, regardless of the cooling rate. This clearly indicates that at this temperature the ash is non reactive. The lime-pozzolan pastes made with ash fired at 900 °C did set, but CH consumption between 7-28 days was reportedly low (see Fig. 6), thus indicating that the pozzolan did not react much. This is consistent with the results from compressive strength (3.5 MPa) that fell very much under the expectations

However, at 120 days the pastes did show a significant increase in compressive strength, especially for those made with ash cooled rapidly. The strength rose to 13 MPa, thus indicating that there was a latent hydraulic potential in the pozzolan. It was decided to make a second round of tests, this time adding chemical activators, such as sodium sulphate, which can act as both a set-accelerator and strength-enhancer. [13,14]. For these tests 4% sodium sulfate was added by mass of lime-pozzolan binder. Testing was done at 7 and 28 days.

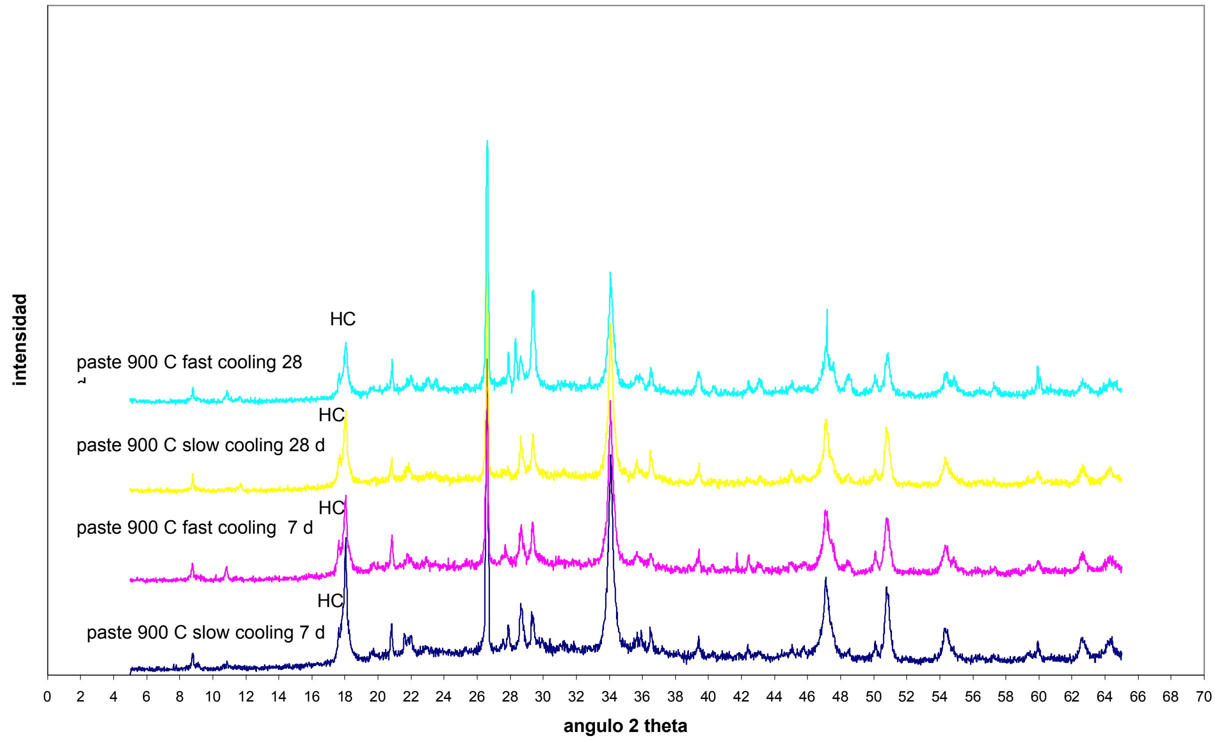

Fig. 6: XRD of pastes made with lime-SFB ashes fired at 900 °C with no chemical activator.

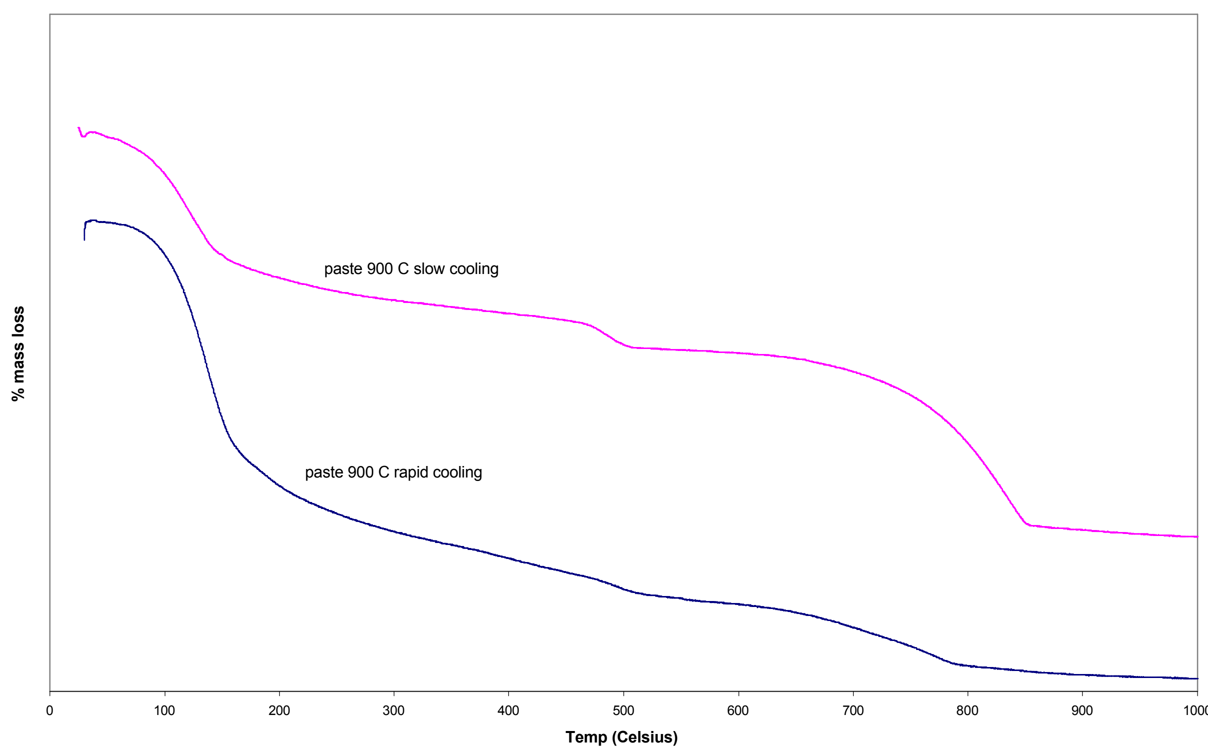

Fig. 7: TG of pastes age 28 days made with ashes from SFB, activated with sodium sulphate

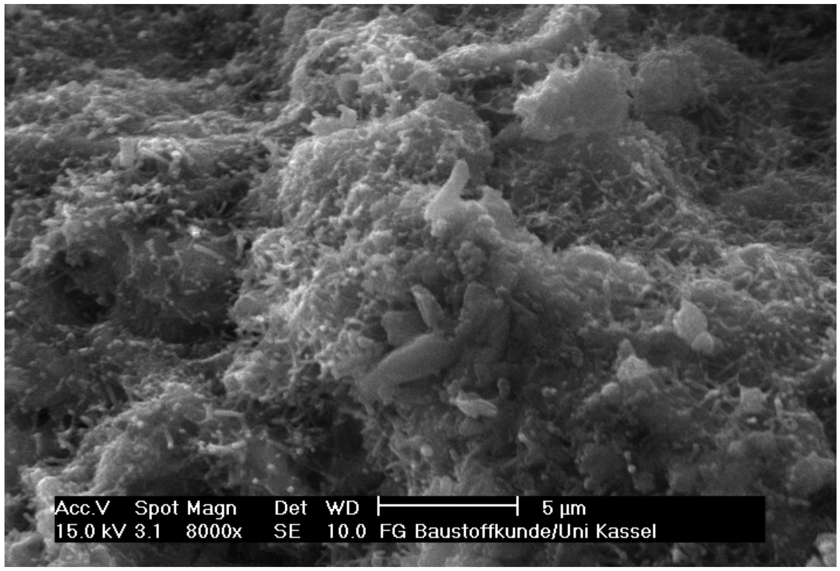

Fig. 8: SEM picture of a fracture surface of a 28 d paste made with SFB ash cooled rapidly at 900 C, activated with sodium sulphate

The pastes made with sodium sulphate with ash burnt at 900 ^oC and rapidly cooled showed higher strengths in comparison with all of the pastes evaluated before. The compressive strength was 12 MPa at 7 days, 16 MPa at 28 days, and 18 MPa at 60 days. XRD and TG diagrams showed that most of CH was consumed at 7 days (see Fig. 7). The SEM pictures show a very dense network of needle-like CSH phases close to the pozzolan grains (see Fig. 8). The pastes made with ash burnt at 900 ^oC and cooled down slowly showed poorer performance at early ages. However, beyond 60 days both pastes had approximately the same strength regardless the cooling regime.

This research is still underway, and other cooling methods are under investigation, such as cooling the ash as it falls from the burning chamber of brick kilns into the ash tray. This research is expected to contribute to widening the application of the SFB for production of useful energy and by providing a suitable use for the waste ash as a replacement material for Portland cement in concrete and masonry construction.

Concluding remarks

There is a great potential to produce high quality building materials through recycling agriculture wastes, especially wastes from the sugar industry. Many types of biomass have application to produce useful energy when fired. If some care is taken, pozzolanic ashes can be produced during this process that can result in a contribution to low-cost sustainable industries, including the construction industry. Feasibility studies to produce a pozzolan from biomass firing must take into consideration methods to control the burning temperature and residence time in the burning chamber as well as to address the cooling rate of the ash.

A promising procedure, reported here, is to produce solid fuel blocks (SFBs) out of clay and waste biomass. This solution enables the production of a reactive pozzolan and the SFB can be used to drive practical industrial processes.

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