Pergamon

Cement and Concrete Research 33 (2003) 517–524

CEMENT AND CONCRETE RESEARCH

Kinetics of the pozzolanic reaction between lime and sugar cane straw ash by electrical conductivity measurement: A kinetic–diffusive model

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Received 4 December 2001; accepted 16 September 2002

Abstract

The kinetics of the pozzolanic reaction between lime (calcium hydroxide) and sugar cane straw ash (SCSA) with 20% and 30% of clay burned at 800 and 1000 °C is studied. A simple experimental technique was used in which the conductivity is the experimental variable. For correlating the conductivity with the concentration of calcium hydroxide (CH), a calibration curve was established. We elaborated a mathematical model that allows us to describe the process in either kinetic or kinetic–diffusive regimes. The fitting of the model by computerized methods enables us determine the parameters that characterize the process: i.e. the diffusion coefficient and reaction rate constant. The pozzolanic activity is evaluated according to the obtained values of the reaction rate constant. The results show that SCSA has a good pozzolanic activity comparable to that of the rice husk ash (RHA).

Keywords: Pozzolans; Pozzolanic reactions; Kinetics

1. Introduction

Pozzolans are incorporated as active additions to Portland cement and concrete due to their capacity for reacting to lime, principally originated during the hydration of Portland cement. The result is the formation of stable, hydraulic and insoluble compounds, principally calcium silicate hydrated (CSH) phases [1] due to the chemical reactions of the amorphous silica presents in the pozzolan with lime.

This pozzolanic reaction modifies some properties of the cement and of the resulting concrete. Although lime pozzolan cements were some of the earliest building materials widely used for all kinds of construction, only recently have lime–pozzolan binders become an interesting alternative for social construction in developing countries. Recent studies [2] have shown that wastes from the sugar industry, mainly sugar cane straw ash (SCSA), have pozzolanic activity derived from the high content of amorphous silica in this material.

Several methods have focused on the assessment of the pozzolanic activity of a material considering the complexity of its "pozzolanicity," where different mechanisms of the pozzolan/CH interaction exist and where there is a considerable variation in the nature of materials showing this property.

It is known that the development of the pozzolan/CH reaction causes the formation of stable and insoluble products, therefore diminishing the CH [$Ca(OH)_2$] concentration in the solution. As a consequence, a decrease of conductivity takes place. In other words, a decrease of free Ca^{2+} ions due to the increase of the CSH-like phase (or reaction product) produces a decrease of conductivity whose change rate depends on whether the reactivity of the pozzolan is higher or lower.

Conductometric techniques have been applied for different purposes in the field of cement. A considerable number of papers have been published on the application of electrical conductance methods (and its reciprocal, resistance) in the study of the early hydration of ordinary Portland cement, some of the early works being traced back to the 1930s and extending until the present day [3–9].

Rassk and Bhaskar [10], however, were the first to design a method for evaluating pozzolanic activity by measuring electrical conductivity. This method allows the measuring of the amount of silica dissolved in a solution of hydrofluoric acid (HF) in which the active material is dispersed. From this, a pozzolanic index is calculated.

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PII: S0008-8846(02)00998-5

Luxán et al. [11] proposed a simple and very fast method for the indirect evaluation of the pozzolanic activity of natural pozzolans. It is based on the electrical conductivity measurement of a calcium hydroxide–pozzolan suspension. They establish an index given by the variation between the initial and final conductivity for a time of only 120 s. This time proved to be sufficient to obtain a stabilization of the curve of conductivity versus time in several materials studied.

Afterwards, Sugita et al. [12,13] evaluated the pozzolanic activity of rice husk ash (RHA) according to Luxán's method. They found a good correlation between noncrystalline silica content in RHA samples and the variation in electrical conductivity of RHA/saturated lime suspensions.

In cement pastes containing a pozzolan, Tashiro et al. [14] proposed a fast method for evaluating pozzolanic activity by measuring electrical resistance (only 72 h for testing were required).

Recently, Payá et al. [15] proposed a methodology for evaluating fly ash. They calculated the pozzolanic activity as the percentage of loss in conductivity at several reaction times (100, 1000 and 10,000 s).

The above methods for evaluating pozzolanic activity are aimed at the qualitative aspect of the behavior of these pozzolanic materials rather than at the quantitative aspect of the lime–pozzolan reaction (this last being the computing of kinetic coefficients). The knowledge of the kinetic coefficients is a good criterion for evaluating the pozzolanic activity of the materials.

As it is known, lime (or cement)–pozzolan reactions are not yet very well understood and have been the subject of investigation of many researchers. The study of the pozzolanic reaction kinetics is of great scientific interest and of technological importance as well.

Several models have been developed for describing the pozzolanic reaction. From the scientific point of view and for numerous applications, simple but accurate models describing this phenomenon is important. The most popular models are those of Jander [16] and Kind and Zhuralev [3]. Other authors [17–21] have developed mathematical models for describing the pozzolanic reaction kinetics, but they do not always agree with the experimental results.

In this research, the electrical conductivity is recorded experimentally. It can be easily determined and correlated with the $Ca(OH)_2$ concentration. This allows us to follow the kinetics of the reaction of the artificial pozzolans (SCSA and RHA with 20% and 30% of clay, burned at 800 and 1000 °C) without quite big experimental requirements. We have worked out a mathematical model that allows us to describe the process in a kinetic–diffusive or kinetic regime. This model fitted by computerized methods lets us determine process parameters, such as the diffusion coefficient and the reaction rate constant. It allows us to evaluate the pozzolanic activity of these materials in an economical, effective and rigorous way.

2. Experimental

2.1. Materials

The pozzolanic ashes were obtained from two kinds of biomasses. The sugar cane straw (SCS) was recollected in the vicinity of the sugar factory "10 de Octubre" in the province of Villaclara, Cuba. The rice husk (RH) was obtained from a rice thresher in the same province.

The chemical composition of these starting materials is shown in Table 1.

Clay was used as an agglutinant, which is constituted fundamentally by a mixed-layer mineral called mica-montmorillonite, as clay mineral. Also, several nonclay minerals were identified as well, such as quartz, calcite, goethite and chlorite. The clay can be activated thermally and become a pozzolanic material. This allows us to obtain a solid fuel block (SFB) that can also be used as an alternative energy source. The energy produced by the self-combustion of the SFB (at temperatures above 400 °C) can be used with different purposes. For example, in the production of lime and silico-calcareous bricks in the building materials industry [22], etc.

A saturated solution of calcium hydroxide, prepared with deionized water and $Ca(OH)_2$, was used. This was valued with hydrochloric acid. The concentration obtained was 0.040 mol/l.

2.2. SFB obtainment

A densification process was carried out to obtain the SFB. This process began with the preparation of the biomass. The RH was used under real conditions as agricultural waste, with approximately 5 mm of particle size and the presence of characteristic powders. The SCS was used in a dry natural state, after milling fibers between 4 and 5 mm of length were obtained. Twenty percent and 30% of clay (depending on the total weight of SFB) and a constant amount of biomass (200 g) were employed. Water was added to the clay–biomass until an appropriate plasticity degree was reached.

Thereafter, the SFB was compacted by using the Proctor Standard Test [23], which reduces the volume and therefore facilitates the transportation. Also the density increases and it makes the combustion more efficient.

Table 1
Chemical composition of the starting materials

Compound	Sugar cane straw (%)	Rice husk (%)
Ca	1.110	0.076
Mg	0.056	0.033
Na	0.057	0.037
Zn	0.0074	0.065
Fe	2.17	0.38
K	0.480	0.250
Cu	0.0037	0.0007

Table 2
Chemical composition of the materials calcined at 800 °C

Compound	Materials (ashes)			
	RH + 20% clay (RHA1)	RH + 30% clay (RHA2)	SCS + 20% clay (SCSA1)	SCS + 30% clay (SCSA2)
SiO_2	62.69	57.30	64.02	62.62
Al_2O_3	14.93	10.36	11.29	13.79
Fe_2O_3	8.60	6.11	6.59	7.65
TiO_2	0.86	0.60	0.67	0.76
CaO	3.15	2.90	3.65	4.41
MgO	3.49	2.87	2.76	3.14
Na_2O	2.58	1.92	1.88	2.22
K_2O	1.36	1.64	2.35	1.91
Ignition loss	2.04	14.21	4.88	3.30
Total	99.70	97.91	98.09	99.80

Finally, the samples were extracted and subjected to a drying process in the open air with the purpose of eliminating the water and to facilitate the combustion.

2.3. Pozzolanic materials and experimental procedure

The combustion process was carried out in a muffle furnace at 800 and 1000 °C. Ashes were screened and a particle size of 0.15 mm was fixed.

The chemical composition of ashes is shown in Tables 2 and 3.

In the conductivity measurement, ash/water solutions were also employed. Its use was to find out the contribution to the conductivity of Na^+, K^+, Mg^{2+} and other ions present in the solution (although in low concentration).

For both, the ash/CH solution sample and the ash/water, 2.10 g for each ash were weighed and then 70 ml of CH solution and 70 ml of deionized water were added, respectively. For measuring the variation of conductivity of the ash/CH solution samples, the contribution to conductivity of ash/water was subtracted.

The conductivity measurements were made in a METROHM microconductimeter (Sweden) at 28 ± 1 °C at different times. The samples were closed tightly to avoid carbonation. To correlate the CH concentration with the conductivity of the CH solution, a calibration curve was established (Fig. 1).

Table 3
Chemical composition of the SCSA calcined at 1000 °C

Compound	Materials (ashes)	
	SCS + 20% clay (SCSA3)	SCS + 30% clay (SCSA4)
SiO_2	66.96	65.50
Al_2O_3	12.72	13.80
Fe_2O_3	6.94	7.65
TiO_2	0.71	0.76
CaO	4.53	3.65
MgO	3.14	3.35
Na_2O	2.02	2.22
K_2O	1.91	1.84
Ignition loss	0.82	0.55
Total	99.75	99.32

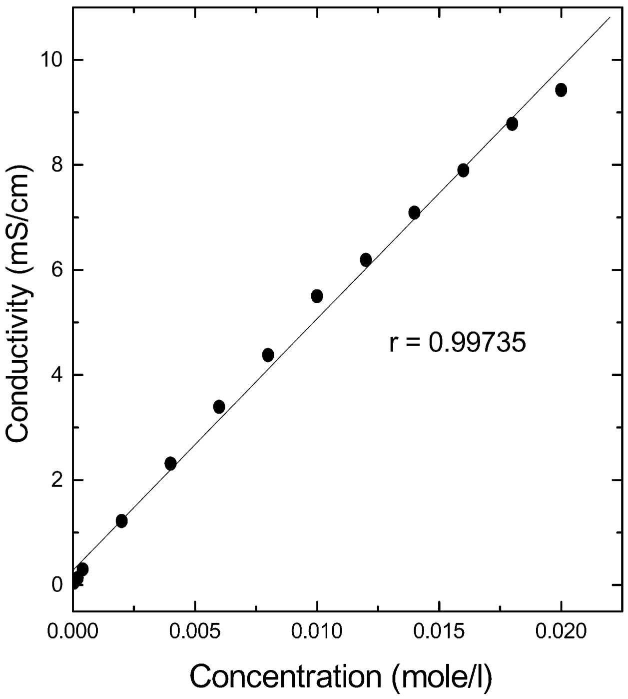

Fig. 1. Conductivity–concentration calibration curve.

3. Formulation of the problem

Several methods have been applied for evaluating the pozzolans [9–11,14,24–28]. These contemplate chemical, physical and mechanical viewpoints and yield qualitative and quantitative evaluations. They are based, in most cases, on the analysis of the pozzolanic reaction in CH/pozzolan systems. Since neither the mechanism nor the kinetics of the pozzolanic reactions are well understood at present, disparity of opinions about how to evaluate the properties of a pozzolan arises. The pozzolanic reaction is heterogeneous. This can be considered about solid–solution type:

$$A_{(L)} + bB_{(S)} \rightarrow E_{(L)} + F_{(S)} \qquad (1)$$

Several models [29] have been proposed for describing reaction (1). In the present paper, we use the Decreasing Nucleus Model (DNM). In accordance with this model, when solution A (with a given concentration C_b) reacts on the surface of the solid reactant B (initially with radius r_s), a layer of reaction products F is formed around the nucleus of reactant B that has not reacted (nucleus without reacting, with radius r_c) which decreases gradually. If layer F is porous, the reaction takes place by diffusion of A through the layer F until it is verified on the interface between F and the nucleus without reacting. The temperature is considered uniform in all the heterogeneous region.

$E_{(L)}$ in Eq. (1) accounts for fluid products of the solid–solution type reaction that could be formed.

The following assumptions are made:

- The spherical form of the granule is kept and the densities of F and B are the same. Consequently, the total radius of the granule r_s (considering the reaction product layer and the nucleus without reacting) does not change with time and an intermediate region does not exist between the nucleus and the layer of product [30].
- The movement rate of the reaction interface dr_c/dt is small in comparison to the diffusion speed of A through the product layer (pseudo-stable state) [31]. This is valid when the density of the fluid in the pores of F is smaller than the density of the solid reactant, which is certain in general.

In Fig. 2, we show a scheme of the concentration profiles according to DNM.

In the case of the pozzolan/lime solution system, the reaction occurs through the following stages [32]:

- Diffusion of the Ca^{2+} ions from the solution to the surface of the pozzolan particle.
- Adsorption of the Ca^{2+} ions on the surface of the pozzolan particle.
- Diffusion of the Ca^{2+} ions through the layer of reaction product.
- Chemical reaction between the Ca^{2+} ions and the pozzolan particle.

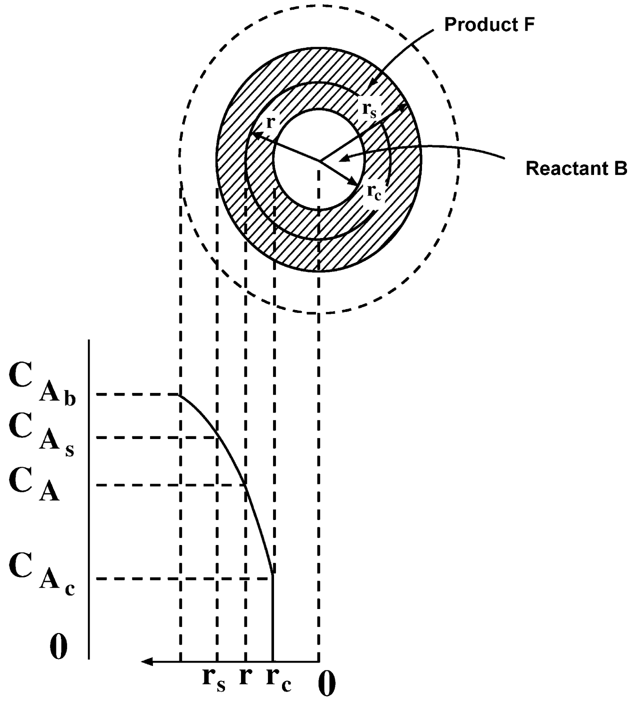

Fig. 2. Scheme showing concentration variations according to DNM.

Under pseudo-stable state conditions, the speed equations, expressed as mole of solution A (CH solution) that disappears per unit of time per particle, are identical:

$$\frac{dN_A}{dt} = 4\pi r_s^2 K_m[(C_A)_b - (C_A)_S] \quad \text{external diffusion} \tag{2}$$

$$\frac{dN_A}{dt} = 4\pi r_s^2 D_e \left[\frac{dC_A}{dr}\right]_{r=r_C} \quad \text{diffusion through the product} \tag{3}$$

$$\frac{dN_A}{dt} = 4\pi r_c^2 K(C_A)_C \quad \text{reaction on the interface } r = r_c \tag{4}$$

In Eq. (4), a first-order irreversible chemical reaction is assumed.

If we handle Eqs. (2), (3) and (4), we obtain the one that relates the decreasing of the nucleus in terms of the exterior concentration of CH with time.

$$-\frac{dr_c}{dt} = \frac{bM_B K(C_A)_b}{\rho_B[1 + (r_c^2/r_s^2)(K/K_m) + (Kr_c/D_e)(1 - (r_c/r_s))]} \tag{5}$$

where K_m is the external mass transfer coefficient, D_e is the effective diffusion coefficient of A through of the porous layer of product F and K is the reaction rate constant.

Since the functional dependence of r_c with time is not known, it is difficult to apply Eq. (5) directly to the experimental results, that are the variation of $(C_A)_b$ (CH concentration) with t. For that reason, it is necessary to consider a behavior that allows us to relate the external concentration $(C_A)_b$ to time.

According to the small particle size and the morphology of the product layer F [2], the decrease of the nucleus to react should follow a similar behavior to the change of the concentration (or conductivity) in the outer solution (Fig. 3). This change shows a fast decrease at early ages and an asymptotic behavior for long times. In accordance to the abovementioned, this behavior of r_c with t is adjusted to a dependence of the type:

$$r_c = r_s \exp(-nt)$$

where n is related to the diminishing speed of the nucleus.

Therefore, Eq. (5) is:

$$nr_s \exp(-nt) = \frac{C_t K(4/3)\pi r_s^3}{\left[1 + \left(\frac{(r_s \exp(-nt))^2}{r_s^2}\right)\left(\frac{K}{K_m}\right) + \left(\frac{Kr_s \exp(-nt)}{D_e}\right)\left(1 - \frac{r_s \exp(-nt)}{r_s}\right)\right]} \tag{6}$$

where $bM_B/\rho_B = V = 4/3\pi r^3$ is the volume of the particle and $(C_A)_b = C_t$.

Since the displacement time of the ions in the solution is much smaller than the necessary time for the diffusion and reaction inside the particle, we can consider the external

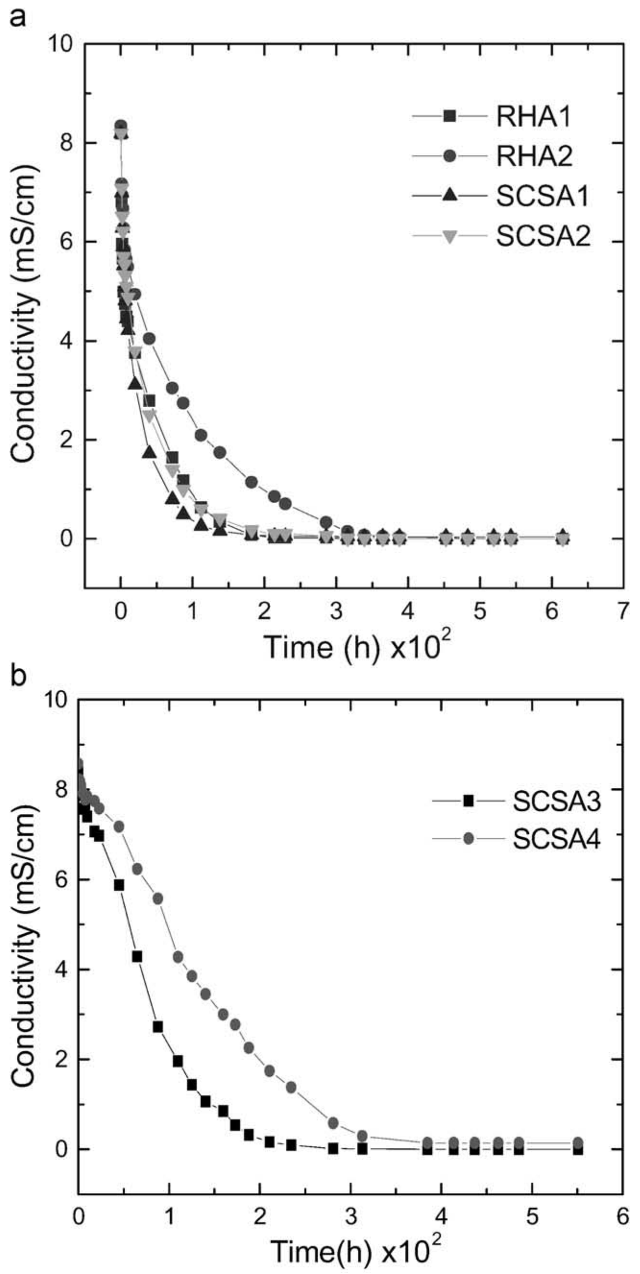

Fig. 3. (a) Variation of conductivity with time for samples burned at 800 °C. (b) Variation of conductivity with time for samples burned at 1000 °C.

mass transfer coefficient as very large and Eq. (6) is reduced to:

$$C_t = \frac{1.59153\exp(-3nt)[-1+\exp(nt)]n}{D_\mathrm{e}} + \frac{10.61032\exp(-nt)n}{K} \tag{7}$$

where $r_\mathrm{s} = 0.15$ mm.

Eq. (7) represents a kinetic–diffusive model. This expresses the variation of CH concentration with time. The lineal relationship between the CH concentration and conductivity allows their direct correlation.

As was previously expressed, the pozzolanic reaction develops by stages. It is known that the resistances of these stages are usually very different and that the stage presenting a bigger resistance (i.e., that lapses more slowly) controls the process. According to this, it is possible in certain cases to have a diffusive (described by the first term of Eq. (7)), kinetic (second term) or kinetic–diffusive (both terms) behavior. The fitting of the model (Eq. (7)) allows us to determine the kinetics coefficients (diffusion coefficient and reaction rate constant) and, therefore, a rigorous characterization of the process.

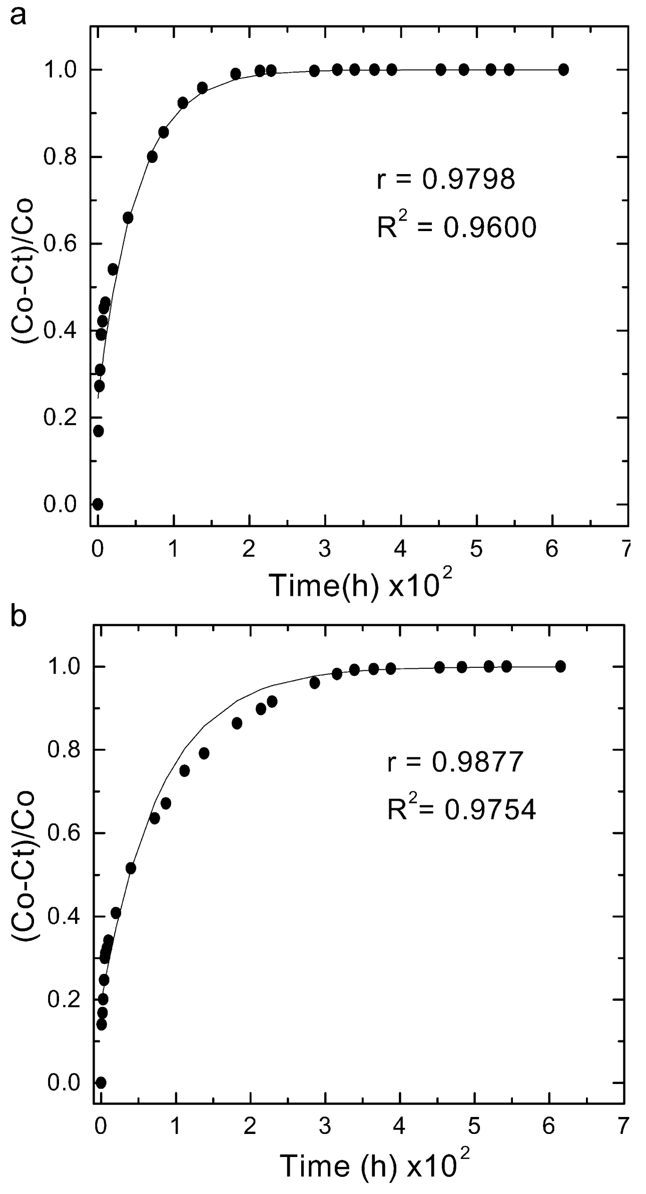

Fig. 4. (a) Relative loss in conductivity for RHA1 burned at 800 °C. ● Experimental, — Model. (b) Relative loss in conductivity for RHA2 burned at 800 °C. ● Experimental, — Model.

4. Results and discussion

In Fig. 3a and b, the conductivity variations versus time for the pozzolans/CH suspensions are shown. A decrease of the electrical conductivity of the suspension is appreciated. This behavior is attributed to the formation of insoluble products with the corresponding decrease of the CH concentration in the solution. As result of this, conductivity decreases.

A considerable variation (loss) of conductivity in early ages is appreciated. The stabilization of the curve (to very close to zero values) is reached for long times and it depends on the analyzed sample. This indicates the moment when the reaction has finished practically.

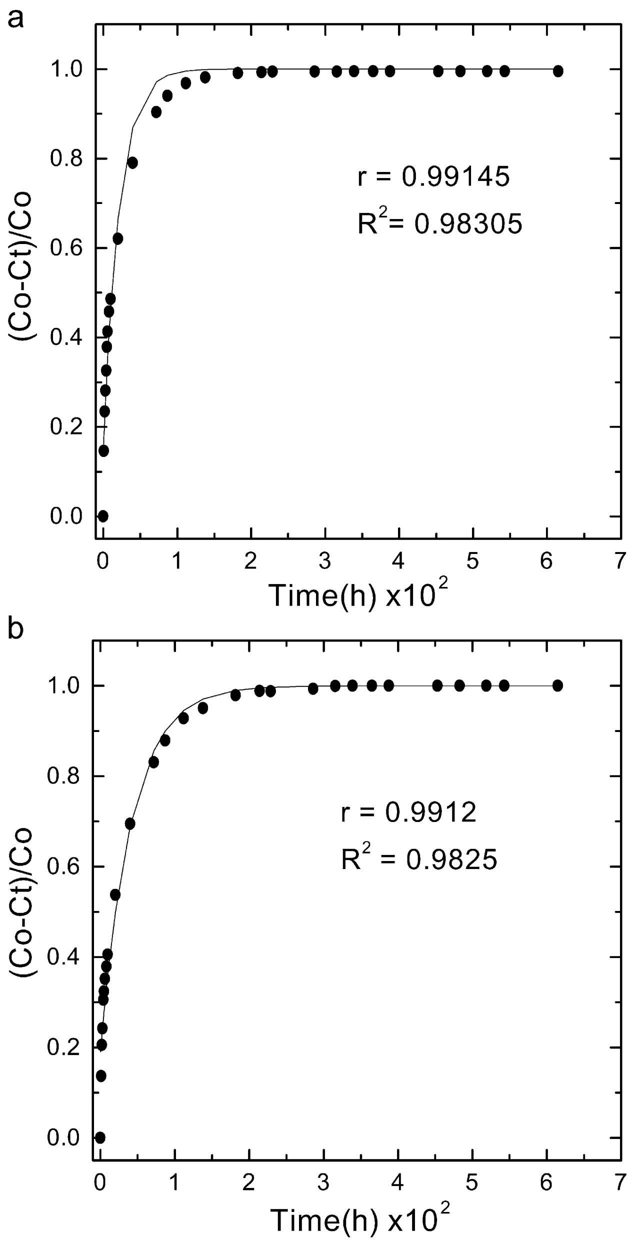

Fig. 5. (a) Relative loss in conductivity for SCSA1 burned at 800 °C. ● Experimental, — Model. (b) Relative loss in conductivity for SCSA2 burned at 800 °C. ● Experimental, — Model.

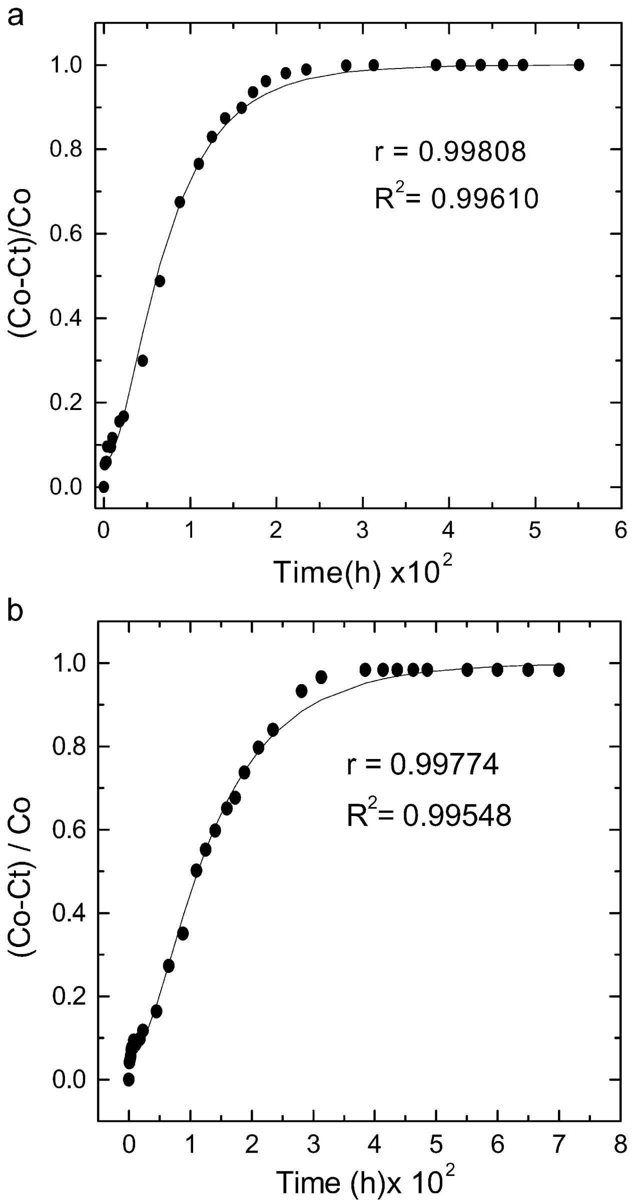

Fig. 6. (a) Relative loss in conductivity for SCSA3 burned at 1000 °C. ● Experimental, — Model. (b) Relative loss in conductivity for SCSA4 burned at 1000 °C. ● Experimental, — Model.

For pozzolanic samples calcined at 800 °C, a greater reactivity is qualitatively appreciated for SCS1 followed by SCS2, RHA1 and RHA2, respectively. For 1000 °C, SCS3 is more reactive than SCS4.

For comparing data, it is convenient to calculate the loss as relative according to the following equation:

$$\xi = \frac{C_0 - C_t}{C_0} \tag{8}$$

where ξ is the relative loss of conductivity, C_0 the initial conductivity and C_t the absolute loss of conductivity with time for pozzolan/lime suspension.

Table 4
Reaction rate constants and n parameter for pozzolans calcined at 800 °C

Material (ash)	n	Reaction rate constant K (h^{-1})
RHA1	$1.95 \times 10^{-2} \pm 0.21 \times 10^{-2}$	$3.34 \times 10^{-2} \pm 0.39 \times 10^{-2}$
RHA2	$1.25 \times 10^{-2} \pm 0.10 \times 10^{-2}$	$1.98 \times 10^{-2} \pm 0.15 \times 10^{-2}$
SCSA1	$4.72 \times 10^{-2} \pm 0.45 \times 10^{-2}$	$7.12 \times 10^{-2} \pm 0.52 \times 10^{-2}$
SCSA2	$2.40 \times 10^{-2} \pm 0.22 \times 10^{-2}$	$3.84 \times 10^{-2} \pm 0.32 \times 10^{-2}$

The use of Eq. (8) allows us to correlate concentration and conductivity taking into account their linear dependence. It also lets us work with a dimensionless magnitude.

According to Eq. (8), Eq. (7) is transformed into:

$$\xi = 1 - \left(\frac{1.59153}{C_0} \frac{\exp(-3nt)[-1+\exp(nt)]n}{D_e} + \frac{10.61032}{C_0} \frac{\exp(-nt)n}{K} \right) \quad (9)$$

Shown in Figs. 4a and b, 5a and b, 6a and b are the relative loss of conductivity ξ versus time for the CH/pozzolans samples calcined at 800 and 1000 °C. Solid lines represent the curves of the fitted model. The fitting of the model (Eq. (9)) permitted us to determine the parameters n, D_e and/or K in each case.

In the case of the samples calcined at 800 °C, a kinetic behavior was appreciated. For this statement was took into account the accuracy in the fitting of the model and statistical parameters such as: correlation coefficient (r), coefficient of multiple determination (R^2), 95% confidence intervals, residual scatter, residual probability and variance analysis. This means that the chemical interaction speed on the surface of the nucleus without reacting is smaller than the diffusion speed of the reactant through the reaction product layer. As a result of this, the general speed of the whole process is determined by the lowest stage (chemical reaction). The values of the n parameter and the reaction rate constant K are given in Table 4. In the figures, the correlation coefficient r is shown.

According to these results, the SCS1 sample shows the highest reactivity (bigger K) followed by SCS2, RHA1 and RHA2. These results agree with the qualitative analysis carried out previously. The K value directly reflects the reactivity of the pozzolan and is a direct index of the pozzolanic activity.

In the case of samples calcined at 1000 °C, a kinetic–diffusive behavior is accepted taking into account the same previous considerations. This means that the chemical reaction speed and diffusion speed are comparable under these conditions. Therefore, both processes determine the general speed of the whole process. The values of n, diffusion coefficient (D_e) and the reaction rate constant (K) are shown in Table 5.

According to these results, the highest reactivity was shown by SCS3 followed by SCS4.

It is appreciated (qualitative and quantitatively) that the SCS ashes diminish their reactivity as the calcination temperature increases. This may be due to the loss of reactivity of SCS silica, due to calcination at a higher temperature that increases the crystallinity of the silica produced [2,19,33,34].

According to the kinetic coefficients K obtained, the SCSA calcined at 800 °C shows a high reactivity, even above RHA considered of good pozzolanic qualities, guaranteed in numerous works.

These results coincide with the results of the experimental tests [2] (X-ray diffraction [XRD], thermogravimetry [TG], mercury intrusion porosimetry [MIP] and scanning electronic microscopy [SEM]) for the pozzolanic characterization of this material.

These experimental tests proved that the ashes based on sugar cane straw are pozzolans with high reactivity that fulfills the principal requirements for pozzolanic materials, which is comparable to ash based on RH.

5. Conclusions

1. The conductometric changes allow the characterization of SCSA as a material with good pozzolanic activity comparable to that of RHA based on the determination of kinetic parameters.
2. The kinetic–diffusive model proposed here allows describing the pozzolanic reaction kinetics in CH/(SCS + clay, RH + clay) systems by previously determining the kinetics coefficient (diffusion coefficients and reaction rate constants). The reaction rate constants give a very exact index of the reactivity or pozzolanic activity of the materials analyzed.
3. The ashes obtained starting from burning the SFB show both high reactivity and good pozzolanic qualities. Besides, they may constitute an alternative source of energy in countries lacking energy reserves that possess high volume of wastes due to their agricultural economy.
4. This method can be used for determining the pozzolanic activity in a direct, economical and rigorous way.

Table 5
Reaction rate constants, diffusion coefficients and n parameter for SCSA pozzolans calcined at 1000 °C

Material (ash)	n	Diffusion coefficient D (mm^2/h)	Reaction rate constant K (h^{-1})
SCSA3	$1.43 \times 10^{-2} \pm 0.04 \times 10^{-2}$	$2.48 \times 10^{-3} \pm 0.22 \times 10^{-3}$	$1.94 \times 10^{-2} \pm 0.07 \times 10^{-2}$
SCSA4	$7.95 \times 10^{-3} \pm 0.22 \times 10^{-3}$	$1.39 \times 10^{-3} \pm 0.12 \times 10^{-3}$	$1.03 \times 10^{-2} \pm 0.03 \times 10^{-2}$

Acknowledgements

The authors wish to thank to Dr. José Fernando Martirena its collaboration and to Dr. Israel Quiroz for reading the manuscript.

References

[1] H.F.W. Taylor, Cement Chemistry, Academic Press, London, 1993.

[2] J.F. Martirena, B. Middendorf, H. Budelman, Use of wastes of the sugar industry as pozzolan in lime–pozzolan binders: Study of the reaction, Cem. Concr. Res. 28 (1998) 1525–1536.

[3] V. Kind, V.F. Zhuralev, Electrical conductivity of setting Portland cements, Tsement 5 (1937) 21–26.

[4] N. Petin, E. Gajsinivitch, A study of the setting process of cement paste by electrical conductivity methods, J. Gen. Chem. USSR 2 (1932) 614–629.

[5] W.B. Boast, A conductimetric analysis of Portland cement pastes and mortars and some of its applications, J. Am. Concr. Inst. 33 (1936) 131–146.

[6] E. Hammond, T.D. Robson, Comparison of the electrical properties of various cements and concrete, Engineer 21 (1955) 78–80.

[7] F. Tamas, Electrical conductivity of cement paste, Cem. Concr. Res. 12 (1982) 115–120.

[8] M.G. Abd-el-Wahed, I.M. Helmy, H. El-Didamony, D. Ebied, Effect of admixtures on the electrical behaviour of Portland cement, J. Mater. Sci. Lett. 12 (1993) 40–42.

[9] W.J. McCarter, H.C. Ezirim, Monitoring the early hydration of pozzolan–$Ca(OH)_2$ mixtures using electrical methods, Adv. Cem. Res. 10 (1998) 161–168.

[10] E. Rassk, M.C. Bhaskar, Pozzolanic activity of pulverized fuel ash, Cem. Concr. Res. 5 (1975) 363–376.

[11] M.P. Luxán, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural products by conductivity measurement, Cem. Concr. Res. 19 (1989) 63–68.

[12] S. Sugita, M. Shoya, H. Tokuda, Evaluation of pozzolanic activity of rice husk ash, Proceedings of the 4th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, vol. 1, Amer. Concr. Inst., Detroit, USA, 1992, pp. 495–512, ACI SP-132.

[13] S. Sugita, Q. Yu, M. Shoya, Y. Tsukinaga, Y. Isojima, in: H. Jutnes, A.B. Amrkai (Eds.), Proceedings of the 10th International Congress on the Chemistry of Cement, vol. 3, 1997, Gothenborg, 3ii 109.

[14] C. Tashiro, K. Ikeda, Y. Inoue, Evaluation of pozzolanic activity by the electric resistance method, Cem.Concr. Res. 24 (1994) 1133–1139.

[15] J. Payá, M.V. Borrachero, J. Monzó, E. Peris-Mora, F. Amahjour, Enhanced conductivity measurement techniques for evaluation of fly ash pozzolanic activity, Cem. Concr. Res. 31 (2001) 41–49.

[16] W. Jander, Reaktionen im festen Zustande bei hohoren Temperaturem, Z. Anorg. Allg. Chem. 163 (1–2) (1927) 1–30.

[17] A. Bezjak, V. Alujevic, A kinetic study of hydrothermal reactions in C_2S–quartz system: I. Determination of rate constants for processes with two acceleration periods, Cem. Concr. Res. 11, (1981) 19–27.

[18] V. Alujevic, A. Bezjak, A kinetic study of hydrothermal reactions in C_2S–quartz system: II. Influence of granulometry of quartz and the treatment of samples, Cem. Concr. Res. 13 (1983) 34–40.

[19] P.R. Khangaonkar, A. Rahmat, K.G. Jolly, Kinetic study of the hydrothermal reaction between lime and rice-husk-ash silica, Cem. Concr. Res. 22 (1992) 577–588.

[20] C. Shi, R. Day, Pozzolanic reaction in the presence of chemical activator: Part I. Reaction kinetics, Cem. Concr. Res. 30 (2000) 51–58.

[21] R. Kondo, K. Lee, M. Diamon, Kinetics and mechanism of hydrothermal reaction in lime–quartz–water systems, J. Ceram. Soc. (Japan) 84 (1976) 573–578.

[22] N. Hill, Energy and cementitious materials: a burning problem? Basin News, 6 July (1993).

[23] N.C. Norma, 054-148: 1978 "Suelos, ensayos de compactación proctor estándar y modificado".

[24] W.T. Moreau, J.L. Gliland, Summary of methods for determining pozzolanic activity, Material in Mortars and Concretes, ASTM Spec. Tech. Publ. (1950).

[25] R. Talero, Qualitative analysis of natural pozzolans, fly ashes and blast furnace slags by XRD, J. Mater. Civ. Eng. 2 (1990) 106–115.

[26] R.C. Sharma, N.K. Jaim, S.N. Ghosh, Semitheoretical method for the assessment of reactivity of fly ashes, Cem. Concr. Res. 23 (1993) 41–45.

[27] M.I. Sánchez, M. Frias, The pozzolanic activity of different materials, its influence on the hydration heat in mortars, Cem. Concr. Res. 26 (1996) 203–213.

[28] J. Cabrera, M. Frías, Mechanism of hydration of the metakaolin–lime–water system, Cem. Concr. Res. 31 (2001) 177–182.

[29] J.M. Smith (Ed.), Engineering of Chemical Kinetics, Continental, Mexico, 1991, in Spanish.

[30] S. Yagi, D. Kunii, Chem. Eng. (Japan) 19 (1955) 500.

[31] K.B. Bishoff, Chem. Eng. Sci. 18 (1963) 711.

[32] A.C. Rabilero, PhD Thesis, University of Oriente, Cuba, 1996, in Spanish.

[33] A.A. Boateng, D.A. Skeete, Incineration of Rice Hull for use a cementitious material: The Guyana experience, Cem. Concr. Res. 20 (1990) 795–802.

[34] S.K. Malhotra, N.G. Dave, Investigations into the effect of addition of fly ash and burnt clay pozzolana on certain engineering properties of cement composites, Cem. Concr. Compos. 21 (1999) 285–291.