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The effect that different pozzolanic activity methods has on the kinetic constants of the pozzolanic reaction in sugar cane straw-clay ash/lime systems: Application of a kinetic–diffusive model

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Abstract

The reaction kinetics of a mixture of sugar cane straw with 20% and 30% of clay burned at 800 and 1000 °C and lime (calcium hydroxide) is studied. A direct method (accelerated chemical method) based on the measurement of the amount of lime reacted as the reaction proceeds is applied. A kinetic–diffusive model published in a previous paper by some authors of this research is used. The fitting of the model by computerized methods allows determining the kinetic coefficients that characterize the process: in particular, the reaction rate constant. The index of pozzolanic activity evaluated according to the obtained values of the reaction rate constant permits to characterize the pozzolanic activity of these materials in a rigorous way. The results are compared with the results obtained applying an indirect method (conductometric method). The kinetic results obtained in the current paper allow affirming that the kinetic–diffuse model used in order to evaluate the pozzolanic reaction is valid, independently of the method used for the evaluation of the pozzolanic activity.

Keywords: Pozzolans; Kinetics; Pozzolanic reactions; Diffusion

1. Introduction

It is known that the incessant generation of solid waste materials represents a serious problem. For that reason it is very important to study and develop any technology, procedure or method that may help to exploit them efficiently.

At present, pozzolanic materials are, in most cases, industrial by-products and solid wastes that can be used as active additions to Portland cement. This is due to their capacity for reacting with calcium hydroxide (CH), produced during the hydration of the Portland cement. It is well known that the hydrated compounds formed during the pozzolanic reaction improve the performance of new cements elaborated with them [1,2].

The incorporating of agricultural wastes once calcined at high temperatures, as pozzolans of high activity; such as rice husk ash, have been studied with positive results in the manufacture of mixed cement [3]. These ashes are characterized by its very low density and very high volume. This fact can have negative aspects when they are transported and stored.

In Cuba, important amounts of sugar cane are processed which generate high volumes of solid waste. These wastes are deposed and burnt in open landfills, thus having a negative impact on the environment. Recent studies [4] have shown that sugar industry solid wastes such as sugar cane straw ash (SCSA) has pozzolanic activity derived from its high content of amorphous silica.

In recent years [5], the possibility of mixing this solid waste of sugar cane with clay has been evaluated by getting an agglutinative material which permits an easy handling as well as an improvement in the environmental aspects. Martirena et. al. [6] have been the first in to conceive and develop the idea of

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this solid fluel block (SFB), starting from the waste of the sugar industry. According to this research, waste biomass becomes an attractive alternative for renewable fuel and the integral concepts like the Solid Fuel Block enable interconnected and more efficient systems using appropriate technologies. For the above-mentioned it is important to evaluate the pozzolanic activity of these materials.

The evaluation of the pozzolanic activity of materials has been the focus of numerous works, obtaining different working methods. In general, these methods are classed as indirect or direct, depending on the parameter to study [7–12]. So, Greenberg [7] describes a method based on the use of a conductometric technique to indirectly monitor the depletion of lime by measuring the electrical conductivity of the solution as the reaction proceeds. Rassk and Bhaskar [8] designed 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 in which the active material is dispersed. Recently Payá et al. [9] proposed a methodology for evaluating the activity of fly ash. They calculated the pozzolanic activity as the percentage of loss in conductivity at several reaction times (100, 1000 and 10 000 s).

On the other hand, direct methods have been used. They are based on the measurement of the amount of lime reacted [10,11]. Among these methods, it is also important to note an accelerated chemical method which has been used by some authors in recent years. Sánchez de Rojas et al. [12] used this method for studying the influence of the microsilica state on pozzolanic reaction rate. They confirm in this study the direct relationship between pozzolanic activity of materials (expressed as fixed lime) and the heat of hydration.

Frías et. al. [13] have used accelerated tests to study the pozzolanic reaction in a metakaolin–lime–water system and they proposed a rapid method for determining lime concentration by thermogravimetry and differential thermal analysis of a mixture of lime and metakaolin.

In most of the previous methods, the evaluation of the pozzolanic activity is aimed at the qualitative aspect of the behavior of the pozzolanic materials rather than at the quantitative aspect of the lime/pozzolan reaction (the latter being the computation of the kinetic coefficients).

At present, the researches are focusing on the knowledge of the kinetic coefficients as a good criterion for evaluating the pozzolanic activity of the materials. Precisely, with this purpose, several traditionally mathematical models have been applied to the pozzolanic reaction in last years. So, Khangaonkar et al. [14] proposed a mathematical model for the kinetic study of the hydrothermal reaction between lime and rice husk ash silica. This model involves mechanism of nucleation and growth, phase boundary interaction and diffusion. An equation for each mechanism is proposed. The application of the model was satisfactory only for early ages of the reaction.

Subsequently, Frías et al [15–16] applied the kinetic model of Jander to describe the mechanism of reaction in metakaolin–lime systems at different curing temperatures.

Recently Villar-Cociña et al. [17] proposed a new kinetic–diffusive model that allows characterizing the pozzolanic activity of sugar cane straw+clay ashes (SCSCA) through kinetic constants in the two reaction periods. The results obtained showed a good correlation between the experimental and theoretical data.

In the bibliography, different methods to determine the pozzolanic activity (direct and indirect methods) can be found, as was mentioned above. For this reason, the modeling of a pozzolanic reaction can be influenced by the method used to calculate the experimental data of pozzolanic activity of materials. There is a total absence of investigations in this specific area.

The present research shows the results of an experimental study on the influence of calcining temperature (800 and 1000 °C) as well as clay content (20% and 30%) in the pozzolanic activity of SCSCA–lime systems. The kinetic–diffusive model fitted by computerized methods makes it possible to determine the reaction rate constants and the pozzolanic activity of these materials in a rigorous way. The results are compared with the data obtained by applying an indirect method (conductometric method).

2. Experimental

2.1. Materials

The materials studied in current paper were sugar cane straw-clay ashes (SCSCA) coming from sugar cane straw mixes with 20% and 30% of clay, once calcined at 800 and 1000 °C of temperature. Table 1 shows the samples used in this paper and their designations. The chemical composition of these ashes showed high contents of silica and aluminum oxides above 70%, followed by iron, calcium and magnesium with percentages of about 15%. Further details are shown in Table 2. Fig. 1 shows the XRD patterns for the starting ashes. Albite and quartz were the main crystalline compounds detected in ashes. Minor compounds as calcite, iron oxide (Fe_30_4) and calcium oxide ($Ca0_2$) are also present. The ashes were ground in order to get particle sizes below 90 μm.

2.2. Test methodologies

2.2.1. Pozzolanic activity

To carry out a qualitative or quantitative determination of pozzolanic activity many experimental methodologies

Table 1
Designations of the samples used

Samples/calcining temperature	Designations
SCSCA (20% clay)/800 °C	SCSCA1
SCSCA (30% clay)/800 °C	SCSCA2
SCSCA (20% clay)/1000 °C	SCSCA3
SCSCA (30% clay)/1000 °C	SCSCA4

Table 2
Chemical compositions for the starting ashes

Oxides (%)	SCSCA1	SCSCA2	SCSCA3	SCSCA4
SiO_2	64.02	62.62	66.96	65.30
Al_2O_3	11.29	13.79	12.72	13.80
Fe_2O_3	6.59	7.65	6.94	7.65
CaO	3.65	4.41	4.53	3.65
MgO	2.76	3.14	3.14	3.35
Na_2O	1.88	2.22	2.02	2.22
K_2O	2.35	1.91	1.91	1.84
TiO_2	0.67	0.76	0.71	0.76
LOI	4.88	3.30	0.82	0.55

have been developed. However, most of them are based on the measurement of the reaction of pozzolanic materials with the calcium hydroxide released during cement hydration.

In this work, as in other studies carried out by the authors, an accelerated method was used in order to study the pozzolanic activity of these materials. This method follows the material–lime reaction with time. The test consisted of putting the pozzolanic material (1 g) in contact with a saturated lime solution (75 ml) in individual double cap polyethylene flasks of 100 ml of capacity and kept in a oven at 40 ± 1 °C for 1, 7, 28 and 90 days (two flasks for period).

At the end of each period, the solution was filtered and the chemical determination of CaO in the remaining solution was quantified by using 20 ml of filtered solution and as chemical reagents for titration EDTA (0.0178 mol/L) and calcein. The fixed lime (mmol/L) was obtained by the difference between the concentration in the saturated lime solution and the CaO found in the solution in contact with the sample, at the end of a given period.

2.2.2. Mathematical model

A kinetic–diffusive model [17] is used to describe this pozzolanic reaction in a pozzolan/lime solution system. The model is:

$$\xi = 1 - \left(\frac{2.65259\ Exp(-3nt)[-1 + Exp(nt)]n}{CoD} + \frac{29.4732\ Exp(-nt)n}{CoK} \right) \tag{1}$$

where D is the effective diffusion coefficient, K is the reaction rate constant, Co is the initial concentration of the solution and n is a parameter related to the decreasing speed of the nucleus of pozzolan. The dimensionless magnitude $\xi = (\mathrm{Co} - \mathrm{Ct})/\mathrm{Co}$ represents the relative loss of lime concentration and Ct represents the absolute loss of lime concentration with time for pozzolan/lime system.

It is known that the pozzolanic reaction develops by stages. The resistances of these stages are usually very different and the stages presenting the greatest resistances (i.e. the stages that lapses more slowly) control the process. Accordingly, it is possible in certain cases to have different behavior: diffusive (described by the first term of Eq. (1)), kinetic (second term) and kinetic–diffusive (both terms). Further explanations about the model can be found in the reference cited.

3. Results and discussion

3.1. Pozzolanic activity

The results obtained for pozzolanic activity are shown in Fig. 2 in which the fixed lime content (mmol/L) versus reaction times (days) is represented. The figure clearly s-

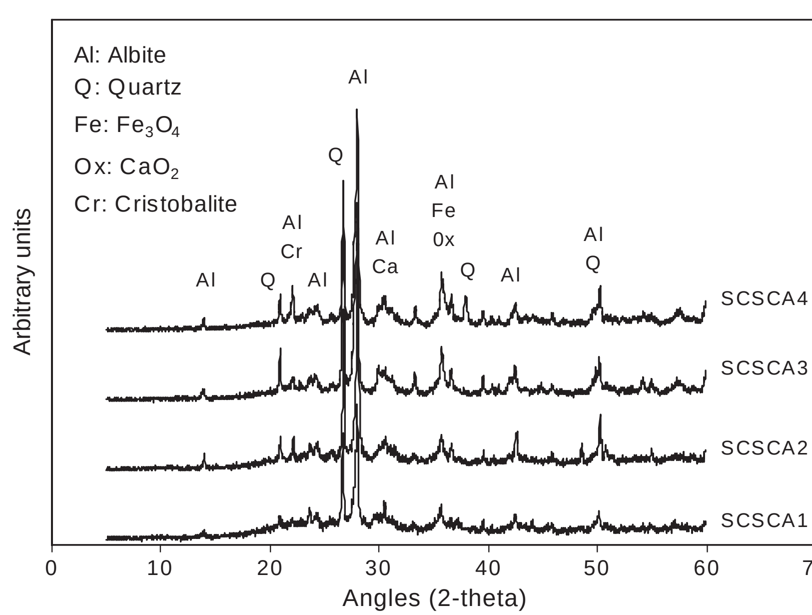

Fig. 1. XRD patterns for the starting ashes.

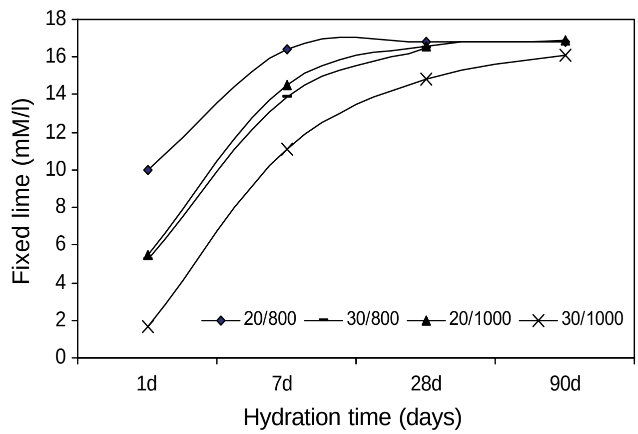

Fig. 2. Pozzolanic activity for calcined samples: fixed lime over time.

hows the pozzolanic behavior of different ashes with the time. After one day, the SCSCA1 shows a high pozzolanic activity, since the sample has fixed 57% of calcium ions (lime). This value is between that for silica fume and metakaolin and, it is higher than that of fly ash [13]. For the rest of the samples, the pozzolanic activity decreases with the increasing clay content as well as calcining temperature (SCSCA1 > SCSCA2 > SCSCA3 > SCSCA4). This same tendency is observed at 7 days of curing, but in this case the SCSCA1 consumed practically all the lime in solution (about 1 mmol/L remaining). With the increasing curing time, the values of fixed lime were very similar for all samples (90 days).

The pozzolanic activity of ashes decreased when the clay content and calcining temperature increased. This fact could be related to the re-crystallization of amorphous silica with increasing calcination temperature [18,19]. Calcined ashes did not show any mineralogical change with calcining temperature, only minor variations in peak intensities were detected. So, for the samples calcined at 1000 °C, an increase in count number of quartz peaks was observed (see Fig. 1 peak at 22.1, 2-theta). Studies in this area are being carried out by the same authors of the current work in order to research various aspects of the pozzolanic reaction of these pozzolans.

From these data of pozzolanic activity, it is important to highlight that all samples showed pozzolanic activity but with different reaction rates. This fact can be an important aspect from the point of view of its recycling as active additions in cements. This range of possibilities has practical applications in the manufacture of SCSCA-blended cements with different properties, such as: high performance cements at early terms, cement with lower hydration heat, etc.

3.2. Application of the mathematical model: determination of the reaction rate constant

The application of the kinetic model was only applied to the SCSCA1 since this sample showed the highest pozzolanic activity. To increase the accuracy in the fitting process of the model 7 experimental points of pozzolanic activity were considered (0 and 2 h, 1, 3, 7, 28 and 90 days).

Fig. 3 illustrates the relative loss of lime concentration versus time for the CH/SCSCA1 system. The solid line represents the curve of the fitted model. Fitting the relative loss of lime concentration versus time successively to the kinetic control model, diffusive control model and a mixed (kinetic–diffusive) control model and carrying out an exhaustive analysis of the important statistical parameters such as correlation coefficient (r), coefficient of multiple determination (R^2), 95% confidence intervals, residual scatter, residual probability and variance analysis (which constitutes a rigorous evaluation of the fitting process of the model to the experimental data), it can be concluded that kinetic control model shows the best correspondence with the experimental data.

This means that the chemical interaction speed on the surface of the nucleus of the pozzolan particle is slower than the diffusion speed of the reactant through the reaction product layer formed around the nucleus. This might be due to high porosity of the reaction product layer in these ashes, which facilitates a quick diffusion process. These findings are in agreement with results published previously [4], which indicated a high porosity for the sugar cane straw ash in pozzolan/CH systems. The study of these materials is recent and very little information is available [4,5].

In the current paper, some statistical parameters are only shown (r, R^2, SE, RSS) since the rest of them (mentioned above) are related to graphic analysis and large tables that would imply a too much large paper.

The values of the n parameter and the reaction rate constant K are given in Table 3. In the figure, the correlation and multiple determination coefficients r and R^2 are shown.

The K values reflect directly the reactivity of the pozzolan and it is a direct index of the pozzolanic activity of this

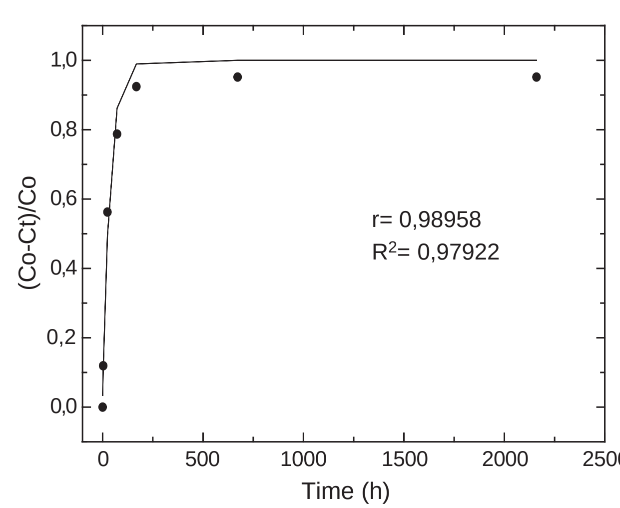

Fig. 3. Relative loss of lime concentration for SCSCA1 burned at 800 °C. ●Experimental ________ Model.

Table 3
Kinetic coefficients and statistical parameters for SCSCA1, obtained through the fitting process of the model to the experimental data, resulting from applying both pozzolanic activity methods

Material (Ash)	Pozzolanic activity method	Kinetic coefficients		Standard Error (SE)	Correlation coefficient (r)	Coefficient of multiple determination (R^2)	Residual sum of squares (RSS)
SCSCA1	Conductimetric method	K	$7.12 \cdot 10^{-2} \pm$	$0.52 \cdot 10^{-2}$	0.99145	0.98305	0.05216
		n	$4.72 \cdot 10^{-2} \pm$	$0.45 \cdot 10^{-2}$			
	Accelerated chemical method	K	$5.25 \cdot 10^{-2} \pm$	$0.48 \cdot 10^{-2}$	0.98958	0.97922	0.02085
		n	$2.95 \cdot 10^{-2} \pm$	$0.26 \cdot 10^{-2}$			

material. The SCSCA1 shows a high pozzolanic activity of order of 10^{-2} h^{-1}.

3.3. Comparative study between methods to evaluate the pozzolanic activity

In order to know the influence that the analytical method used to evaluate the pozzolanic activity of a material, a comparative study of the kinetic parameters between accelerated chemical method and conductometric method was made.

In a previous work [17] these samples were characterized by using a conductometric method. The CH concentration was correlated with the conductivity of the CH solution. In this case a greater reactivity was qualitatively appreciated for SCSCA1 followed by SCSCA2. The samples SCSCA3 and SCSCA4 calcined at 1000 °C showed less reactivity. These findings are totally in agreement with the pozzolanic activity data obtained from accelerated chemical method.

Fig. 4 illustrates the relative loss of conductivity with time for SCSCA1. The solid line represents the curve of the fitted model. In this case a kinetic behavior was accepted taking into account the same consideration expressed previously.

The kinetic parameters were determined in the fitting process of the model (Eq. (1)). According to the value of the kinetic coefficient K, the SCSCA1 shows a high reactivity of the order of 10^{-2} h^{-1}.

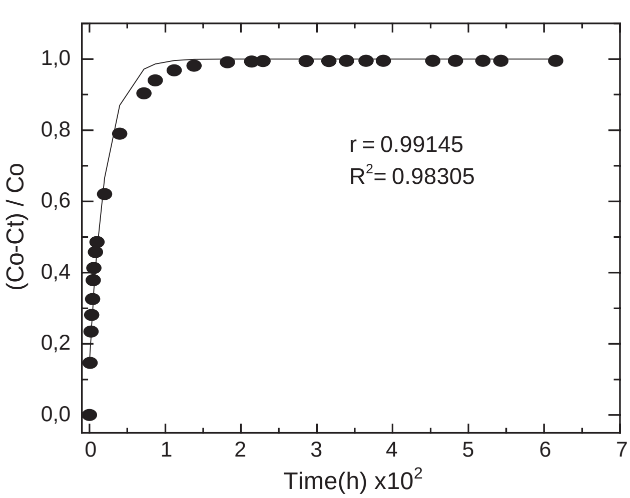

Fig. 4. Relative loss of conductivity for SCSCA1.
● Experimental ________ Model.

Table 3 shows the kinetic coefficients and statistical parameters obtained through the fitting process of the kinetic–diffusive model (with kinetic control) to the experimental results from both pozzolanic activity methods.

Comparing the results obtained by both, the accelerated chemical method and conductometric method for the evaluation of the pozzolanic activity it is possible to state that: the ashes show a high pozzolanic activity. In both methods, a rapid variation (loss) of lime concentration in early ages is appreciated. Thereafter, the variation of lime concentration becomes slow until the stabilization of the experimental curve is reached for long times in dependence of the analyzed sample.

The values of the reaction rate constant, that characterize the pozzolanic activity of the material, are very similar (order of 10^{-2}) in both cases. The statistical parameters show a good correspondence between the model and the experimental data in both cases.

From the results obtained in the current work, it is possible to affirm that the model used for describing the pozzolanic reaction kinetics and for calculating the kinetic coefficients is satisfactory, independently of the method used for the evaluation of the pozzolanic activity. This fact is a very important aspect to take into account when making a modeling of the pozzolanic reaction.

4. Conclusions

From results obtained in this paper, the following conclusions can be raised:

1. All calcined samples present a very high pozzolanic activity, but the fixation rate of lime (pozzolanic reaction) varied in function of calcining temperature and clay content.
2. The ashes of SCSCA with 20% of calcined clay and 800 °C of calcining temperature show the best conditions of activation; since at 1 day of curing, the ash had fixed the 56% of available lime.
3. The values of the reaction rate constant, obtained in the fitting process of the model by using both methods, show a high reactivity for this material (order of 10^{-2}). This gives a direct index of the pozzolanic activity of the material and it allows the pozzolanic characterization of the material in a direct and rigorous way.

4. The results obtained allow us to affirm that the kinetic–diffuse model used for describing the pozzolanic reaction kinetics in SCSCA/lime system by previously determining the kinetic coefficients is satisfactory, independently of the method used for the evaluation of the pozzolanic activity.
5. The availability of ashes with different pozzolanic reaction rates (in relation to calcining temperature and clay content) can become an important technological advantage in the manufacture of new blended cements elaborated with this calcined material; in which, the selection of one ash or another as active pozzolan will depend on the characteristics of the building site.

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