

IC-NOCMAT 2007 Maceió
*International Conference on Non-Conventional Materials and Technologies:
Ecological Materials and Technologies for Sustainable Building
Maceió, Alagoas, Brazil, 14th-17th October 2007
In Honour of Professor R.N.Swamy*

**SUGAR CANE BAGASSE-CLAY ASH AS POZZOLANIC
MATERIAL: STUDY OF THE REACTION KINETICS
AND DETERMINATION OF THE KINETIC
PARAMETERS.**

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ABSTRACT

The paper presents a study of the pozzolanic reaction kinetics between calcium hydroxide (CH) and a mixture of sugar cane bagasse with 20 and 30% of clay, burned at 800 and 1000⁰C (SCBCA) by electrical conductivity measurements. A kinetic-diffusive model carried out by the authors of this research is used. The model was fitted to the experimental data by computerized methods, which allowed the computation of the kinetic parameters of the pozzolanic reaction (reaction rate constant and free energy of activation) that rigorously characterize the pozzolanic activity of the materials. The results show that SCBCA present reactivity and good pozzolanic qualities in the range 800-1000⁰C.

Keywords: solid wastes, pozzolan, kinetics, pozzolanic reaction, and conductivity

1. Introduction.

Pozzolanic materials have been used widely in the manufacture of Portland cement in many applications because of their advantageous properties of the new cementitious matrixes which include a cost reduction, a reduction in hydration heat evolution, a lower permeability, a denser microstructure, a higher durability, chemical resistance etc [1-3].

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 [4, 5].

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 [6]. 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 deposited and burnt in open landfills, thus having a negative impact on the environment. Recent studies [7, 8] have shown that sugar industry solid wastes such as sugar cane straw ash (SCSA) and sugar cane bagasse ash have pozzolanic activity derived from its high content of amorphous silica.

In recent year [9], 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.

At present the researchers are focussing on the knowledge of the kinetic coefficients as a good and rigorous criterion for evaluating the pozzolanic activity of the materials. Precisely, with this propose, several traditionally mathematical models have been applied to the pozzolanic reaction in last years. So, Kangaonkar et. al. [10] 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 74-283, 2003.

Subsequently, PRasRethna [11], JGKedKinetic study of the Jander [12] to describe the mechanism of reaction in metakaolin – lime systems at different curing temperatures.

Kondo et. al. [14] modified the Jander equation to depend on the mechanism (reaction or diffusion) that controls the reaction process. They study the reaction kinetics in a lime–quartz–water system.

Brouwers et. al. [15] proposed a shrinking core model for analyzing the pozzolanic reactivity of flay ash. This model considers the pozzolanic particle composed by two regions (outer hull and inner region). The thermodynamics properties of the flay ashes were derived.

Recently, Villar-Cociña et. al. [16, 17] proposed a new kinetic-diffusive model that allows characterizing the pozzolanic activity of sugar cane straw mixed with clay for all ages of the reaction by computing the kinetic coefficients (reaction rate constant, fundamentally) of the CH/ sugar cane straw-clay ash reaction. The results obtained showed a good correlation between the experimental and theoretical data.

In the present work, the kinetic-diffusive model published by the authors in previous papers is applied. The fitting of the model allows the computing of the kinetic and

thermodynamics parameters (reaction rate constant, diffusion coefficient and free energy of activation) for the pozzolanic reaction in sugar cane bagasse-clay ash/lime systems. This allows us the characterization of the pozzolanic activity of these wastes in a rigorous way.

2. Experimental

2.1 Materials

Sugar cane bagasse-clay ashes (SCBCA) from the combustion of Cuban sugar cane bagasse were obtained in an electric furnace at different temperatures of calcinations: 800 and 1000°C during 20 min. Then the ashes were cooled at room temperature. Table 1 show 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. Ashes were screened and a particle size of 0.15mm was fixed.

Table 1. Designations of the samples used

Samples/Calcining Temperature	Designations
SCBCA (20% clay)/800°C	SCBCA1
SCBCA (30% clay)/800°C	SCBCA2
SCBCA (20% clay)/1000°C	SCBCA3
SCBCA (30% clay)/1000°C	SCBCA4

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

Table 2. Chemical compositions for the starting ashes

Oxides (%)	SCBCA1	SCBCA2	SCBCA3	SCBCA4
SiO_2	60.70	61.46	63.86	62.66
Al_2O_3	14.35	14.70	14.35	15.67
Fe_2O_3	8.60	8.48	8.36	8.33
CaO	3.27	3.02	3.53	3.40
MgO	3.54	3.02	3.54	3.68
Na_2O	2.31	2.41	2.17	2.51
K_2O	1.40	1.40	1.58	1.36
TiO_2	0.83	0.85	0.83	0.87
LOI	3.88	3.85	0.72	0.76

2.2 Test methodologies.

* Pozzolanic activity

To carry out a qualitative or quantitative determination of pozzolanic activity many experimental methodologies have been developed.

In this work, as in other studies carried out by the authors, a conductometric method was used in order to study the pozzolanic activity of these materials.

This method follows the conductivity of the pozzolan-calcium hydroxide solution with reaction time.

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, 2,10g for each ash were weighed and then 70ml of CH solution and 70ml 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 $28^\circ\text{C} \pm 1^\circ\text{C}$ 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).

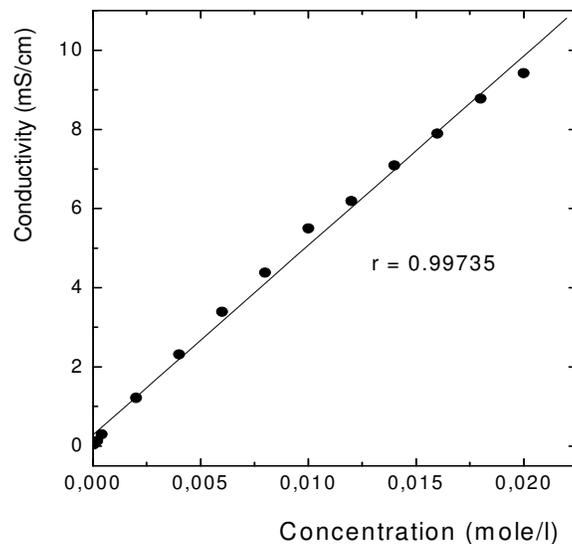
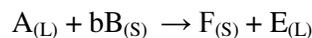


Figure 1. Conductivity-concentration calibration curve.

* Mathematical model

It is known that the pozzolanic reaction in CH/pozzolan systems is heterogeneous and it can be considered about solid-solution type:



When solution A reacts on the surface of the solid reactant B (with stoichiometry coefficient b) a layer of reaction products F is formed around the nucleus of reactant B that has not reacted (nucleus without reacting) which decreases gradually. If the layer F is porous the reaction take place by diffusion of A through the layer F until it is verified on the interface between F and the nucleus without reacting. $E_{(L)}$ accounts for the fluid products of the solid – solution type reaction that could be formed.

The form of the rate equation is determined by the control regime or the rate-limiting step which can be one of the following two, principally [18, 19]: (1) diffusion through the

layer of reaction product (diffusive control), (2) chemical reaction at the surface on the unreacted nucleus (kinetic control).

Villar-Cociña *et. al.* [16, 17] proposed a kinetic-diffusive model for describing the pozzolanic reaction in sugar cane straw-clay ash/CH systems:

The model is:

$$\xi = \frac{C_0 - C_t}{C_0} = 1 - \frac{0.23 \cdot \text{Exp}\left(\frac{-3t}{\tau}\right) \cdot \left(-1 + \text{Exp}\left(\frac{t}{\tau}\right)\right) \cdot \frac{1}{\tau}}{C_o D_e r_s} + \frac{0.23 \cdot \text{Exp}\left(\frac{-t}{\tau}\right) \cdot \frac{1}{\tau}}{C_o K r_s^2} \quad (1)$$

where D_e is the effective diffusion coefficient, K is the reaction rate constant, C_o is the initial concentration of the solution and τ is a constant of time (time interval in which the radius of the nucleus of pozzolan diminish to 37% of its initial radius (r_s)). The initial radius r_s of the pozzolan particles was taken as 0.15 mm.

The magnitude ξ is the relative loss of conductivity, C_o the initial conductivity and C_t the absolute loss of conductivity with time for pozzolan/lime suspension. This magnitude allows us to correlate concentration and conductivity taking into account their linear dependence. It also let us work with a dimensionless magnitude.

As the pozzolanic reaction develops by stages, it is possible that the rate-limiting stage corresponds with the diffusion through the layer of reacting product or with the chemical reaction at the surface on the unreacted nucleus.

For that reason, it is possible in certain cases to have different behavior: Diffusive (described by the 2nd term of Eq.(1)), kinetic (3rd term) and kinetic-diffusive (both term). Further explanations about the model can be found in Villar-Cociña *et. al.* [16, 17].

3. Results and discussion

3.1 Pozzolanic activity

In figures 2a and 2b 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.

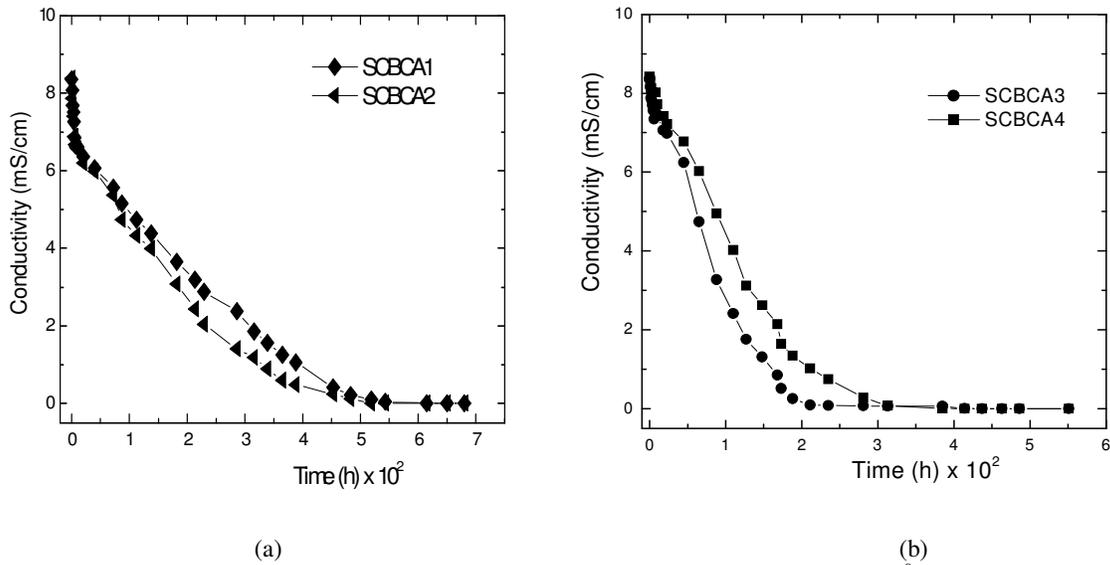


Figure 2. Relative loss in conductivity for: a) SCBCA1 and SCBCA2 burned at 800⁰C, b) SCBCA3 and SCBCA4 burned at 1000⁰C

• Experimental _____ Model

For pozzolanic samples calcined at 800 ⁰C a greater reactivity is qualitatively appreciated for SCBCA2 followed by SCBCA1. For 1000 ⁰C, SCBCA3 is more reactive than SCBCA4.

3.2 Application of the mathematical model: determination of the reaction rate constant and the free energy of activation

The kinetic-diffusive model (Eq. 1) was applied for all samples. Figures 3a, 3b, 4a and 4b illustrate the relative loss of lime concentration versus reaction time for the SCBCA/CH system. The solid line represents the curve of the fitted model.

The model was fitted to the relative loss of conductivity-time data, considering a kinetic control model, diffusive control model and a mixed (kinetic-diffusive) control model successively.

An exhaustive analysis of the most important statistical parameters such as: correlation coefficient (r), coefficient of multiple determination (R²), residual sum of squares (RSS), 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), allows us to conclude that: In the case of the samples calcined at 800⁰C, a the kinetic control regime predominates showing 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 agreement with results published previously [20, 21], which indicated a high porosity and slow reactivity for the sugar cane bagasse ash (calcined at 800⁰C) in pozzolan/CH systems.

For the case of the samples calcined at 1000⁰C, a kinetic-diffusive regime is accepted taking into account the same previous considerations. This means that the chemical reaction speed are comparable under these conditions. Therefore, both determine the general speed of the whole process.

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

The values of the parameters (τ , D , K and ΔG^\ddagger .) so obtained are given in Table 3 and 4, while the correlation and multiple determination coefficients r and R^2 are shown in Figs 3 and 4.

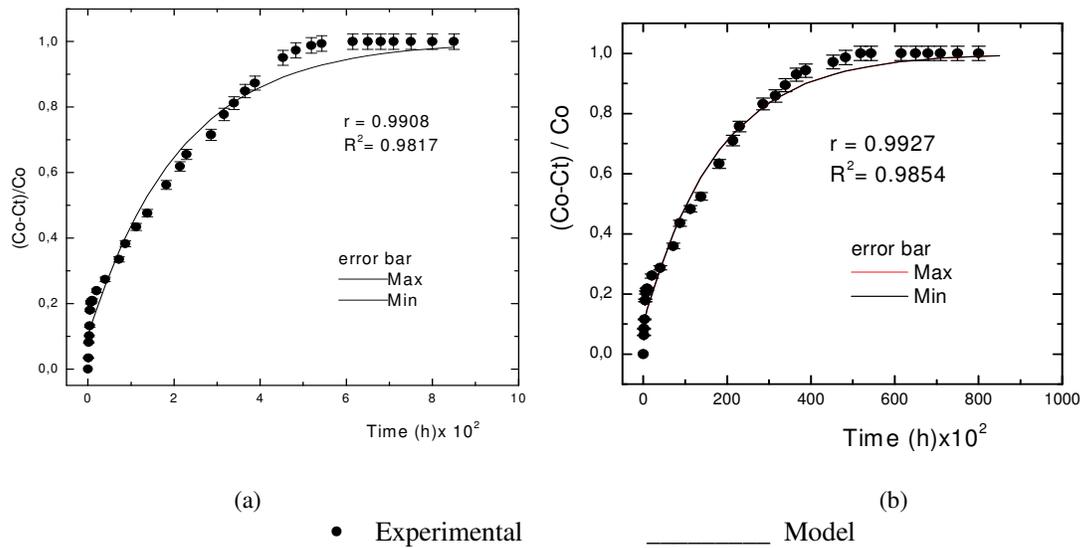


Figure 3. Relative loss of conductivity versus reaction time: a) SCBCA1, b) SCBCA2, calcined at 800⁰C.

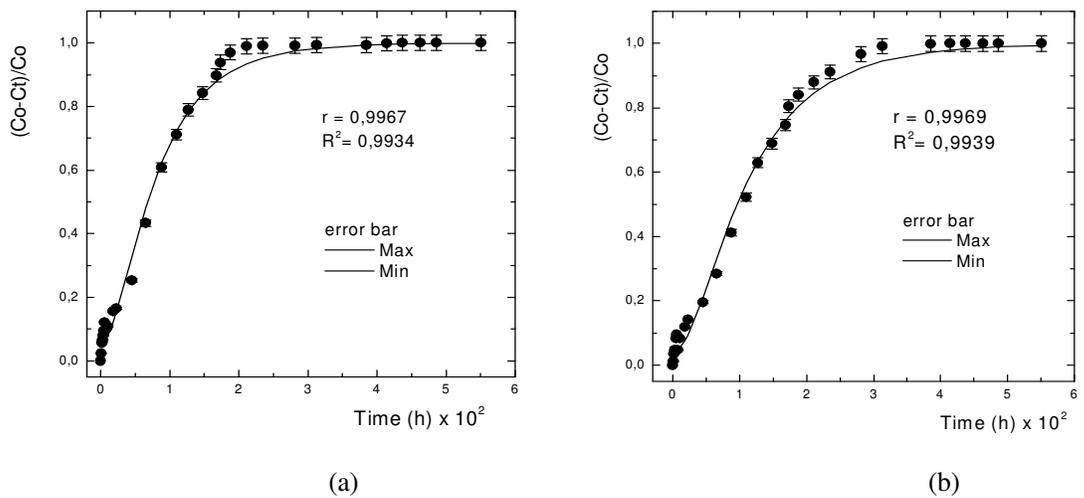


Figure 4. Relative loss of conductivity versus reaction time: a) SCBCA1, b) SCBCA2, calcined at 1000⁰C.

• Experimental _____ Model

One of the most important parameter that characterizes the reactivity of the materials is the thermodynamic parameter of activation called free energy of activation. This parameter can be calculated by using the Eyring equation of “The absolute theory of rate processes” [22].

The Eyring equation is given by:

$$K = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\#}{R T}\right) \quad (2)$$

Where: k_B is the Boltzman constant, h the Planck constant and R the constant of the gases.

T is the temperature and K the reaction rate constant

$\Delta G^\#$ is the free energy of activation, which characterize the change of free energy of the system when passing from the initial state to the transition state

It is well-known that big values of $\Delta G^\#$ are correlated with stability kinetics, i.e. low reactivity (small values of K). On the other hand, small values of $\Delta G^\#$ are correlated with instability kinetics, i.e. high reactivity (big values of K). The knowledge of $\Delta G^\#$ allows us to characterize how fast the reaction occurs, to big $\Delta G^\#$ values the reaction will be more slowly and vice versa.

The study about the free energy of activation in pozzolanic reactions is very scarce. In the bibliography only have been reported values of free energy of activation for some specific systems [15, 19, 23].

For the SCBA-lime system in the international bibliography not have been reported values of activation parameters of the pozzolanic reaction.

In this research, the free energies of activation were calculated by substituting Eq. (2) in the model (Eq.1). The resultant equation was fitted to the experimental data (relative loss of conductivity versus reaction time) and the values of $\Delta G^\#$ were determined. The values of $\Delta G^\#$ so obtained are given in Table 3 and 4.

The K and $\Delta G^\#$ values provide a direct index of the pozzolanic activity of the materials.

Table 3 - Reaction rate constants, τ parameter, free energy of activation and statistical parameters for SCBCA calcined at 800°C.

Material (Ash)	τ (h)	Reaction rate constant (h^{-1})	Free energy of activation $\Delta G^\#$, kJ/mol	Correlation coefficient (r)	Coefficient of multiple determination (R^2)	Residual sum of squares
SCBCA1	214.6 ± 10.5	(6.60 ± 0.29). 10 ⁻³	106.84 ± 0.11	0.9909	0.9819	0.0789
SCBCA2	177.1 ± 8.4	(8.04 ± 0.34). 10 ⁻³	106.31 ± 0.10	0.9928	0.9957	0.0616

Table 4 - Reaction rate constants, τ parameter, diffusion coefficients, free energy of activation and statistical parameters for SCBCA calcined at 1000°C.

Material (Ash)	τ (h)	Diffusion coefficient (mm^2/h)	Reaction rate constant (h^{-1})	Free energy of activation $\Delta G^\#$, kJ/mol	Correlation coefficient (r)	Coefficient of multiple determination (R^2)	Residual sum of squares
SCBCA3	77.7 ± 3.1	(2.26 ± 0.37). 10 ⁻³	(1.75 ± 0.08). 10 ⁻²	104.35 ± 0.11	0.9967	0.9934	0.0333
SCBCA4	108.1 ± 3.6	(1.55 ± 0.22). 10 ⁻³	(1.23 ± 0.04). 10 ⁻²	105.23 ± 0.09	0.9969	0.9938	0.0295

According with the values of the reaction rate constant (K), the SCBCA3 shows the highest reactivity (bigger K) followed by SCBCA4, SCBCA2 and SCBCA1. These results agree with the qualitative analysis carried out previously in section 3.1.

Similarly, the values of $\Delta G^\#$ reflects the same tendency for the pozzolanic activity of the ashes, i.e. the SCBCA3 shows the highest reactivity (smaller $\Delta G^\#$) followed by SCBCA4, SCBCA2 and SCBCA1.

It is appreciated (qualitatively and quantitatively) that the ashes increase their reactivity as the calcination temperature increases. The SCBCA calcined at 1000⁰C has a higher reactivity (order of 10⁻² h⁻¹) in comparison with the SCBCA2 calcined at 800⁰C (order of 10⁻³ h⁻¹). However, all ashes show a high pozzolanic reactivity (in the order of 10⁻² – 10⁻³ h⁻¹).

Future studies include the analysis of the influence of calcining temperature on the pozzolanic activity of these ashes.

3. Conclusions

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

1. The conductometric changes allow the characterization of SCBCA as a material with good pozzolanic activity based on the determination of kinetic parameters.
2. The kinetic-diffusive model used here allows describing the pozzolanic reaction kinetics in CH/SCBCA system by previously determining the kinetics coefficient (diffusion coefficients, reaction rate constants and free energy of activation). The reaction rate constants jointly with the free energy of activation give a very exact index of the reactivity or pozzolanic activity of the materials analyzed.
3. Sugar cane bagasse-clay ashes can be used as active additions once calcined in the temperature range of 800⁰C-1000⁰C.
4. The sugar cane bagasse with 20 and 30% of clay can become pozzolanicly active in the range 800⁰C-1000⁰C. However, its activation rate was found to vary substantially (order of 10⁻² h⁻¹ for calcining temperature of 1000⁰C and order of 10⁻³ h⁻¹ for 800⁰C).
5. The availability of ashes with different pozzolanic reaction rates can become an important technological advantage in the manufacture of new blended cements elaborated with the calcined materials: 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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