CHARACTERIZATION OF THE POZZOLANIC ACTIVITY OF VARIOUS AGROINDUSTRIAL WASTES: KINETIC PARAMETERS

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In this research work a quantitative characterization of various materials (sugar cane waste ashes, bamboo leaf ash, calcined paper sludge, loessic soils, zeolite and fly ash) as pozzolanic materials based on the computing of the kinetic parameters of the pozzolanic reaction in pozzolan/calcium hydroxide systems is offered. The paper presents a synthetic overview of the more relevant results in the quantitative characterization of the pozzolanic reaction (computing of the kinetic parameters) of different materials carried out by the authors, Other experimental techniques, such as X-ray diffraction (XRD) and scanning electron microscope (SEM), were also employed.

Two pozzolanic activity tests (conductometric method and accelerated chemical method) are employed. A kinetic-diffusive model (published by the authors in previous works) is used to describe the pozzolanic reaction. The kinetic parameters that characterize the process (in particular, the reaction rate constant and free energy of activation) are determined with relative accuracy in the fitting process of the model. The pozzolanic activity is quantitatively evaluated according to the values obtained of the kinetic parameters. This allows the comparison in a direct way of the pozzolanic reactivity of the materials, which is very useful for the employment of these materials. The values of the reaction rate constant jointly with the free energy of activation give a precise index of the reactivity or pozzolanic activity of the materials.

According to the values calculated of the reaction rate constant K, bamboo leaf ash shows the highest reactivity $(8.41 \times 10^{-1} \text{ h}^{-1})$ followed by fly ash $(1.76 \times 10^{-1} \text{ h}^{-1})$, sugar straw ash $(8.11 \times 10^{-3} \text{ h}^{-1})$, sugar cane bagasse ash $(1.91 \times 10^{-2} \text{ h}^{-1})$, loessic soil $(1.23 \times 10^{-3} \text{ h}^{-1})$, calcined paper sludge $(8.69 \times 10^{-3} \text{ h}^{-1})$ and Zeolite $(6.88 \times 10^{-3} \text{ h}^{-1})$.

Keywords:
pozzolanic activity
kinetic parameters
materials characterization

1. Introduction

Nowadays, some industrial by-products and wastes are attracting much research because of their high silica and/or alumina content for the use as additions in commercial Portland cement. It is well-known that hydrated phases formed during pozzolanic reaction commonly improve the performance of concrete [1, 2].

The reuse of waste materials for concrete production is a worldwide practice. It is known that the incessant generation of solid waste materials represents serious environmental and technical problems. Also, the assessment of the pozzolanic activity of cement replacement materials is becoming increasingly important because of the need for more sustainable cementing products. The majority of the wastes are disposed in landfills having an adverse effect on the environment, creating air pollution due to small dust. Using waste ashes as pozzolanic materials to replace cement...
can reduce the consumption of cement and reduce landfill are requirements. This in turn helps solve environment problems caused by cement production, decreasing both energy used and CO₂ emissions.

In recent years, the use of agro-industrial solid wastes and zeolitic minerals as pozzolans in the manufacture of blended mortars and concrete has been the focus of new researches [3-8]. In the most of these researches, the methods for evaluating pozzolanic activity of the materials are focused on the qualitative aspect of the behavior of the pozzolanic materials rather than the quantitative aspect of lime- pozzolan reaction, with the latter regarding computation of kinetic parameters. The investigation of the kinetics of pozzolanic reactions is an important experimental task that gives characteristic constants for the reaction rate. Using them, one can evaluate the effectiveness of applying different type of pozzolanic materials as additives to mortars and concretes, as well as to compare their properties.

At present, researchers are beginning to focus on known kinetic coefficient as an acceptable and rigorous criterion for evaluating the pozzolanic activity of the materials. With this precise purpose, several traditional mathematical models have been applied to the pozzolanic reaction [9-15] which describe with more or less accurately the experimental results. Recently Villar-Cocina et. al. [16-18] proposed a kinetic-diffusive model that allows characterizing the pozzolanic activity of sugarcane wastes for all ages of the reaction. The results obtained showed a good correlation between the experimental and theoretical data.

The present paper shows the characterization of various pozzolanic materials (sugar cane bagasse ash (SCBA), sugar cane straw ash (SCSA) bamboo leaf ash (BLA), calcined paper sludge (CPS), loessic soils (LS), zeolite and fly ash (FA) based on the computing of the kinetic parameters of the pozzolanic reaction by applying the kinetic-diffusive model reported by the authors in previous papers. This allowed the pozzolanic activity of these materials to be characterized in a rigorous way through the computing of the kinetic parameters, which also gives the possibility of comparing in a direct way the pozzolanic behavior of the materials. The above is very useful for the selection of one material or another preferred pozzolan, which will depend on the characteristics needed for the building site. Also, in the elaboration of ternary cements, of great importance in the actuality due to the present word-wide economic crisis, it is very important the knowledge of the kinetic parameters as a fundamental tool for quantifying the reactivities of the pozzolanic materials that will be added to the cement.

2. Materials and Methods

2.1 Materials

The materials analyzed involve both artificial (thermally activated waste) and natural pozzolans. For the selection of the calcining temperature employed for the activation of the materials was taken into account the best results (high reactivity), obtained in previous research works of the authors [18-21]

Sugar cane wastes

The pozzolanic ashes were two types of biomasses. The sugar cane straw (SCS) and sugar cane bagasse (SCB) were recollected in the vicinity of the sugar factory “J. P. Carbó” in Villaclara, Cuba. Sugar cane straw ash (SCSA) and sugar cane bagasse ash (SCBA) were obtained in an electric furnace at 800ºC calcining temperature for 20-minute duration. Once calcined, the ashes were ground and sieved to <90 µm, finesses similar to Portland cement. More information about the influence of calcining temperature on the reactivity of these materials can be found in reference [18, 19].

Bamboo leaf ash

The bamboo leaves were recollected in the vicinity of the Faculty of Animal Science and Food Engineering of the Sao Paulo University, Pirassununga, Brazil. The bamboo leaf ashes were obtained in a laboratory electric furnace at 600ºC calcining temperature for 2h of retention. Once
Calcined, the ashes were ground and sieved below 90 µm.

**Calcined paper sludge**
The paper waste used in this study was newsprint paper sludge with a high clay component from a newsprint paper company in Madrid, Spain, which uses exclusively recycled paper as raw material. The paper sludge was dried and it was burnt in an electrical laboratory furnace at 600°C during 2h. The activated product was cooled at room temperature and ground and sieved to below 90 µm. More information about the influence of calcining temperature on the activation of this material can be found in Frías et al. [20].

**Loessic soil**
A typical stratigraphical column of Pampean Loessic sediments, located at center of Cordoba Province, Argentina, was sampled. Diverse layers of loess were identified. In this paper only the intermediate layer was chosen, 5.50m thick, with sandy layers and cemented layers of loess. More information about the different layers can be found in Quintana and Villar-Cociña [22].

**Zeolite**
A natural zeolitic rock from Tasajeras deposits situated in province of Villaclara, Cuba was used. The zeolite was ground and sieved to below 90 µm, with grain size average of 84.8 µm. More information about the influence of grain size on the pozzolanic activity can be found in Rosell-Lam et. al [23].

**Fly Ash**
The fly ash utilized in this work was originated in the burning process of mineral coal-fired thermoelectrical plant, located in Capivari de Baxio, Santa Catarina, Brazil. Such ash is produced in an electrostatic precipitator and corresponds to about 80 wt% of the total ashes generated for this station. The ashes have a fine granulometry below 90 µm with average grain size of 49.7µm. Table 1 show the samples designations and the activation conditions

**Lime**
The lime used in the pozzolan/calcium hydroxide system was an analytical grade calcium hydroxide (95% of minimum purity, 4.8% of maximum magnesium and alkaline salts content, and 0.5% of maximum insoluble substance content).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Designations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar cane straw ash (calcined at 800°C)</td>
<td>SCSA</td>
</tr>
<tr>
<td>Sugar cane bagasse ash (calcined at 800°C)</td>
<td>SCBA</td>
</tr>
<tr>
<td>Bamboo leaf ash (calcined at 600°C)</td>
<td>BLA</td>
</tr>
<tr>
<td>Calcined Paper sludge (calcined at 600°C)</td>
<td>CPS</td>
</tr>
<tr>
<td>Fly ash (uncontrolled temperature)</td>
<td>FA</td>
</tr>
<tr>
<td>Loessic soil (natural pozzolan)</td>
<td>LS</td>
</tr>
<tr>
<td>Zeolite (natural pozzolan)</td>
<td>Zeolite</td>
</tr>
</tbody>
</table>

**2.2 Test methodologies**

**2.2.1 Pozzolanic activity methods**
To carry out a qualitative or quantitative determination of pozzolanic activity many experimental methodologies have been developed [24-26]. In this research, as in other studies carried out by the authors [18, 27-29] were applied two different pozzolanic activity methods. Both methods are based in the monitoring of the lime consumption with the reaction time and they can be used indistinctly. The computing of the kinetic parameters of the pozzolanic reaction by applying the kinetic-diffusive model that will be used in this research is independent of the method used for the evaluation of the pozzolanic activity as it was demonstrated in a previous paper [28].

a)-Conductometric method
This method follows the conductivity of the pozzolan – calcium hydroxide solution with reaction time.

A saturated solution of calcium hydroxide (CH), prepared with deionized water and Ca(OH)$_2$ was used. To obtain the solution, the Ca(OH)$_2$ in excess was mixed with deionized water and stirred for 2h, after which the solution was maintained at rest for 24 h. Thereafter, the solution was filtered and it was valued with hydrochloric acid (HCL).

For each 100 ml of saturated Ca(OH)$_2$ solution were mixed with 2.10 g of pozzolanic material (which is the proportion commonly found in the literature for similar experiments) and magnetically stirred. Immediately after the pozzolan was mixed with the CH solution, the conductivity measurements began.

The measurements of conductivity were made at 40 ± 1 ºC at different times. To correlate the CH concentration with the conductivity of the CH solution a calibration curve that demonstrates a linear dependence, was applied [16, 22, 27]

b)- Accelerated chemical method
This method also follows the pozzolanic-calcium hydroxide reaction over time. The test consisted of putting the pozzolanic material (1g) in contact with a saturated lime solution (75 mL) at 40 ± 1 ºC for 1, 7, 28 and 90 days. At the end of each period, CaO (quicklime) concentration in the solution was analyzed. The fixed calcium hydroxide (mmol/L) was obtained as the difference between the original concentration of a solution of saturated calcium hydroxide and the CaO found in the solution in contact with the sample, at the end of a given period [30].

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

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

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 yet reacted (unreacted nucleus within) which decreases gradually. If the 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. 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 [31, 32]: (1) diffusion through the layer of reaction product (diffusive control), (2) chemical reaction at the surface on the unreacted nucleus (kinetic control).

Villar-Cocía et. al. [16, 17] proposed a kinetic-diffusive model for describing the pozzolanic reaction in sugar cane straw-clay ash/CH systems. Thereafter, for the case of sugar cane straw ash/CH and sugar cane bagasse ash/Ch systems, a correction term ($C_{corr}$) was added to the model to account for the remainder concentration of CH that is not consumed in the reaction. In some systems the CH is not consumed totally. The corrected model is [18]:
\[
\xi = C_o - C_t = \frac{0.23 \cdot \text{Exp}\left(\frac{-3t}{\tau}\right) \left(-1 + \text{Exp}\left(\frac{t}{\tau}\right)\right) \cdot \frac{1}{\tau} + 0.23 \cdot \text{Exp}\left(-\frac{t}{\tau}\right) \frac{1}{\tau}}{C_o \cdot D_e \cdot r_s} - C_{corr}
\]

where \( D_e \) is the effective diffusion coefficient of A through the porous layer of product F, \( K \) is the reaction rate constant, \( C_0 \) is the initial concentration of the solution and \( \tau \) 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 radius \( r_s \) of the pozzolan particles was taken as the average size particle for each analyzed material. The dimensionless magnitude \( \xi = (C_0 - C_t)/C_0 \) represents the relative loss of lime concentration and \( C_t \) represents the absolute loss of lime concentration with time for the pozzolan/CH system.

As the pozzolanic reaction develops in 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 (2\textsuperscript{nd} and 3rd term). Further explanations about the model can be found in the references cited [16, 17].

The fitting of this model allows determining the kinetic parameters (effective diffusion coefficient and reaction rate constant) and, therefore, a rigorous characterization of the process.

### 3. Results and discussion

#### 3.1 Chemical and mineralogical characterization

The chemical compositions of the ashes were determined by an X-ray fluorescence (XRF) technique (Table 2).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SCSA (%)</th>
<th>SCBA</th>
<th>BLA</th>
<th>CPS</th>
<th>LS</th>
<th>zeolite</th>
<th>FA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>70.20</td>
<td>58.61</td>
<td>80.4</td>
<td>20.94</td>
<td>62.20</td>
<td>66.78</td>
<td>60.1</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>1.93</td>
<td>7.32</td>
<td>1.22</td>
<td>13.86</td>
<td>13.19</td>
<td>11.89</td>
<td>24.0</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>2.09</td>
<td>9.45</td>
<td>0.71</td>
<td>0.51</td>
<td>4.65</td>
<td>4.04</td>
<td>6.70</td>
</tr>
<tr>
<td>CaO</td>
<td>12.20</td>
<td>12.56</td>
<td>0.99</td>
<td>35.06</td>
<td>4.39</td>
<td>3.32</td>
<td>1.60</td>
</tr>
<tr>
<td>MgO</td>
<td>1.95</td>
<td>2.04</td>
<td>5.06</td>
<td>2.36</td>
<td>1.46</td>
<td>0.45</td>
<td>0.37</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>4.10</td>
<td>0.53</td>
<td>1.07</td>
<td>0.28</td>
<td>0.25</td>
<td>0.25</td>
<td>0.26</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>3.05</td>
<td>3.22</td>
<td>1.33</td>
<td>0.39</td>
<td>1.81</td>
<td>0.97</td>
<td>2.53</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>0.50</td>
<td>0.92</td>
<td>0.08</td>
<td>0.06</td>
<td>3.10</td>
<td>1.22</td>
<td>0.35</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.02</td>
<td>0.34</td>
<td>0.1</td>
<td>0.26</td>
<td>0.26</td>
<td>0.02</td>
<td>1.39</td>
</tr>
<tr>
<td>LOI</td>
<td>1.81</td>
<td>2.73</td>
<td>8.04</td>
<td>25.90</td>
<td>na</td>
<td>10.36</td>
<td>2.03</td>
</tr>
</tbody>
</table>

SCSA=sugar cane Straw ash; SCBA=sugar cane bagasse ash; BLA=bamboo leaf ash; PL=paper sludge; FA=flay ash; na=not applicable

The main oxide present in SCSA and SCBA ashes is SiO\(_2\), followed by CaO. Other oxides such as Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), K\(_2\)O and SO\(_3\) are present in smaller amounts. Figure 1a and 1b show the XRD patterns for the starting ashes. The SCSA samples show a very low crystallinity. A wide band is observed between 15 and 32 (2 theta), which implies the presence of vitreous matter. For SCBA, quartz is detected as the main crystalline compound.

For the case of BLA silica (SiO\(_2\)) is the major component in ash, following by CaO, K\(_2\)O, Al\(_2\)O\(_3\) and SO\(_3\) in concentrations of 5.1, 1.3, 1.2 and 1.1 respectively. Oxides as Fe\(_2\)O\(_3\), MgO, O\(_3\) and MnO show contents below 1% and the rest of oxides (Na\(_2\)O, ZnO) are present in percentages under 0.1%.

Figure 1c shows the XRD pattern for bamboo ash, a highly amorphous nature is observed, which
corresponds with the broad localized about 20-30° 2θ. The presence of crystalline minerals was not detected. The band form of this ash is similar to that showed by silica fume, a highly active addition used normally for high performance concrete manufacture [33].

![XRD patterns for the starting ashes](image1)

**Fig. 1** XRD patterns for the starting ashes, a)-SCSA, b)-SCBA, c)-BLA, d) – FA

For CPS the main oxides present in are silica (SiO₂) 20.94%, alumina (Al₂O₃) 13.86%, calcium oxide (CaO) 2.36%. The rest of the oxides were below 0.9%. The crystalline mineralogical phases present in this waste are calcite, kaolinite and other minerals such as talc and quartz [34].

For the case of LS the main oxides present in the samples were SiO₂ and Al₂O₃ (more than 75%). Other oxides as Fe₂O₃, CaO, SO₃, Na₂O and K₂O were minor components. The mineralogical analysis confirmed the presence of the glassy fraction, mainly acid volcanic glass, with a low refractive index in variable percentages (49-54%). The large amount of amorphous silica and the scarcity of carbonates confirm the pozzolanic reaction as the cause of the natural cementation.

In the case of the zeolita the main oxides present are SiO₂ (about 67%), followed of Al₂O₃ (about 12%). Other oxides such as Fe₂O₃, CaO, Na₂O and MgO are present in small amounts. The
crystalline mineralogical phases present in this material are heulandite-clinoptilolite as principal crystalline compounds, followed by mordenite. Plagioclase, calcite and quartz are present as minor compounds.

For FA the main oxides present in fly ash (Table 2) are: SiO$_2$ as the major component in ash following Al$_2$O$_3$, Fe$_2$O$_3$, CaO and TiO$_2$. The rest of the oxides were below 0.5%. The XRD pattern (Figure 1d) suggests the presence of mullite, quartz, hematite and kyanite. The halo observed between 15 and 30$^\circ$ (2 theta) implies the presence of vitreous matter.

3.2 Pozzolanic activity

The results obtained for pozzolanic activity are shown in Figures 2 and 3. In Figure 2 the conductivity variations versus time for the pozzolans/CH suspensions are shown for zeolite, LS, FA and BLA pozzolans; while Figure 3 shows the results of accelerated pozzolanic tests for CPS, CSCA and CSBA ones up to 90 days of reaction. It is necessary to highlight for the present study the not influence of the pozzolanic activity methods on the computing of the kinetic parameters [28].

![Fig. 2 Variation of conductivity with reaction time for zeolite, loessic soil (LS), fly ash (FA) and bamboo leaf ash (BLA)](image)

The conductometric test (Fig. 2) showed a decrease of the electrical conductivity of the suspensions. This behavior was attributed to the formation of hydrated phases with the corresponding decrease of the CH concentration in the solution, which leads to a decrease in conductivity.

A considerable variation (loss) of conductivity in early ages is obtained; the BLA shows the more rapid variation in early ages, followed by LS, FA and zeolite. The stabilization to the curve is rapidly reached for BLA (only 30 h are needed approximately), followed by LS. For the other materials, the stabilization to the curve is reached for long times. This indicates the moment when the reaction has finished practically.

According with the above-mentioned might be possible to conclude that a greater reactivity is qualitatively observed for BLA, followed by LS, FA and zeolite. However, another important factor that must be taken into account when an evaluation of the reactivity is carried out is the difference between the initial and final conductivities (stabilized electrical conductivity) in the different solutions pozzolan / CH (a major difference, the reactivity of the material will be higher [3]). This could be related with the amount consumed of calcium hydroxide, a great difference corresponds to a greater consume of CH in comparison with a minor difference.

For the case of the materials shown in Figure 2 is evident that FA consumes more CH than the LS. It is clear that qualitatively, is very difficult to have an accurate idea of the pozzolanic activity. For that reason an evaluation from the point of view quantitative of the pozzolanic reactivity that involves all this aspects and that allows the computation of the kinetic parameters is very important.
SEM observations were carried out after conductivity testing with the aim of corroborating the presence of hydrated phases (calcium silicate hydrate (C-S-H) fundamentally) in the samples. Figure 4 shows scanning electron microscope images of SCBA burned at 800°C after the reaction. The presence of C-S-H can be seen forming a reaction product layer around the pozzolanic particles. In Figure 5 (for BLA after conductivity testing) the SEM observation shows the formation of C-S-H gels, rough zones having a sponge-like morphology.

For the case of the zeolite (Figure 6), the morphology 7 days after the reaction with CH is shown. The morphology of calcium silicates forming on the surface of a zeolite grains is appreciated (zone 1). The variation of the Si/Al relation carried out by sounding shows the diminishing of this relation in the zone 1 in comparison with another zones typical of the zeolite (zones 2 and 3). The above shows the formation of reaction products during the pozzolanic reaction. The SEM images for fly ash sample (Figure 7) also shows the presence of C-S-H gels on the surface of the pozzolanic particles.

On the other hand, the results of accelerated pozzolanic tests for reaction times of up 90 days are shown in Figure 3. The absolute loss of lime concentration plotted against reaction time for the pozzolans/CH samples is shown.

![Figure 3](image)

**Fig. 3** Variation of lime concentration with reaction time for calcined paper sludge (CPS), sugar cane straw ash (SCSA) and sugar cane bagasse ash (SCBA)

A considerable loss of lime concentration in early ages is obtained for all samples (SCSA, SCBA and PL). The stabilization of the curve was reached after long period of time and it depends on the analyzed sample. A qualitative analyses show a greater reactivity for SCSA followed by SCBA and CPS. This fact could be related to the higher alumina content in CPS than for SCSA and CSBA respectively, forming also hexagonal plaques of calcium aluminates (C₄AH₁₃) as shown in Figure 8 [35].
Fig. 4 (a) SEM of a detail of SCBA sample burned at 800ºC and reacted with calcium hydroxide, showing the layer of reaction products around the nucleus of the pozzolan particle; (b) microanalysis of the zone A (nucleus without reacting); (c) microanalysis of the zone B (layer of reaction products)

Fig. 5 C-S-H gels morphology by SEM (sample of BLA)

Fig. 6 SEM picture of the zeolitic material 7 days after of the reaction with calcium hydroxide

Fig. 7 Micrograph showing the presence of C-S-H gels on the surface of the pozzolanic particles of FA

Fig. 8 SEM micrograph of hydrated calcium aluminate (C₄AH₁₃)
3.3 Application of the mathematical model. Determination of the kinetic parameters.
As above-mentioned, the knowledge of the kinetic parameters of the pozzolanic reaction is a good criterion for evaluating quantitatively the pozzolanic activity of the materials. In the international bibliography the values reported of kinetic parameters for pozzolan/CH solution are very scarce. We have not encountered in the literature at our disposal any attempt of reporting kinetic parameters for various pozzolanic materials that give the possibility of comparing quantitatively the reactivity of same ones. With the aim of computing the kinetic parameters, the kinetic-diffusive model (Eq. (1)) was applied for all samples. Figures 9, 10 and 11 illustrate the relative loss of lime concentration plotted against reaction time for SCSA/CH, SCBA/CH, BLA/CH, CPS/CH, LS/CH, Zeolite/CH and FA/CH respectively. The solid and dash lines represent the curves of the fitted model.

**Fig. 9** Relative loss of lime concentration versus reaction times for SCSA, SCBA and CPS
Black circle (experimental), solid, dash and dots line (model).

**Fig. 10** Relative loss of conductivity versus reaction times for Zeolite, FA and LS
Black circle (experimental), solid, dash and dots line (model).

**Fig. 11** Relative loss of conductivity versus reaction times for BLA
Black circle (experimental), solid line (model).
The fitting of the model (Eq. (1)) allowed us to determine the parameters $\tau$, $D_e$, $K$ and $\Delta G^\#$ in each case. The $\Delta G^\#$ was calculated by using the Eyring equation of “The absolute theory of rate processes” [36], which is given by:

$$K = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\#}{RT}\right)$$  \hspace{1cm} (2)$$

where $k_B$ is the Boltzman constant, $h$ is the Planck constant and $R$ is the universal gas constant. $T$ is the temperature, $K$ is the reaction rate constant, and $\Delta G^\#$ is the free energy of activation, which characterizes the change of free energy of the system when passing from the initial state to the transition state.

It is well-known that large 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 (large values of $K$). The knowledge of $\Delta G^\#$ allows us to characterize how fast the reaction occurs; for large $\Delta G^\#$ values the reaction will be slower.

Fitting the relative loss of lime concentration versus reaction 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 sum of squares (RSS), residual scatter, residual probability and variance analysis, it can be concluded that:

For the case of SCSA, SCBA, BLA, CPS and LS the 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 the high porosity of the reaction product layer in these materials, which facilitates a quick diffusion process.

For the samples of zeolite and FA, a kinetic-diffusive control regime predominated 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 was comparable with the diffusion speed of the reactant through the reaction product layer around the nucleus. Therefore, both processes determine the general speed of the whole process.

The values of the parameters ($\tau$, $D_e$, $K$ and $\Delta G^\#$) are given in Table 3.

### Table 3 Reaction rate constants, $\tau$ parameter, free energy of activation, $C_{corr}$ parameter and statistical parameters for the pozzolanic materials

<table>
<thead>
<tr>
<th>Material (Ash)</th>
<th>$\tau$ (h)</th>
<th>Reaction rate constant ($h^{-1}$)</th>
<th>Free energy of activation $\Delta G^#$ (kJ/mol)</th>
<th>$C_{corr}$</th>
<th>Correlation coefficient ($r$)</th>
<th>Coefficient of multiple determination ($R^2$)</th>
<th>Residual sum of squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCSA</td>
<td>23.3 ± 1.8</td>
<td>(8.11±0.67). 10^{-2}</td>
<td>104.63±0.19</td>
<td>0.088±0.012</td>
<td>0.9988</td>
<td>0.9976</td>
<td>0.0022</td>
</tr>
<tr>
<td>SCBA</td>
<td>100.3 ± 9.8</td>
<td>(1.91±0.38). 10^{-2}</td>
<td>108.39±0.47</td>
<td>0.051±0.038</td>
<td>0.9894</td>
<td>0.9788</td>
<td>0.0020</td>
</tr>
<tr>
<td>BLA</td>
<td>4.1 ± 0.2</td>
<td>(8.41±0.29). 10^{-1}</td>
<td>98.56±1.24</td>
<td>0.09 ± 0.008</td>
<td>0.9958</td>
<td>0.9916</td>
<td>0.0293</td>
</tr>
<tr>
<td>CPS</td>
<td>34.8 ± 3.4</td>
<td>(8.69±0.94). 10^{-3}</td>
<td>110.46±0.42</td>
<td>2.39 ± 0.51</td>
<td>0.9860</td>
<td>0.9722</td>
<td>0.0062</td>
</tr>
<tr>
<td>LS</td>
<td>48.4 ± 4.6</td>
<td>(1.23±0.21). 10^{-2}</td>
<td>109.55±0.36</td>
<td>0.19 ± 0.01</td>
<td>0.9925</td>
<td>0.9851</td>
<td>0.0370</td>
</tr>
<tr>
<td>Zeolite</td>
<td>78.1±1.6</td>
<td>(6.88±0.24). 10^{-3}</td>
<td>111.06±0.72</td>
<td>3.09 ± 0.02</td>
<td>0.9998</td>
<td>0.9996</td>
<td>0.0002</td>
</tr>
<tr>
<td>FA</td>
<td>101.9±1.7</td>
<td>(1.76±0.04). 10^{-1}</td>
<td>102.63±0.25</td>
<td>0.01±0.004</td>
<td>0.9972</td>
<td>0.9943</td>
<td>0.0595</td>
</tr>
</tbody>
</table>

According to the values of the reaction rate constant $K$, BLA shows the highest reactivity (larger value of K) followed by FA, SCSA, SCBA, LS, CPS and Zeolite. These results agree with the qualitative analysis carried out previously in the Pozzolanic Activity section above. Similarly, the values of $\Delta G^#$ reflect the same tendency for the pozzolanic activity of the
ashes, that is, BLA shows the highest reactivity (smaller $\Delta G^*$) followed by FA, SCSA, SCBA, LS, CPS and Zeolite.

4. Conclusions

1. Chemically, all samples are formed by the same oxides but with different contents. The main oxides are silica and alumina (although CPS shows a 35% of CaO) whose contents are: 84.1% (FA), 81.62% (BLA, presents the highest content of SiO$_2$ of 80%), 78.67% (zeolite), 75.39% (LS), 72.13% (SCSA), 65.93% (SCBA) and 34.80% (CPS)

2. According to XRD analysis, for the cases of SCSA, SCBA, BLA, FA, the halo observed in the patterns suggests the presence of amorphous material in the samples. It is necessary to highlight the highly amorphous nature for the case of bamboo ash.

3. The values of the reaction rate constant and free energy of activation, obtained in the fitting process of the kinetic-diffusive model, show that the bamboo leaves ashes calcined at 600 °C have a very high pozzolanic reactivity, followed by FA, SCSA, SCBA, LS, CPS and Zeolite.

4. The assessment from the quantitative point of view of the pozzolanic reactivity through the calculation of the kinetic parameters allows a direct comparison between different pozzolanic materials.

5. The availability of materials with different pozzolanic reaction rates can become an important technological advantage in the manufacture of new blended cements that include both natural pozzolans as thermally activated material. The selection of one addition or another as the preferred pozzolan will depend on the characteristics needed for the building site.

Acknowledgements

The authors thank FAPESP (Brazil) (process 2011/12691-2) and CNPq (Brazil) (401704/2013-0) for the financial support to carry out and to conclude this research work. Also, the authors would like to thank the FAPESP (process n. 2011/16842-5) and to CSIC-FAPESP program (i-Link+2013, project ref: i-link0675) for their financial support, and to the Framework Agreement of Collaboration between IETcc/CSIC (Spain) and FZEA/USP (Brazil).

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