



## New method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical conductivity measurements in lime:pozzolan suspensions

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Received 31 January 2014

Accepted 11 April 2014

Available on line 24 September 2014

**ABSTRACT:** A very simple method based on electrical conductivity and pH measurements was proposed for assessing reactivity of pozzolans. Calcium hydroxide:pozzolan water suspensions were monitored by means of measurements of electrical conductivity and pH values. In these suspensions, Ca(OH)<sub>2</sub> in solid state was initially present, being them, thus, saturated in this reagent. Three testing temperatures were selected (40, 50 and 60 °C). In the experiments carried out, calcium hydroxide was suspended in deionized water for yielding a lime saturated suspension. The addition of siliceous pozzolan (two types of rice husk ash RHA and two types of densified silica fume DSF were tested) to the saturated lime suspension can produce the unsaturation of the system, depending on the testing time, testing temperature and reactivity of pozzolan. When unsaturation was reached, the loss of electrical conductivity was higher than 30% and the variation of pH was higher than 0.15 units. These threshold values were selected for characterizing the reactivity of pozzolans by means of a proposed template, classifying the pozzolan in three different reactivity levels.

**KEYWORDS:** Reaction; Characterization; Siliceous pozzolan; Silica fume; Rice husk ash

**Citation / Citar como:** Tashima, M.M.; Soriano, L.; Monzó, J.; Borrachero, M.V.; Akasaki, J.L.; Payá, J. (2014) New method to assess the pozzolanic reactivity of mineral admixtures by means of pH and electrical conductivity measurements in lime:pozzolan suspensions. *Mater. Construcc.* 64 [316], e032 <http://dx.doi.org/10.3989/mc.2014.00914>.

**RESUMEN:** Nuevo método para evaluar la reactividad puzolánica de adiciones minerales por medio de medidas de pH y conductividad eléctrica en suspensiones cal:puzolana. En este trabajo se propone un método simple basado en medidas de conductividad eléctrica y pH. Se determinaron los valores de conductividad eléctrica y pH de suspensiones acuosas de hidróxido cálcico:puzolana. En las suspensiones, había inicialmente Ca(OH)<sub>2</sub> en estado sólido, de manera que dichas suspensiones estaban, por tanto, saturadas respecto a ese reactivo. Se seleccionaron tres temperaturas de trabajo (40, 50 and 60 °C). En las experiencias, el hidróxido cálcico fue mezclado con agua desionizada, generando una suspensión saturada en cal. La adición de puzolana silíceas (se ensayaron dos tipos de ceniza de cáscara de arroz y dos tipos de humo de sílice densificado) a la suspensión saturada de cal puede producir la insaturación del sistema, dependiendo del tiempo, temperatura y reactividad de la puzolana. Cuando se alcanza la insaturación, la pérdida de conductividad eléctrica fue mayor a 30% y la variación de pH fue mayor que 0.15 unidades. Estos valores umbral fueron seleccionados para caracterizar la reactividad de las puzolanas por medio de una plantilla propuesta al efecto, clasificando la puzolana en tres niveles de reactividad diferentes.

**PALABRAS CLAVE:** Reacción; Caraterización; Puzolana silíceas; Humo de sílice; Ceniza de cáscara de arroz

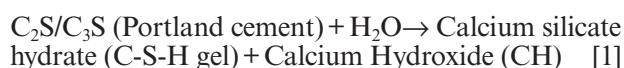
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## 1. INTRODUCTION

In the last decades, several technological and scientific discussions are focusing on the durability and mechanical properties of conventional binders (1, 2). In most cases, the use of blended cements can contribute to the improvement of these properties. Several waste materials have been assessed as supplementary cementitious material (SCM) in blended cements, contributing on the reduction of landfilling areas and also on diminishing the CO<sub>2</sub> emission associated to the production of Portland cement clinker that is responsible for about 5–8% of the global CO<sub>2</sub> emission (3).

Supplementary cementitious materials may be used by blending Portland cement at cement plant, or by replacing Portland cement at the concrete plant. In some cases, these SCM are pozzolans, siliceous or silicoaluminous mineral admixtures which, in itself, possess little or no cementitious value, but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide, released during Portland cement hydration, to form compounds possessing cementitious properties, mainly calcium silicate hydrate.

Calcium silicate hydrate (C-S-H gel), the main product formed during the Portland cement hydration, is responsible for the mechanical strength of hardened cements. C-S-H gel is produced by hydration of C<sub>3</sub>S and C<sub>2</sub>S. Portlandite (calcium hydroxide) is also formed as a reaction product as can be observed in Eq.[1]. In a simple way, the reaction between pozzolan and calcium hydroxide, also named pozzolanic reaction, can be represented as Eq.[2].



Pozzolanic reaction involves two main parameters: the maximum calcium hydroxide consumption and the rate of reaction. These parameters depend mainly on the nature of pozzolanic material, it means, on the chemical and mineralogical composition of pozzolans and on its particle size (4).

Several techniques to characterize pozzolanic reactivity of SCM have been performed such as pozzolanic activity index (5), thermogravimetric analysis (TGA) of Portland cement pastes or calcium hydroxide pastes (6) and electrical conductivity measurements of lime/pozzolan suspensions (7) and blended Portland cement mortars (8). Among these methods, techniques based on electrical conductivity measurements are considered easy and rapid tests to evaluate the pozzolanic reaction, when compared with the existent techniques.

The first study related to electrical conductivity measurements to determine the pozzolanic activity of mineral additions was proposed by Raask and Bhaskar in 1975 (9). In that method, the soluble silica in HF solution was indirectly determined by means of the measurement of electrical conductivity due to the formation of SiF<sub>6</sub><sup>2-</sup> and H<sup>+</sup> ions. The pozzolanic activity index was calculated indirectly by comparison to amorphous silica.

In 1989, Luxán et al. (10) proposed an electrical conductivity method to evaluate the reactivity of natural pozzolans in a saturated hydrated lime solution. Luxán's method consists on analyze the reduction in the electrical conductivity of a hydrated lime/pozzolan suspension by means of interaction of Ca<sup>+2</sup> and OH<sup>-</sup> ions with amorphous silica phase present in the pozzolan, to form insoluble compounds (C-S-H gel). The main problem of Luxán's method is the difficult on preparation saturated calcium hydroxide solution due the low dissolution rate of Ca(OH)<sub>2</sub> at 40 °C, that required at least 24 h to yield saturation equilibrium.

In order to simplify the Luxán's method, Payá et al. (11) proposed the use of unsaturated hydrated lime solutions. In this case, the preparation of unsaturated solutions took only 1 h. Another important change proposed by Payá et al. (11) was to take into account the contribution, in the electrical conductivity and pH measurements, of ions released to aqueous medium provided by the mineral admixture that was not considered by the Luxán's method.

All methods mentioned above focus only on the qualitative aspect of the pozzolanic reaction. In 2003, Villar-Cociña et al. (12) proposed a kinetic-diffusive model based on the electrical conductivity measurements to describe pozzolanic reaction in calcium hydroxide/pozzolan suspensions. This proposed method was based on the Decreasing Nucleus model (DNM). This model proposes a quantitative evaluation of lime-pozzolan reaction, determining kinetic coefficients (diffusion coefficients and reaction rate constants). In this context, several papers have been published by these authors (13).

Recently, the use of ordinary Portland cement solution in the electrical conductivity measurements was proposed by Sinthaworn and Nimityongskul (14). For this method, OPC solution was prepared with 350 g of ordinary Portland cement and 1000 mL of water. The solution was stirred and stored for about 30 minutes to allow sedimentation take place. After the mixture was clear, it was carefully poured, and kept the clear solution (without dregs) in a sealed container to protect against carbonation. Evaluation of pozzolanic activity was performed using 200 mL of OPC solution and 1 g of pozzolan under continuous stirring at 80 °C during 24 h (14).

In this paper, a new alternative method is proposed to assess the reactivity of pozzolanic materials by means of pH and electrical conductivity

measurements. In this case, the pozzolanic reactivity analysis is performed on saturated suspensions with excess of calcium hydroxide in solid state. This type of suspension is different from all previous papers reported previously in the literature. The main advantage of using this new method is, on one hand, the easy preparation of calcium hydroxide suspensions respect to the suspensions used in the Luxán's method (10) and, on the other hand, the new method allows assessing the maximum calcium hydroxide consumption and the pozzolanic reaction rate in these conditions. In order to validate the new proposed method, four siliceous pozzolans with different reactivity, six different CH:pozzolan mass ratio systems and three working temperatures (40, 50 and 60 °C) were performed.

## 2. EXPERIMENTAL

### 2.1. Materials

Calcium hydroxide (95% purity) supplied by Panreac S.A. was used to prepare CH suspensions. Deionized water, plastic film, Erlenmeyer flasks of 100 mL were also used for the analysis.

To validate this new method, four selected pozzolanic materials with different reactivity were assessed: a high-degree densified silica fume (DSF-H), a low-degree densified silica fume (DSF-L), an amorphous rice husk ash (RHA-A) and a crystalline rice husk ash (RHA-C). Table 1 summarizes the chemical composition of selected pozzolans, determined by means of X-ray fluorescence analysis. In the same way, Figure 1 shows the XRD patterns for these pozzolanic materials.

Table 1 show that all pozzolanic materials are siliceous material (silica content higher than 85%). The main difference among these materials is related to their mineralogy and to their particle size distribution.

Both DSF-H and DSF-L are characterised as amorphous materials, determined by the deviation in the baseline in the range  $2\theta = 15\text{--}30^\circ$ , as shown in Figure 1. Small peaks of cristobalite and X silica (PDFcard# 341382) were found. RHA-A sample can also be considered an amorphous material due to the deviation on the baseline. Nevertheless, the presence of small amounts of cristobalite (PDFcard# 270605) and tridymite (PDFcard# 181170) can also

be identified in this sample. RHA-C is a rice husk ash obtained from a non-controlled combustion at high temperatures and has its mineralogical structure formed mainly by tridymite (PDFcard# 181170).

Table 2 shows the particle size distribution and amorphous silica content for tested pozzolans. The amorphous silica content was performed using the selective chemical analysis proposed by Payá et al. (15).

DSF-H is a silica fume sample showing high-degree densification. It has a mean particle size about  $246.7\ \mu\text{m}$  and 50% of particles under  $186.9\ \mu\text{m}$  (16). On the other hand, DSF-L is a low-degree densified silica fume with a mean particle size of  $23.2\ \mu\text{m}$  and 90% of particles under  $42.6\ \mu\text{m}$  (17). Despite both DSF samples presented similar mineralogy, significant differences on particle size distribution were observed. This fact has an important influence on the content of amorphous silica: for the coarsest pozzolan (DSF-H), the amorphous silica content was only 80.5%, unlike the finest one (DSF-L) which had 98.2% of reactive silica.

RHA-A is a waste material with 99% of amorphous silica and a mean particle diameter about  $14\ \mu\text{m}$ . The high pozzolanic reactivity of RHA-A was confirmed in previous studies through pozzolanic activity index and thermogravimetric analysis of calcium hydroxide and Portland cement pastes (17). RHA-C presented a very low amorphous silica content (10.1%) and had a mean particle diameter similar to RHA-A. The low pozzolanic reactivity of RHA-C was previously reported by Payá et al. (11).

### 2.2. Equipments

A pHmeter Crison micro PH2001 and an electrical conductivitymeter Crison micro CM2201 were used to measure the pozzolanic reaction progress. A shaking water bath JULABO - SW22 working in the temperature range of  $20\text{--}99.9\ ^\circ\text{C}$  was used to control the test temperature.

### 2.3. Considerations about the proposed method

The new proposed method to assess the pozzolanic reaction consists on monitoring CH:pozzolan aqueous suspensions in different proportions during 7 days by means of pH and electrical conductivity

TABLE 1. Chemical composition of selected pozzolanic materials (wt%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	LOI
DSF-H	90.77	0.46	4.53	0.78	0.23	0.02	0.21	0.37	3.43
DSF-L	91.73	0.29	0.14	0.37	0.36	0.54	–	–	4.61
RHA-A	83.53	1.42	0.86	1.79	0.36	0.45	0.96	0.78	5.28
RHA-C	90.29	–	–	0.41	–	0.35	0.11	0.27	0.14

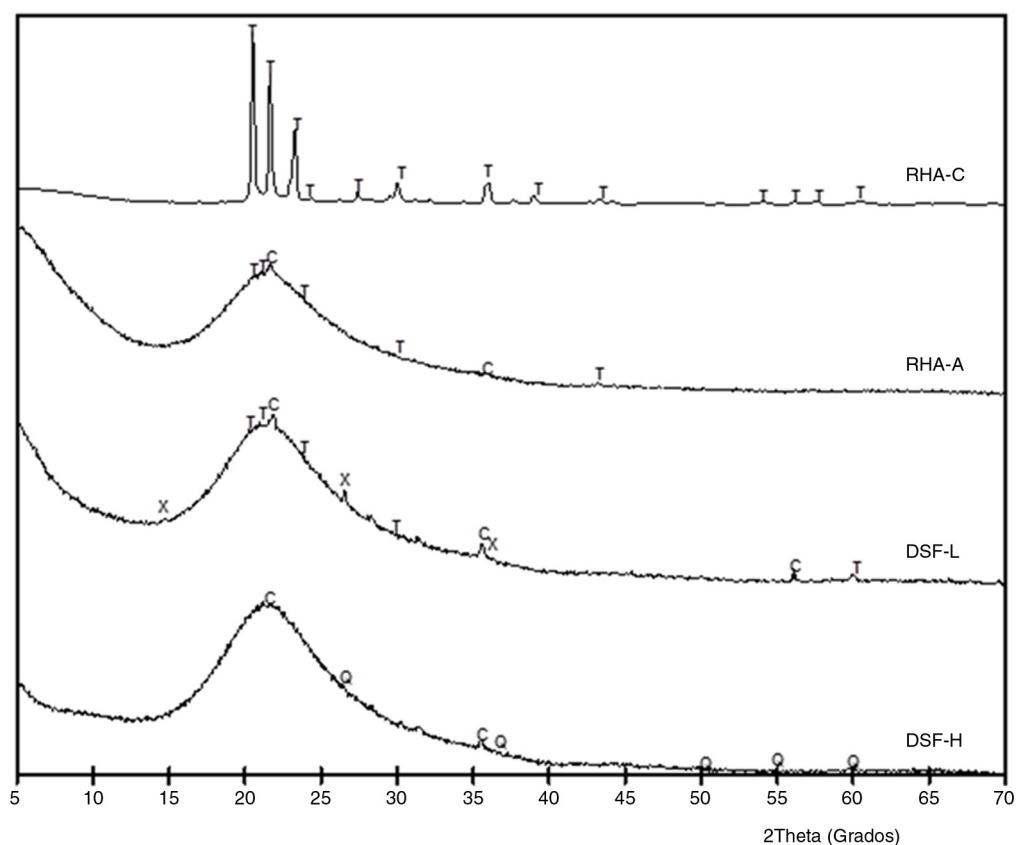


FIGURE 1. XRD patterns for selected pozzolans. (Keys: C- Cristobalite; Q- quartz; T- tridymite; X- silica X).

measurements. At the beginning of test, all prepared suspensions are saturated in calcium hydroxide with excess of calcium hydroxide in solid state.

During the testing period, a reduction on the pH and electrical conductivity values can be observed for the suspensions, indicating the unsaturation of the suspension respect to calcium hydroxide due to the pozzolanic reaction progress. The reduction on pH and electrical conductivity values are due the reaction of dissolved  $\text{Ca}^{+2}$  and  $\text{OH}^{-}$  ions with pozzolan particles to form stable and insoluble products (10).

The presence of calcium hydroxide in solid state maintain approximately constant the concentration of dissolved  $\text{Ca}(\text{OH})_2$  in the suspension (saturated

system) and, when the ions dissolved in the solution are consumed, solubilization of calcium hydroxide took place quickly, reaching again the saturation of the solution. The solubilization process is finished when calcium hydroxide in solid state is exhausted. From this moment (unsaturated system), when the CH in solid state is totally dissolved, a reduction on pH and electrical conductivity values can be detected, indicating the beginning of the unsaturation step.

Six different CH:pozzolan mass ratios (2:8; 2.5:7.5; 3:7; 3.5:6.5; 4:6; 4.5:5.5) were tested, taking into account that the total mass of solid was constant in 1.0 g. Initially, 50 mL of deionized water was added to Erlenmeyer flasks, which were sealed with

TABLE 2. Particle size distribution and amorphous silica content for all pozzolanic materials

	Mean particle size ( $\mu\text{m}$ )	d(0.1)	d(0.5)	d(0.9)	amorphous silica (%)
DSF-H	246.7	18.27	186.9	565.57	80.5
DSF-L	23.25	3.61	18.44	42.66	98.2
RHA-A	13.68	2.19	8.58	31.53	99.3
RHA-C	14.15	2.12	9.19	32.54	10.1

a plastic film and put into the thermostatic bath in order to reach the temperature of test (40 °C, 50 °C or 60 °C). After 30 minutes, calcium hydroxide was added in the flasks to saturate the suspension. All suspensions prepared are saturated of  $\text{Ca}(\text{OH})_2$  and the presence of CH in solid state can be observed, even for suspension initially with 0.2 g of calcium hydroxide (solubility of  $\text{Ca}(\text{OH})_2 \sim 0.185 \text{ g}/100 \text{ mL}$  at 25 °C and its solubility decreases with the increasing of temperature). Once again, flasks were sealed to avoid water evaporation and carbonation. Then, flasks were put into in the thermostatic bath for 15 minutes. After that, pH and electrical conductivity for all CH suspensions were measured ( $\text{pH}_0$  and  $C_0$ , respectively). For suspensions tested at the same temperature,  $\text{pH}_0$  and  $C_0$  values are similar, independently on the amount of CH in the suspension (suspensions are saturated in calcium hydroxide). Finally, pozzolanic material was added to the suspension. From this moment, CH:pozzolan suspensions were monitored during 7 days.

The pH (represented as concentration of hydroxyl anions,  $[\text{OH}^-]$ ) and electrical conductivity curves for CH:pozzolan suspensions can present basically three different behaviors along 7 days of test, as depicted in the curves represented in Figure 2. These curves are the typical ones that have been obtained for this new method.

Firstly, “Suspension a” represents a typical curve for low pozzolanic reactivity materials. There is practically no change on the  $[\text{OH}^-]$  values and electrical conductivity measurements along the 7 days of test (see Figure 2a and Figure 2b) due to the low reaction of  $\text{Ca}^{+2}$  and  $\text{OH}^-$  with pozzolan particles (crystalline phases are not able to combine with calcium hydroxide). In some cases, this type of curve can also represent an excess of calcium hydroxide in the suspension, fact that restrain the unsaturation of suspension.

Secondly, “Suspension b” represents a typical curve for pozzolanic materials that in the first hours of test is not able to get unsaturation in the suspension. Nevertheless, due the progress of pozzolanic reaction, all calcium hydroxide in solid is exhausted and then, a reduction on the pH and electrical conductivity values can be observed for long periods of test (suspension b, Figure 2a and Figure 2b).

And thirdly, the curve represented by “Suspension c” indicates a very rapid consumption of calcium hydroxide and, consequently, a reduction on the pH and electrical conductivity values in the first hours of test. This behavior is characteristic of high reactivity pozzolanic materials and/or for suspensions with low initial calcium hydroxide content.

As can be observed in the typical curves for the proposed method, both electrical conductivity measurements and  $[\text{OH}^-]$  values are sensible enough to detect variations on the CH:pozzolan suspension. Nevertheless, variations on the electrical conductivity values are easily detected. Hence, authors decide to use  $[\text{OH}^-]$  values just as a confirming parameter of pozzolanic reactivity measurements. In order to elucidate the analysis of experimental data, authors propose to represent the electrical conductivity results in terms of loss of conductivity ( $\text{Lc}(\%)$ ). Hence, the loss of electrical conductivity will be the main parameter for this analysis. The  $\text{Lc}(\%)$  is calculated according to the following equation (Eq.[3] and [4]):

$$\text{LC}(\%)_t = \frac{C_0 - C_{t,c}}{C_0} * 100 \quad [3]$$

$$C_{t,c} = C_t - C_{t,poz} \quad [4]$$

Where:

$C_0$  is the electrical conductivity of calcium hydroxide suspension before addition of pozzolan;

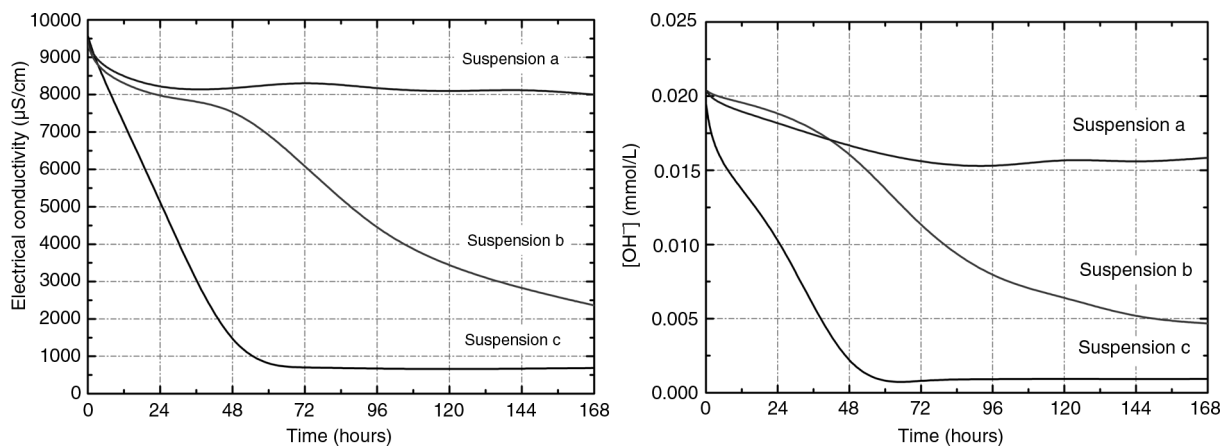


FIGURE 2. Typical curves obtained from the new proposed method after 7 days of test: a) electrical conductivity values; b)  $[\text{OH}^-]$  values.

$C_t$  is the electrical conductivity measured for  $t$  hours;  
 $C_{t,poz}$  is the electrical conductivity released by pozzolan for  $t$  hours;  
 $C_{t,c}$  is the electrical conductivity corrected for  $t$  hours.

According to recommendations of Payá et al. (11), the ions released to aqueous medium provided by the mineral admixture would be considered in this new method. Thus, an Erlenmeyer flask containing 50mL of deionized water and 1g of pozzolan was also monitored and electrical conductivity value  $C_{t,poz}$  was determined for each testing time. The electrical conductivity of CH:pozzolan suspension ( $C_t$ ) minus  $C_{t,poz}$  was calculated (Eq.4), for yielding the corrected  $C_{t,c}$  value.

Typical curves of loss of electrical conductivity are represented in Figure 3. “Suspension a” present a low and constant values during all the period of test. It indicates a low reactive pozzolan or an excess of  $Ca(OH)_2$  in the suspension.

For “Suspension b” there is no change on the  $L_c$  (%) values in the first hours of test, indicating the saturation of suspension. Nevertheless, after 48 hours of test, an increment on the loss of conductivity can be observed due the progress of pozzolanic reaction. “Suspension c” indicates a high reactive pozzolanic material that is able to react with  $Ca(OH)_2$  in few hours, yielding a unsaturated suspension.

### 3. RESULTS AND DISCUSSION

The new method allows evaluating both the maximum calcium hydroxide consumption and the rate of pozzolanic reaction. In this section, the obtained results for all selected pozzolans are presented. Tested pozzolans did not show an important contribution to electrical conductivity when added to deionized water. Thus, these values were lower than 100  $\mu S/cm$  for all tested pozzolans. This behavior

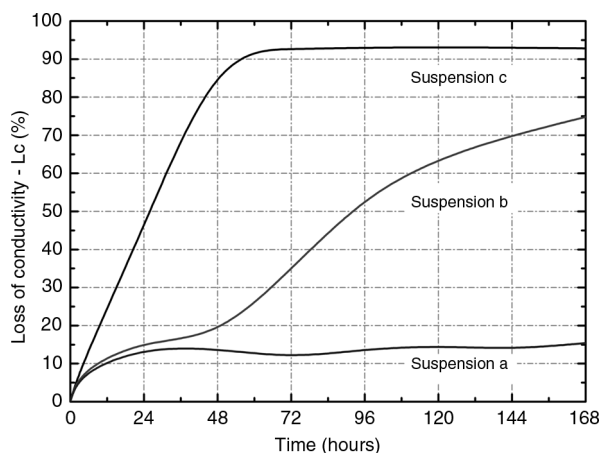


FIGURE 3. Typical curves for loss of electrical conductivity,  $L_c$  (%), during 7 days of test.

means that  $C_{t,poz}$  values were negligible if compared to  $C_t$  values. Consequently, one could simplify and propose as follows (Eq.[5]):

$$C_{t,c} = C_t - C_{t,poz} \approx C_t \quad [5]$$

#### 3.1. Influence of pozzolan type and CH:pozzolan mass ratio on the electrical conductivity of suspensions

Initially, all CH:pozzolan suspensions were tested at 40 °C during 7 days. Six different CH:pozzolan mass ratio for all pozzolans (DSF-H, DSF-L, RHA-A, RHA-C) were performed summarizing a total of 24 tested suspensions. In some cases, selected CH:pozzolan suspensions were tested at least 3 times in order to assess the reproducibility of the new proposed method. In this study of repeatability, some changes on the pH and electrical conductivity values for a given suspension were noted but, in all cases, the deviation was less than 1.0% for pH values and no more than 8% for electrical conductivity values. Hence, the obtained deviation is considered acceptable, fact that confirms the reproducibility of the new proposed method.

##### 3.1.1. Loss of electrical conductivity for CH:DSF-H system tested at 40 °C

Figure 4 show the loss of conductivity for CH:DSF-H suspensions. Only suspension 2:8 presented a significant  $L_c$  (%) value during the test period of 7 days at 40 °C, yielding  $L_c$  (%) = 40% after 48 hours and 70% after 168 hours of test. Suspension 2.5:7.5 presented some changes on the  $L_c$  (%) only after 120 hours of test, yielding 26% after 168 hours of test. The others CH:DSF-H systems did not present any change after the 7 days of test. Although DSF-H is considered a high reactive pozzolanic material,

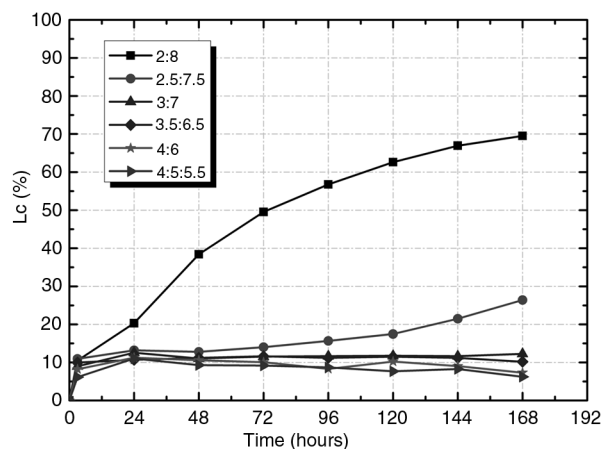


FIGURE 4. Loss of electrical conductivity for CH:DSF-H suspensions at 40 °C.

it is observed that its pozzolanic reactivity is limited due the densified state of silica fume particles (16).

3.1.2. Loss of electrical conductivity for CH:DSF-L system tested at 40 °C

The loss of conductivity values for CH:DSF-L suspensions tested at 40 °C are depicted in Figure 5. Suspensions 2:8, 2.5:7.5 and 3:7 presented a significant reduction on their electrical conductivity values yielding about 60% of Lc (%) for suspension 3:7 after 168 hours. Suspensions with more than 0.3 g of calcium hydroxide (3.5:6.5, 4:6 and 4.5:5.5 systems) did not present any important changes on the Lc (%) values during the 7 days of test, meaning that unsaturation of suspension was not reached in these cases. Comparing the obtained results for DSF-L (see Figure 5) and DSF-H (see Figure 4), it is clearly that the degree of densification affects the reaction between mineral admixture and calcium hydroxide. This fact is related to the decrease on the mean particle diameter for DSF-L that promoted an increase in the pozzolanic reaction rate.

3.1.3. Loss of electrical conductivity for CH:RHA-A system tested at 40 °C

Figure 6 shows the Lc (%) values for different CH:RHA-A proportions tested at 40 °C. It can be noted that, suspensions with low calcium hydroxide content presents high values of Lc (%) since the first hours of test. Suspension 2:8 yields about 90% of Lc (%) after only 48 hours of test. In the same way, suspension 2.5:7.5 have a similar behavior to suspension 2:8. In both cases, a very rapid reaction of Ca<sup>2+</sup> and OH<sup>-</sup> with RHA-A particles can be observed.

The Lc (%) values for suspensions 3:7, 3.5:6.5 and 4:6 are practically constant in the first 24 hours of test. Nevertheless, after a period of time an increment in the loss of conductivity values can be observed.

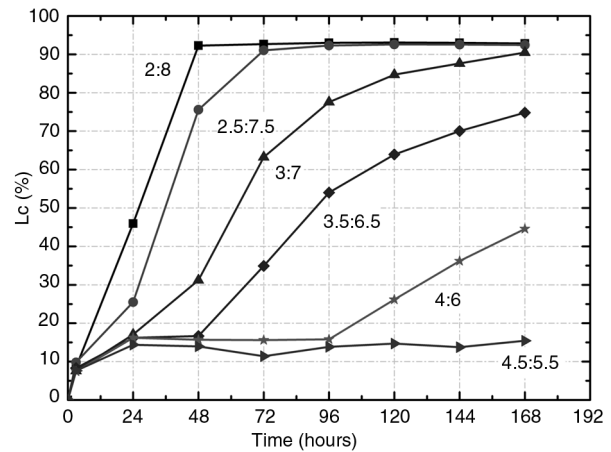


FIGURE 6. Loss of electrical conductivity for CH:RHA-A suspensions at 40 °C.

It indicates that suspensions became unsaturated of calcium hydroxide due to the pozzolanic reaction progress. Thus, an important increase of Lc (%) value was observed for 3:7 system after 24 hours, for 3.5:6.5 system after 48 hours and for 4:6 system after 96 hours.

For suspension 4.5:5.5 no significant changes on the Lc (%) values was observed during all the testing period. It indicates that for this proportion, RHA-A is not able to consume completely solid calcium hydroxide present in the suspension. The obtained results confirm the high pozzolanic reactivity of RHA-A as previously reported by Tashima et al. (17).

3.1.4. Loss of electrical conductivity for CH:RHA-C tested at 40 °C

Figure 7 shows the loss of conductivity for CH:RHA-C suspensions. As it was expected, no significant changes on the Lc (%) values are observed. As reported by Payá et al. (11), RHA-C is a crystalline

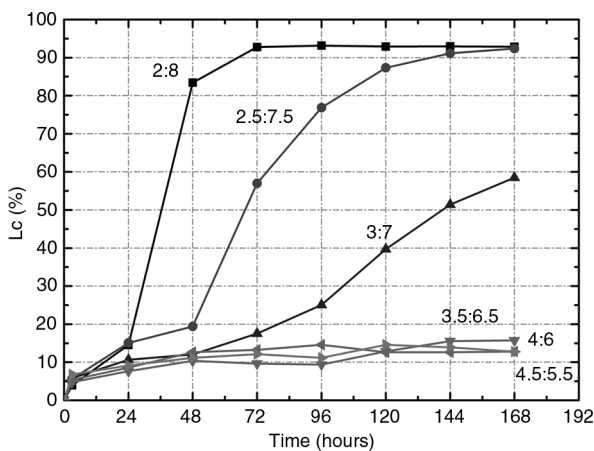


FIGURE 5. Loss of electrical conductivity for CH:DSF-L suspensions at 40 °C.

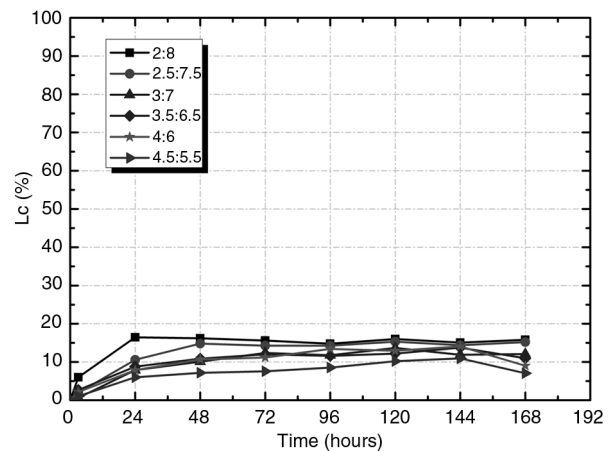


FIGURE 7. Loss of electrical conductivity for CH:RHA-C suspensions at 40 °C.

pozzolan with only 10.1% of amorphous phase. These results confirm the sensibility of the new method proposed in distinguish the behavior between amorphous and crystalline materials, it means, between reactive and non-reactive pozzolans.

### 3.2. Influence of testing temperature on the electrical conductivity of suspensions

In this section the influence of testing temperature for CH:pozzolan suspensions is assessed. According to the literature [18], high temperature promotes an increase on the hydration reaction of Portland cement. Hence, it is expected that CH:pozzolan suspension present similar behavior.

#### 3.2.1. Loss of electrical conductivity for CH:DSF-H systems

Figure 8 shows the Lc (%) values for CH:DSF-H suspensions tested at 50 °C and 60 °C. In this case, no significant changes were observed for CH:DSF-H suspensions. Only suspensions with low calcium hydroxide content presented a variation on the electrical conductivity values. For DSF-H systems the positive effect of increasing temperature was not observed. It is probably due the high-degree densification of silica fume that promotes some divergent results.

#### 3.2.2. Loss of electrical conductivity for CH:DSF-L systems

Figure 9 shows the variation of Lc (%) with time for CH:DSF-L suspensions tested both at 50 °C and 60 °C. The increment on the testing temperature causes a increasing on the degree of reaction between DSF-L and calcium hydroxide. About 60% of loss of conductivity was yielded for 3.5:6.5 suspension tested at 60 °C. For this CH:DSF-L proportion, no significant changes on the Lc (%) values were observed for suspensions tested both at 40 °C

and 50 °C (see Figure 5 and Figure 9a). Despite of increasing testing temperature 4:6 and 4.5:5.5 systems did not reach unsaturation.

#### 3.2.3. Loss of electrical conductivity for CH:RHA-A systems

Figure 10a shows the loss of conductivity for CH:RHA-A suspensions tested at 50 °C. An increment on the temperature accelerated the pozzolanic reaction promoting an increment on the Lc (%) for the earliest ages of test. This behavior can be observed for all suspensions, excepted for suspension 4.5:5.5 that maintains its Lc (%) values constant during the 7 days of test.

Figure 10b shows the loss of conductivity for CH:RHA-A suspensions tested at 60 °C. In this case, the behavior of 3:7 is similar to those obtained for suspensions 2:8 and 2.5:7.5. Another significant change is observed for suspension 4.5:5.5 which for this testing temperature was able to get unsaturation in the suspension yielding approximately 40% of loss of conductivity after 168 hours of test. This result confirms that high temperature contributes positively with the pozzolanic reaction progress.

#### 3.2.4. Loss of electrical conductivity for CH:RHA-C systems

For CH:RHA-C suspensions tested at 50 °C, the loss of conductivity curves are depicted in Figure 11a. All suspensions tested did not present any significant variation on the Lc (%) values indicating that this material is a very low reactive pozzolan.

However, when suspensions were tested at 60 °C, a different behavior for suspensions 2:8 and 2.5:7.5 was observed (see Figure 11b). After 96 hours of test, suspension 2:8 began to increase its Lc (%) values, yielding 61.4% after 168 hours of test. A similar behavior is observed for suspension 2.5:7.5 that starts to change its Lc (%) values after 144 hours of test.

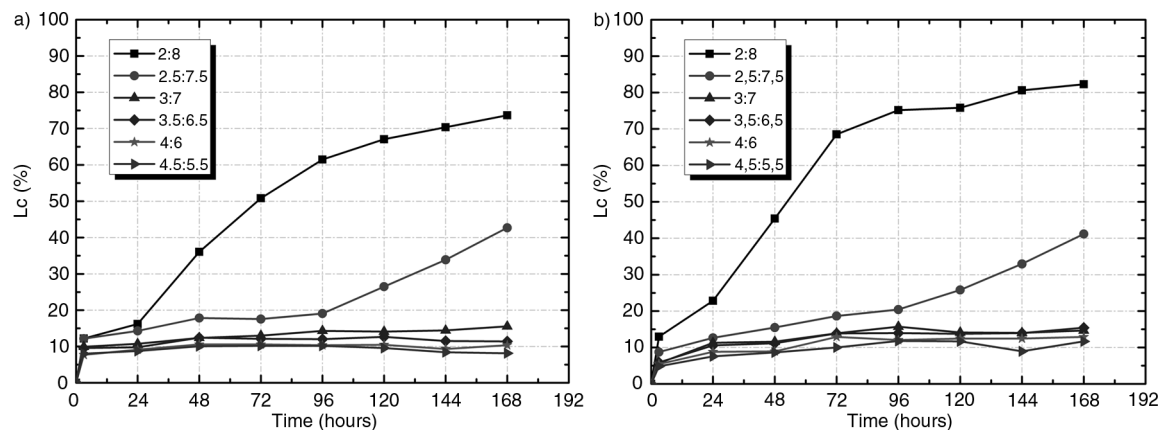


FIGURE 8. Loss of electrical conductivity for CH:DSF-H suspensions: a) test temperature of 50 °C; b) test temperature of 60 °C.



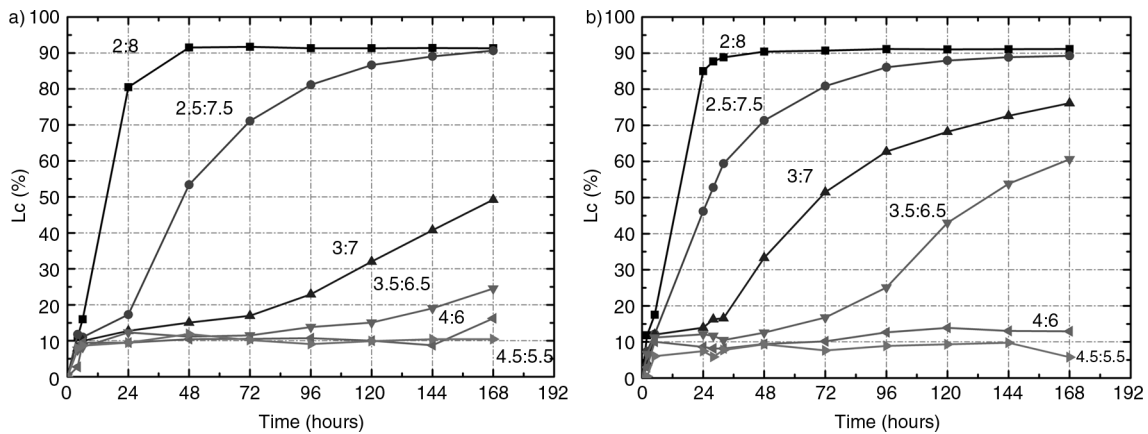


FIGURE 9. Loss of electrical conductivity for CH:DSF-L suspensions: a) test temperature of 50 °C; b) test temperature of 60 °C.

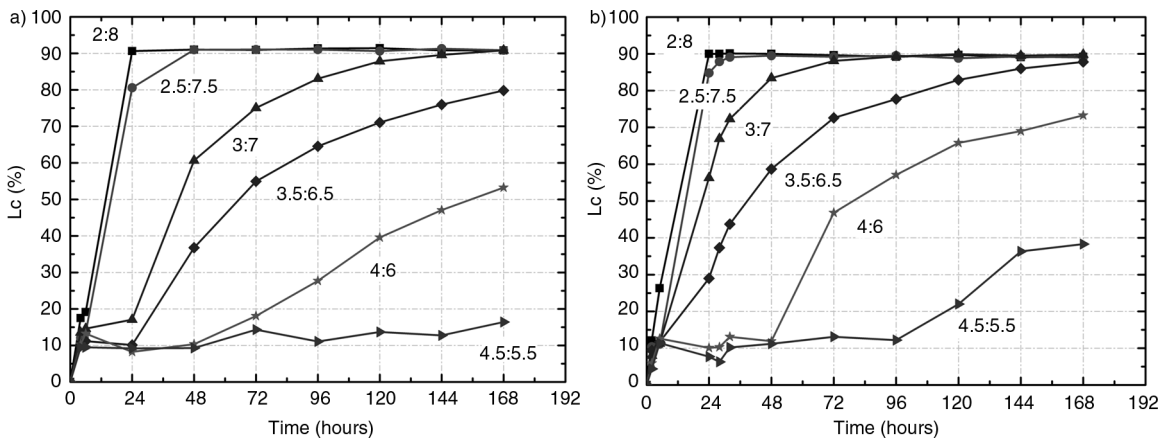


FIGURE 10. Loss of electrical conductivity for CH:RHA-A suspensions: a) test temperature of 50 °C; b) test temperature of 60 °C.

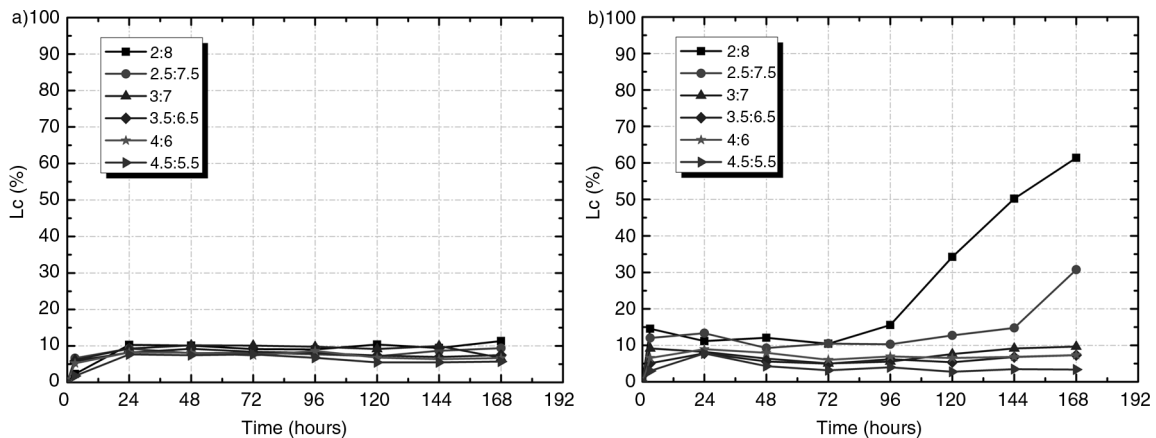


FIGURE 11. Loss of electrical conductivity for CH:RHA-C suspensions: a) test temperature of 50 °C; b) test temperature of 60 °C.

### 3.3. Assessment of pH values for CH:pozzolan suspensions

This parameter was used just to confirm the obtained results for loss of electrical conductivity test. Some selected systems, that represent all the possible

cases obtained for pH values, were depicted in Figure 12 and Figure 13. For CH:DSF-L suspensions, it can be noted that suspensions containing initially less than 0.35 g of calcium hydroxide (2:8, 2.5:7.5 and 3:7 systems) presented a significant variation on the pH values due the reaction of OH<sup>-</sup> groups with

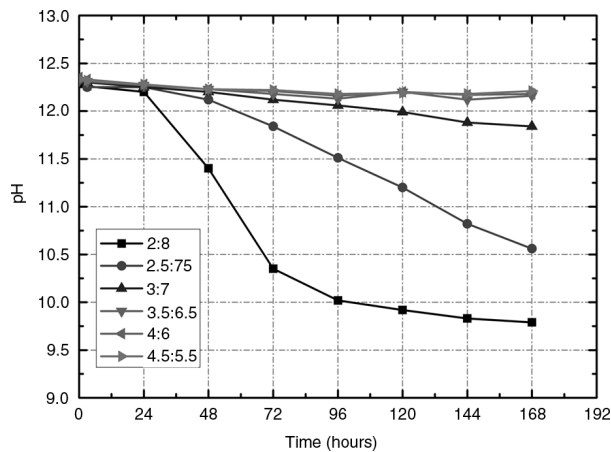


FIGURE 12. pH values for CH:DSF-L suspensions tested during 7 days at 40 °C.

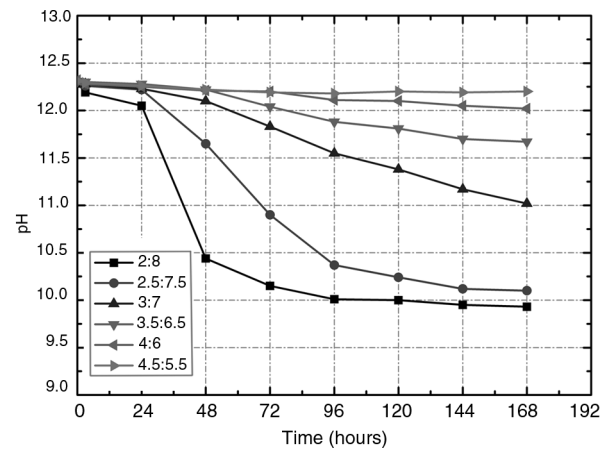


FIGURE 13. pH values for CH:RHA-A suspensions tested during 7 days at 40 °C.

pozzolans. For suspensions 3.5:6.5, 4:6 and 4.5:5.5 no important changes were observed both for pH values and Lc (%) values during 7 days of test.

Figure 13 shows the variation of pH values for CH:RHA-A suspensions tested during 7 days at 40 °C. In this case, four suspensions presented an important reduction on the pH values. Suspension 4:6, even presenting a slight decrease on the pH value, this suspension present about 44% of loss of electrical conductivity after 7 days (see Figure 6). This fact confirms the unsaturation of the 4:6 suspension respect to calcium hydroxide.

Hence, after assess the obtained results for selected suspensions, it can be concluded that pH values are also a sensitive parameter to assess the pozzolanic reaction of CH:pozzolan suspensions.

### 3.4. Criteria for the classification of pozzolanic materials

The new method proposed to assess the reactivity of mineral admixtures by means of pH and electrical conductivity measurements in CH:pozzolan suspensions showed very interesting results, presenting sensibility to differentiate amorphous material and a crystalline one. Analyzing the obtained results, a classification for mineral admixtures is proposed according to their pozzolanic reactivity, in terms of variation of electrical conductivity and pH.

The Lc (%) value of 30% is set with a safety margin, above which the system should be unsaturated in calcium hydroxide. For those systems in which one can assume that suspension is saturated in calcium hydroxide, calculated of Lc (%) values were lower than 30%. The time required for getting calcium hydroxide unsaturation in the suspension (unsaturation time,  $t_{\text{uns}}$ ) was calculated based on the Lc (%) values for all testing temperatures.

Analogously, the pH values for saturated calcium hydroxide system was maintained constant through

the test, and slight variations about 0.15 units respect to the initial pH value ( $t=0$ ) were recorded. Hence,  $\Delta\text{pH}$  higher than 0.15 units represented the unsaturation of CH:pozzolan suspensions. Table 3 show the  $\Delta\text{pH}$  value and unsaturation time for all tested suspensions.

The unsaturation time, that is associated to the Lc (%) = 30% could be used to assess the pozzolanic reaction rate. Hence, for a same CH:pozzolan proportion, it can be observed that RHA-A yielded the unsaturation before the others pozzolans. From Table 3, it can be noticed that unsaturation of the system is mainly produced for the highest temperature and for the lowest CH:pozzolan ratio, and also depends, obviously, on the reactivity of the pozzolan. In order to classify the mineral admixture according to their reactivity, a template is proposed (see Figure 14). Three different zones were distinguished for this classification: zone 1 for low reactivity pozzolan, zone 2 for medium reactivity and zone 3 for high reactivity pozzolan.

To fill the template, for suspensions that yielded unsaturation after 7 days of test, a mark should be placed in the template for its corresponding CH:pozzolan proportion and testing temperature. Different marks were used for each tested pozzolan. Figure 15 shows the fulfilled template using experimental data for DSF-H, DSF-L, RHA-C and RHA-A.

For a given pozzolan, when a mark was placed in the zone 3, this pozzolan should be considered a high reactivity material. Thus, the assessed pozzolans are classified according to Table 4.

## 4. CONCLUSIONS

A very simple method based on electrical conductivity and pH measurements of CH:pozzolan suspensions was proposed for assessing reactivity of pozzolans. In this method, a saturated suspension

TABLE 3.  $\Delta\text{pH}$  values and unsaturation times ( $t_{\text{uns}}$ ) for all tested suspensions

		40°C		50°C		60°C	
		$\Delta\text{pH}$	$t_{\text{uns}}$ (h)	$\Delta\text{pH}$	$t_{\text{uns}}$ (h)	$\Delta\text{pH}$	$t_{\text{uns}}$ (h)
DSF-H	2:8	0.18	36.9	0.39	40.7	0.18	31.6
	2.5:7.5	–	–	0.21	131.4	0.19	134.1
	3:7	–	–	–	–	–	–
	3.5:6.5	–	–	–	–	–	–
	4:6	–	–	–	–	–	–
	4.5:5.5	–	–	–	–	–	–
DSF-L	2:8	0.89	29.4	0.84	9.9	0.97	8.5
	2.5:7.5	0.49	54.7	0.37	32.4	0.30	15.0
	3:7	0.34	104.1	0.23	114.5	0.29	44.9
	3.5:6.5	–	–	–	–	0.32	102.6
	4:6	–	–	–	–	–	–
	4.5:5.5	–	–	–	–	–	–
RHA-A	2:8	0.24	15.0	1.51	8.7	1.72	6.1
	2.5:7.5	0.66	26.2	0.45	10.4	1.01	9.9
	3:7	0.22	45.0	0.42	31.1	0.40	12.9
	3.5:6.5	0.27	65.5	0.17	41.9	0.23	24.5
	4:6	0.27	129.2	0.28	100.6	0.28	60.4
	4.5:5.5	–	–	–	–	0.16	133.4
RHA-C	2:8	–	–	–	–	0.18	114.6
	2.5:7.5	–	–	–	–	0.22	166.9
	3.5:6.5	–	–	–	–	–	–
	3:7	–	–	–	–	–	–
	4:6	–	–	–	–	–	–
	4.5:5.5	–	–	–	–	–	–

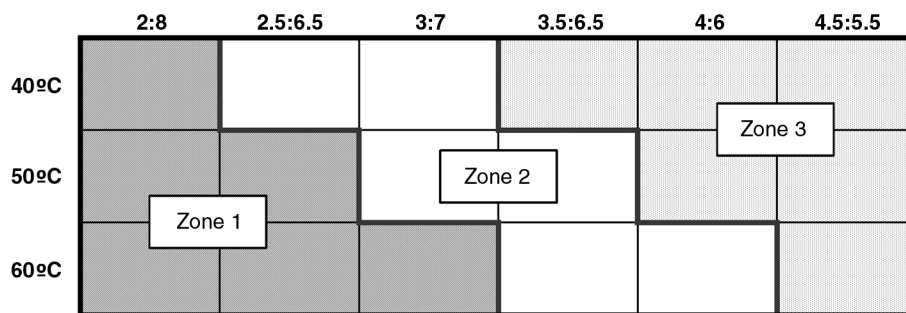


FIGURE 14. Template for classification of pozzolan reactivity.

with excess of calcium hydroxide in solid state was used. In these conditions the maximum calcium hydroxide consumption and the pozzolanic reaction rate can be assessed. Pozzolanic materials showing high reactivity, yielded easily unsaturation in high content calcium hydroxide suspensions: unsaturation was reached at shorter testing times when testing temperature was increased. Unsaturation was established when loss on conductivity was higher

than 30% respect to a calcium hydroxide saturated suspension and also when the decreasing of pH was higher than 0.15 units. Different behaviors can be identified depending on the reactivity of pozzolanic material. A classification for pozzolanic materials is proposed based on the obtained results and a template was established for the assessing the pozzolanic reactivity: three reactivity levels (high, medium and low) have been proposed.

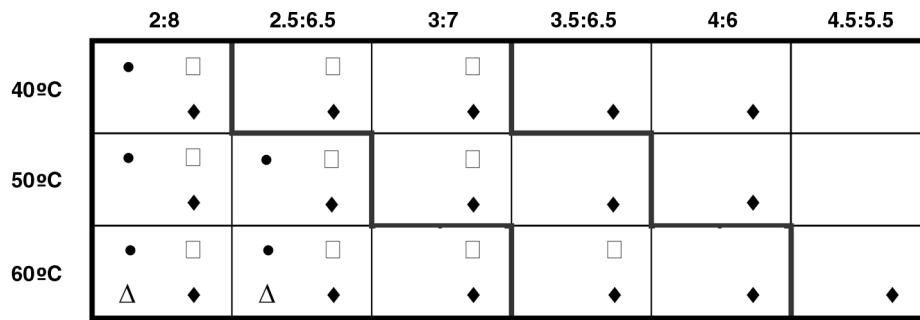


FIGURE 15. Fulfilled template for selected pozzolanic materials. Keys: ● - DSF-H; □ -DSF-L; △ - RHA-C and ◆ - RHA-A.

TABLE 4. Classification of pozzolan according to the proposed method

Pozzolan	Zone	Reactivity
DSF-H	1	low
DSF-L	2	medium
RHA-A	3	high
RHA-C	1	low

Amorphous rice husk ash was classified as high reactivity material, and crystalline rice husk ash was a low reactivity material. For silica fume, depending on the densification state, low and medium reactivity materials were identified.

**ACKNOWLEDGEMENTS**

This paper is a part of the Mauro M. Tashima’s Doctoral Thesis: thanks are given to Pedro Garcés (Universidad de Alicante), Francisca Puertas (CSIC – Eduardo Torroja Institute) and Arnaldo Moreno (Universitat Jaume I) for their comments and advice in the preparation of the doctoral thesis.

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