

CORRELATIONS BETWEEN POZZOLANIC EVALUATION METHODS, ELECTRICAL CONDUCTIVITY AND CHEMICAL SHRINKAGE TEST

U. Hernández-Toledo¹, P. Valdez-Tamez¹, G. Fajardo¹, P. Montes², A. Durán-Herrera¹

¹ Universidad Autónoma de Nuevo León (UANL), FIC, Nuevo León, México

² Instituto Politécnico Nacional, CIIDIR Oaxaca, Oaxaca, México

*Corresponding author; e-mail: ur.hernandeztl@uanl.edu.mx

Abstract

The use of pozzolans is one of the main strategies of the cement industry to reduce the CO₂ emissions; however, one barrier to increase the use of pozzolans is the local availability. Rapid pozzolanic evaluation methods can facilitate the search for new pozzolanic materials and their quality control. The pozzolanic activities of eleven materials which include two class f fly ash, two silica fumes, metakaolin, ground granulated blast furnace slag, ground glass, sugar cane bagasse ash and three natural pozzolans were evaluated with two types of ordinary Portland cement and calcium hydroxide (CH). The strength activity index (mortar mixtures at 7 and 28 days of age), the Chapelle test (10.57 g/L CH and 4 g/L pozzolan suspension at 80 °C for 16 h), chemical shrinkage (cement pastes with 10 or 20% of pozzolan at 60 °C for 3 days) and a proposed electrical conductivity method (800 mg/L CH and 302.7 mg/L pozzolan suspension) were compared. Simple and multivariable linear regression analysis were employed to identify possible correlations between methods and physicochemical characteristics of materials. Only a significant correlation ($R^2=0.84$) was found between the CH consumption of Chapelle and the loss of conductivity of conductivity tests. Based on this finding, the proposed conductivity method may be useful for estimate the CH consumption of the Chapelle method.

Keywords:

Strength activity index; calcium hydroxide/pozzolan ratio; electrical conductivity; Chapelle test

1 INTRODUCTION

Pozzolans and supplementary cementitious materials, including fly ash, silica fume, ground granulated blast furnace slag, calcined clays and natural pozzolans (sugar cane bagasse ash and rice husk ash) are commonly used in the manufacture of cements and concretes. In 2003 the global average content of clinker for the manufacture of Portland cement was 85%, in 2010 was 77% and is expected to continue declining to 71% [Schneider 2011].

To evaluate the pozzolanicity of a material techniques such as differential scanning calorimetry, scanning electron microscopy and isothermal calorimetry can be used [Scrivener 2015]. In practice, the standard methods such as the strength activity index (SAI), the Frattini and Chapelle test are the most used. Rapid methods represent an alternative to facilitate the preliminary pozzolanic evaluation of materials. An interesting proposal is the method based on the measurement of electrical conductivity (EC) in a suspension with calcium hydroxide (CH) or with Portland cement (PC) and pozzolan. Raask and Bhaskar proposed for the first time to measure the EC

in a suspension of fly ash in a 0.1 M hydrofluoric acid solution. They classified the reactivity according to the dissolved reactive material [Raask 1975]. Luxán et al. present a very fast method where the EC is recorded in saturated CH and natural pozzolans suspensions for 120 s at 40 °C, with a calcium hydroxide/pozzolan (CH/P) ratio of approximately 0.056. The method is only applicable to natural pozzolanic materials, such as opal rocks or diatomaceous earths [Luxán 1989]. Payá et al. presents improvements to the Luxán's method, they used an unsaturated CH solution with CH/P ratio of 0.04, monitoring up to 10,000 s from 40 to 80 °C, and subtracting the conductivity of the pozzolan. The method is applicable for fly ash with low calcium content [Paya 2001]. Sinthaworn y Nimityongskul propose a method where the EC is measured in PC and pozzolan suspensions at 80 °C for 28 h [Sinthaworn 2009]. Some studies have focused on the effect of the alkaline solution concentration, CH/P ratio and reaction temperature [Sinthaworn 2009; Velázquez 2014a; Velázquez 2014b]. In general, these studies show that loss of conductivity increases with increasing temperature and with decreasing CH/P ratio. Saturated CH solutions delay the onset of EC

decrease. Tashima et al. presents a method where the EC of 18 suspensions with 6 CH/P ratios from 0.25 to 0.81 and 3 temperatures (40, 50 and 60 °C) for 7 days were measured. Pozzolans are classified according to a template, in which the suspensions that have a LC greater than 30% are marked [Tashima 2014]. Most of the time these methods do not correlate well with the SAI or Frattini methods because the test conditions are generally modified to accelerate the reactions and reduce the test time [Donatello 2010]. A rapid pozzolanic evaluation method that could estimate measures of widely used methods would have the practical advantage of being able to compare its results with much more information available in the literature or of own experiences. Additionally, chemical shrinkage tests have been widely used to compare the hydration rate of PCs and blended PCs. Recent studies indicate a good relationship between chemical shrinkage and calorimetry isotherms, and are considered as an economical method with great potential for conducting evaluations even in the long term [Kocaba 2012; Pang 2013]. In this paper, we study the correlation between Chapelle, SAI, electrical conductivity, chemical shrinkage methods and the physicochemical characteristics of the materials by simple and multivariate linear regression analysis. The main objective is to propose a rapid method based on EC tests, either individually or in conjunction with chemical shrinkage and physicochemical variables of the materials. The proposed method must be useful to estimate the values of SAI or the CH consumption as the Chapelle does.

2 EXPERIMENTAL

2.1 Materials

Eleven different natural and artificial pozzolans were tested. Densified silica fumes (HS1; Master Life SF 100, BASF and HS2; Eucon MSA, Euclid Chemical), fly ash (CV1-100; obtained from José López Portillo power plant, Coahuila, México and CV2-100m; from Plutarco Elías Calles power plant, Guerrero, México), sugar cane bagasse ash (CBC-200; from Constancia sugar factory, Veracruz, México) natural pozzolans of volcanic origin (PN1, PN2 y PN3; provided by Holcim Mexico); ground granulated blast-furnace slag (EAH; provided by Holcim Mexico), ground waste glass (VM; waste glass of industry in Monterrey, México) and metakaolin (MK; Metaforce provided by Cementos Chihuahua). Ordinary Portland cement with high early strength (CPO III; fulfilling with ASTM Type III cement), ordinary Portland cement with high sulfate resistance (CPO V; fulfilling with ASTM Type V cement) and standard graded sand ASTM C 778 was used. Calcium hydroxide (98.6%, J.T. Baker) for the conductivity measurements and calcium carbonate (99.9%, J.T. Baker), sucrose (J.T. Baker), nitric solution 0.1 N, ethyl alcohol, and phenolphthalein for Chapelle test were analytical-grade reagents were used. Distilled water was used in all the tests.

The post-treatments applied to the pozzolans prior usage are shown in Tab. 1. Non-commercial pozzolans were dried in an oven at 105 °C for 1 day before treatment. Materials with size greater than 5 mm were ground with a disc or jaw crusher before sieving or grinding. Grinding was applied in a high-energy vibrating mill, Sweco DM1, for one hour with 65 kg of steel balls and 4 kg of material. All batches of

pozzolans and cements were homogenized. Density was determined using a Le Chatelier Flask and kerosene (ASTM C 188). The loss on ignition was determined by gravimetric analysis, calcinating the sample cements and pozzolans in an electric furnace at 950 °C and 750 °C respectively, during 1 hour in oxidizing ambient atmosphere (ASTM C 114 and C 311). The particle size distribution was analyzed by laser diffraction using isopropanol as a dispersant agent in a Microtrac, Microtrac Inc. equipment. For the analysis a low flow rate was used (45%, is suitable for fine powders). To estimate the deagglomeration produced by the mechanical mixing, 90 s of ultrasound with 40 W of power were applied as deagglomeration is significant in densified silica fumes. This time was determined experimentally.

Tab. 1: Post-treatments applied to pozzolans.

Pozzolans	Type of treatment
HS1, HS2 y MK	As received (commercials)
CV1-100	Sieving by the mesh #100 (150µm)
CV2-100m	Sieving by the mesh #100 (150 µm) and grinding
CBC-200	Sieving by the mesh #200 (75µm)
PN1, PN2, PN3, EAH, VM	Crushing and grinding

Specific surface area was determined by N₂ adsorption (NOVA 2000E, Quanta Crom) using the Brunauer-Emmett-Teller (BET) method. Chemical analysis of the major elements was determined by X-ray fluorescence (XRF) spectrometry using an Epsilon 3-XL PANalytical. Chemical and physical characteristics of cements and pozzolans are reported in Tab. 2. Micrographs of all pozzolans and cements were taken at different magnifications to identify the different morphologies using a JEOL SM 6510-LV Scanning Electron Microscopy (SEM). Only the most relevant micrographs are shown (Fig. 1). The powder samples were sprinkled on a double sided adhesive carbon tape attached to a sample holder. With the silica fume a suspension was prepared with acetone and a drop was placed on the carbon tape. Each sample was coated with a thin layer of gold to make it electrically conductive.

The SEM images of HS1 are shown in Fig., 1a and 1b, whereas HS2 are shown in Fig. 1c and 1d. It is observed that HS1 is constituted by spheres of smaller size than HS2, but HS1 agglomerates appear to have a higher degree of fusion than HS2. This can be supported by the results from the particle size distribution test (Tab.2 and Fig. 1), since HS2 agglomerates reach smaller particle diameters by the application of ultrasound. It is known that densified silica fume may have different degrees of agglomeration before to mixing and during mixing its deagglomeration is also variable and depends on the degree of fusion of the particles in the agglomerates [ACI 234 Committee 2006]. CV1-100 presents cenospheres and some carbon particles (Fig. 1e). CBC-200 presents large quartz particles, with cellular structure particles and particles with carbon. The other pozzolans are mostly composed of angular particles with variable size as a result of the grinding process.

2.2 Chapelle test

The pozzolanic activities of the materials were evaluated with the modified Chapelle test in accordance with the NF P 18-513 (Annex A) standard. This test estimates the amount of CH consumed by the pozzolan during 16 hours in a CH/P = 2.64 solution at 85 ± 5 °C. 1 g of pozzolan is mixed with 2 g of CaO and 250 mL of distilled CO₂ free water, which is continuously stirred during the test. Also, a blank with 2 g of CaO was tested. The CaO was obtained from the calcination of a CaCO₃ at 1000 °C for at least 30 minutes. When the reaction ended, 250 mL of a saccharose solution (250 g/L) was added and stirred during 15 min. After that, 200 mL of the resultant solution were filtrated and taken 25 mL to titrate with

0.1 N HCl and some drops of 0.1% phenolphthalein in a 50% ethanol solution. The consume Ca(OH)₂ was calculated according to Ec. 1:

$$\text{mg of Ca(OH)}_2 \text{ fixed} = 2 \times \frac{V_1 - V_2}{V_1} \times \frac{74}{56} \times 1000 \quad (1)$$

where, V₁ (mL) is the volume of 0.1 N HCl necessary for 25 mL of solution of the blank test, V₂ (mL) is the volume of 0.1 N HCl necessary for 25 mL of the suspension containing the pozzolan. It was verified that for the blank test the result of 56/2 x V₁ was be less than 1000. The repeatability of Chapelle test is 10%. All pozzolans were evaluated by duplicate. EAH was not evaluated because Chapelle test is not applicable to metallurgical slags [Quarcioni 2015].

Tab. 2: Chemical and physical characteristics of cements and pozzolans.

	CPO III	CPO V	HS1	HS2	CV1- 100	CV2- 100m	CBC- 200	PN1	PN2	PN3	VM	EAH	MK
Chemical composition (%)													
SiO ₂	17.90	26.4	95.58	97.16	61.70	62.09	63.87	70.24	74.43	57.04	94.73	43.01	67.00
Al ₂ O ₃	4.86	3.27	1.01	0.78	26.29	18.28	15.86	14.10	11.97	17.94	2.08	7.76	25.45
Fe ₂ O ₃	2.01	4.42	1.22	0.05	5.43	8.17	7.69	3.07	2.15	7.96	0.21	0.33	1.37
CaO	63.96	59.3	0.47	0.42	2.15	6.26	2.47	1.69	0.81	7.54	0.11	34.98	4.50
MgO	1.22	1.14	0.85	0.36	0.71	1.11	1.20	0.19	-	2.37	-	8.14	-
SO ₃	NA	NA	-	-	0.46	0.33	0.33	-	-	0.11	-	4.08	0.73
Na ₂ O	0.69	-	-	-	0.33	0.49	0.34	3.66	2.92	3.59	2.49	-	-
K ₂ O	0.89	0.57	0.48	0.82	1.42	1.38	5.07	6.03	7.14	1.96	0.17	0.48	0.33
TiO ₂	0.23	0.18	-	-	1.16	1.05	1.07	0.48	0.17	0.83	0.01	0.87	0.11
P ₂ O ₅	0.11	-	0.35	0.37	-	0.17	1.32	-	-	0.09	-	-	0.05
MnO	0.50	0.08	0.05	0.03	0.02	0.05	0.23	0.07	0.04	0.13	-	0.12	0.21
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃			97.8	98.0	93.4	88.5	87.4	87.4	88.5	82.9	97.02	51.10	93.82
Loss on ignition	1.8	2.0	3.2	2.0	2.8	4.7	8.7	2.9	2.0	0.8	0.3	1.1	2.3
Physical properties													
Density (g/cm ³)	3.09	3.22	2.22	2.27	1.92	2.54	2.17	2.37	2.35	2.72	2.27	2.88	2.62
Fineness 45 µm (retained %)	4	23	47	3	56	16	35	7	17	11	2	33	17
d ₉₀ (µm)	34.8	49.5	143.0	33.1	130.5	72.4	80.2	35.3	57.9	45.4	33.3	156.7	63.2
d ₅₀ (µm)	15.4	18	42.5	16.1	51.9	15	34.8	9.8	17.6	12.2	14.10	18.8	15.1
d ₁₀ (µm)	4.6	3.54	12.8	7.6	12.1	3.29	12.5	2.7	3.6	2.2	4.28	1.6	2.2
Laser diffraction area (m ² /kg)	180	195	88	178	103	260	100	370	255	362	256	410	358
BET surface area (m ² /kg)	4,600	3,620	21,630	27,170	3,500	7,210	35,990	4,110	3,800	5,400	3,530	5,250	11,280

2.3 Strength activity index (SAI)

SAI measures the contribution of the pozzolanic reaction to the compressive strength, which is dependent on the densification of the cement matrix and the packing effect produced by the pozzolan [Pourkhorshidi 2010; Tironi 2013]. The SAI at 7 and 28 days was evaluated according to ASTM C311 and the complementary standards. Control mortars cubes were prepared by mixing 1375 g sand, 500 g cement and 242 g water in a planetary orbital mixer. Test samples were prepared in the same manner, except that 20% of cement was replaced by the test pozzolan and the water content was adjusted to obtain a flow ± 5 as control mixture. In the case of the silica fumes (HS1 and HS2) the replacement was 10% according with the ASTM C 1240. The mix composition and water requirement of pozzolans are presented in Tab.3. All cubes were placed in moist room for 24 h, then placed in a water bath with 1.65 g/L of Ca(OH)₂ at 23 °C until the time of the test. When ready, the cubes were removed from the bath, surface dried and tested to determine the 7 and 28 days compressive strength. Results reported are the averages of three tests and

are presented as % relative strength to the respective control mortar. The SAI is calculated according to the Ec. 2:

$$SAI = (A/B) \times 100 \quad (2)$$

where *A* is the average compressive strength of test mixture cubes (MPa) while *B* is the average compressive strength of the control mix cubes (MPa).

2.4 Electrical conductivity in calcium hydroxide-pozzolan suspensions

Considerations about the test conditions

The reaction between calcium hydroxide (CH) and the pozzolanic material in suspension produces a decrease in the electrical conductivity (EC) due to the decrease in the concentration of Ca²⁺ and OH⁻ [Luxán 1989].

In a CH-pozzolan suspension where the amount of pozzolan is several times greater than CH the EC decreases rapidly and stabilization of the system occurs in less time. Because CH is limited it can be exhausted by reacting mostly with the fine fraction of pozzolan.

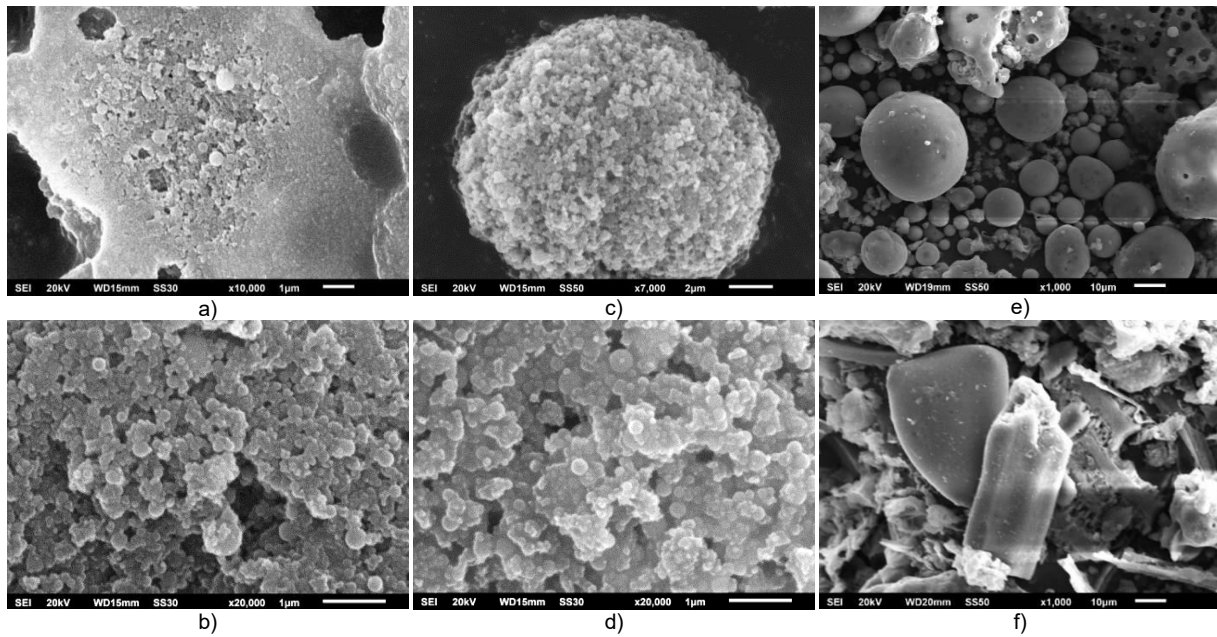


Fig. 1: SEM images of HS1 (a, b), HS2 (c, d), CV1-100(e) and CBC-200 (f).

Tab. 3: Composition of mixtures for the SAI test and water demand of pozzolans.

	CPO III	CPO V	HS1	HS2	CV1- 100	CV2- 100m	CBC- 200	PN1	PN2	PN3	VM	EAH	MK
Control mixtures													
Cement (g)	500	500											
Sand (g)	1375	1375											
w/c	0.484	0.484											
Flow (%)	95	93											
Mixtures with pozzolan													
CPO III cement (g)			450	450	400	400	400	400	400	400	400	400	400
Sand (g)			1375	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375
Pozzolan (g)			50	50	100	100	100	100	100	100	100	100	100
w/b			0.52	0.50	0.50	0.50	0.61	0.49	0.47	0.475	0.475	0.465	0.50
Flow (%)			91	90	96	95	99	100	96	91	94	95	99
Water requirement (%)			107	103	103	103	126	101	97	98	98	96	103
CPO V cement (g)			450	450	400	400	400	400	400	400	400	400	400
Sand (g)			1375	1375	1375	1375	1375	1375	1375	1375	1375	1375	1375
Pozzolan (g)			50	50	100	100	100	100	100	100	100	100	100
w/b			0.545	0.52	0.50	0.50	0.61	0.48	0.47	0.484	0.48	0.475	0.495
Flow (%)			95	89	93	92	95	92	92	90	93	89	96
Water requirement (%)			113	107	103	103	126	99	97	100	99	98	102

This fraction may not be representative of all pozzolans. In the case of suspensions where the amount of pozzolan is much lower than CH, the decrease in EC is lower, and less and less evident as the CH/pozzolan ratio increases. Therefore, seems reasonable to propose a CH/pozzolan ratio close to 1.

In the suspension of the Chapelle test and in the mortars for the SAI test the CH is under supersaturation condition. In this condition the CH crystals can function as nucleation points that accelerate the formation of C-S-H. It may be desirable to have the same mechanism in EC testing to improve the relationship with the mentioned methods. However, in supersaturated solutions at the start of the test, a quantity of pozzolan reacts with CH without changes in the EC. The EC begins to decrease only until the CH has dropped below the saturation point. With unreactive pozzolans, the decrease in EC may be very low or negligible. Based on previous experimentation and other investigations [Payá 2001; Sinthaworn 2009;

Sinthaworn 2011; Velázquez 2014a; Tashima 2014], it was decided to use an unsaturated CH solution with a CH/pozzolan ratio equal to 1.0. A test temperature of 80 °C was also established due to it accelerates the pozzolanic reaction and changes in EC occur in less time [Payá 2001; Sinthaworn 2011].

Electrical conductivity test in CH-pozzolan suspensions of 0-24 h

Based on the above, a first evaluation of the EC method was performed with the following conditions. A suspension with 800 mg/L CH and 800 mg/L pozzolan (CH/pozzolan ratio of 1.0) was used with continuous stirring at 80 ± 1 °C for 24 h in a high density polypropylene flask with 230 mL suspension. An Orion 4-Star Plus conductivimeter and a water bath arrangement with stirring and digital temperature control were used. EC was measured every 10 s for the first 5 min, then every 10 min until 24 h. A concentration of 800 mg/L of CH was chosen because

is below the saturation point at 80 °C (960 mg/L) and has also been proposed in previous works [Payá 2001; Sinthaworn 2011]. The relative conductivity loss is calculated according to the equation (Ec. 3) proposed by Paya et al. [Payá 2001]:

$$(\%LC)_t = \frac{C_0 - (C_P)_t}{C_0} 100 \quad (3)$$

where $(\%LC)_t$ is the % of loss in electrical conductivity for a given suspension and a given time t ($t=24$ h), C_0 the conductivity of CH solution before pozzolan addition and (C_P) the absolute loss in conductivity for CH/pozzolan suspension at given time, t .

In the method proposed by Paya et al. [Payá 2001] the conductivity contributed by the pozzolan is subtracted. In the present work, this is not essential and it can be omitted because the CH/pozzolan ratio is 25 times higher than the used in the method of Paya et al., and the EC contributed by the pozzolan is very low. It was determined that the EC of the pozzolans studied is less than 1% with respect to the CH solution.

This first technical proposal presented in this paper is useful to evaluate the pozzolanic capacity of the materials, however, a low correlation ($R^2 = 0.44$) was observed with the Chapelle test. Further experimentation was carried out in which the effect of the variables including the CH/pozzolan ratio, concentration of the suspension and test time was studied to try to improve the correlation mentioned. It was found that the best correlation is achieved using the reaction conditions of the Chapelle test with a subsequent adjustment in the concentration of the suspension before taking the EC reading at the end of the test. This adjustment consists in diluting the suspension at the end of the reaction time, modifying the condition of CH of super saturated to unsaturated in order to detect changes in EC due to the consumption of this.

Electrical conductivity method in suspension correlated with the Chapelle test

A CH-pozzolan suspension containing 8.00 g/L of CaO (10.57 g/L $\text{Ca}(\text{OH})_2$) and 4.00 g/L of pozzolan (CH/pozzolan ratio of 2.64) was used for this purpose. The suspension was kept sealed and shaken for 16 h at 85 ± 1 °C in a high density polypropylene vessel with 35 mL suspension.

At the end of the reaction time the suspension was diluted, in order to observe decreases in the EC with respect to the blank with CH. Distilled and boiled water was added at 85 °C to complete 462.5 mL of suspension. The suspension was constantly stirred and maintained at 85 °C, then, the EC at 60 s was measured after dilution. This time for measurement (60 s) is important because it appears that part of the C-S-H formed during the reaction time is soluble at a lower concentration.

With dilution, the final concentration before reading should be 800 mg/L $\text{Ca}(\text{OH})_2$ and 302.7 mg/L pozzolan. Since EC is not measured continuously and only one reading is taken at the end of the test, simultaneous testing can be performed including a blank. This proposed method correlates with CH consumption of the Chapelle test. The loss of conductivity is calculated according to the following equation (Eq. 4):

$$\%LC = \frac{C_c - C_p}{C_c} 100 \quad (4)$$

where $\%LC$ is the % of loss in conductivity of a pozzolan evaluated, C_c the conductivity of the CH solution at the end of the test (blank) and C_p the loss in conductivity of the CH-pozzolan suspension at the end of the test.

2.5 Chemical shrinkage

The measurement of the chemical shrinkage is based on the fact that the volume occupied by the hydration products is lower than that of the reactants. This reduction in volume that occurs during hydration is known as chemical shrinkage. In general, when pozzolans are present the magnitude of the contraction is related to the magnitude of the hydration reactions of the cement plus the pozzolanic reactions [Bouasker 2008; Kocaba 2012; Pang 2013; Yodsudjai 2013].

In this research, the chemical shrinkage was measured in pastes with the same proportions of binders used in the SAI tests. The dilatometry (volumetric) method was applied according with ASTM C 1608, with some modifications. It was measured for 72 h at 60 °C of temperature to increase the rate of contraction [Geiker 1983; Pang 2013]. A w/c ratio of 0.5 was used to allow homogenous mixing in the mixtures with pozzolan replacement. The pastes were mixed for 5 min at 1300 rpm. Two replicates were tested in each sample. In each serie two blanks were included to verify that there were no errors due to sealing or significant expansions in the rubber stoppers. The chemical shrinkage per unit mass of cement at time t was estimated as (Ec.5):

$$CS(t) = \frac{[h(t) - h(60 \text{ min})]}{M_{\text{cement}}} \quad (5)$$

where $CS(t)$ is the chemical shrinkage at time t (mL/g cement) and $h(t)$ is the water level in the capillary tube at that time t (mL).

2.6 Linear regression analysis (LRA)

Simple and multivariable linear regression analysis were employed using the SPSS® statistical software, to identify possible correlations between the methods and the physicochemical characteristics studied. In Tab. 4 the configuration used in the analysis is shown. We used 1 to 10 dependent variables simultaneously to perform the LRA.

Tab. 4: Variables configuration in the LRA.

Depend variables	Independent variables
Chapelle test	Electric conductivity, physicochemical characteristics (oxides %, sizes and surface areas)
SAI (7 and 28 days)	Chapelle test, chemical shrinkage, electrical conductivity, physicochemical characteristics.

3 RESULTS AND DISCUSSION

3.1 Chapelle test

The results of the CH consumption per gram of pozzolan are presented in Fig. 2. It can be observed that materials known as highly reactive have the highest consumption, such as silica fumes (HS1 and HS2), sugar cane bagasse ash (CBC-200), finely ground glass (VM) and metakaolin (MK). Fig. 2 also shows a good performance of the two natural pozzolans (PN1 and PN2). It is well known that fly ash has a lower reaction rate than the rest, and because of

the short testing time the results for CV1-100 and CV2-100m are reasonable. However, in the case of the used MK, which is a commercial product, the consumption would be expected to be somewhat higher than that obtained from the test, since a metakaolin of medium reactivity has a consumption of about 850 mg of CH [Ferraz 2015; Quarcioni 2015]. In conclusion, no correlation between CH consumption and chemical composition, particle sizes or surface areas (BET or LD area) was found in simple and multivariate linear regression analysis.

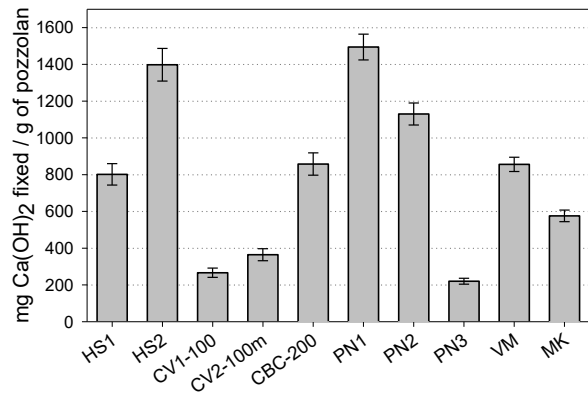


Fig. 2: CH consumption by pozzolans from the Chapelle test.

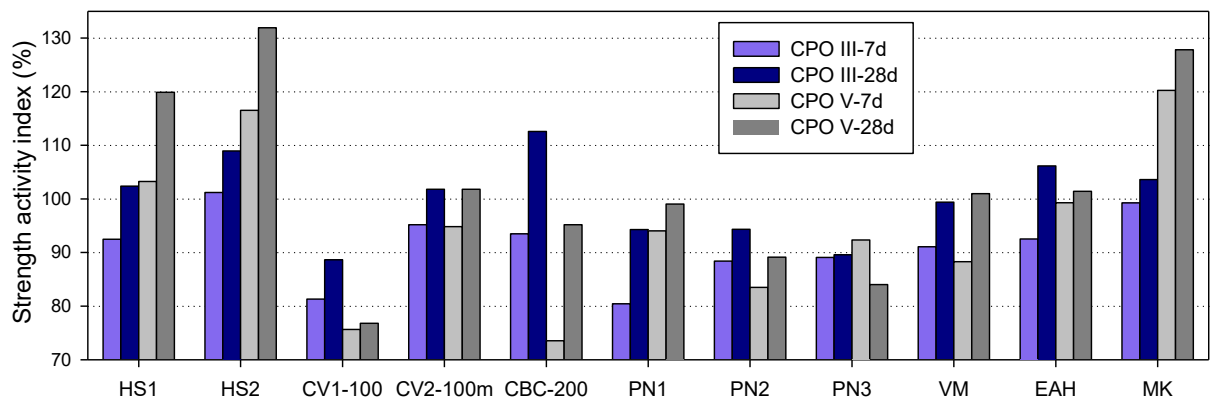


Fig. 3: Summary of SAIs at 7 and 28 days with CPO III and CPO V cements (20% of replacement, except in HS1 and HS2 is 10%)

3.2 Strength activity index (SAI)

In Fig. 3 the SAIs of the pozzolans at 7 and 28 days are presented. At 28 days the HS1, HS2, CV2-100m, VM, EAH and MK values of SAI with both cements are equal to or greater than 100%. This indicates that the influence of the materials on the compressive strength due to the pozzolanic and filler effect is higher than the dilution effect caused by the increase in the effective w/c ratio of the mixture. The effective w/c in the control mortar (0.484) is increased in the other mixtures due to the replacement of cement by the pozzolans. For example, with the replacement of 10% (with HS1 and HS2) the effective w/c is 0.537 and with 20% is 0.605. But the increase in a/c to maintain fluidity must also be considered. The CBC-200 showed a significant increase in water demand (126%), however, it presented a compressive strength value higher than the control with CPO III and only slightly lower with the CPO V. The pozzolans PN1, PN2 and PN3 exhibit acceptable reactivity, CV1-100 shows low activity probably due to its larger particle size. All pozzolans, except CBC-200 at 7 days with CPO V cement, exceed the 75% of the SAI value at 7 and 28 days, which is established by the ASTM C 618.

3.3 Electrical conductivity in CH-pozzolans suspensions

Test in CH-pozzolans suspensions of 0-24 h

The LC behavior in time of some pozzolans studied is shown in Fig. 4. There is a clear difference in the behavior of each pozzolan. HS1 and HS2 induce CH fixation rapidly (started at 1000 s). For example, HS2 show an LC of 86% at 24 h indicating that it has consumed most of the CH. Less reactive materials

such as CV1 and CV2 begin the ascent in LC after 10,000 s and only register 10% in LC at 24 h. The proposed test conditions are adequate to demonstrate the pozzolanic behavior of materials, however, the LC (24 h) present a very low correlation ($R^2=0.44$) with the CH consumption from the Chapelle test.

Correlation between the electrical conductivity and the Chapelle tests

When the reaction conditions of the EC tests (CH/pozzolan ratio and concentration) are modified changes that improve the correspondence with CH consumption are also observed (Fig. 5). For example, the LC of PN2 was underestimated, obtaining only 19% with the initial technique (Fig.4) whereas 60% was obtained with the current technique (Fig.5).

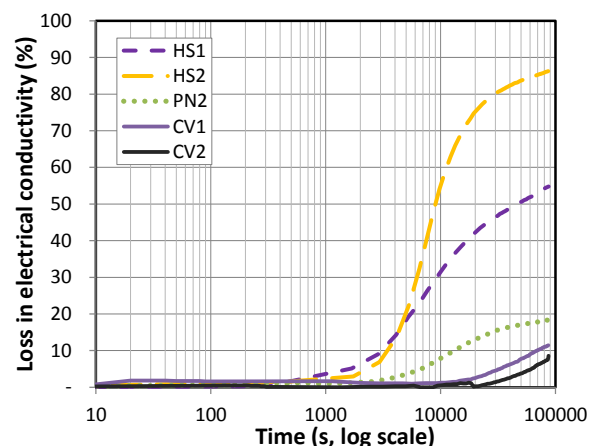


Fig. 4: Loss of EC in 800 mg/L CH and 800 mg/L pozzolan suspensions at 80 °C for 0 to 24 h.

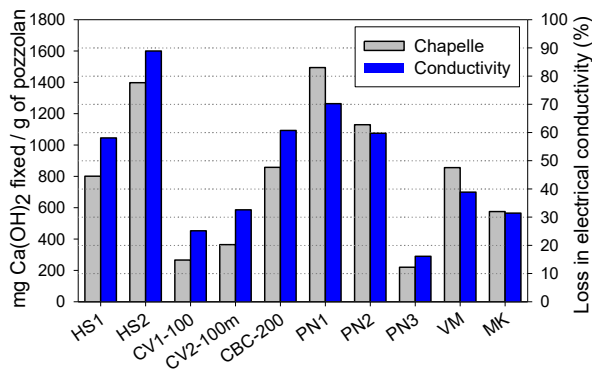


Fig. 5: Loss of EC in 10.57 g/L of CH and 4 g/L of pozzolan suspension at 85 °C after 16 h, and CH consumption from Chapelle test.

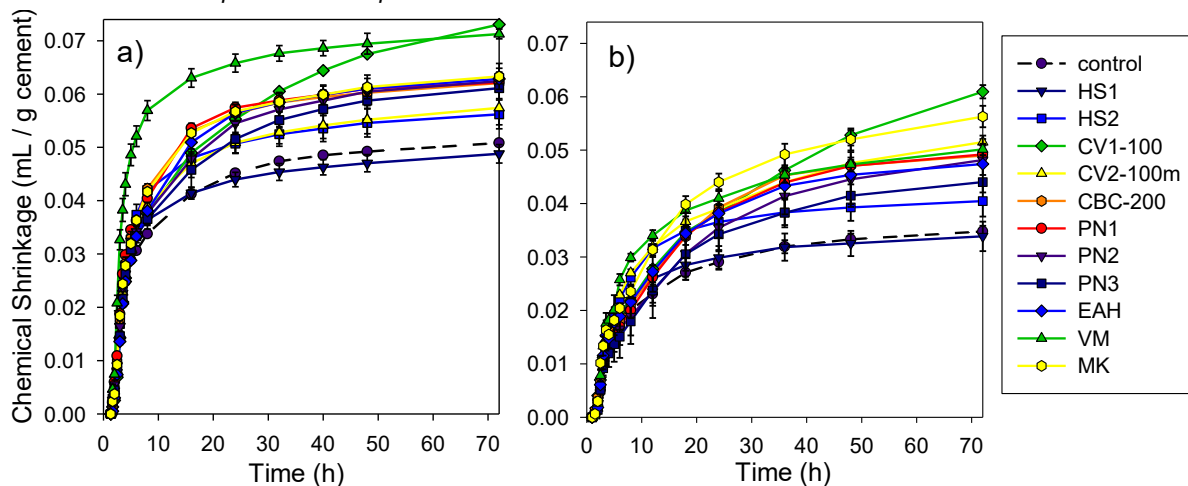


Fig. 6: Chemical shrinkage in pastes with w/c=0.5, replacement level of pozzolans of 20% (HS1 and HS2 is 10%) at 60 °C of temperature with, a) CPO III and b) CPO V.

The characteristics of the cement that allow a high initial resistance such as the higher content of C₃A, C₄AF and alkalis and smaller particle size also increase the rate and magnitude of the chemical shrinkage [Yodsudjai 2013]. As example, the CPO V shrinkage at 72 h was reached by the CPO III at only 10 h reaction. All pastes with pozzolan presented a greater shrinkage per g of cement when compared to the control, this is due, among other things, to the fact that retraction increases with the higher effective w/c ratios, by the formation of cement hydrates due to the filler effect [Bouasker 2008; Pang 2013]. In case of HS1 and HS2, a greater contraction was expected based on the reactivity observed in the other methods studied. It should be mentioned that bubbles were observed on the surface of the paste of the two replicates of HS1 and HS2 with both cements. These bubbles could be hydrogen since there are reports showing their formation in concrete with silica fume cured at temperatures higher than 40 °C, as a result of the reaction of residual metallic silica [ACI 234 Committee 2006]. The total volume of bubbles was arbitrarily subtracted from the shrinkage profile by applying a linear decrement in the range of 6-72 h. Therefore only the contraction at 72 h is considered correct. Based on this fact the obtained profile is a simulation. Even with such a correction the contraction values for HS1 and HS2 are low. This could be caused by the pressure produced by the gas which was present inside the paste limiting the absorption of water. It has been also reported a good correspondence between chemical shrinkage and

Some differences between the Chapelle and EC methods can be observed; however, in general there is correspondence between the values (Fig. 5) as dictated by the reasonable determination coefficient obtained ($R^2=0.84$).

3.4 Chemical shrinkage

In Fig. 6 the cumulative chemical shrinkage curves of the pastes are shown. The paste prepared with CPO III cement has a higher shrinkage rate than the paste prepared with CPO V cement and also has a higher shrinkage value at 72 h, this is 0.050 versus 0.035 mL/g, respectively. This occurs because each phase of the cement has a different temperature sensitivity [Pang 2013], so that the increase in shrinkage rates is not always proportional between cements.

calorimetry of isotherms of slags with the same type of cement [Kocaba 2012]. However, the correspondence between these methods can be achieved only in the same paste at the same temperature [Pang 2013]. In general, no relationship was observed between the chemical shrinkage at 72 h (Fig. 7) and the results of SAI or the Chapelle test, even when the results of the silica fume specimens were not considered for the analysis.

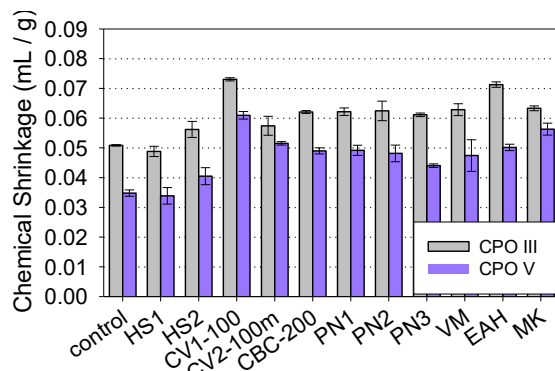


Fig. 7: Chemical shrinkage at 72 h (from Fig. 6).

3.5 Correlation between methods

The LRAs show that the %LC variable in conjunction with the %NaO variable can estimate the Chapelle variable with a 95% of confidence interval (Tab. 5). Other models with more variables involved and $R^2>0.90$ values were found; however, some of the

independent variables are not significant since the P values were higher than 0.05.

Although, the model 2 has a higher R^2 and a smaller standard error than model 1, for practicality model 1 is considered more feasible to estimate the CH fixed in the Chapelle test as only includes the independent variable %LC (Tab.5 and Fig. 8). In this research, no model was found that could predict the SAI. Because of that, it is inferred that the chemical composition and fineness of pozzolans is not sufficient to explain the development of compressive strength, especially with pozzolans of different types.

Although the CH/pozzolan ratio in the Chapelle test and the SAI test are close in value, there are differences between the CH solution and the cement mortar pore solution. In cement, the presence of alkali metal ions (Na^+ and K^+) decreases the solubility of CH approximately of 20 mmol/L to 1-5 mmol/L depending on alkaline activity [Donatello 2010]. Variables such as the amount of amorphous material in pozzolans or the contribution of filler effect could contribute to the estimation of the SAI; however, its determination requires techniques which consume more time and resources (Rietveld analysis, SAI with fillers).

Tab. 5: Estimated coefficients for the simple and multiple regression model to estimate the Chapelle variable.

	%LC	%NaO	cte	R^2	e
Model 1	1809.8 (0.001)		-75.7 (0.611)	0.849	185.4
Model 2	1872.8 (0.001)	84.7 (0.018)	-223.2 (0.082)	0.936	128.8

() values in parentheses are P values.

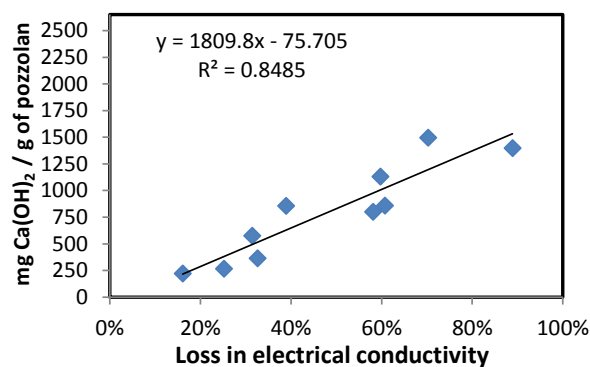


Fig. 8: Correlation between LC and CH consumption from Chapelle test.

4 CONCLUSIONS

Base on the simple and multivariable LRAs of the results the following conclusions can be drawn:

- There is no significant correlation between the physico-chemical characteristics of the studied pozzolans and their pozzolanic activity.
- A significant correlation between the Chappelle and the electrical conductivity methods was found ($R^2=0.84$). When the %NaO was considered in the analysis the correlation considerably improved ($R^2=0.93$). Therefore, the proposed method of electrical conductivity can be a feasible alternative

to predict the CH consumption from the Chapelle test.

- There is no significant correlation or model to predict the Strength Activity Index of the studied pozzolans. It is inferred that the chemical composition and fineness of the pozzolans are not sufficient to explain the development of the compressive strength.

5 RECOMMENDATIONS

In order to improve the correlation between the SAI and the other methods the inclusion of variables such as the amorphous content of the pozzolan and the filler effect has to be considered; thermally controlled strength test can be useful as well. Simultaneous measurements of pH and electrical conductivity can also be useful to improve their correlation with the Chapelle test results.

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