EVALUAREA ACTIVITĂȚII PUZZOLANICE ÎN SISTEMUL HIDROXID DE CALCIU – PUZZOLANĂ ARTIFICIALĂ
POZZOLANIC ACTIVITY EVALUATION IN ARTIFICIAL POZZOLANAS-CALCIUM HYDROXIDE SYSTEMS

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Results of interrelated tests for physical-chemical and microstructural properties of four synthetic pozzolanas evaluating the hydration rate in blends with calcium hydroxide are presented. The pozzolanic activity of silica fume, classified fly ash, raw fly ash and commercial metakaolin was estimated. Results showed a clear relationship between the calcium hydroxide consumption and the reactive phase content, specific surface area and porosity of the pozzolans. The calcium hydroxide-silica fume blend consumed 98% of portlandite after 21 days, whereas the system with metakaolin also presented an effective pozzolanic activity with 94% depletion. The fly ashes were the less effective pozzolans of the study.

Keywords: *D. Pozzolans; D. Mortar; C. Mechanical properties; B. X-ray methods; B. Porosity*

1. Introduction

In recent years a wide variety of industrial by-products such as fly ash, silica fume, metallurgical slags, rice husk or sugar cane bagasse ashes, among others, had been widely investigated with the objective of its utilization as partial cement replacement in the concrete industry. Reduction in wastes accumulation, and the technological advantages provided by these materials such as strength development and durability of structural and precast concrete cured under severe conditions [1-2], make these constituents a real and a very attractive alternative in the search of sustainable construction materials. These constituents can be regarded as artificial pozzolanas, as they comply with the ASTM definition of chemical reactivity with $Ca(OH)_2$ when finely grounded to form hydrated products similar than those generated by Portland cement [3].

The pozzolanic materials can be classified according its origin in natural or synthetic, and also according the differences in chemical composition or the needing for thermal or chemical activation; however, there are a number of intrinsic and extrinsic variables which must be taken into account when classifying them based on their pozzolanic potential, such as the vitreous network, particle size and distribution, specific surface area, porosity, $Ca(OH)_2$ content, temperature, humidity or alkaline hydroxides presence. In the other hand, pozzolanic reaction has been widely studied on pastes, mortars and concretes by several techniques demonstrating that the reactive fraction is activated with the portlandite released by the cement reaction to form C-S-H type products improving the mechanical strength and the impermeability of the binding matrix [4]. Nevertheless, there is discussion in the acceptance of some methods and its usefulness in predicting the behavior of the materials according workability or durability, which is due to the aforementioned factors. Therefore, it is also convenient to evaluate the effect of the pozzolanic activity on the setting times, pH evolution and the morphological and physical characteristics of the pozzolanas affecting the water absorption, and thus the reaction itself as hydroxides concentrations are diminished in the pore solution, impacting both the rheological properties and the paste ability to prevent corrosion on the metallic reinforcement of concrete.

In consideration of all these features, it is necessary to understand the relationship between the physical, chemical and morphological properties of artificial pozzolanas in order to establish a correct understanding on the mechanical and kinetic processes provoked in Portland cement hydration and its hydration products. This study presents a comparison of scientific characterization of four different synthetic pozzolanas, as a complement to a prior contribution conducted on four natural pozzolanic

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compounds [5], in order to increase the knowledge of the pozzolanic effects on construction materials based on Portland cement.

2. Materials and experimental procedures

Reactive grade calcium hydroxide with >95% of purity was used for the pozzolanic evaluation. The pozzolanic materials were: Condensed silica fume (**SF**), commercial metakaolin (**MK**), type C classified fly-ash from Boral Material Technologies with a mean particle size of 3 μm (CFA3) and type F raw fly-ash (FA) from a local thermoelectric in Nava, Coahuila, Mexico. Ordinary Portland cement (**OPC 40**) from CEMEX that fulfill ASTM C 150 and NMX-C-414 standards was used for reference purposes; also ASTM C 778 graded sand was used for mortars fabrication.

Chemical composition of the raw materials was obtained by X-ray fluorescence using a Bruker AXS equipment. Specific surface area and porosity were determined by adsorption of nitrogen with the BET method using a Quantrachrome Nova 2000e facility. The size particle distribution of the pozzolanas was measured via laser diffraction with a Malvern Mastersizer 2000 instrument using methanol as dispersant. X-ray powder diffraction (XRD) was used to evaluate the mineralogical phases and the vitreous fraction; a Bruker D8 Advance diffractometer with Cu *Kα* radiation (λ=1.5418 Å) was used for a scanning range of 10-50°2θ with a step size 0.05°2θ and an incidence time of 0.5 s/step. Compressive strength (CS) assays were performed after 7 and 14 days of curing according the standard test method described in ASTM C 311-93 [6] for cubic mortar samples of 5 cm (30% calcium hydroxide - 70% pozzolanas) cured at 55±1.7°C. The water/binder ratios (w/b) were fixed in a variable range for constant flow of 110 ± 5% (ASTM C 109) depending on the formulation prepared. The cubes were left to set isothermically at 20°C for 24 ± 2 h, the samples were later stored in a moist curing furnace at the temperature described above (55±1.7°C) until mechanical testing. Additionally, mortars of Portland cement partially replaced by pozzolanas (20%) were prepared and cured at 23±2ºC in a moist curing room (95±3% RH) for up to 56 days until strength tests.

To evaluate the pozzolanic activity, pastes of the same formulations of the mortars (calcium hydroxide-pozzolanas) were prepared and placed inside polyethylene bags; they were cured for up to 21 days in the same conditions as the mortars. The pastes were then saturated with acetone and manually grounded to pass the # 150 sieve mesh (100 μm). After stirring, the pastes were filtered using a # 41 Whatman paper and dried at 100°C for 30 min. The remaining lime was then determined by the alternative A test method procedure (Franke modified) depicted in ASTM C114-99 [7].

3. Results and Discussion

3.1. Physicochemical properties of the pozzolanas

Table 1 shows the chemical composition in main oxides of the materials used as binders and Table 2 exhibits its physical properties. It can be seen that in all cases, the sum of SiO_2, Al_2O_3 and Fe_2O_3 for the pozzolanas is higher than the 70% that ASTM standard [3] refers as the minimum for the materials to be used in concrete. It is interesting to note that the CaO content in the classified fly ash (CFA3) is greatly augmented in comparison to the raw type F fly ash (FA), while the SiO_2% is lower than the latter and can be almost considered an “acidic pozzolana” [8]. This could imply that the CFA3 has an enhanced “hydraulic potential” or ability to produce C-S-H products *per se*, relative to the other materials merely activated by the pozzolanic reaction. However, as ASTM does not specify microstructural or morphological characteristics that these materials should have, it is noteworthy to discuss the results of Table 2 in order to establish a correct approach to a comparative analysis of the pozzolanic activity.

Table 1

Chemical composition of raw materials, (%) by mass

OXIDE	OPC 40	SF	MK	CFA3	FA
SiO_2	19.28	94.05	52.66	48.51	60.42
Al_2O_3	5.03	0.13	42.29	25.30	27.28
Fe_2O_3	1.79	0.09	0.68	3.13	4.07
CaO	64.31	0.32	0.14	14.65	2.47
MgO	1.68	0.7	0.00	2.56	0.91
SO_3	3.07	0.00	0.03	1.07	0.34
Na_2O	0.23	0.88	0.00	0.52	0.62
K_2O	0.95	0.51	0.30	1.01	1.11
TiO_2	0.22	0.01	2.07	1.47	1.09
P_2O_5	0.09	0.07	0.09	0.21	0.09
Mn_2O_3	0.04	0.04	0.00	0.06	0.02
SrO	0.07	0.00	0.00	0.30	0.04
LOI 950°C	3.24	2.91	1.03	0.69	1.00
Sum	**100.00**	**99.71**	**99.29**	**99.48**	**99.46**
Na_2O eq.	0.86	1.22	0.20	1.18	1.35
$SiO_2+Al_2O_3+Fe_2O_3$	26.10	94.27	95.63	76.94	91.77

It can be seen in Table 2 that except for the non-classified fly ash (FA), the other three pozzolanas have a particle size distribution that ranges totally under 45 microns, however the specific surface area is significantly higher in the cases of the SF and MK. It is important to mention that the siliceous pozzolana was condensed to increase its bulk density perhaps forming agglomerates; therefore, its average particle size (11 μm) is higher than the normally reported for this kind of material [9,10]. Special attention

should be made to the CFA3 that denotes an average particle size as low as 3 μm but reaches only 2.5 m^2/g of BET fineness; this could be related to the reduced porosity (or a more solid structure) of 2.8% observed in Table 2 relative to the SF and MK (>35%), suggesting a lower reactivity than those materials probably for a more severe thermal shock during their respective thermal processing that lead to less porous particles with smooth surfaces. It can be also seen in Table 2 that the density of the pozzolanas is somewhat similar in the four cases and is slightly lower than that of the Portland cement, signifying a potential increase in the total volume of cementing materials for a same cementitious mass in the fabrication of concretes, which could improve the impermeability and durability.

Table 2

Physical properties of the cementing materials

Material	Density (g/cm^3)	Average particle size (μm)	BET specific surface area (m^2/g)	% Passing sieve 325 (45 μm)	BET porosity (%)
OPC 40	3.05	16.0	3.8	92.2	4.1
SF	2.16	11.0	25.8	100.0	35.7
MK	2.56	5.9	21.0	100.0	35.2
CFA3	2.52	3.0	2.5	100.0	2.8
FA	2.11	59.4	3.2	35.2	1.6

Figure 1 shows the particle size distribution of the artificial pozzolanas simultaneously with the OPC 40 included as reference. It can be seen a narrower and finer granulometric distribution for the CFA3 in comparison to the other materials, which coincides well with the lower average particle diameter of this pozzolana presented in Table 2. Similarly, the curves for the MK and the SF denotes somewhat similar distributions, that are also a finer granulometry than that of Portland cement with 5.9 and 11.0 μm of average particle size (see Table 2), respectively. In the other hand, the FA shows a far more extended curve in the *x* axis than the other materials revealing a coarser granulometry for a higher average particle size, that explained a lower BET fineness (3.2 m^2/g). These results could be interpreted as the FA being the less reactive pozzolan of the study by means of physical characteristics.

3.2 Mineralogical characteristics

Figure 2 shows the XRD spectra of the four pozzolanas where it can be well appreciated the reflections of the amorphous hump between 15 and 30°2θ in all cases as a consequence of the reactive vitreous network. It is also presented the phase-mineral compositions for each material. It is clear that according the intensity of the amorphous halo; the SF could promote a better reactivity for a larger vitreous content than the other materials, reaching ~100 cps with mineral inclusions of quartz

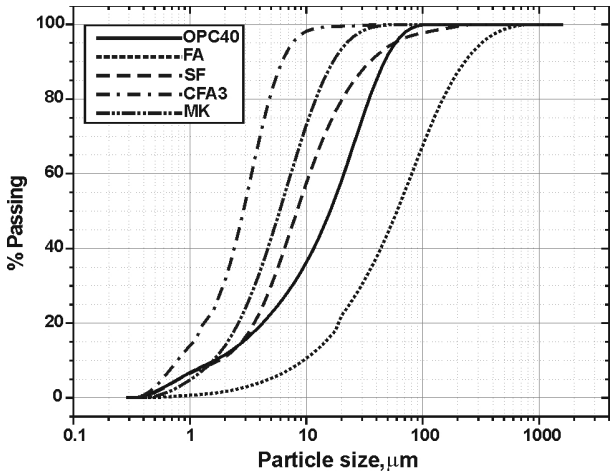

Fig. 1 - Particle size distribution of the artificial pozzolans.

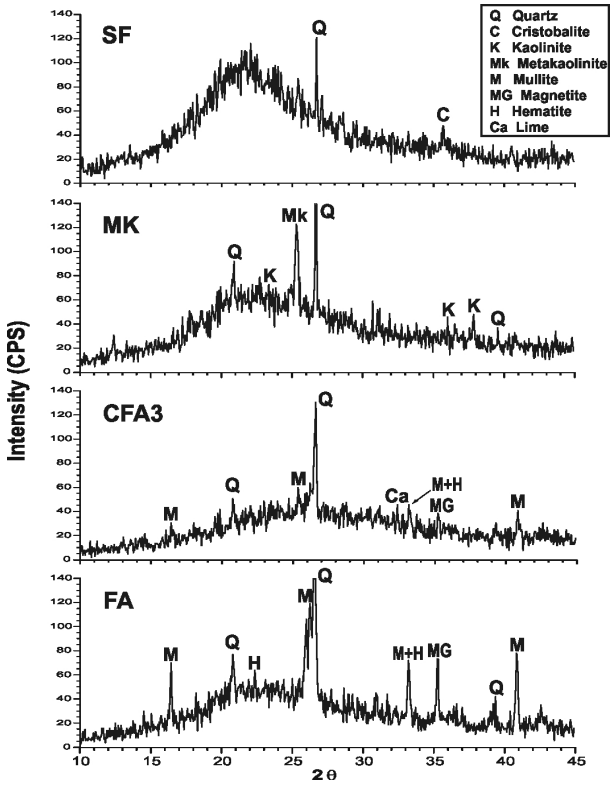

Fig. 2 - XRD patterns of the artificial pozzolans.

and some cristobalite. The hump for the MK reached 70 cps of intensity with disordered kaolinite (Mk), kaolinite and quartz as the crystalline fraction. Although the crystalline phases possess poor dissolution and consequently a poor hydraulic behavior [11], the compounds with disordered or metaestable state as in the case of cristobalite and Mk presents indeed some reactivity [5].

On the other hand, the CFA3 and FA patterns in Figure 2 exhibited a diminished intensity of the halo (~42 cps) relative to the SF and MK; however, the pattern of the non-classified fly ash indicated a higher content of crystalline phases, revealed by the presence of hematite and

Table 3

Physical properties for systems of 30% calcium hydroxide–70% pozzolans

Pozzolan used	Mortars: w/b ratios for 110±5% flow	Mortars: *Compressive Strength (MPa) 7 d	Mortars: *Compressive Strength (MPa) 14 d	Pastes: w/b ratios for Normal Consistency	Pastes: Setting times (h:min) Initial	Pastes: Setting times (h:min) Final
SF	0.53	12.8	17.0	0.43	2:13	2:54
MK	0.45	12.2	15.2	0.36	1:39	2:35
CFA3	0.46	9.4	10.4	0.25	3:10	3:57
FA	0.55	3.9	5.2	0.29	3:05	3:42

** Determined according ASTM C-311-93 for curing at 55ºC*

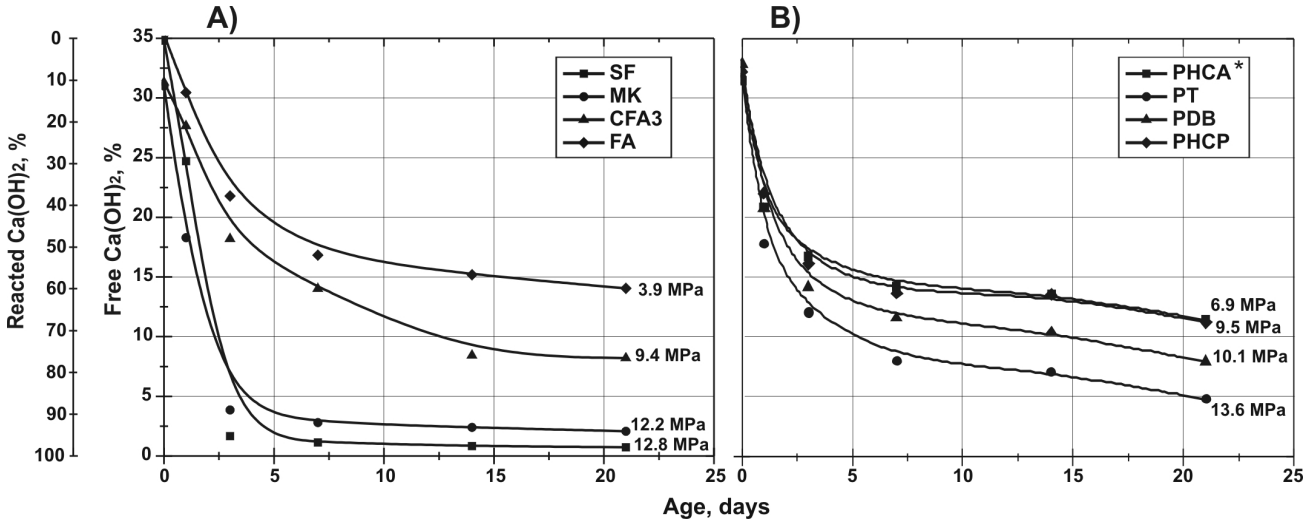

Fig. 3 - $Ca(OH)_2$ consumption obtained by the Modified Franke Test Method for 1, 3, 7, 14 and 21 days. (A) Results from artificial pozzolanas; (B) Results from natural pozzolanas adapted from [5]. Strength data: Mortars at 7 days of curing. *Abbr: no specific meaning

the broadened and/or increase of the main peaks of mullite, magnetite and quartz (encountered also in the CFA3) at 25.9°, 35.5° and 26.6°2θ, respectively. The latter shows that according the mineralogy and/or vitreous fraction, the fly ashes of this study represented the less reactive materials, while the SF had the best characteristics followed by the MK. However, between the two coal combustion materials, the CFA3 seems to possess a better reactivity than the FA due to a lower content of crystalline phases and probably a lower oxidizing state, evidenced by the occurring of hematite (Fe_2O_3) in the FA from the oxidation of magnetite (Fe_3O_4).

3.3. Pozzolanic activity and Strength development

Table 3 shows some physical properties of the mixes studied where it can be appreciated the w/b ratios used for the pastes and the mortars. It should be noted that water requirements for same workability increase as the specific surface area of the powders also increase, therefore the w/b ratio in the case of the pastes is higher for materials with SF (see Table 2) followed by the MK and finally the fly ashes. However, for the mortars the w/b was higher for the FA; considering the results of section 3.1 no explanation was found for this, taking also in consideration that the spherical morphology of fly ash should represent a better lubrication between particles [4]. In the other hand, it is interesting to note in Table 3 the initial setting time spanned more than 3 h in the case of the pastes with FA and CFA3, that represented almost the double of time relative to the MK and practically one hour more than the SF; however, it only takes a period of 37 min in the case of the compound with FA to reach the final setting time, implying very slow initial reactions but being accelerated once they have begun.

Figure 3 presents the results of the pozzolanic activity as a function of the consumed hydrated lime obtained by the Modified Franke Test Method (Alternative Test Method A) described in ASTM C 114-99 [7]. The tendency of the curves in Figure 3 corresponds to a potential decreasing curve; therefore, its equations (Table 4) allow to interpret the kinetic of the pozzolanic reaction for each case from the time the powders are mixed with water. In general, the results in Figure 3A display a good correlation with the properties of the materials already discussed in

sections 3.1 and 3.2: It can be seen that after one day the MK greatly diminishes the initial $Ca(OH)_2$ to 18.5% that meant ~48% of the total calcium hydroxide to produce phases of the type C-S-H. In contrast, the other pozzolanas oscillated from 13-29% of consumed $Ca(OH)_2$ for the same time, indicating a strong initial reactivity by the calcined kaolinite.

After 3 days, the SF increase significantly the rate of the reaction, decreasing the free $Ca(OH)_2$ to only 1.5% (95% of depletion). This trend is maintained for further ages reaching 97.8% of reacted portlandite after 21 days, representing the highest consumption of the study. Meanwhile, the MK showed a somewhat similar behavior than the SF, exhibiting also a pronounced slope in the corresponding curve of Figure 3A reaching 89% of reacted $Ca(OH)_2$ at 3 days and 94% after 21 days, suggesting also a steady behavior after this age. These results evidences that these two pozzolanas present the highest reactivity of the study, as demonstrate the powers of the equations in Table 4 and the strength values in Table 3. In contrast, the fly ashes reached after 3 days contents of 21.5 and 18.5% free $Ca(OH)_2$ for the FA and the CFA3, respectively (38 and 48% of depletion), while its consuming of calcium hydroxide after 21 days is 76 and 60%. Nevertheless, attention should be made to the shape of the CFA3 and FA curves: less pronounced slope but with tendency to decline after 21 days, especially for the FA. It is important to mention that ASTM C 618-89 limit the compressive mechanical strength at 7 days to 5.5 MPa minimum; it can be seen in Table 3 that all the studied mixtures exceeded notably this requirement, except for the binder with FA that merely surpassed this value until 14 days as a consequence of its limited reactivity.

Table 4

Correlation of the pozzolanic reaction curves for systems in Figure 3

Pozzolan used	Equation and Corr. Coef.
SF	$y = 7.6256 x^{-0.824}$ $R^2 = 0.87$
MK	$y = 10.15 x^{-0.557}$ $R^2 = 0.92$
CFA3	$y = 21.003 x^{-0.269}$ $R^2 = 0.87$
FA	$y = 25.533 x^{-0.186}$ $R^2 = 0.93$
PT*	$y = 16.004 x^{-0.3385}$ $R^2 = 0.97$
PDB*	$y = 19.107 x^{-0.2563}$ $R^2 = 0.98$
PHCP*	$y = 20.89 x^{-0.1927}$ $R^2 = 0.98$
PHCA*	$y = 20.757 x^{-0.1817}$ $R^2 = 0.99$
** Adapted from [5] Abbrev: No specific meaning.*	

Figure 3 draws a comparison of the synthetic materials studied with the results of the activity of four different natural pozzolanas (incise B) performed by the same authors and reported elsewhere [5]. Those materials were dried at 110°C for 24 h, crushed, pulverized and grinded until 90 to 94% of the material passed through a 325 mesh sieve (45 μm). The chemical composition in terms of $SiO_2+Al_2O_3+Fe_2O_3$ wt% were 81.2, 79.6, 86.5 and 84.7% for PT, PDB, PHCA and PHCP, respectively. In that report, it was concluded that the pozzolana denominated PT was the most reactive because of its higher specific surface area, since the chemical composition, the glassy structure content and the particle size distributions were very similar among all the studied materials of igneous origin.

It can be seen in Figure 3 that except for the MK, the natural pozzolanas consume portlandite more rapidly after 24 h than the synthetic materials; however, after 3 days the SF and MK combine $Ca(OH)_2$ much faster than the PT at a rate of more than 20% (see equations in Table 4). It is noteworthy the 7 day strength for the PT-$Ca(OH)_2$ mortars (13.6 MPa) that surpass that of the MK and SF systems even for more than 10% less combined portlandite than the former. This behavior could be attributed to the significantly higher specific surface area of 63.1 m^2/g in pozzolana PT [5] than that of the artificial pozzolans reported in Table 2.

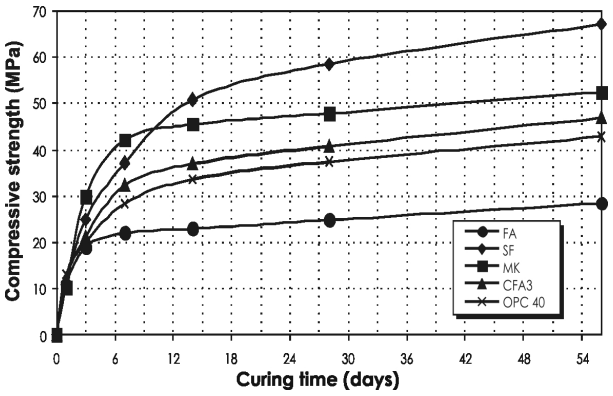

Fig. 4 - Strength of partially replaced Portland cement mortars (20% pozzolan) cured at 23±2°C.

Figure 4 presents the results of compressive strength for the partially replaced Portland cement mortars that fit well with the pozzolanic activity discussed from results in Figure 3 and Table 4: After 3 days the MK compound reach 30 MPa followed by the SF mortar (25 MPa), both surpassing the 100% Portland cement system and the samples with fly-ashes. This trend is maintained for up to 7 days; however, after 14 days the SF accelerates the pozzolanic reaction (note the pronounced slope) and reaches more than 50 MPa (44 MPa for the MK mortar) well above the reference OPC system (33 MPa). The increasing of strength for the SF mortar is sustained for up to 56 days (67 MPa); however, the tendency in the curves indicates further gain in

all cases. It is clear that the SF, MK and CFA3 enhance the mechanical properties at later stages of curing by means of C-S-H formation by pozzolanic reaction improving the performance of neat Portland cement mortars (42 MPa at 56 days). Nevertheless, the mortars with FA reached only 28 MPa for all the studied period.

4. Conclusions

- There is a direct relationship in the portlandite consumption and the strength development with the reactive vitreous content and the specific surface area of the pozzolana: As the surface area increases and the crystallinity of the pozzolana decreases, the $Ca(OH)_2$ consumption and the strength are augmented.

- Calcium hydroxide-SF system consumed 98% of the initial amount of portlandite at 21 days of curing. SF being the pozzolana with higher surface area and the lowest content of crystalline phases, while the system with MK consumes 94%, the CFA3 combines 76% and the FA transforms only 60% of portlandite by means of pozzolanic reaction.

- The pozzolanic and strength performance for the studied materials can be summarized as follows: SF>MK>classified fly ash>raw fly ash.

- This information is useful to establish the kinetics of the pozzolanic behavior of the artificial pozzolans studied.

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