Activación de arcillas de bajo grado a altas temperaturas

Activation of low grade clays at high temperatures

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Resumen

Se presenta una propuesta de producción de puzolanas artificiales a partir de activar arcillas de baja pureza, como alternativa de producción de Metacaolín. Se trabajó básicamente con tierra rica en minerales arcillosos, principalmente caolín. Este material fue sedimentado y luego calcinado a 900 grados Celsius. Igual proceso se realizó al material original sin sedimentar. Producto de la calcinación disminuyó considerablemente la superficie específica, y por ende la actividad puzolánica, que fue evaluada monitoreando el consumo de HC en pastas a varias edades, y la resistencia a compresión en morteros. El material calcinado, aparentemente inerte, fue molido hasta una alta finura. Se introdujo una serie experimental con ceniza de paja de caña, como referencia de puzolana anteriormente estudiada. Las arcillas calcinadas molidas incrementaron cuantiosamente su actividad puzolánica, caracterizado por un mayor consumo de HC en pastas, y una mayor resistencia a compresión en morteros. Aparentemente este cambio se debe al efecto del molido sobre la reactividad de los suelos arcillosos calcinados. Los mejores resultados se obtuvieron para las muestras sedimentadas antes de calcar. La resistencia a compresión de morteros, sustituyendo un 30% del peso de cemento por dicho material, es similar al control (100% cemento) a 7 días, y mayor a 28 y 60 días. Aunque dicha sustitución no disminuye la porosidad total, se disminuye la sorptividad, principalmente en muestras producidas con material sedimentado calcinado y molido. Posiblemente este fenómeno ocurra por un proceso de refinación de poros capilares inducido por la precipitación de productos de la reacción puzolánica.

Palabras Clave: Puzolanas, arcillas calcinadas, microestructura, porosidad, sorptividad

Abstract

This paper introduces a proposal to produce artificial pozzolans by means of activation of low grade clays, as an alternative to metakaolin production. Basically the work considered clay mineral enriched soils, mainly kaolin. Such material was sediment and later calcined at 900 Celsius degrees. The same process was conducted with non-sediment material. Due to calcinations, the specific surface decreased significantly, and therefore, its pozzolanic activity, which was assessed by monitoring the CH consumption in cement pastes of several ages, as well as compressive strength in cement mortars. Calcined material, apparently inert, was ground until achieving high finesse. An experimental series made of sugar cane straw ash was introduced, as a reference to the pozzolans previously studied. Ground calcined clays increased its pozzolanic activity at a huge extent, which is characterized by a higher consumption of CH in cement pastes and by a higher compressive strength in cement mortars. Apparently this change takes place due to grinding effect on the reactivity of calcined clayey soils. The best results were obtained from sediment samples before their calcinations. The compressive strength of cement mortars, replacing a 30% the cement weight by such material, is similar to the control (100% cement) at 7 days, and higher at 28 and 60 days. Although such replacement does not decrease total porosity, it does decrease sorptivity, mainly in samples produced with calcined and ground sedimented material. Probably this phenomenon occurs because of pores capillary refining process induced by the precipitation of products of pozzolanic reaction.

Keywords: Pozzolans, calcined clays, microstructure, porosity, sorptivity

1. Introduction

1.1 Work Context

Nowadays, due to economical and environmental reasons, concrete industry is looking after an optimization to replace clinker cement by other supplementary cementitious materials. Such is the case for pozzolans, which constitute a possibility of achieving a reduction of cement consumption,

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either as addition in the cement production process or as its replacement in the concrete elaboration. In both cases, it's well known that pozzolans modify concrete physical and mechanical properties, which supply diverse benefits to the use engineers, civil constructors and researchers design for it.

Depending on the source, Pozzolans can be classified as natural or artificial. Natural pozzolans are actually rocks existing in nature and, to be used they do not require anything else but a grinding process, their main characteristic is its chemical composition rich in silica, aluminum and iron content. Such content is not uniformly distributed on the Earth planet however, there are some areas having plenty of them, especially in the so called "fire belt" (Martirena, 2003). On the other side, artificial pozzolans are sub-products of high energy consumption processes, either due to high temperatures required by calcinations or raw material combustion processes, or the high technological cost involved. Artificial pozzolans are mainly produced by developed countries, where materials such as fly ash, silica fume, blast furnace slag and calcined clays (metakaolin) are broadly accepted for the production of blended cements.

Pozzolanic reaction is characterized by the consumption of calcium hydroxide (CH) by reactive silica or alumina contained in pozzolans, forming calcium hydro silicate (C-H-S). Gel content of reactive products is generally increased, providing a minor pores capillary and therefore, higher strength and durability (Taylor, 1990; Feldman, 1984; Agarwal, 2006).

The use of pozzolans is restricted because of limited worldwide availability as well as relatively low reactivity of some of them. Such is the case of fly ash (Thomas et al., 1999) together with the above mentioned technical-economic aspects which threaten a proliferate use of pozzolans, being this phenomenon even more serious in undeveloped countries.

1.2 Pozzolans made out from calcined clays

Presently, one of the most used and studied supplementary cementitious materials are calcined clays in form of metakaolin.

Such materials are obtained from thermal-treated natural kaolin mineral deposits, which have excellent pozzolanic properties mainly because of their chemical composition, amorphous structure, and high specific surface. During this thermal treatment, factors such as temperature, calcinations time, shape and size of particles influence metakaolin reactivity (MK) (Bich et al., 2009; Gonçalves et al., 2009; Samet et al., 2007).

Clay calcination temperature affects the pozzolanic properties of resulting material. The major reactivity is reached when calcination process causes dehydroxylation, which leads to a collapsed and untidy clay structure. The optimal activation seems to depend on the material purity level and its involved minerals. Some authors have widely reviewed this parameter during previous researches, concluding that optimal activation temperature for kaolin is the range between 630-900 °C (Fernandez, 2009; Sabir et al., 2001).

MK is well known by its contribution to concrete improvements, when used as partial substitute of Portland cement. Studies have proved that at early age mortars and concrete strengths are increased, due to filler effect and accelerated cement hydration, which results in a porous structure refinement (Agarwal, 2006; Lawrence et al., 2005). Besides, its contribution in reducing alkali-silica reaction has also been demonstrated, as it reacts under the presence of water with the calcium hydroxide contained in the porous solution, to create in this way cementitious calcium hydro silicate phases.

The inconvenience of MK use is centered on the availability of pure Kaolin mineral clays, as raw material for its production, besides high costs of energy involved in the calcination elaboration process. A feasible solution to decrease such disadvantage factor could be the use of lower grade clays as well as an effective energetic production process during calcination.

Former experimental studies contribute to elaborate a more feasible calcination process for these clays. Such is the case of solid fuel block matter, which guaranteed the calcination process at temperatures reaching 900 °C (Martirena, 1999).

Taking this factor into account, an experimental kiln was elaborated to burn a densified biomass combination with clay, in order to collect waste material from this process and evaluate its potential as pozzolan. After a detailed study of clay resulting from the combustion of solid fuel block, it was found that clay had a deficient pozzolanic activity. Uncontrolled burning conditions provoked the presence of high content of non-calcinated material and carbon waste present in the resulting ashes, thus seriously affecting its reactivity. A decision was made: to process and study the clay material separately.

A previous study, conducted for other purposes, employed clay from the same source, the same sedimentation process and thermal treatment (Fernandez, 2009). The study demonstrated that when calcination temperature rose from 600 ° C to 1000 ° C, the specific surface decreased (approximately from 40 m²/g to less than 5 m²/g), basically because of particle agglomeration and due to the liquid phase sintering phenomena. Therefore this clay reactivity was significantly affected. The present research includes ground clays resulting from 900 ° C calcination, in order to reverse such phenomenon.

This research poses a solid proposal: the utilization of local materials, in this case of a clayed soil containing low grade kaolinite mineral, as a natural source for production of highly reactive pozzolans resulting from a calcination thermal treatment. Such clay soil is widely present in Cuba (Delgado, 2003), which ensures the availability of raw material for possible production of this pozzolan.

The energetic consumption involved in these clays calcination process, intended to achieve highly reactive pozzolans, can be developed in an effective way by employing as alternative fuel a biomass resulting from agro-industry processes. That is why the solid fuel block allows the development of a feasible cost effective calcination process which is less dependent on an external energy source (Martirena et al., 2007). A fundamental fact is the employment of appropriate technologies leading to an efficient alternative fuel combustion process,

for instance the vertical shaft brick kiln for elaboration of ceramic bricks, because in this way, a guaranteed reduction of coal content in waste ashes is achieved, thus increasing the pozzolanic properties of burned material.

This paper introduces a work program for the study and understanding of elaborated pozzolans, in order to introduce its application as a substitute for ordinary Portland cement (OPC). The same study consider stages from clay sedimentation, calcination and grinding processes up to its addition and study in cement pastes and mortars.

Cement pastes were elaborated to study the effect of employed additions, in its fresh state as well as for the micro-structural changes in its hardened state. On the other hand, mortars were elaborated to evaluate the influence of such materials on compressive strength and durability.

Durability analysis was developed by means of the capillary water absorption technique. The effect of concrete quality, in locations close to exposed surfaces, is closely linked to the grade and type of aggressive agents that can penetrate it. Such properties controlling the transport of these materials inside the concrete mass or towards the reinforcement are of great relevance such as permeability and sorptivity. The extent a concrete absorbs water in contact with its surface is related to several durability aspects. Two basic parameters related with absorption are effective porosity (water mass required for material saturation) and sorptivity (penetration extent) (Khelam, 1988; Hanzic and Ilic, 2003; Muhammed Basheer, 2001).

2. Materials and experimental methods

2.1. Raw Materials

Studies are developed at the Laboratory of Construction Materials (LMC), EPFL, in Switzerland in cooperation with the Centre for Research and Development of Structures and Materials (CIDEM), UCLV, Cuba. For elaboration of pastes and mortars Normo 3-cement was employed, which is produced in Switzerland, with a 32 MPa compressive strength at 28 days that is ranked as Type I, by the American regulation ASTM C150-2. A summary of its physical composition and some physical features are indicated in Table #1.

Two types of calcined clays were basically studied: clayey soil, designated as T120 and sedimented clay, resulting from such soil settlement designated as AS-900. Both materials were calcined at 900 °C during one hour, under controlled temperature conditions by a laboratory furnace and, ground during 120 minutes by a ball-mill with 600-liters capacity.

The material used to elaborate both calcined clays consisted in a clay soil from the county central zone, traditionally used for the production of ceramic elements, mainly bricks and ceramic blocks. This soil is characterized by containing a clay mineral mixture, basically kaolinite and montmorillonite, all of them with a low purity grade (Fernandez et al., 2008).

Another addition employed was sugar cane straw (SC), in order to conduct a comparative analysis using a previously studied pozzolan (Martirena et al., 2009), which was ground under same conditions that calcined clays. Besides, only in order to compare the action of active mineral additions, calcareous filler (F) was employed as a reference. The later was ground during 60 minutes, until reaching a similar finesse than the rest of additions. Physical properties of all additions employed in the present study are also shown in Table #1.

Tabla 1. Composición química y propiedades físicas de los cementos y adiciones utilizadas
Table 1. Chemical composition and properties of employed cements and admixtures

Propiedades/Properties	CP N3	SC	T120	AS-900	F
SiO ₂	21.01	70.40	57.74	43.89	0.20
Al ₂ O ₃	4.626	2.42	18.71	24.73	0.50
Fe ₂ O ₃	2.603	1.38	7.07	11.13	0.13
CaO	64.18	9.76	1.85	1.38	54.78
MgO	1.823	2.28	1.80	2.63	0.27
SO ₃	2.78	0.35	0.02	0.08	0.1
K ₂ O	0.939	3.60	0.65	1.10	0.10
MnO	0.029	0.10	0.12	0.14	0.01
Na ₂ O	0.197	0.23	2.68	1.99	0.10
PPI	1.26	3.97	8.57	9.81	43.00
Álcalis/Alcali % (Na ₂ O) eq	0.82	2.60	3.11	2.70	0.17
Superficie específica/Specific surface (m ² /g)	0.79	3.25	7.05	5.19	1.09
Densidad/Density (g/cm ³)	3.17	2.58	2.86	2.59	2.70
Tamaño medio de grano/Average grain size (μm)	28.21	5.49	3.83	7.47	13.01

In Figure 1, granulometric curves of all employed additions and cement obtained by means of laser granulometry, studied by this research, are compared. It is noticed that Portland cement 3 (CP-N3) has at 28.21 μm the thicker average particle size. By means of respective treatments on additions, it was possible to reach and to employ finer materials than the used Portland cement, reaching an average particle size: SC 5.49 μm , T120 3.83 μm , AS-900 7.47 μm and F 13.01 μm .

The fact that sediment clay, after calcination and blending processes (AS-900), yields higher particle sizes regarding the non-previously calcined and ground material (T120) is due to the latter has small impure quartz particles, coming from the original soil, which act as blending agents in this process and they are harder than the rest of materials involved. On the other side, when eliminating these quartz particles by means of sedimentation process, material obtained increased its clay fraction and consequently also the plasticity associated to such materials. It may have lead to a higher agglomeration among the clay grains during blending process, enabling the presence of a small group of particles of sizes higher than 100 μm in AS-900 material.

Figura 1. Distribución de tamaño de partícula de las materias primas
Figure 1. Particles size distribution of raw materials

2.2 Experimental Method

The present study was generally divided into the following experimental phases:

Phase 1: Sedimentation and calcination process of a clay soil and sediment clay.

The settlement process was developed due to the need of studying purified clay coming from a clay soil. In order to conduct an effective process, to reach the smallest grain sizes as possible, it was necessary to deflocculate clay particles. Sodium silicate was employed as deflocculating agent, at a 0.02% concentration, due to its dispersing features exposed by producers. For calcination, materials were arranged in melting pots inside a laboratory muffle. The temperature was increased up to 900 °C, at a rate of 300 °C/hour, and after reaching limit it was maintained at a constant rate during 1 hour.

Phase 2. Activation of calcined clay, sugar cane straw ash and calcareous filler by means of grinding.

Once calcined material was obtained, it was necessary to conduct an activation process in order to reverse problems found in its pozzolanic reactivity. Since such deficiencies rose due to a considerable decrease of specific surface, mainly because of particles agglomeration and due to the liquid phase sintering phenomena, it was decided to conduct a grinding process.

On the other hand, materials would be assessed when replacing a 30% of ordinary Portland cement in the elaboration of cement pastes, mortars and concrete. By employing a lower average particle size for such replacement, besides guaranteeing a higher matrix compaction it would also affect water demand and therefore, rheological properties of afore mentioned systems, mainly its fluidity.

In order to assess the finesse effect of different cementitious systems, a Marsh cone test was developed on cement pastes – addition, as established by the Cuban regulation NC 461:2006 which is based on the American regulation ASTM C 939-97: “Standard test method for flow of grout for preplaced – aggregate concrete (flow cone method)”. The study was conducted on a calcined non-sedimented clay soil, since it was the finest addition material, as it was proven later. To this effect, cement pastes were made with 0.4 steady water – binder ratio and a 30% replacement rate for blended systems. 60 and 120 minutes grinding time were basically assessed, and the minimum chemical additive percentage was determined for them in order to reach a desired fluidity (30 – 40 seconds) the same as in the cement control paste without mineral addition.

For each percentage of additive, determined in accordance with the total weight of binder (cement + addition), four test repeated samples were made. MAPEFLUID N-200 was employed as super-plasticizing liquid admixture water reducer. Results obtained are shown in Table 1.1 and depicted in Figure 1.1.

Phase 3: Study on cement pastes of reactivity for different materials

All cement pastes were made by employing Normo 3 cement as main binder. All of them, except pure Portland mixture, employed levels of 30% weight cement replacement. The ratio 0.4 % water / binder were maintained constantly for all cases.

Reactivity in calcined clay pastes, as well as for the rest of additions, was studied in time by means of the calcium hydroxide's (CH) consumption evolution. The peak follow-up of portlandite in cement pastes by means of x-rays diffraction (Figure 2), its quantification by means of thermo-gravimetric analysis (Figure 3), and the amount of chemically combined water, allowed the detection of pozzolanic activity at 1, 7 and 28 days of age.

The reactivity blending effect on calcined clays was also assessed by thermo-gravimetric analysis. Two experimental series were employed, designated as T0 for clay soil and AS-0 for sediment clay, both calcined and non-ground materials. Results are shown in Figure 5.

In order to study the effect of mineral additions on material porosity, all cement pastes were evaluated at 7 and 28 days by a mercury intrusion porosimeter. The results of such experiment are expressed in Figure 6, where porosity accumulated values are related in function of pore size.

Phase 4: Application and Study on mortars

40x40x160-mm-mortar specimens were made according to procedures of regulation EN 1015-2:1998/A1:2006, by employing as main binder material Normo 3 Portland cement. Cement was replaced in a 30% by additions, always employing water binder ratio of 0.5. Later the flexural and compressive strength tests at 1, 7, 28 and 60 days were performed according to requirements EN 1015-11:1999/A1:2006. Standard Sand (SIA 162) was employed for all mortar samples.

The following day specimens are unmolded and arranged for conservation at 30 °C waiting for the test date. Figure 7 shows the average of six compressive strength values for each mortar sample at different test ages.

Hydration rate of all mortar samples were determined at 7 days, in order to correlate the compressive strengths values with the reactivity showed by pozzolans at such age. Hydration rate, expressed in percentages, is referred to the volumetric comparison of anhydride cement, at a given test age, in relation with the original formula (Scrivener, 2004). Therefore, the mortar samples were prepared as polished sections to be analyzed by the electronic scan microscope. By means of images analysis from the microscope and by using specialized software the hydrated and anhydride phases, pores and aggregates were identified and quantified. Figure 10 shows the results obtained from this analysis.

The present research included a capillary water absorption test in order to determine different elaborated mortars' sorptivity, and later evaluate the effect of pozzolans employment on material durability. 15 cm height x 15 cm diameter concrete cores were taken from a 15x15x15 cm. cube elaborated with the same dosages used in mortar mixtures, at different ages, for each kind of addition to be analyzed. They were cut into three sections of similar height thus becoming the test samples. Such samples were placed, perfectly hardened, into a container holding a 3 mm-water film and liquid intrusion was measured in time by means of weight differences. They were evaluated at 3, 7 and 28 days. The average of 3 measures per age for each kind of mortar is indicated by results shown in Figures 11 and 12. Sorptivity was obtained for each sample and test age, under the expression:

$i = S\sqrt{t}$, meaning:

i : absorbed water volume per transverse section unit (mm) or (mm³/mm²)

S : sorptivity (mm/ $\sqrt{h}$)

t : time (h)

Another remarkable durability factor for elaborated material is capillary porosity.

It was determined by percentually relating completely hardened mass in tested samples to the saturate weight without surface humidity. The samples were subjected to extreme saturation by placing them inside a water vacuum container during 24 hours. Results are expressed in Figure 13.

3. Results and Discussion

3.1 Analysis of Pastes Results

Marsh cone test allowed the assessment of finesse effect on cement – addition pastes fluidity, which behavior may be correlated with possible rheological changes on mortars and concretes elaborated with such materials. The basic test procedure consists in measuring the time spent in filling 1 liter of cement paste, which has to continuously flow from the cone. Results are indicated in Table 1.1.

Tabla 1.1 Resultados del ensayo del cono de Marsh
Table 1.1 Mash cone test results

Aditivo según peso aglom. (%) Admixture as per binder weight (%)	valores medios de fluidez (s) Fluidity average values (s)			
	CPO OPC	Suelo arcilloso Clay soil		F
		60 min	120 min	
0.10	35.50	-	-	47.75
0.15	-	-	-	34.75
0.20	19.75	x	x	23.75
0.30	-	x	-	18.25
0.40	12.00	x	x	16.50
0.50	-	x	x	-
0.60	-	60.25	33.25	-
0.70	-	42.50	20.25	-
0.80	-	35.75	15.75	-
0.90	-	27.75	-	-
1.00	12.25	23.00	-	-

- no realizado/non developed x no pasa por el cono/x doesn't pass the cone

Figure 1.1 graphically depicts the behavior of results from the test. It demonstrates that by grinding calcined clayey soil during 60 minutes, fluidity values similar to pure cement control paste are reached when super-plasticizing additive is poured at a 0.8% rate of total binder weight. On the other side, similar fluidity values are shown by ground calcined clay soil for 120 minutes when using the chemical additive at a 0.6% rate of total binder weight.

The required selection was settled at minimum amount of additive needed to reach a desired fluidity and, grinding times for calcined clays were settled in 120 minutes.

Figura 1.1 Comportamiento de la fluidez en pastas de cemento – adición

Figure 1.1 Fluidity behavior on cement – admixture pastes

The x-ray technique allowed monitoring in time the pozzolanic reaction process, demonstrating portlandite peak intensity (18° and 34°) for each paste (Figure 2). All studied systems showed a portlandite peak most intense at 7 days, in relation to the calcium hydroxide of the cement matrix due to the Portland cement hydration during the first days. Afterwards, at 28 days, lower peak intensity levels were detected, because of the characteristic portlandite consumption of pozzolanic reaction. The cement – calcined clay (AS-900) system, the peak CH decrease between 7 and 28 days is sensitively deeper than in the other systems, which indicates that a relevant pozzolanic activity took place.

The thermal-gravimetric results (TG) in Figure 3 indicate that calcium hydroxide is lower for all pozzolanic systems in comparison to the reference (CH consumption), which is even deeper for the case of calcined clay (AS-900) and demonstrate that this material seems to be the most reactive of all studied ones.

Figura 2. Evolución de hidróxido de calcio en pastas de cemento por XRD

Figure 2. Evolution of calcium hydroxide on cement pastes by XRD

Figura 3. Contenido de HC en pastas de cemento por TG

Figure 3. CH content in cement pastes by TG

Figura 4. Agua químicamente combinada

Figure 4. Chemically combined water

Figure 4 shows results for chemically combined water content, on different systems in time. This study was conducted by monitoring the hydration products formation, by means of a differential thermal analysis (DTA), applied on the thermal-gravimetric technique (TG) (Ramachandran, 2001). As expected pure Portland cement (CP N3) shows highest values, because it initially has higher amount of cement than others. Therefore, the filler system (F) will serve as a reference, since it has the same cement amount than other pozzolanic systems. That is why the values higher than the filler may be considered only as water consumption by the pozzolanic reaction. For early ages (1d), sugar cane straw (SC) and calcined clay soil (T120) systems have values higher than the filler, which is an index of pozzolanic activity. However, the fact that both additions had the smallest grain sizes may have influenced a higher hydrate formation at this early age.

The behavior of sedimented calcined clay (AS-900) at this age is quite different, which has a chemically combined water percentage slightly lower than the filler reference, which indicates there is few or none pozzolanic activity. It may be explained by higher reactive alumina content in such pozzolan (Table #1), since it favors the hydration in this phase over the cement pastes. It may also have influenced the low contents of CH, which indicate that these results cannot always be attributed to consumption by pozzolanic activity only, but also to a limited portlandite formation coming from Portland cement hydration.

This phenomena has been previously referenced by Fernandez in 2009 (Fernandez, 2009), who demonstrated by means of calorimetric tests, the presence of a given threshold value of reactive alumina content which is higher than the value cement silica reaction is altered.

However, at 7 days values showed by AS-900 increased, since values higher than other systems are obtained, except for pure Portland (CP N3) values, thus demonstrating an important pozzolanic reaction process for this period. At this age there is plenty of portlandite coming from cement hydration phases, which reaction to pozzolan facilitate an extra formation of hydrate products. This pozzolanic activity increased continuously for calcined clay systems (AS-900 and T120) even exceeding the chemically combined water values, at 28 days, showed by the pure Portland system (PC N3). Finesse material effect (Table #1) for pastes fabricated with calcined clay soils (T120) may have slightly influenced higher hydrate formations at 28 days, compared to other systems, although the active mineral addition system showed a lower portlandite consumption at this age (Figure 3).

The thermal-gravimetric test demonstrated the grinding effect on calcined clay reactivity. Figure 5 evidences that non-ground systems do not reflect a considerable pozzolanic activity, since both have higher values of portlandite content in relation to the reference. However, by grinding calcined clays, the calcium hydroxide consumption by cement pastes at 28 days may decrease in approximately 65% the original non-ground condition.

Figura 5. Efecto del molido en el consumo de CH

Figure 5. Effect of grinding on CH consumption

Porosity in such pastes was also studied by employing a mercury intrusion porosimeter (MIP). As indicated in Figure 6, all pastes have a reduction of total porosity between 7 and 28 days, which is a well known aspect due to the formation in time of hydration products, provoked by the pozzolanic reaction (Feldman, 1984; Gonçalves et al., 2009). Besides it is important to highlight that, only in systems of active mineral additions, a pore structure refining takes place in comparison to reference, being this phenomenon even higher for the case of calcined clay (AS-900). This phenomenon can be seen by analyzing the pore structure behavior in pastes at 28 days. Table #2 shows a summary of pastes pure structures, classified in accordance with the International Union of Applied Pure Chemistry (Everett, 1972). It can be observed that the replacement of ordinary Portland cement by active mineral additions, a micro-structural change takes place, since it evidences a reduction of macro-pores proportion and an increase of meso-pores proportion. It leads to the refining observed at 28 days, as indicated in Figure 6, being most significant for calcined sedimented clay (AS-900).

Figura 6. Porosidad por Intrusión de Mercurio en pastas a 7 y 28 días
Figure 6. Porosity by Mercury Intrusion in pastes, at 7 and 28 days

Tabla 2. Distribución de tamaños de poros, pasta 28 días

Table 2. Distribution of pore sizes, paste at 28 days

Tamaño del poro d/Pore Size d (nm)	CP/PC	AS-900	F	SC	T120
Macroporos/Macropores d>50 nm	N3	1.17	4.00	2.84	1.68
Mesoporos/Macropores 2.0<d<50 nm	2.68	98.84	96.00	97.18	98.32
Microporos/Macropores d<2.0 nm	96.92	0.00	0.00	0.00	0.00

Such phenomenon has previously been referenced by literature. Such is the case of studies conducted by R.F Feldman in 1984, which demonstrated that by using mineral additions in cement pastes, hydration products of lower permeability are achieved than those in pure Portland systems (Feldman, 1984). Similar results were achieved by J.P. Goncalves in 2009, which proved that when using industrial or laboratory metakaolin, or ground bricks for Portland cement replacement, mixtures with finer pore structures can be obtained (Goncalves et al., 2009).

As this device is based on mercury intrusion, the first porosity values to be yielded are those referred to material external pores. This principle indicates that AS-900 mixture, at 28 days, shows an external porosity lower than the rest of pozzolan mixture, which is an index closely linked to its reactivity and quite favorable against the action of external aggressive agents.

In the same figure it may be observed that addition systems do not reach total porosity values lower than the reference, in spite of the effect of pozzolanic reaction. It can be explained due to the fact that solid volume of OPC hydration products is higher than the volume of pozzolanic reaction, which is further increased by the internal porosity of employed pozzolans (Feldman, 1984; Goncalves et al., 2009). As reference system consumes more water during hydration process, there will be more space available for hydration products to be formed, being those volumetrically higher in this pure Portland mixture. Total porosity is higher in mineral addition systems; however, the compressive strength of mortars is higher than the reference system. Apparently it is not only volume, but also pores distribution and morphology, either macros or micros, internal or external; it plays an important role for the definition of mechanical strengths.

3.2 Analysis of mortars results

The reactivity showed by paste pozzolans, as well as porosity associated to them, influenced compressive strength of elaborated mortars. Results of compressive strength test on mortars (Figure 7) indicate that the pozzolanic reaction process at early ages (up to 7 days), in spite of being the stage having the higher increase proportion for strength values in the mixtures, does not achieve the results yielded by the pure Portland system.

From 28 days on compressive strength of pozzolanic systems is higher than the reference system, specially calcined clay (AS-900), which shows an increased strength of 30% in relation to pure Portland system at such age, which makes it the most reactive mineral addition of all.

Figura 7. Resistencia a la compresión en morteros

Figura 7. Mortars compressive strength

Lime consumption in pastes, obtained by means of thermal gravimetric analysis, was related to compressive strength on each mortar. Since cement amounts in addition mixtures are lower than in the reference system, the increase of strength of each addition with cement-filler system was compared, provided that 30% replacement is also the same for the other systems. Figure 8 shows a table with percentage values of calcium hydroxide content and compressive strength in pozzolan mixtures in relation to filler mixture, having both the same cement amount. For example, the AS-900 system, at 1 day has a portlandite content equivalent to 71% in filler system, and its strength at that age is 84% of the total achieved by the mortar made of filler. In this figure it can be observed that all pozzolanic systems, as time went by (1, 7 and 28 days) moved points towards the left symbolizing portlandite consumption. It has a direct effect on compressive strength; therefore, the increased values are also noticed. It is remarkable that calcined clay (AS-900) has the lowest CH consumption and, at the same time highest strength values.

The increase of mechanical strength apparently takes place due to the pozzolans activation by means of grinding process. Figure 9 shows that non-ground systems have compressive strength values in mortars quite lower than the reference system,

except for non-ground calcined clay, which reaches similar values than pure Portland system only at 60 days. Above demonstrates that calcined clay, that initially has low reactivity, may become a quite reactive pozzolan by means of grinding process. The harmful effect of having a low specific surface due to particle agglomeration and sintering effect by high temperatures may be reversed by blending process, which increases the specific surface and also the reactivity of such material.

Figura 8. Desarrollo de la reacción puzolánica
Figure 8. Pozzolanic reaction development

Figura 9. Efecto del molido en la resistencia a la compresión
Figure 9. Grinding effect on compressive strength

As observed in Figure 10, at 7 days mortars elaborated with additions have higher OPC hydration degree compared to pure Portland reference system. This is because cement is replaced by a finer material, which particles allow higher compaction in the mixture, thus enhancing hydration process.

Generally, there is more water amount available per cement gram, since water cement ratio increases because of replacement. For the case of mortars with calcined clay (AS-900), the fact that the CH content assessed in pastes has a lower value at the same age, as well as the filler effect, may have influenced a higher hydration degree in such mortars compared to others.

Figura 10. Grado de Hidratación en morteros a 7 días según BSE-IA

Figure 10. Hydration degree on mortars at days, according to BSE-IA

Another remarkable factor, to be taken into consideration when employing active mineral additions as replacement of regular Portland cement, is its contribution to changes in the pores structure, which are determinant for the new material durability. It was proven by employing a capillary water absorption test (Figure 11), being also able to measure its sorptivity (Figure 12).

Logically curves in Figure 11, in time, show a decrease of water absorption for all specimens, which apparently take place because of microstructure densification due to hydrates formation. This phenomenon is accentuated for the case of calcined sedimented clay (AS-900), which at 28 days is the system showing the lowest water absorption values.

Both, the calcined sedimented clay (AS-900) and the (CP N3) cement, show an increase of sorptivity values from 3 to 7 days, as shown in Figure 12. It may be explained due to porosity refinement, provided the relevant chemical reaction taking place during such time interval. As pore closes, capillary tension increases, allowing a fast water intrusion (higher sorptivity), but at lower volume (lower absorption).

For the case of AS-900, this refinement is evidenced as well by the fact it became the second system in absorbing more water at 3 days, only superseded by filler system and also, the second of lower absorption at 7 days, quite similar to values shown by the calcined clay soil (T120) system.

Calcined clay (AS-900) is shown once again as the mineral addition with the best behavior, which in this case reaches the lowest sorptivity values at 28 days. It demonstrated that by employing this type pozzolan as Portland cement replacement, it is possible to decrease water intrusion degree in the concrete mass, which avoids strong and direct effects from aggressive agents that may compromise material durability.

Figura 11. Absorción de agua en morteros, primeras 8 horas
Figure 11. Water absorption by mortars, during the first 8 hours

Figura 12. Sorptividad en morteros

Figure 12. Mortars Sorptivity

Figura 13. Porosidad capilar en morteros con adiciones

Figure 13. Capillary porosity in mortars with additions

Figure 13 shows the use of calcined clay as replacement cement material for Portland cement, which reduces material capillary porosity more than 60% compared to the reference system.

There is a close relation between material capillary porosity and durability. This study has employed two techniques to determine porosity: MIP and water saturation. Results for both cases are different and therefore contradictory. On one hand, MIP reaches pore sizes corresponding to nanometers, when water absorption only provides information about capillary pores registered by microns. It may be concluded that Portland cement replacement by pozzolanic additions preferably reduces macro porosity and at lower extent micro porosity, which generally indicates a capillary porosity refining and, therefore, a material permeability improvement.

All micro structural tests developed by this research justify the favourable behaviour of employed additions regarding mortars compressive strength. Micro structural analysis techniques served as interpretation tools for physical mechanical properties of elaborated mixtures, as well as for its features at macro scale.

4. Conclusiones

Following conclusions were reached by the current study:

- Mortars mechanical properties, by replacing a 30% cement by SC, T120 and AS-900, were:
 - Similar to the reference system, at 7 days
 - Higher than reference system, as from 28 days
- All active mineral additions developed an adequate pozzolanic reaction process, being calcined clay (AS-900) significantly remarkable.
- Raw materials grinding process have a great influence on reactivity of clayey soils and sedimented clays. Due to such grinding process (besides the calcium hydroxide increased consumption by such systems in comparison to the reference system), there is a mixture compaction increase by employing finer materials than Portland cement.
- The use of active mineral additions leads to a material pores structure refinement.
- Pores distribution and morphology seem to directly affect the definition of mechanical strengths.
- Mortars obtained from clay systems (T120 and AS-900) decreased its sorptivity at 28 days, in comparison to the pure Portland reference.
- The use of active mineral additions reduces material capillary porosity, mainly calcined clay with a decrease over 60% regarding the reference sample.
- Provided that calcined clays, from low purity grade clay soils, are finely ground at 900 Celsius degrees, they can reach a relevant pozzolanic activity. This can broaden the application fields for reactive pozzolans production.

- Clays' thermal activation process can be effectively conducted by burning a solid fuel block. The vertical shaft brick kiln technique guarantees an adequate combustion process, which minimizes coal contents in calcined material.

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