Pozzolanic improvements to fly ash when removing unburned carbon

Mejoras puzolánicas a la ceniza volante al retirar carboncillo

Walter Roldán Latorre (Main and Corresponding Author)
Departamento de Ingeniería Civil. Universidad Católica del Norte
Av. Angamos 0610. Antofagasta (Chile)
wroldan@ucn.cl

Jorge Garcés Arroyo
Laboratorio LIEMUN. Universidad Católica del Norte
Av. Angamos 0610. Antofagasta (Chile)
Jorge.ig.ga@gmail.com

Manuscript Code: 1027
Date of Acceptance/Reception: 30.07.2018/21.12.2017
DOI: 10.7764/RDLC.17.2.296

Abstract
Through a very simple washing process with water, the unburned carbon is separated and removed from the fly ash. In this work, mixtures of mortar with 30% Portland cement replacement are made by different additions: integral fly ash (obtained from thermoelectric), washed fly ash (removing unburned carbon by washing), unburned carbon and limestone filler (limestone rock dust). To determine better the pozzolanic contribution of the additions, 5% gypsum (with respect to the weight of the binder) is added to the mixtures not hardened. With these mixtures, specimens are made for tests to rupture at 7, 28 and 90 days of age, kept submerged in water and also special specimens kept in similar condition measuring length variations. It is detected that the substitution of portland cement by unburned carbon, significantly reduces the mechanical resistance at any age and does not contribute to protection against sulphate attacks. It is concluded that the unburned carbon does not possess pozzolanic properties and its withdrawal generates benefits to the fly ash in the search to improve the pozzolanic performance in concrete mixtures.

Key words: Pozzolanic enhancements; unburned carbon removed; fly ash washing; pozzolanic portland cement; concrete and mortar.

Resumen
A través de un proceso de lavado con agua muy simple, se separa y se retira el carboncillo de la ceniza volante. En este trabajo se elaboran mezclas de mortero con 30% de reemplazo de cemento portland por distintas adiciones: ceniza volante integral (obtenida de termoeléctrica), ceniza volante lavada (retirando carboncillo por lavado), carboncillo y filler calizo (polvo de roca caliza). Para determinar de mejor manera el aporte puzolánico de las adiciones, se adiciona 5% de yeso (con respecto al peso del conglomerante) a las mezclas en estado fresco. Con estas mezclas se elaboran probetas para ensayos a rotura a 7, 28 y 90 días de edad, mantenidas sumergidas en agua y también probetas especiales mantenidas en similar condición midiendo variaciones de longitud. Se detecta que la substitución de cemento portland por carboncillo, reduce significativamente a toda edad la resistencia mecánica y no contribuye a una protección frente a ataques de sulfatos. Se concluye que el carboncillo no posee propiedades puzolánicas y su retiro genera beneficios a la ceniza volante en la búsqueda de mejorar el desempeño puzolánico en mezclas de hormigón.

Palabras clave: Mejoras puzolánicas; retiro de carboncillo; lavado a la ceniza volante; cemento portland puzolánico; hormigón y mortero.

Introduction

Flying ash has recognized pozzolanic properties that can be used in the preparation of cementitious mixtures in replacement of Portland cement (Metha and Monteiro, 2006 & Malhotra and Metha, 1996). The reduction of Portland cement in the concrete helps to reduce the pollution associated with the production of cement (Raggiotti, Positieri, Locati, Murra, & Marfil, 2015); the replacement of cement by fly ash reduces costs (Roldan. 2011) and helps solve environmental problems in the accumulation of waste in the industrial processes of electricity production (Pavez, 2012).

However, the fly ash contains carbon particles, which for some reason have not been completely incinerated in the home and which are also dragged by the flow of incandescent gases to the chimney of exit in the plant thermoelectric, where they are trapped by electro-static precipitators together with the fly ash (Velasquez, de la Cruz, Sanchez & Marin, 2007). The presence of this unburned material in the fly ash is variable and depends on the origin and quality of the carbon; its presence causes unwanted spots and reduces the resistant capacity of the concrete (Pavez, 2012).

Some research indicates that the removal of unburned carbon is factible, but they do not account for the pozzolanic benefits that this withdrawal represents; rather they do it to reuse and re-burn (Velasquez et al, 2007). Others realize that the unburned carbon content is important, since it acts as a strong adsorbent reducing workability (Lorenzo, 1993), so its content must be strictly delimited.

For which the study seeks to achieve the following objectives: Check that removal of unburned carbon improves the pozzolanic condition of fly ash. The specific objectives is: Define the effect of the presence of unburned carbon in flying ash on mechanical resistance; Check that the removal of unburned carbon from the fly ash improves the durability conditions providing better protection against sulphate attack; and Quantify objectively the improvement of pozzolanity conditions when removing unburned carbon from fly ash from the point of view of the mechanical strength of compression and from the point of view of durability conditions.

Methodology

An experimental plan is developed with mortar mixtures using binder 100% portland cement and, similarly, mortars with binder type "portland cement-pozzolan", where 30% of portland cement is replaced by a pozzolanic addition.

For the achievement of the objectives, different specimens are prepared with the use of pozzolanic addition in the binder, which are subjected to mechanical strength tests and measurements of length changes, curing them in an environment of humidity saturation (under water) and in an environment aggressive (sulfate attack); results that are compared with mortar specimens using binder 100% portland cement, which provide reference values.

As a pozzolanic addition, in principle integral fly ash is considered, as it is extracted from thermoelectric, without removing unburned carbon; then the pozzolanic addition is changed to washed fly ash (unburned carbon has been removed). To prove that the unburned carbon harms the cementing mixture that contains it, 30% of portland cement is also replaced by unburned carbon, as if the unburned carbon was pozzolanic material and to prove that the charcoal does not have pozzolanic properties, 30% is also made of portland cement replacement by calcareous filler (rock dust) that does not possess pozzolanic properties.

Used Materials

Obtaining unburned carbon by washing fly ash

The integral fly ash, as obtained from the thermoelectric, is subjected to a simple washing process with water with the purpose of separating unburned carbon particles. Density differences are exploited since the fly ash particles oscillate between 2.4 and 2.9 g/cm^3, while the unburned carbon between 1.3 and 1.5 g/cm^3. The procedure has allowed to separate approximately 25 grams of unburned carbon from 1000 g of integral fly ash; this amount will depend on the origin characteristics of the fly ash.

Figure 1. Unburned carbon extracted and dried after the wash treatment to fly ash. Own-elaboration.

During the wash the unburned carbon is concentrated as foam in flotation, which facilitates the separation through a procedure that is described below.

a) In a container, integral fly ash is poured up to 2/3 of the capacity. Pressurized drinking water is added to almost fill the container. It is stirred with a metal spatula, trying to dissolve any material agglomerations, letting decant for 15 minutes.

b) The unburned carbon remains floating on the surface and can be removed by suction with the use of a washing flask, taking care not to extract the fines from the fly ash that has not yet decanted. The removed unburned carbon should be deposited in a temperature resistant container. The unburned carbon adhering to the walls of the washing container can be removed manually using a metal spatula. The unburned carbon adhering to the spatula is washed off and added to the container that receives the unburned carbon.

c) Once the previous separation process has been carried out, both the washed fly ash and the unburned carbon should be dried as they remain with saturation humidity, so the drying of these materials must be carried out in an oven at a temperature of 90 °C for a 24 hours time. The dry state is obtained during a time in which the weight is controlled with differences of 0.1% between successive weighings.

Chemical properties of fly ash and unburned carbon

X-Ray Fluorescence Spectrometry (xRF) tests are carried out on integral fly ash FA(i) from the thermoelectric plant in Tocopilla, Chile; the results are described in Table 1, together with the analysis carried out on the washing derivatives, such as the washed fly ash FA(w) and the unburned carbon removed Cr.

Table 1. XRF analysis to cementing materials used. Source: Applied Geochemistry Laboratory. U. Católica del Norte. Antofagasta, Chile.

Compound	FA(i)	FA(w)	Cr	CF	OPC
SiO_2 (%)	54.8	55.8	49.1	5.35	14.02
Al_2O_3 (%)	21.2	21.4	24.1	3.88	3.23
Fe_2O_3 (%)	7.5	8.1	9.6	0.98	2.08
CaO (%)	3.9	3.7	5.3	48.3	73.2
MgO (%)	2.7	2.7	4	0.59	0.58
K_2O (%)	2	2	2.2	0.7	0.6
Na_2O (%)	1.4	1.2	1.9	0.18	0.48
SO_3 (%)	0.3	0.1	1.4	-	2.56
LOI (%)	3.3	2.4	1.5	39.51	0.4
Otros (%)	2.9	2.6	0.9	0.51	-

FA(i): Integral Fly Ash– FA(w): Washed Fly Ash – Cr: Unburned Carbon – CF: Calcareous Filler – OPC: Portland Cement.

The integral fly ash FA(i), the washed fly ash FA(w) and the unburned carbon Cr, individually meet requirements for chemical composition (ASTM C618-17), which in principle is indicative of having pozzolanic properties. The loss of ignition LOI, allows indirectly estimate the amount of unburned carbon, although there are technically more precise ways to quantify it (Mohebbi, Rajabipour & Scheetz, 2015), since the amount LOI is not only due to the burning of organic carbon, but also to other possible reactions such as the calcination of some compounds, the physical and chemical desorption of molecular water and the release of gases.

Characteristics of the Portland cement used

Table 2. Anhydrous phases of Portland Cement OPC. xRD analysis and Rietveld quantification. Source: Applied Geochemistry Laboratory. U. Católica del Norte. Antofagasta, Chile.

Compound	%
C_3S	56.1
C_2S	4.2
C_3A	17.8
$CaCO_3$	12.6
C_4AF	9.3

Water

The water used in the preparation of mortar specimens is potable, from the network of the LIEMUN.

Arid used

Siliceous sand is used whose properties are indicated in Table 3.

Calcareous Filler CF

Limestone rock powder is used; it is a material without pozzolan property (Lawrence, Cyr & Ringot, 2003 & Diaz, Mejia de Gutierrez, Izquierdo & Gordillo, 2013) that is obtained by grinding using a pulverizing mill and sieving under 80 µm. The xRF analysis performed is indicated in Table 1 above.

Table 3. Properties of sand used. Source: Own elaboration.

Density Real dry	Kg/m^3	2,630
Density Real saturated	Kg/m^3	2,650
Density Apparent loose	Kg/m^3	1,650
Density Apparent compact	Kg/m^3	1,850
Absortion	(%)	1.1
Fineness Modulus		3.02

Gypsum

For the addition of calcium sulphate to the binder, white gypsum type plaster is used, with hemi-hydrated calcium sulfate contents between 73-90%, calcium carbonate between 5-16% and less than 1% free crystallized silica. It has a grinding fineness of more than 60% under 149 µm and more than 96% under 44 µm.

Experimental laboratory development

For compression strength tests, a set of three prismatic specimen of 40x40x160 mm are prepared for each type of mixture. Also for each type of mixture a set of 2 prismatic specimens of 50x50x250 mm is made, with cylindrical teflon rods of 5 mm in diameter, which are placed at the ends of each specimen, to measure the variation of length with the comparator of lengths. Dosage is established according to the following proportions (by weight): water/binder/sand = 1/2/6.

As a binder 100% portland cement OPC or the combination "70% OPC + 30% Pozzolans" is used, as appropriate. As a pozzolan in replacement of Portland cement, the addition of FA(i), FA(w), Cr and CF in the indicated proportion is indistinctly considered; to emulate severe attack by sulfates conditions, gypsum is added to the fresh mortar mixture in amount of 5% of the weight of the binder. Table 4 describes the amounts of material used in the preparation of mortar specimens for the different binder mixtures.

Table 4. Dosages used to make mortar specimens (quantity in grams). Source: Own elaboration.

Binder mixture	OPC	Sand	Water	FA(w)	FA(i)	Cr	CF	G
100% OPC	450	1,350	225	-	-	-	-	-
70% OPC + 30% FA(w)	315	1,350	225	135	-	-	-	-
70% OPC + 30% FA(i)	315	1,350	225	-	135	-	-	-
70% OPC + 30% Cr	315	1,350	225	-	-	135	-	-
70% OPC + 30% CF	315	1,350	225	-	-	-	135	-
100% OPC + 5% G	450	1,350	225	-	-	-	-	22.5
70%OPC + 30%FA(w) + 5%G	315	1,350	225	135	-	-	-	22.5
70%OPC + 30%FA(i) + 5%G	315	1,350	225	-	135	-	-	22.5
70%OPC + 30%Cr + 5%G	315	1,350	225	-	-	135	-	22.5
70%OPC + 30%CF + 5%G	315	1,350	225	-	-	-	135	22.5

OPC: Portland Cement; FA(i): Integral Fly Ash; FA(w): Washed Fly Ash; Cr: Unburned Carbon; CF: Calcareous Filler; G: Gypsum

The specimens are demold to 24 hours and kept submerged in water in a room with humidity and controlled temperature.

Mechanical resistance to compression

Results of resistance to compression at age 7, 28 and 90 days of curing, are indicated in Table 5.

Table 5. Mortars. Mechanical compression resistance. Source: Own elaboration.

	Compression Resistance [MPa]		
Binder Mixture	7 days	28 days	90 days
100% OPC	45.3	55.6	57.2
70% OPC + 30% FA(w)	36.6	47.3	58.3
70% OPC + 30% FA(i)	37.0	45.4	54.0
70% OPC + 30% Cr	22.8	29.7	37.0
70% OPC + 30% CF	28.8	39.2	44.7
100% OPC + 5% G	40.7	50.2	52.5
70%OPC+30%FA(w)+5%G	33.1	44.8	55.4
70%OPC+30%FA(i) + 5%G	30.2	42.1	50.8
70%OPC + 30% Cr + 5%G	18.0	25.9	33.5
70%OPC + 30% CF + 5%G	24.7	34.6	40.2

Mortar expansion

It is known that sulfates damage the cement matrix, which degrades mechanical strength. The sulphate's aggressiveness manifests itself in a high humidity environment to form expansive compounds (Zhao, He, Gao & Li, 2008). On the other hand, the protection benefits reported by pozzolans in environments with sulphate are known (Paya, Borrachero, Monzo, Peris-Mora & Bonilla, 2002); then, to properly study the pozzolanic contributions of the additions that make up the different conglomerating mixtures, similar mortar specimens are exposed to high humidity conditions (submerged in water), without gypsum and with gypsum in the binder. When adding gypsum to the interior of the mass, the specimens are subjected to severe attack of calcium sulfate, observing and comparing the expansive reactivity with the curing time.

To observe the development of volumetric changes, the expansion of the mortar in a principal direction is measured, measuring the variation of length "Δl [%]" as an average of two expansion specimens using the length comparator. This procedure starts immediately after demolding, keeping a record of measurements over time until the age of 90 days of curing, compatible with the mechanical resistance record.

$$\Delta l\ [\%] = 100 \bullet (L_t - L_1)/L_1 \qquad (1)$$

were:
L_1: Average effective length of the specimen at the age of 1 day (after the demolding)
L_t: Average effective length of the specimen at age "t" days

It is understood by "Effective length", the length of the central segment of the specimen comprised between extreme rods. The following graphically shows results of measured expansions for the different mortar mixtures, without gypsum and with gypsum in the binder.

Figure 2. Longitudinal expansion of mortars, according to the age of curing; without addition of gypsum. Source: Own elaboration.

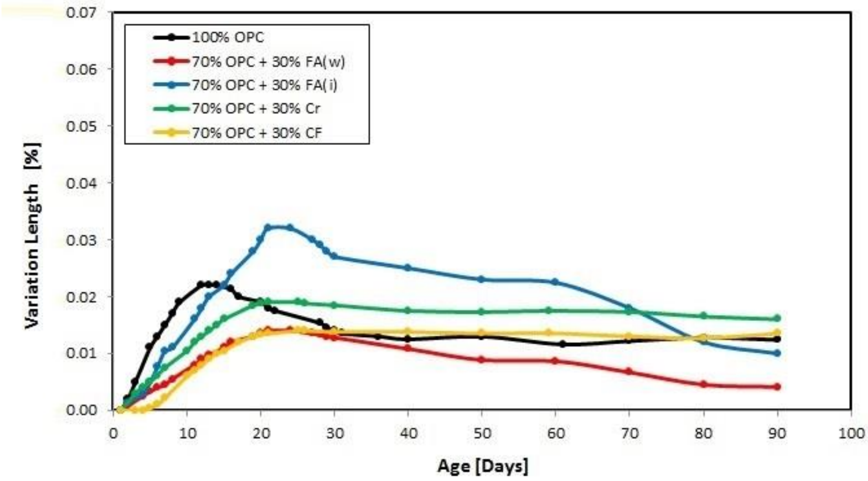
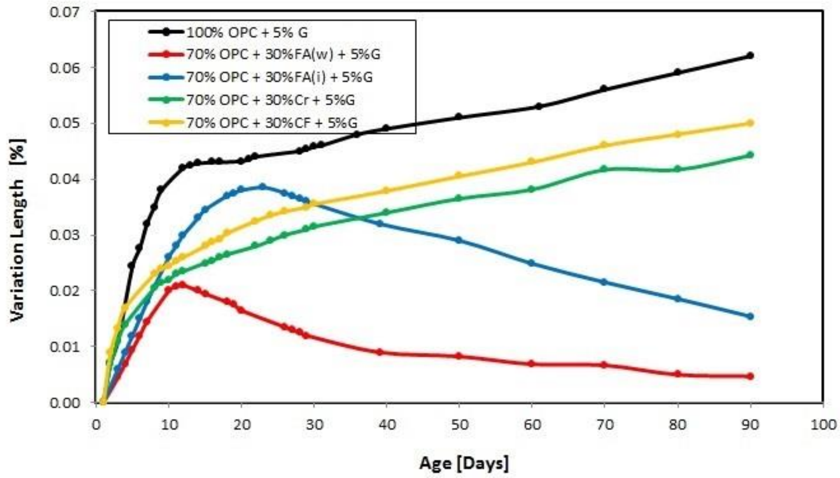


Figure 3. Longitudinal expansion of mortars, according to the age of curing; with addition of gypsum. Source: Own elaboration.



The previous figures show the variation in length experienced by the specimens with different binder mixtures and show the expansive effect that causes a severe attack by sulphate inside the mass, in a high humidity environment. Proof of this is that the mortar specimens made with 100% OPC change their expansive behavior with the contributions of gypsum to the clinker showing a moderate and controlled expansion when no gypsum is added (see Figure 2), to a condition of growing expansion over time, without apparent limit, product of the addition of 5% gypsum to the binder (Figure 3).

The previous figures show remarkable differences in expansion when a material with pozzolanic properties participates in the binder. The specimens that contain active pozzolana, such as washed fly ash FA(w) and integral fly ash FA(i), in an environment with a lot of sulphate as the present experience, show a lower expansive behavior than the specimen of well-known pozzolanic activity that contains calcareous filler CF (Figure 3).

Another significant condition is highlighted, as a result of the attack by sulphates, the specimens with active pozzolanic material develop expansion from an early age but at a certain moment the expansive development stops, continuing with a contractive process; at the same time, the specimens with calcareous filler CF, of no pozzolanic condition, before the attack of sulphate, the expansion develops always increasing in time, without apparent limit.

The expansive development of the specimens with unburned carbon Cr, is similar to specimens with calcareous filler CF; this allows to assert that the unburned carbon also has no pozzolanic condition.

The present investigation demonstrates that the removal of unburned carbon improves the pozzolanic properties of fly ash; in addition, it proposes a simple system of extraction by washing with the idea of facilitating the removal since its presence reduces conditions of mechanical resistance and durability to cementitious mixtures.

Regarding compression strength

- In all cases, the mechanical resistances of the specimens increase with the age of curing, in the same way as with traditional portland cement mixtures.
- The attack of sulphate carried out with the addition of gypsum to the fresh mortar, reduces the mechanical resistance with respect to similar mortars without gypsum, stating that at all ages the sulphate degrades the cementing mixture.
- The unburned carbon as a replacement of Portland cement in the mixtures, significantly impairs the mechanical resistance, demonstrating that the unburned carbon does not possess pozzolanic properties.
- The unburned carbon present in the integral fly ash FA(i), even in small quantities, harms the development of mechanical resistance, which is evident when comparing compression resistance results with the use of washed fly ash FA(w).
- The mortars that present a smaller reduction in the mechanical resistance at all ages before the attack of sulphates, have turned out to be those that use washed fly ash FA(w), demonstrating that the removal of unburned carbon made improves pozzolanic conditions to the fly ash.
- The calcareous filler CF, even though material without pozzolanic properties, shows better mechanical resistance than unburned carbon Cr; most likely, CF as an addition material manifests in a better way the nucleation effect or particle effect in this type of mixtures (Soriano, 2007).
-

Regarding the expansion

- The concept of durability can be quantified by the behavior and record of expansions since, by adding gypsum to the mortar mix, an environmental condition of highly contaminating and degrading performance is represented.
- The effect of a pozzolanic addition can be observed through the expansive behavior shown by the samples in a humid environment with sulfate as the one produced here.
- According to the previous comments, of all the additions tested in Portland cement replacement, the FA(w) in sulphate environment, is the addition that generates smaller expansions, demonstrating having better pozzolanic active conditions.
- The addition of unburned carbon Cr in an environment with sulphate develops a growing expansion over time, with a tendency similar to calcareous filler CF, proving not to be an active pozzolan.
- The specimens with addition of integral fly ash FA(i), also show to have pozzolanic properties since they control the expansion in a similar way to the washed fly ash FA(w); however, having unburned carbon, they show an expansive development greater than FA(w), which shows that the presence of unburned carbon impairs the durability performance of the fly ash that contains it, validating the recommendation to extract the unburned carbon to improve the pozzolanic condition of fly ash.
-

General conclusions

- In general, the pozzolanic addition slows down the development of compression resistance up to 28 days of age, which is the one used to refer values of mechanical resistance; it is evident that the development of pozzolanic hydration compounds that contribute, require more time and depending on the percentage of portland cement replacement, can exceed 100% cement, as it has been shown here.
- Given that the best mechanical strength results at 90 days of age are obtained for mixtures with FA(w), exceeding mixtures with FA(i) and given that the smaller expansions in time are also obtained for mixtures with FA(w), it is demonstrated that the removal of unburned carbon improves the pozzolanic condition of the fly ash.
- It is demonstrated that the presence of unburned carbon Cr impairs pozzolanic action reducing mechanical resistance and affecting durability in aggressive environmental conditions, it is considered appropriate to recommend the removal of this inert material in the fly ash by washing treatment.
- The unburned carbon Cr despite having high contents of SiO_2, Al_2O_3 and Fe_2O_3, these lack pozzolanic reactivity so the mineralogical composition alone (Table 1) is not an indicator of the pozzolanic condition of a material; it is essential to demonstrate reactivity, a condition that can indirectly be detected through tests of mechanical resistance and expansion in an aggressive environment such as those carried out here.

ASTM C618-17. (2017). *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete.* ASTM International, West Conshohocken, PA, 2017.

Díaz, J., Mejía de Gutiérrez, R.; Izquierdo, S. & Gordillo, M. (2013). Mezcla ternaria de cemento portland, escoria de alto horno y piedra caliza: resistencia mecánica y durabilidad. *Revista de la Construcción, 12*(3), 53-60. doi: 10.4067/S0718-915X2013000300006.

García, M., Blanco-Varela, M., De La Torre, A., Bruque, S. y Zúñiga, F. (2003). Cuantificación Mineralógica Directa de Cementos Portland por el Método de Rietveld. *Cemento y Hormigón*, N°850. ISSN 0008-8919.

Lawrence, P., Cyr, M. & Ringot, E. (2003). Mineral admixtures in mortars Effect of inert materials on short-term hydration. *Cement and Concrete Research 33*, 1939-1947.

Lorenzo, M. P. (1993). *Influencia de dos cenizas volantes españolas en la microestructura y durabilidad de la pasta de cemento portland hidratado.* Tesis doctoral. Universidad Complutense de Madrid. Facultad de Ciencias Químicas. Madrid-España. 258 p.

Malhotra, V.M. & Metha, K. (1996). *Pozzolanic and cementitious Materials.* Gordon and Breach Publishers, Ottawa, 1996.

Metha, K. & Monteiro, P. (2006). *Concrete. Microstructure, Properties, and Materials.* Third Edition. McGraw-Hill. New York-USA. 647 p.

Mohebbi, M., Rajabipour, F. & Acheetz, B. (2015). *Reliability of loss on ignition (LOI) test for determining the unburned carbon content in fly ash.* 2015 World of Coal Ash (WOCA) Conference in Nashville. Cement & Concrete II Session.

Pavéz, H. (2012). *Factibilidad de fabricación de Hormigón con Cenizas Volantes a nivel industrial en la Región de Antofagasta.* Tesis de Título, Departamento Ingeniería Civil, U. Católica del Norte. Antofagasta, Chile.

Paya, J., Borrachero, MV., Monzo, J., Peris-Mora, E. & Bonilla, M. (2002). Long term mechanical strength behaviour in fly ash/Portland cement mortars prepared using processed ashes. Journal of Chemical Technology & Biotechnology, 77(3), 336–344. doi.org/10.1002/jctb.580.

Raggiotti, B., Positieri, MJ., Locati, F., Murra, J. & Marfil, S. (2015). Zeolite, Study of Aptitude as a Natural Pozzolan Applied to Structural Concrete. *Revista de la Construcción, 14*(2), 14-20.

Roldán, W. (2011). *Materiales puzolánicos para uso en conglomerantes especiales basados en yeso.* Tesis doctoral. Universidad Politécnica de Valencia. Departamento de Ingeniería de la Construcción y de Proyectos de Ingeniería Civil. Valencia, España. 362 p.

Soriano, L. (2007). *Nuevas aportaciones en el desarrollo de materiales cementantes con residuo de catalizador de craqueo catalítico usado (FCC).* Tesis doctoral. Universidad Politécnica de Valencia. Departamento de Ingeniería de la Construcción y de Proyectos de Ingeniería Civil. Valencia, España. 354 p.

Velásquez, L., De La Cruz, J., Sánchez, J. & Marín, M. (2007). Remoción del carbón inquemado de las cenizas volantes producidas en el proceso de combustión de carbón. *Revista Energética*, N° 38.

Zhao, S.B., He, R.C., Gao, R.D. & Li, QB. (2008). Research on mechanism of sulfate attack on concrete by TG-DSC method. Advances in Concrete. Structural Durability. Proceedings of ICDCS2008, Vol 1 and 2, Pages: 549-555.