Influence of cement properties in the reaction rate and mechanical behavior of concrete with high fly ash content

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Abstract

The use of fly ash (FA) as an admixture to concrete is broadly extended for two main reasons: the reduction of costs that supposes the substitution of cement and the micro structural changes motivated by the mineral admixture. Regarding this second point, there is a consensus that considers that the ash generates a more compact concrete and a reduction in the size of the pore. However, the measure in which this contributes to the pozzolanic activity or as filler is not well defined. There is also no justification to the influence of the physical parameters, fineness of the grain and free water, in its behavior.

This work studies the use of FA as a partial substitute of the cement in concretes of different workability (dry and wet) and the influence in the reactivity of the ash. The concrete of dry consistency which serves as reference uses a cement dose of 250 Kg/m^3 and the concrete of fluid consistency utilized a dose of cement of 350 Kg/m^3. Two trademark of Portland Cement Type 1 were used. The first reached the resistant class for its fineness of grain and the second one for its composition. Moreover, three doses of FA have been used, and the water/binder ratio was constant in all the mixtures. We have studied the mechanical properties and the micro-structure of the concretes by means of compressive strength tests, mercury intrusion porosimetry (MIP) and thermal analysis (TA).

The results of compressive strength tests allow us to observe that concrete mixtures with cements of the same classification and similar dosage of binder do not present the same mechanical behavior. These results show that the effective water/binder ratio has a major role in the development of the mechanical properties of concrete. The study of different dosages using TA, thermo-gravimetry and differential thermal analysis, revealed that the portlandite content is not restrictive in any of the dosages studied. Again, this proves that the rheology of the material influences the reaction rate and content of hydrated cement products.

We conclude that the available free water is determinant in the efficiency of pozzolanic reaction. It is so that in accordance to the availability of free water, the ashes can react as an active admixture or simply change the porous distribution. The MIP shows concretes that do not exhibit significant changes in their mechanical behavior, but have suffered significant variation in their porous structure.

Originality

The work tries to establish the influence of the ash as admixture in two extreme doses (low and high volume) of cement. Both dosages are allowed by the EHE-98 Construction Code (Spain). It also tries to evaluate the contrast that the fineness of the grain and the composition of the cement have on the pozzolanic reactions of the ash for cements cataloged under the same designation of common cements.

Finally, the proposed tests try to compare the influence of the rheological changes produced in the material when the volume of fly ash increases significantly. The experimental campaign aim is to determine the influence of various parameters in the mechanical behavior and microstructure. Low and high volumes of ash have been used to distinguish the changes in the parameters to be analyzed: effective free-water, rheology, and cement/binder ratios.

Chief contributions

The work evidences the influence of the doses of cement and the effective water/binder ratios, over the effectiveness of the doses of fly ash used. It also shows the variations in the mechanical properties and the micro-structure of concretes that use fly ash and cement that acquire their resistance class by different ways (fineness of grain or composition). Ultimately, the influence of the rheology of the material, the development of resistance to compression, and the reaction rate are observed.

Keywords: *concrete, microstructure, porosimetry, thermal analysis and fly ash*

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Introduction

Environmental requirements promote the employment of high doses of fly ash (FA) in concretes. The decrease of the doses of cement in the mixtures of concrete abates the material costs, diminishes the pollution associated with the production of cement and helps solve the problem of ash eradication. The manufacturers produce a variety of cements with similar physical characteristics, using different doses of raw material. Cements with low contents of tri calcium silicate (C_3S) reach the same strength than those cements with higher contents of C_3S when increasing the fineness of the cement particles. This provides a higher amount of accessible C_3S for hydration and, as a consequence, an acceleration of the hydration reactions. As a result, the markets provide cements under the same designation of common cements which significantly vary in mineralogical composition and granulometric distribution (Fernández, 2007). These factors contribute to the increase of the uncertainty in the behavior of the resultant material.

The influence of the composition and physical properties of the cements in the micro-structure and its effect over the mechanic properties of concrete with FA is not well defined yet. The need for more research that explores the micro-structural development in the concretes that use FA is evident.

The objective of this research is to study the use of FA as a partial substitute of cement in concretes of different consistencies and doses, and the influence of such in the reactivity of the FA. In order to achieve these objectives, various rehearsals of compressive strength, mercury intrusion porosimetry (MIP), and thermogravimetry/differential thermal analysis (TG/DTA) were carried out.

Materials

EHE-98 specifies that concretes made with FA must be manufactured with CEM 1 cement. In this work, CEM I 42.5 R has been adopted. We have selected two cements with different relations of C_3S/C_2S: the first one reaches the strength class for its grain size, which it is denominated *F*, and the second one, denominated as *G*, for its composition. Table 1 presents the mineralogical composition of the cements. Figure 1 shows the results of the granulometric analysis of the cements. The size distribution of the particles was determined through laser diffraction in suspension, according to ISO 13320.

The aggregates used in the mixtures are of siliceous. Coarse aggregates with a maximum size of 20 mm, and its granulometric module is of 7,08. The granulometric analysis of the aggregates was carried out in accordance to UNE-EN 933-1. The FA employed are of a siliceous nature and low content in calcium oxide, classified as a type *V* in accordance to the *Instrucción para la Recepción de Cementos* (RC-03). Moreover, these fulfill the standards UNE EN 450-1 and UNE EN 450-2.

Table 1: Mineralogical compositions of the cements

Mineral	*Holcim (F)*	*Cemex (G)*
C_3S	56,06	65,13
C_2S	17,56	5,84
C_3A	9,84	12,12
C_4AF	7,51	8,24

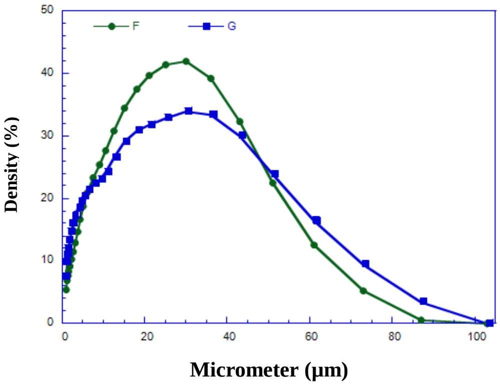

Figure 1: Cements' granulometric analysis

Dosages and testing

In this work two concretes of reference were designed and built. The first was designed to obtain a dry consistency and the second for a fluid consistency. On both cases, the dose of aggregates was done through the Bolomey method. The reference doses of dry consistency employed 250 kg of the cement per m^3 of concrete and the reference dosage of the concrete of fluid consistency employed 350 kg per m^3. The water/cement ratio stayed in 0,65 in both of them. The doses of concrete with FA followed the recommendation of UNE 83414. Table 2 shows the dosages. The process of mixing and curing followed the recommendations ASTM C 192. Table 3 enumerates the tests performed.

Table 2: Doses of concrete by m^3

Ash / Cement	Dry consistency concrete					Fluid consistency concrete				
	Cement (kg)	Ash* (kg)	Sand (kg)	Gravel (kg)	Plasticizer (kg)	Cement (kg)	Ash* (kg)	Sand (kg)	Gravel (kg)	Plasticizer (kg)
0,00	250	0	1050	808	1,25	350	0,0	918	780	0,00
0,15	239	36	1022	808	1,20	335	52	879	780	0,00
0,35	226	79	988	808	1,13	317	111	831	780	0,00
0,50	217	109	964	808	1,09	304	152	798	780	0,00

* Efficiency coefficient, K = 0,30, has been embraced

Results

Compressive strength: Figures 2 up to the 5 show the results of the compressive strength tests. Figures 2 and 3 correspond to the dry consistency concretes and Figures 4 and 5 belong to the mixtures of fluid consistency concretes.

Table 3 Tests completed

Tests	Time Period (days)				Standards
	7	28	91	365	
Mechanical	X	X	X		UNE-EN 12390-3
MIP			X		ASTM D4404-84*
TG/DTA		X	X	X	ASTM E1131-03*

* Adjusted experimentally

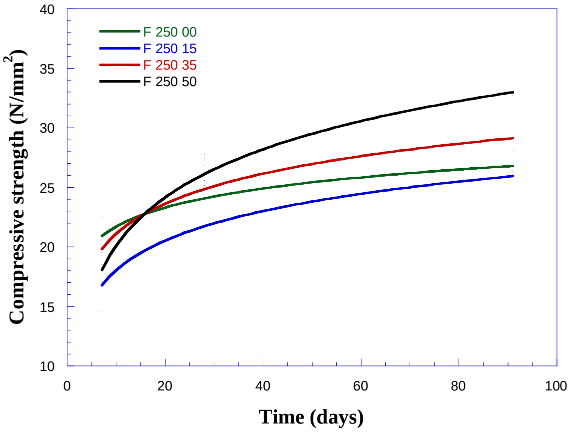

Figure 2: Compressive strength: 250 Kg/m^3 of *F*

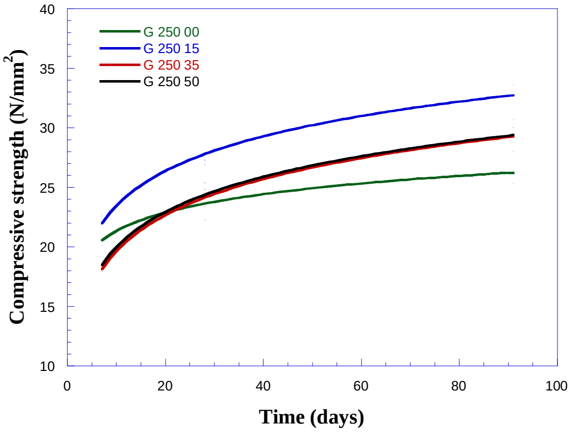

Figure 3: Compressive strength: 250 Kg/m^3 of *G*

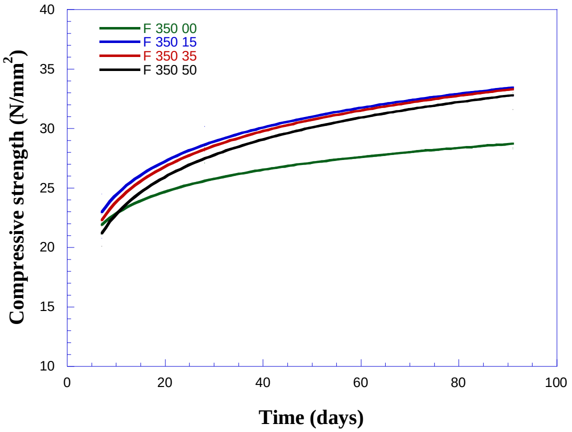

Figure 4: Compressive strength: 350 Kg/m^3 of *F*

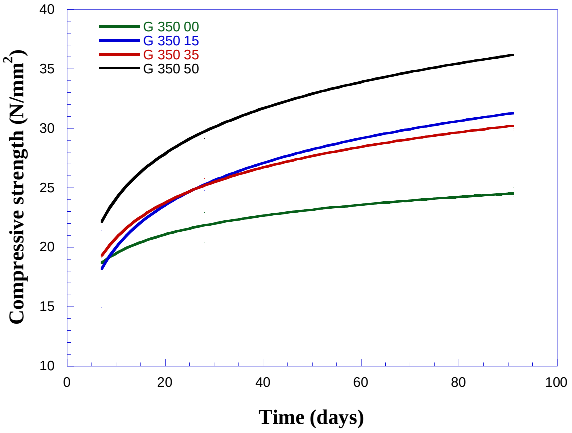

Figure 5: Compressive strength: 350 Kg/m^3 of *G*

In the case of the mixtures of fluid consistency, the reference concretes mixed with *F* offers superior values of compressive strength to those concretes built with *G*. The incorporation of FA improves the strength of the concretes at 28 days and in a considerable number of cases in or before the 7 days. The doses of FA vary their behavior by the type of cement. The concretes manufactured with *F* behave better when using moderate doses (≤ 35%) while the concretes built with *G* react better with high doses (> 35%).

As comparing the compressive strength values it is seen that the mixtures of dry consistency prepared with *F* show lower values of strength than its equivalents of fluid consistency (350 Kg/m^3), in all ages studied. Nevertheless, the concretes of dry consistency prepared with cement *G* show greater compressive strength values than its analogs of fluid consistency when low doses are employed (< 35%) and the opposite occurs for moderate or high doses (≥ 35%), at all ages studied.

Thermal Analysis: Figures 6 up to 9 show the results of the loss of hydration water for each concrete studied along hydration time. Figures 6 and 7 correspond to the concretes of dry consistency and Figures 8 and 9 belong to the mixtures of fluid consistency. The TG/DTA of the mixtures of dry consistency prove how reference concretes manufactured with *F*, at early ages, are more reactive than the concretes manufactured with *G*. The use of FA seems to be more effective when combined with *G* in a short period of time and with *F* on a long term. The incorporation of high doses of FA (35% and 50% in concrete built with *G*, proves an increase in hydration water at early ages, from 2.2% in reference concrete to 2.6% and 2.8% in the case of 35% and 50% of FA incorporation respectively, but decrease at 1.6% at 365 days independent of FA addition. In contrast, concretes mixed with *F*, the addition of high volume of FA (35% and 50%) produces an increase of hydration water in the long run, 365 days, from 2% of hydration water to 2.2% and 2.8%.

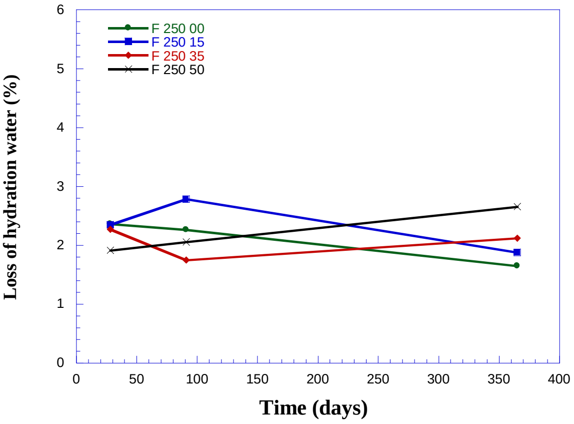

Figure 6: Loss of hydration water: 250 Kg/m^3 of *F*

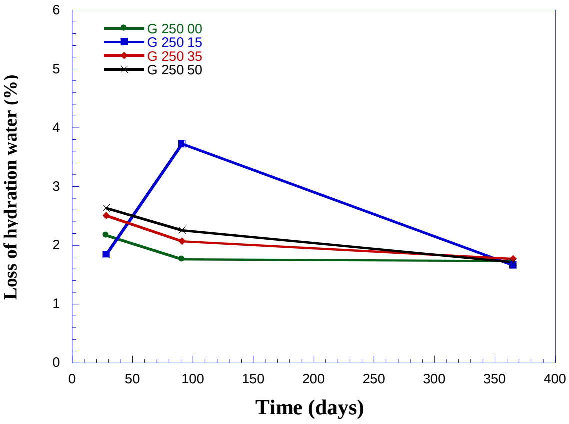

Figure 7: Loss of hydration water: 250 Kg/m^3 of *G*

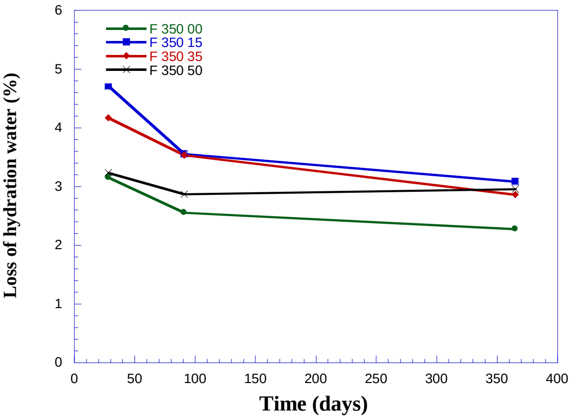

Figure 8: Loss of hydration water: 350 Kg/m^3 of *F*

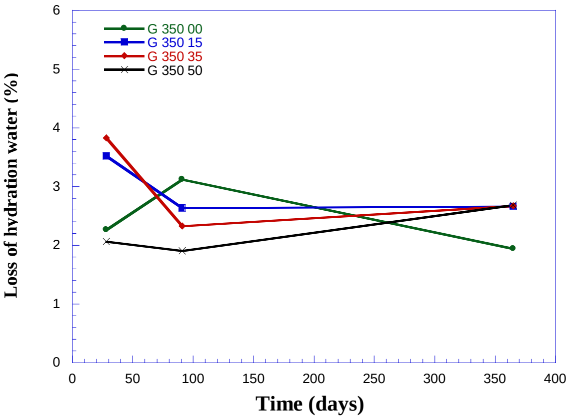

Figure 9: Loss of hydration water: 350 Kg/m^3 of *G*

The behavior of the reference concrete could be associated with greater fineness of *F* when comparing it with *G*. This is due to the greater contact surface that presents *F* to react with water. In the case of concrete with FA, the behavior could be associated with a decrease of the cement dose, which determines a lower hydration heat. This slowdown the hydration process of the cements

(Neville, 1999) and this simultaneously delays the pozzolanic reaction. The concretes mixed with *G* benefit of their higher amount of de C_3S to obtain a greater quantity of hydrated products than the concretes manufactured with *F* in a short period of time.

In the mixture of fluid consistency the behavior of the reference concrete has similar performance than the mixture of dry consistency, the concrete manufactured with *F*, seems to be more reactive that those manufactured with *G*. The incorporation of FA accelerates the reactivity in both concretes for moderate doses of ashes (≤ 35 %). Nevertheless, for high doses (50%) seems to slow down the hydration reactions. The use of ashes seems to be more effective when combined with *F* than with *G* for moderate doses of ash, while *G* assimilates better the insertion of high volumes of FA than *F*.

Just as the mixtures of dry consistency, the results of the reference concrete could be associated with the fineness of the cement. In the case of concretes with moderate doses of FA, the behavior of both concretes improves due to a better hydration of the Portland cement and the pozzolanic activity of the FA. It is known that FA can accelerate the C_3S hydration, its fineness and the quick absorption of Ca^{2+} makes it ideal for precipitation of C-S-H (Hewlett, 2004). The adding of FA in *G* increases the content of hydrated products significantly compared to the doses prepared with *F*. Despite this fact, none of the doses studied with the addition of FA in *G* surpasses the content of products hydrated with *F*. When comparing the TG/DTA it can be observed how the mixes of fluid consistency, prepared with *F* present a greater volume of the hydrated products at an earlier age than its equivalents of dry consistency. A similar tendency is appreciated when *G* is employed.

Mercury Intrusion Porosimetry: Figures 10 up to the 13 show the results of the cumulative volumes of MIP at 91 days. The values presented correspond to the average intrusion of the two cylinders tested. A mortar sample was extracted manually from each cylinder of hardened concrete, 3,5g ±0,3g.

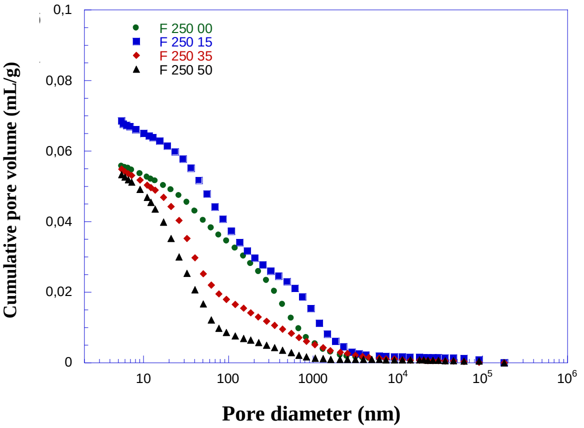

Figure 10: Cumulative pore volume: 250 Kg/m^3 of *F*

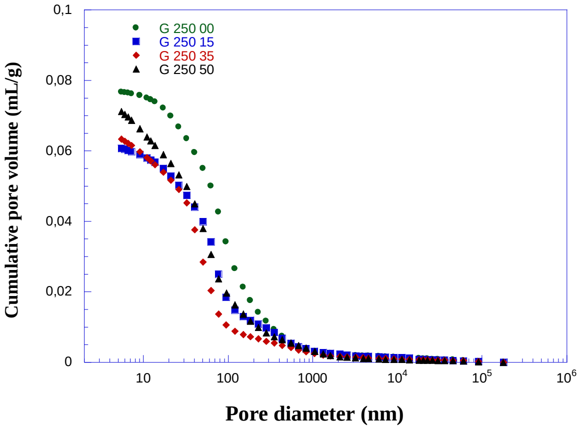

Figure 11: Cumulative pore volume: 250 Kg/m^3 of *G*

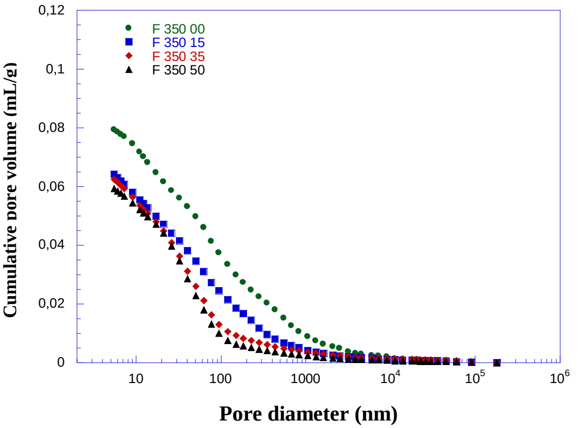

Figure 12: Cumulative pore volume: 350 Kg/m^3 of *F*

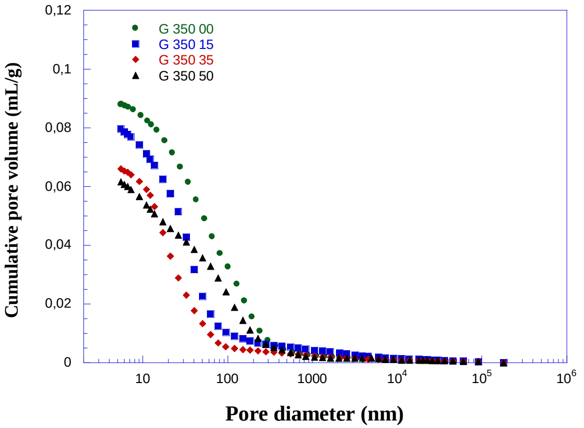

Figure 13: Cumulative pore volume: 350 Kg/m^3 of *G*

In the mixtures of dry consistency, the doses of FA vary its behavior by the type of cement used; the concretes of reference built with *F* offer a minor volume of total mercury intrusion that the concretes mixed with *G*. In concretes mixed with *F*, the incorporation of FA betters the resistance to the mercury penetration for all the cases studied with the exception of 15% of FA addition. The concretes built with *G* behave better once low doses are used (< 35%) while those concretes built with *F* react satisfactory when introducing higher doses (> 35%).

In the results of the mixtures of fluid consistency, the reference concretes of built with *F* offer a smaller total volume of mercury than the concretes made with *G*. The inclusion of FA decreases the mercury penetration for all of the cases studied. The addition of FA in concrete *F* and *G*, produces a refinement of the microstructure which provoking a decrease in the porosity of these concrete independent of percentage of FA added. However, it is possible to detect a different evolution of the porosity in concrete *F* and *G*. In the case of concrete built with *G* a significant reduction of porosity is observed, but in the case of the 50% of FA, the cumulative pore volume curve has a different evolution. It shows a great amount of pores with a diameter close to 100 nm. This behavior could have implications in the mechanical properties and durability along time.

Discussion

As previously stated, in the mixtures of dry consistency the reference concrete built with *F* offer compressive strength values superior to those concretes made with *G*. This could be explained through the TG/DTA and the MIP where the concretes built with *F* are more reactive and offer a minor volume of total porosity than the concretes made with *G*. The inclusion of FA equals of improves the compressive strength. This behavior cannot be explained in composition terms due to the fact that the TG/DTA shows a slowdown of the hydration reactions. However, the MIP shows an improvement in the resistance to mercury penetration for most of the cases studied.

It is valid to highlight that the compressive strength varies its behavior depending on the type of cement used and the doses of FA. The concretes built with *G* act better when using low doses (< 35%) while the concretes produced with *F* react better when introducing high doses (> 35%). This is contradictory with the findings of the TG/DTA where: superior doses (≥ 35%) seem to slowdown the hydration reactions in the *F* and accelerate in *G*. Nevertheless, the results of the MIP coincide with the mechanical behavior due to the fact that in this test the concretes made with *G* act better when employing low doses (< 35%) while those mixed with *F* react positively when introducing higher doses (> 35%). When referring to the mixtures of fluid consistency, the concretes of reference prepared with *F* offer values of compressive strength superior to those manufactured with *G*. This is consistent with the TG/DTA, where the concretes built with *F* get to be more reactive than the concretes manufactured with *G*. Likewise, the results of the MIP are coherent with the mechanical behavior; when the concretes mixed with *F* offer a minor total intrusion volume than the concretes fabricated with *G*.

In general terms, the incorporation of FA improves the compressive strength in the concretes from early stages. It is important to establish that the concretes made with *F* act better when using moderate doses (≤ 35%) while the concretes mixed with *G* react better when higher doses are introduced (> 35%). The TG/DTA supports this behavior when observing that the use of ashes is more effective when combined with *F* than with *G* for moderate doses of FA, while the *G* assimilates better the introduction of high doses of FA. Likewise, the MIP shows how the concretes built with *G* act more effectively when using high doses (> 35%) while those elaborated with *F* react better when introducing low doses (< 35%). When comparing the consistency it was observed that the mixtures of dry consistency prepared with *F*, present less compressive strength values than those with fluid consistency. Nevertheless, this behavior does not coincide with the concretes prepared with *G*. These vary in its behavior depending on the doses of FA. On the TG/DTA it can be seen that the mixtures of fluid consistency, prepared with *F* and *G* show a greater volume of hydrated products at an earlier age than its equivalents of dried consistency. However, when comparing the total volume of intrusion, it can be examined that the mixtures of dry consistency prepared with *F* and *G* present a minor degree of total porosity than its equivalents of fluid consistency in most of the cases.

Conclusions

- It can be concluded that different behaviors in function of concrete consistency exist: fluid or dry. In fluid concrete (high doses of cement), the concrete *F* reacted better when using moderate doses of the ashes (≤ 35%). Nevertheless, concretes where *G* was used reacted better when using high doses of the FA (50%). On the dry concretes (low doses of cement) it is harder to establish a behavior patter due to its higher difficulty to compaction. However, in general terms a better action can be seen in the concretes having *G* when using low doses of the FA (15%). The concretes that use *F* act better when using high doses of FA (50%).

- The loss of hydration water throughout time show a delay in the reactions of concrete built with *G* when compared with those made with *F*. Concretes in which FA are used present a greater proportion of hydrated compounds. In both cases it is very important the type of cement used: C_3S/C_2S ratio and consistency of cement.

- In most cases, the total porosity of the concretes built with *F* is less than the concretes that used *G*. The diminishing of total porosity reaches a maximum limit (where the reduction of total porosity is minimal) once the dose of FA increases. The doses necessary to reach this value vary depending on the cement studied.

Final Considerations: The effective free water available marks the efficiency of the pozzolanic reaction of the FA. According to that, various proportions of the added FA come to act as active admixture (strength effect) or modify the porous distribution (changes in porosity). The behavior of the concretes with FA varies in function to the physical and chemical characteristics of the cements used, even when these are under the same designation of cements.

References

Fernández Cánovas, M., 2007. *Hormigón.* 8th ed. Madrid: CICCP.
EHE-98 Instrucción Española de Hormigón Estructural. 1998, Ministerio de Fomento.
ISO 13320-1:1999 Particle size analysis -- Laser diffraction methods -- Part 1. 1999, ISO.
UNE-EN 933-1:1998. Ensayos para determinar las propiedades geométricas de los áridos. 1998, AENOR.
RC-03 Instrucción para la Recepción de Cementos. 2003, Ministerio de Fomento.
UNE-EN 450-1:2006. Cenizas volantes para hormigón. Parte 1. 2006, AENOR.
UNE-EN 450-2:2006. Cenizas volantes para hormigón. Parte 2. 2006, AENOR.
UNE 83414:1990 EX. Adiciones al hormigón. Ceniza volante. 1990, AENOR.
Neville, A.M., 1999. *Properties of concrete*. 4th ed. London: Pearson Education Limited.
Hewlett, P.L., 2004. *Lea´s Chemestry of Cement and Concrete*. 4th ed. Boston: Elseiver.