



Hydration and properties of ternary cement with calcareous filler and slag

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ABSTRACT

The calcareous filler produces an increase in early hydration due to the physical effects (filler and heterogeneous nucleation). The dilution effect counteracts this benefit and limits its content. Slag reacts slowly, causes the refinement of grains and pores, and improves the mechanical and durable properties. This paper is a study on the hydration of cements with filler (0 to 20%) and slag (0 to 35%), utilizing the Powers model for slag expanded by Chen & Brouwers. The mechanical resistance of the concrete ($a/mc = 0.50$) and the segmentation of the pores in relation to the capillary absorption rate are analyzed from the hydration results. The results show a limit on the filler content to obtain an adequate response for the mechanical and durable resistances at a greater age, and a limit on the slag content to obtain appropriate values at an early age.

Keywords: Calcareous filler; Slag; Resistance; Capillary absorption; Hydration.

RESUMEN

El filler calcáreo produce un incremento de la hidratación temprana debido al efecto físico (relleno y nucleación heterogénea). El efecto de dilución contrarresta este beneficio y limita su contenido. La escoria reacciona lentamente, provoca el refinamiento de granos y poros, y mejora las propiedades mecánicas y durables. En este trabajo se estudia la hidratación de cementos con filler (0 a 20 %) y Escoria (0 a 35%), empleando el modelo de Powers ampliado por Chen & Brouwers para escoria. A partir de los resultados de la hidratación, se analizan la resistencia mecánica del hormigón ($a/mc = 0.50$), y el proceso de segmentación de poros en relación con la tasa de absorción capilar. Los resultados muestran una limitación del contenido de filler para obtener una respuesta adecuada de la resistencia mecánica y durable a largas edades, y del contenido de escoria para obtener valores apropiados a temprana edad.

Palabras clave: Filler calcáreo, escoria, resistencia, absorción capilar, hidratación

RESUMO

Filler calcáreo produz uma aceleração da hidratação nas primeiras idades devido ao efeito físico (compactação e nucleação heterogênea). O efeito de diluição neutraliza os benefícios e limita o seu conteúdo. A escória reage lentamente, fazendo com que o refinamento dos grãos e poros, e melhora as propriedades mecânicas e duráveis. Neste trabalho a hidratação do cimento com filler (0-20%) e escória (0-35%) é estudada usando o modelo de Powers ampliado por Chen Brouwers para escória de alto forno. A partir dos resultados de hidratação, é analisada a resistência do concreto (com $a/c = 0,50$), e o processo de segmentação de poros é analisado com relação a taxa de absorção capilar. Os resultados mostram que o teor de filler deve ser limitado para obter uma resposta de resistência mecânica e de durabilidade. Também o conteúdo de escória deve ser limitado para obter propriedades adequadas nas primeiras idades.

Palavras chave: Filler calcáreo, escória, resistência, absorção capilar, hidratação.

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1. INTRODUCTION

The addition of minerals has taken vital importance in the formulation of cement mixtures due to the need to reduce energy consumption, protect natural mineral resources, and reduce gas emissions that contribute to the greenhouse effect. In order to meet sustainability objectives, it is also necessary for the formulated mixture to contribute to a longer working life for the concrete structures of which it will form part. Over the past few decades, there has been an increase in efforts to understand the behavior of concrete with the addition of natural minerals (pozzolans, calcareous filler), thermally activated additives (calcined clay), or industrial sub-products (fly ash, blast furnace slag, silica fume) (CEMBUREA, 2000 – 2010). In order to formulate binary cements, various mineral additions within the limits of the resources available in each region or country have been used. As of 1990, the use of ternary or cement compounds formulated with Portland clinkers and two mineral additions has increased given that it has various advantages over binary cements. The European (EN 197-1), Mexican (NMX C-414-0), and Argentinean (IRAM 5000) standards for cement have standardized cement compounds that contain up to 35% in weight a combination of two additives, and currently it is planned to increase this percentage up to 55%. In the United States, the ASTM C 1157 standard incorporated hydraulic cements based on performance that do not limit the type and quantity of the mineral additions that could be mixed with Portland cement.

Additives to be combined are chosen in such a manner that the deficiency of a mineral addition is compensated by virtue of the other, and the synergy produced improves the behavior of the ternary cement material. Finally, the mechanical and durable properties of the concrete will depend on the hydration process, which will determine the porosity and connectivity of the porous structure of the matrix, as well as the improvement of the paste-added interface (Soroka, 1979).

The hydration of Portland cement is a complex natural physicochemical process influenced by factors of the Portland cement itself (mineralogical composition, alkali, sulfates, finesse, etc.), the conditions of the mixture (*a/c* relation, unitary content of the cement), and the environment (temperature and relative humidity). When the mineral additions have been incorporated with the Portland cement, the effects produced on the hydration can be arbitrarily divided into three (Cyr et al., 2006):

- The **dilution effect** is the consequence of the partial replacement of a part of the cement by the mineral addition, which decreases the quantity of the cement and, consequently, creates an increase in the effective water/cement ratio. For an equal hydration grade of the cement material, this effect implies a lower volume of hydration products for the cement.

- The **physical effects** produced by the finely ground additions are: the filler effect and heterogeneous nucleation. The filler effect makes the fine particles of the additions fill the empty spaces between the cement grains, modifying its granular packaging, which implies a change in the initial porosity of the paste. This effect positively or negatively modifies the demand for water required to maintain the workability given the particle size and the ratio of the additions.

- The **chemical effect** is the pozzolanic reaction of the mineral addition in which the previously hydrated phases play a role at varying degrees, such as is the case for calcium hydroxide (CH). In the particular case of the calcareous filler, the reaction of calcium carbonate and tricalcium aluminate of Portland clinker produces the formation of hydrated calcium carboaluminate (general phase AFm: mono-substituted aluminoferrite) (Bonavetti et al., 2001); however, this addition does not generate hydrated calcium silicate (CSH) during its hydration (Sersale, 1992).

When inactive mineral additions are used, the influence of the first two effects is easy to quantify with the chemically combined water and the Powers and Brownyard model (Powers, 1948;

Brouwers, 2004, 2005), as is the case of the calcareous filler already mentioned (Bonavetti et al., 2003; Bentz et al., 2009; Bonavetti et al., 2013). Whereas when the addition presents a chemical effect, quantification becomes more complex and requires models that allow the determination of the contribution of the addition to the parameter.

The properties of concrete and its evolution with the passage of time depend in great measure on the advancement of the cement hydration which determines the evolution of the porosity of the matrix (Bentz et al., 2009). In ternary cements comprised of filler and slag, this process depends in great measure on the relative ratios of the components. The filler contributes to hydration in the initial stage and the slag contributes to hydration in the midterm, and the properties of the concrete they comprise vary in accordance to the evolution of this process.

The objective of this paper is to analyze the compression strength and the rate of capillary absorption in concrete elaborated with cement compounds that contain calcareous filler and blast furnace slag with regard to the hydration process of the cement material.

2. PROCEDURE

In the concretes studied, normal Portland cement (CPN, IRAM 50000), resistance class CP40 ($f^c > 40$ MPa at 28 days) with low C_3A ($< 3\%$) content was utilized. The additions utilized were calcareous filler (F) and granular blast furnace slag (E). F originates from limestone with a high ground calcite content at a Blaine finesse of $522 \text{ m}^2/\text{kg}$. E is a cooled slag ground to a Blaine finesse of approximately $450 \text{ m}^2/\text{kg}$. The slag has a high activity classification according to the index of determined cement in accordance with the standard ENV 196-1. The combinations of binary and ternary cements utilized can be found in Table 1.

The concretes were elaborated in two stages utilizing river silica sand as a fine aggregate and crushed granite stone as a thick aggregate (maximum size of 19 mm); the content of the cement material (CUMC) was 350 and $360 \text{ kg}/\text{m}^3$, and in all cases the a/mc (water/cement material) was 0.50. Full details of the first and second stage concretes have been previously published (Menéndez et al., 2006, 2007; Carrasco et al., 2003).

The resistance was determined in cylindrical test tubes (100 x 200 mm), cured 24 hours in molds and subsequently in water saturated with lime at 20 ± 1 °C until reaching the trial age. The informed values are the average of five test tubes. For the first stage concretes, the compression strength was determined at 3, 7, 28, 90, and 360 days, and for second stage concretes at 2, 7, and 28 days.

In first stage concretes, the capillary absorption coefficient was determined in prismatic test tubes whose lateral faces were painted with epoxy paint, except for the face corresponding to the mold where a 100 cm^2 area was left unpainted. The prisms were consecutively submerged at a constant depth of 1 cm. The quantity of water absorbed was measured as the weight gain at 1, 5, 10, 15, 30, 60, 120, 240, 360, 720, 1440, and 2880 minutes, and the capillary absorption rate (S) of the concretes was measured as the slope of the graph between the water quantity absorbed per unit area versus the square root of time in the zone comprised between 1 hour as long as linearity was maintained (Menéndez et al., 2002).

The quantity of non-evaporable water (W_n) was determined from the fragments obtained from the tested samples in accordance with the procedure proposed by Powers (Powers, 1949; Escalante-García, 2005). For the average mineralogical composition of the Portland cements utilized, the quantity of non-evaporable water of the cement used to achieve total hydration was 0.195 g of water per g of cement. Assuming the hypothesis of the hydration model proposed by Chen & Brouwers (2007a), for the total hydration of the slag utilized, 0.20 g of water per g of slag is

required. For this particular case, due to the small difference between the total W_n for the hydration of the type of cement utilized (low C_3A), there is an assumed value of 0.20 g/g for the cement and slag. By having the total W_n values coincide, it is possible to calculate the degree of hydration for the combined cement material. With the degree of hydration calculated using the Powers model (Powers, 1948; Brouwers, 2004, 2005) and the Chen & Brouwers model (2007b) for the cements with slag, it is possible to estimate the volumes of the hydrated phases assuming that the calcareous filler is hydraulically inactive and that the total of the incorporated slag reacts. Calculating the volume of hydrated products and knowing the free space created by the effective water/cement ratio, the gel-space (X) ratio and the capillary porosity (ϕ) of the cement matrix of the concrete can be calculated following the expressions described previously (Bonavetti et al., 2013).

3. RESULTS AND DISCUSSION

Table 1 shows the results obtained for the combined water (W_n), compression strength ($f'c$) and rate of capillary absorption (S) for the various concretes and the ages included in this study. As was expected, the course of time for curing increases the content of combined water and compression strength, and decreases the capillary absorption rate.

In relation to the reference concrete (CP or CPN), it can be observed that the calcareous filler contributes to the content of W_n at an early age, and that the contribution of slag is appreciable after seven days of hydration. For concretes with binary cement with calcareous filler, the quantity of W_n relative to the content of reactive material increases when the level of early age replacement is increased (Figure 1a), and then the progress of the hydration of the Portland phase tends to minimize this advantage. For binary cements with slag (Figure 1b), the incorporation of slag produces a relative decrease of the W_n at an early age. At 7 days, the slag reacts slowly and the relative W_n increases reaching a similar value to that of the Portland cement reference at 28 days.

Table 1. Composition of the cement material, combined water (W_n), compression strength (f'_c), capillary absorption rate (S); degree of hydration (α), gel/space ratio (X), and capillary porosity (ϕ) of the studied concretes.

Concrete	CUMC, kg/m ³	F, %	E, %	Age days	W_n	f'_c MPa	S , g/cm ² h ^{1/2}	a/c effect	α	X	ϕ , %
CP	350	0	0	3	10.04	18.3	0.222	0.50	0.515	0.536	30.9
				7	11.77	25.5	0.181		0.604	0.603	27.7
				28	13.29	36.0	0.100		0.682	0.657	24.8
				90	16.76	39.0	0.081		0.859	0.768	18.2
				360	17.71	41.3	0.081		0.908	0.796	16.4
CPN	360	0	0	2	10.66	15.9	--	0.50	0.547	0.561	29.8
				7	11.74	27.4	--		0.602	0.602	27.7
				28	14.91	34.0	--		0.764	0.711	21.7
CP12F	350	12	0	3	10.96	20.6	0.214	0.57	0.562	0.520	36.0
				7	14.21	28.3	0.126		0.729	0.630	29.9
				28	15.41	34.5	0.093		0.790	0.667	27.6
				90	17.85	38.4	0.063		0.915	0.736	22.9
				360	18.28	39.6	0.065		0.937	0.748	22.1
CP18F	350	18	0	3	11.36	20.9	0.288	0.61	0.583	0.506	39.5
				7	15.32	27.2	0.214		0.786	0.631	32.0
				28	16.50	35.2	0.097		0.846	0.665	29.7
				90	18.20	37.7	0.068		0.933	0.711	26.5
				360	18.91	38.0	0.062		0.970	0.730	25.2
CPN15F	360	15	0	2	11.66	18.0	--	0.59	0.598	0.531	36.7
				7	12.70	27.0	--		0.651	0.566	34.7
				28	16.10	32.7	--		0.826	0.671	28.3
CP20E	350	0	20	3	9.18	16.6	0.288	0.50	0.471	0.501	32.6
				7	11.72	25.0	0.214		0.601	0.601	27.8
				28	13.72	34.7	0.097		0.704	0.672	24.0
				90	16.95	41.5	0.068		0.869	0.774	17.8
				360	18.46	43.5	0.062		0.947	0.817	15.0
CPN35E	360	0	35	2	8.31	11.1	--	0.50	0.426	0.464	34.2
				7	10.78	21.4	--		0.553	0.566	29.5
				28	13.81	29.0	--		0.708	0.675	23.8

Table 1. (Continued)

Concrete	CUMC, kg/m ³	F, %	E, %	Age days	Wn l	f'_c MPa	S, g/cm ² h ^{1/2}	a/c effect	α	X	ϕ , %
CP12F10E	350	12	10	3	10.39	19.4	0.208	0.57	0.533	0.500	37.1
				7	13.27	28.4	0.147		0.681	0.600	31.6
				28	14.33	36.6	0.111		0.735	0.634	29.6
				90	17.97	39.4	0.069		0.922	0.740	22.7
				360	18.55	40.0	0.063		0.951	0.755	21.6
CP12F20E	350	12	20	3	9.18	15.6	0.236	0.57	0.471	0.453	39.4
				7	11.72	28.2	0.194		0.601	0.547	34.6
				28	13.72	36.9	0.113		0.704	0.614	30.8
				90	16.95	39.3	0.050		0.869	0.711	24.7
				360	18.46	39.7	0.047		0.947	0.753	21.8
CP18F10E	350	18	10	3	11.14	19.1	0.238	0.61	0.571	0.499	39.9
				7	14.55	26.1	0.196		0.746	0.609	33.4
				28	15.68	35.4	0.137		0.804	0.642	31.3
				90	18.27	38.3	0.105		0.937	0.713	26.4
				360	19.13	38.8	0.086		0.981	0.735	24.8
CP18F20E	350	18	20	3	10.92	15.3	0.249	0.61	0.560	0.491	40.3
				7	14.15	24.4	0.199		0.726	0.596	34.2
				28	15.50	34.6	0.126		0.795	0.637	31.6
				90	17.62	37.7	0.061		0.904	0.696	27.6
				360	18.65	38.2	0.062		0.956	0.723	25.7
CPN6F22E	360	6	22	2	9.05	16.3	--	0.53	0.464	0.472	36.0
				7	13.25	27.1	--		0.680	0.628	28.0
				28	14.16	36.9	--		0.726	0.658	26.3
CPN11F11E	360	11	11	2	10.46	18.7	--	0.56	0.536	0.506	36.3
				7	12.89	27.8	--		0.661	0.592	31.7
				28	16.21	34.4	--		0.831	0.696	25.4
CPN22F6E	360	22	6	2	9.84	14.2	--	0.64	0.504	0.435	45.4
				7	14.53	24.6	--		0.745	0.587	36.5
				28	15.42	29.6	--		0.791	0.613	34.8

The contribution of slag to the W_n corresponds to the pozzolanic reaction of the slag, whose main hydration products are the calcium aluminium silicate (C-A-S-H) with a lower C/S reaction than that which corresponds to C-S-H, hydrotalcite (M_5AH_{13}) and ettringite ($C_3A.3CS.H_{32}$) (Chen & Brouwers, 2004). This reaction is initially stimulated by the alkaline solution that contains the CH provided by the hydration of the Portland cement.

For concretes with ternary cements of low (Figure 1c) and high filler content (Figure 1d) and variable slag content, it can be observed that the W_n is slightly greater than the reference concrete for the first case and much greater at an early age for the second case, tending to converge at 90 days.

In line with the previous results on the mortars regarding the hydration of the binary and ternary cement systems with calcareous filler and slag (Menéndez et al., 2003; Carrasco et al., 2007), it can be observed that the effects of the additions (dilution, physical and chemical effects) cause variations in the W_n .

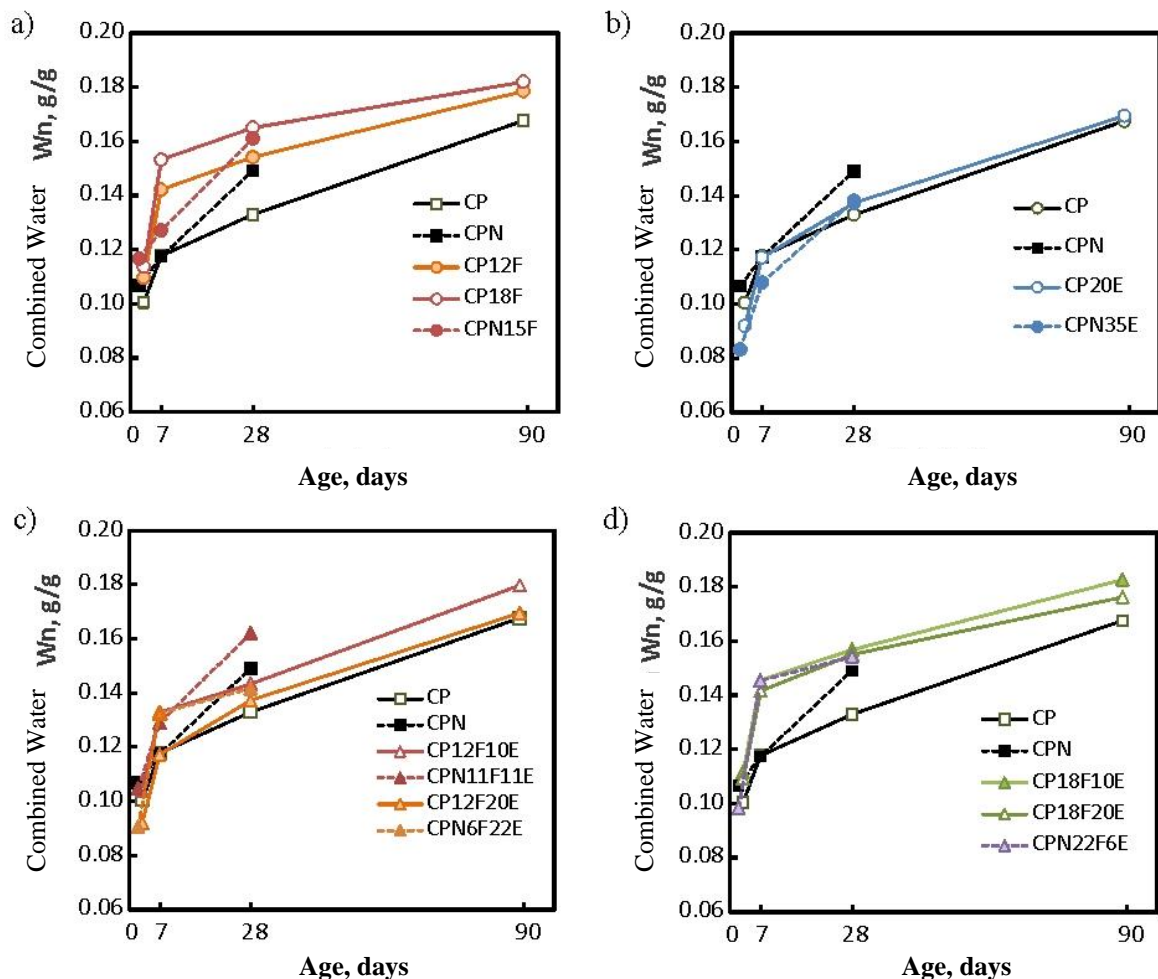


Figure 1: Evolution of the non-evaporable water (W_n) in the concrete matrix in function of time.
 a) Binary cements with calcareous filler; b) Binary cements with slag; c) Ternary cements with low filler ratio; d) Ternary cements with high filler ratio.

The physical effects fundamentally appear during the first days of hydration and the chemical contribution of the slag is appreciable after the first seven days of hydration. Dilution is an effect present at all times.

The increase in the percentage of mineral added to the Portland cement causes the dilution effect, which decreases the quantity of Portland cement and consequently produces a change in the effective water/cement ratio. In the case of the calcareous filler-slag system, the same can be calculated as indicated by the equation below (1).

$$a/c_{\text{effective}} = A / (C + \chi_f F + \chi_E E) \quad (1)$$

Where A, C, F, and E are the quantity in weight of water, Portland cement, calcareous filler, and slag utilized in the mixture. χ_f and χ_E are the efficiency factor of the calcareous filler and of the slag utilized, respectively. This factor represents a measurement of the relative behavior of each addition compared to Portland cement, and this factor also depends on the type of Portland cement utilized, its age, type, and the quantity of the addition utilized in the mixture and the initial a/c ratio (Cyr et al., 2000).

When considering that the calcareous filler is an inactive mineral addition, the efficiency factor χ_f tends to 0 and therefore produces an increment in the effective a/c ratio proportional to the content of the addition in the cement. For slag, the value of χ_E varies with time, the level of replacement, and the cement used. At longer ages (>90 days), the value of $\chi_E > 1$ increases the resistance and decreases the permeability. At 28 days, the value of χ_E varies from 0.79 to 1.5 for a 50% replacement making it necessary to increase the CUMC and decrease the a/mc to reach a similar resistance to that of Portland cement (Boukhatem et al., 2011). In order to simplify the calculations, this study assumes that χ_f is null and that $\chi_E = 1$ for all ages.

For the same degree of hydration as Portland cement, the dilution effect caused by the filler ($\chi_f = 0$) produces a lower volume of hydrated products and therefore a lesser quantity of combined water with regard to the total cement material incorporated. The reduction in volume of the hydrated products at the first ages for elevated percentages of additions leads to a lower compression strength. For low addition percentages (Menéndez et al., 2003), the heterogeneous nucleation increases the degree of reaction of the cement material and can, in part, compensate for the dilution. The filler effect makes the fine particles of the additions fill the empty spaces between the cement grains, modifying its granular packaging, which implies a change in the initial porosity of the paste and consequently the resistance could slightly increase.

In this study a constant a/mc ratio has been used in the concrete mixture, therefore the space to be occupied by part of the hydration products shall be the same. The difference will be given by the quantity of material that has reacted at each age that determines the gel/space ratio of the system. Consequently, in order to know the influence of the content of the addition on any resistant or durable property, it is necessary to study the volume of the hydration products produced in accordance with the degree of hydration (α) of the cement material.

Table 1 shows the effective values of the a/c ratio calculated for each of the concretes studied assuming the stated hypothesis. Starting from the W_n , the degree of hydration of the Portland cement can be estimated, dividing this value by the total necessary water to hydrate the entirety of the Portland cement. Whereas for slag, the degree of hydration was calculated from the difference between the total combined water minus the combined water of the fraction of Portland cement in the mixture, dividing the total necessary water to hydrate the entirety of the slag. Subsequently, the

volume of the hydration products was calculated according to the Chen & Brouwers model (2007b) and finally the gel/space ratio (X) whose values are shown in Table 1.

The compression strength of a material of a cement base (f'_c) can be calculated as the intrinsic resistance (f_0) of the material affected by the gel/space ratio (X) raised to the n (2).

$$f'_c = f_0 X^n \quad (2)$$

Figure 2 shows the relation between the compression strength and the gel/space ratio obtained utilizing this simplified model. The coefficients of the equation (2) obtained through the best approximation by least squares for each type of cement are shown in Table 2. For every group, it can be observed that the intrinsic resistance value of this material of cement base (concrete) is approximately 75 MPa and coefficient n varies from 2.0 to 2.3, whose values are found within reported literature.

This good correlation between the experimental results of the compression strength of the concretes elaborated with different cement materials, with variable ratios of calcareous filler and slag, in binary and ternary mixtures, confirm that those postulated by the simplified hydration models of Powers, which were later revised and expanded on by Chen & Brouwers, are acceptable for the studied system. This observation is important for the design of concretes with multicomponent cements that allow the design of the replacements from the wanted resistance or durability objective.

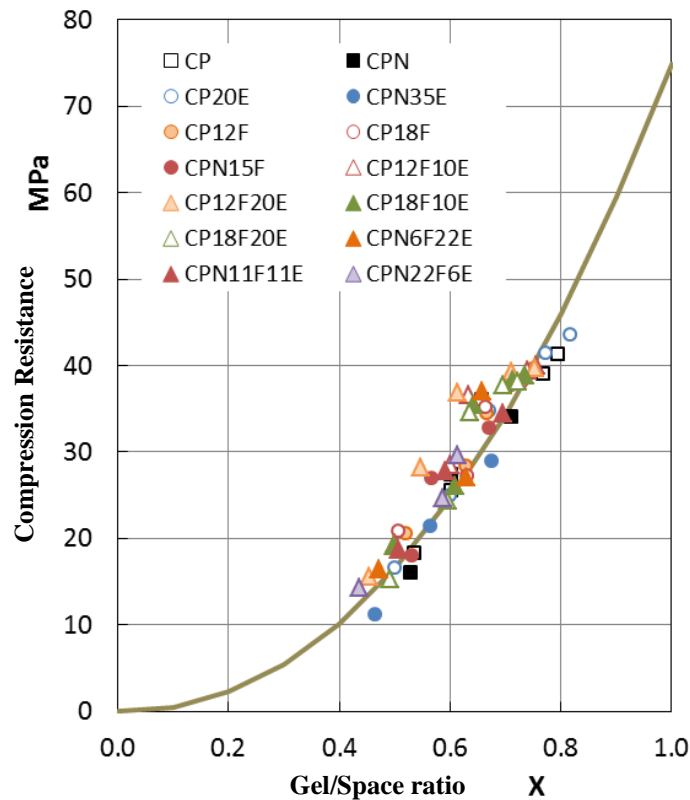


Figure 2: Compression resistance vs. gel/space ratio for all the concretes studied.

Table 2: Coefficients of the equation that relates f'_c and the gel/space ratio.

Concretes included in the correlation	f_0	n	R^2
Portland Cement (CP, CPN)	74.1	2.2	0.84
Binary cements with calcareous filler (CP12F, CP18F, CP15F)	76.7	2.1	0.95
Binary cements with slag (CP20E, CPN35 E)	75.8	2.3	0.96
Ternary cements	76.3	2.0	0.92
All cements	74.9	2.06	0.90

To ensure the durable performance of the concrete before the deterioration processes, the first measure that must be taken is the reduction of the transport processes of water and aggressive substances in its mass. For concretes of Portland cement, it has been assumed that a decrease in the a/c ratio below 0.53 produces a drastic reduction on the permeability when the same has been properly cured and is related to the capillary porosity (Soroka, 1979).

The capillary porosity (ϕ) according to the Powers model for Portland cement depends on the a/c ratio and the degree of hydration (α) of the same (3).

$$\phi (\%) = (a/c - 0.37) * 100 \quad (3)$$

In terms of pore connectivity, the reduction of permeability occurs when the volume of capillary pores in the mixture is below 18% (Winslow et al., 1994). In the case of Portland cement with an a/mc ratio of 0.50, a hydration degree of 0.70 is required to archive a capillary porosity of 18% and thus segment the pores impeding the transportation of water. In concretes of binary or ternary cement, the calculation of capillary porosity also emerges from the analysis of the content of the hydrated cement material in function of the space available to be filled. For this reason, the capillary porosity increases with the increment of the effective a/c and decreases when the degree of hydration of the cement material increases. In function of this model, it is possible to estimate the volumes of the various stages that are found in the cement paste at any of its hydration stages.

Figure 3 shows that for concretes CP and CP20E, when the 18.5% capillary porosity is achieved, segmentation of the pores occurs and the capillary absorption rate changes very little after the first 28 days once the degree of hydration that produces segmentation of the pores is reached. Between 90 and 360 days, the capillary absorption rate does not significantly change. For all the binary and ternary cements that contain 12 and 18% of calcareous filler, even though the degree of hydration is greater, the absorption rate presents a higher value up to the first 28 days due to the increase of the effective a/c ratio. However, the capillary porosity threshold that does not make significant changes in the capillary absorption rate is greater (22 to 24%). This situation is attributable to the fact that the models utilized do not take into account the blockage effect of the pores, which can produce the incorporated calcareous filler particles.

In this manner, it can be concluded that in order to obtain an impermeable concrete with a low water transportation rate per capillarity, it can only be achieved when the segmentation of the pores of the cement matrix is produced; whether through a reduction of the a/mc ratio or an increase in the degree of hydration of the cement material.

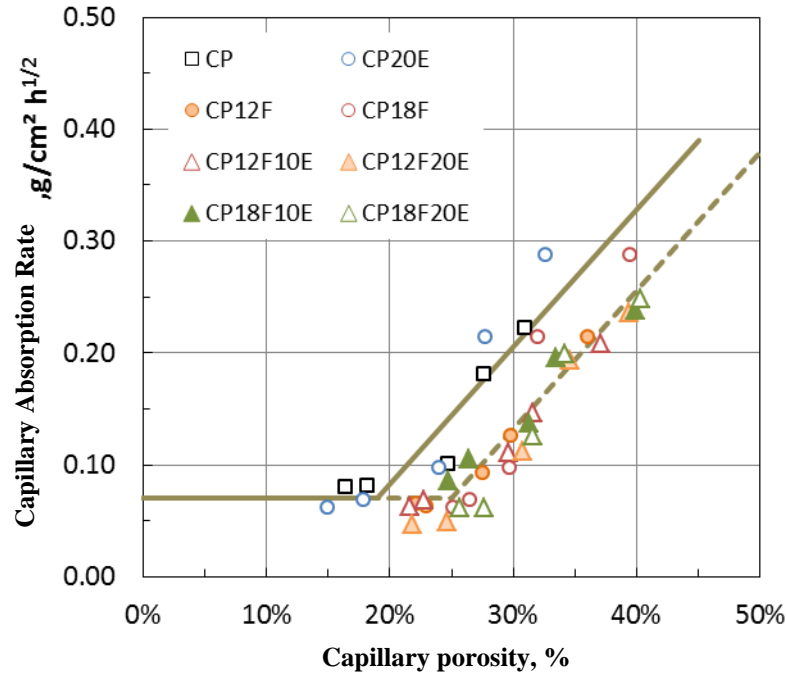


Figure 3. Relation between the capillary absorption rate and the capillary porosity of the matrix.

4. CONCLUSIONS

According to the experimental results and the suppositions made to implement the existent hydration models, the following conclusions can be expressed:

- The evolution of the hydration of the cement matrix of the concrete determines the development of the porous structure and with it, the compression strength and the capillary absorption rate independent of the formulation of the cement mixture utilized.
- For binary compound cements, the evolution of the hydration of the cement can be controlled and modified with the calcareous filler or in the case of cement, with slag through a change in the finesse and the ratios in the mixture. In general, it can be observed that the properly ground calcareous filler contributes to the early hydration and slag contributes to the late hydration. This supplementation allows the development of ternary cements.
- The Powers model and the considerations of Chen & Brouwers for the hydration of slag allow the modeling of the gel/space ration and the capillary porosity of the matrix in the ternary cements. The relation between the results of the models and the experimentally determined properties of the concrete reasonably correspond.

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