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Limestone filler cement in low w/c concrete: A rational use of energy

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Abstract

The effect of limestone filler (up to 20%) on the degree of hydration, the volume of hydration products, and the optimal replacement of limestone filler in cement pastes at different w/cm ratios (0.25–0.50) were investigated by using a quadratic statistical model. The results show an increase in the degree of hydration in very low w/cm ratio paste when the limestone filler content is increased. However, the largest volume of hydration products occurs for high w/cm ratio pastes, for which the available space also increases with the limestone filler content. Finally, for a given cement, the optimum limestone filler content for different w/cm ratios can be obtained by using the gel–space ratio concept. In addition, concrete mixtures (w/cm = 0.30 and 0.34) were made to determine the compressive strength. The results have shown that concretes containing limestone filler cements present a small reduction of strength at 28 days improving the hydration of clinker particles in the system. The strength of concrete depends on the gel–space ratio, which takes into account all of the effects produced by limestone filler addition: the increase of the degree of hydration, the dilution, and the increase of the *effective w/c ratio.*

Keywords: Hydration; Compressive strength; Filler; Cement paste; High-performance concrete

1. Introduction

The use of portland cement containing limestone filler is a common practice in European countries, especially in France. This type of cement is formulated to achieve certain goals in the technical, economic, and ecological fields. Among the technical benefits are the increase of early strength, the control of bleeding in concrete with low cement content, and the low sensibility to the lack of curing [1]. The economic benefits are related to the possibility to obtain a cement with a strength development similar to that of portland cement at low production and investment costs per ton of cement [2]. The ecological advantages are the reduction of CO_2 and NO_x emissions per ton of cement manufactured and the conservation of fossil fuels and mineral resources.

The performance of limestone filler addition to portland cement has been widely studied in pastes, mortars, and concretes [2–6]. In general, limestone filler improves the hydration rate of cement compounds and consequently increases the strength at early ages [7–10]. From a chemical point of view, limestone filler does not have pozzolanic properties, but it reacts with the alumina phases of cement to form an AFm phase (calcium monocarboaluminate hydrate) with no significant changes on the strength of blended cement [11].

The main effects of limestone filler are of physical nature. It causes a better packing of cement granular skeleton and a larger dispersion of cement grains [12]. Furthermore, limestone filler acts as the crystallization nucleus for the precipitation of CH [13]. These simultaneous effects produce an acceleration of the hydration of cement grains.

High-performance concrete (HPC) mixtures contain a large volume of cement content and low w/cm ratio; in addition, high workability can be achieved by using superplasticizer admixture. In these mixtures, there is not available space to locate the hydration compounds and, as a result, a large volume of cement will remain unhydrated causing a nonrational use of resources and energy to produce concrete. In these concretes, the capillary pores become discontinuous relatively early and the improvement of the strength depends on the degree of hydration developed by the cementing materials. Moreover, the large volume of cement could induce an increase of cracking in the concrete structure [14]. Replacing the expensive particles of cement by nonreactive economical particles of filler could offset these disadvantages.

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Table 1
Physical characteristic of cements used

Physical characteristic	Cement		
	C0	C10	C20
Limestone filler content (wt.%)	0	9.3	18.1
Fineness			
Specific surface Blaine (m^2/kg)	317	372	420
Retained 75-μm sieve (#200) (%)	7.8	1.4	1.9
Compressive strength[a] (MPa)			
1 day	10.7	14	11.9
7 days	33.4	41.6	40.1
28 days	44.1	49.2	47.6

[a] Compressive strength of six 40 × 40 × 40-mm^3 prisms ISO-RILEM mortar.

Nedhi et al. [15] investigated the addition of limestone filler on low w/cm ratio mortar and they concluded that cement with limestone filler (up to 10–15%) did not affect the early strength of mortar, but it caused loss of strength at later ages. They proposed the use of ternary blend containing limestone filler, silica fume, and portland cement as the most cost effective mixture evaluated at 28 days. By using the NIST CEMHYD·3D software, Bentz and Conway [16] have recently demonstrated that for the initial w/cm of 0.25 and 0.30 a proportion of coarse cement particles can be replaced by inert filler with a little projected reduction in the compressive strength.

In this article, the use of portland limestone cements (PLC) in low w/cm mixtures is experimentally analyzed. Initially, the degree of hydration, the volume of cementing compound, and the gel–space ratio are analyzed in pastes (w/cm = 0.25–0.50) containing cements with different proportion of limestone filler. Finally, the compressive strength in concrete with low w/cm using these cements is examined to corroborate the effect of limestone addition.

2. Experimental procedure

2.1. Materials

A Type I portland cement (C0) and two PLCs (C10 and C20) obtained from the same portland clinker by an intergrinding process in the cement factory were used. The clinker contained 65% of C_3S and 5.3% of C_3A, limestone contained 85% of $CaCO_3$ in calcite form without clay minerals and quartz as the main impurity, and the limestone contents by mass were 0, 9.3, and 18.1% according to the data supplied by the cement producer. The cements have the same strength class (44.1, 49.2, and 47.6 MPa at 28 days) leading to a larger specific surface area of PLCs: 317, 372, and 420 m^2/kg for C0, C10, and C20, respectively. The physical characteristics of these cements are reported in Table 1.

For concrete mixtures, the coarse aggregate was crushed granite stone with a maximum size of 19 mm obtained from a very sound granite rock with 30.6 and 146 MPa of flexural and compressive strength, respectively. The fine aggregate was natural sand with a fineness modulus of 2.35. A high-range water reducer based on sulfonated melamine formaldehyde containing 22% of active ingredient in aqueous solution was used.

2.2. Cement pastes

For each type of cement, pastes with w/cm of 0.25, 0.30, 0.35, 0.40, and 0.50 were mixed during 3 min in a planetary mixer. The pastes were put in individual sealed plastic bags and stored in a water bath at 21 ± 2 °C until 1, 3, 7, and 28 days. At the time of test, the paste was ground in acetone to stop the hydration, and the nonevaporable water was determined by using the procedure proposed by Powers [17]. The degree of hydration (α) was estimated assuming that the filler is a chemically nonactive addition and that the water needed for the full hydration of the cement used is 0.23.

2.3. Concrete mixtures and test

Two concrete mixtures (w/cm = 0.30 and 0.34) were made for each type of cement used. The cementitious material content was 450 kg/m^3, and the slump was 10 ± 2.5 cm. The mixture proportions and properties of fresh concrete are shown in Table 2. Concretes with PLC require an increase of admixture dosage to achieve the projected slump, which is attributed mainly to the large specific surface of the PLCs.

Compressive strength of concrete was determined on 100 × 200-mm cylinders. Specimens were cast, covered with a plastic sheet, and left in a laboratory environment

Table 2
Concrete mixture proportions and slump

Cement	Proportion of mixture (kg/m^3)						Slump (cm)
	w/cm	Cementitious material	Water	Fine aggregate	Coarse aggregate	Admixture[a]	
C0	0.30	450	135	707	1154	1.2	12.0
C10	0.30	450	135	705	1154	1.4	12.5
C20	0.30	450	135	703	1154	1.4	12.5
C0	0.34	450	157	700	1100	1.0	12.0
C10	0.34	450	157	695	1100	1.2	10.0
C20	0.34	450	157	690	1100	1.2	9.0

[a] Percentage in weight of cemetitious material.

for 24 h. After demolding, the cylinders were cured in water saturated with lime until 3, 7, and 28 days. Fragments of specimens were used to estimate the amount of nonevaporable water and the degree of hydration in concrete by using a similar procedure as described above. Results provided by this method are not accurate enough; nevertheless, they illustrate the hydration reaction progress.

3. Results and discussion

3.1. Influence of limestone filler addition on paste hydration

Fig. 1 shows the evolution of α for active cement grains in pastes containing C0, C10, and C20 cements for the different w/cm ratios used (0.25 to 0.50). For very low w/cm ratio (0.25), the α of portland cement were 0.35 and 0.5 at 1 and 28 days, respectively. The α of active material, however, attained a value of 0.64 for the w/cm ratio commonly used in HPC (0.30–0.35). These results show that more than 35% by mass of active cement grains remain unhydrated after 28 days, acting as an expensive filler material in low w/cm ratio mixtures. Since portland cement is the largest energy-consuming ingredient of concrete, it appears as a nonrational solution for concrete production in the future [18]. According to Powers' model, the complete hydration of cement paste could be obtained in mixtures with w/c greater than 0.42 because it provides enough space to locate the hydration products of cement grains. However, it can be noticed that for pastes with w/cm of 0.50, as used in conventional concrete, the α was 0.80 at 28 days.

In the two pastes containing PLC and very low w/cm ratio (0.25), the α was higher than that of the corresponding portland cement at all ages studied. It is due to the improvement of hydration kinetics at early ages caused by limestone addition and the small grain size of clinker due to the intergrinding process and the high *effective w/c ratio* presented in paste that allow the compound resulting from the progress of cement grain hydration.

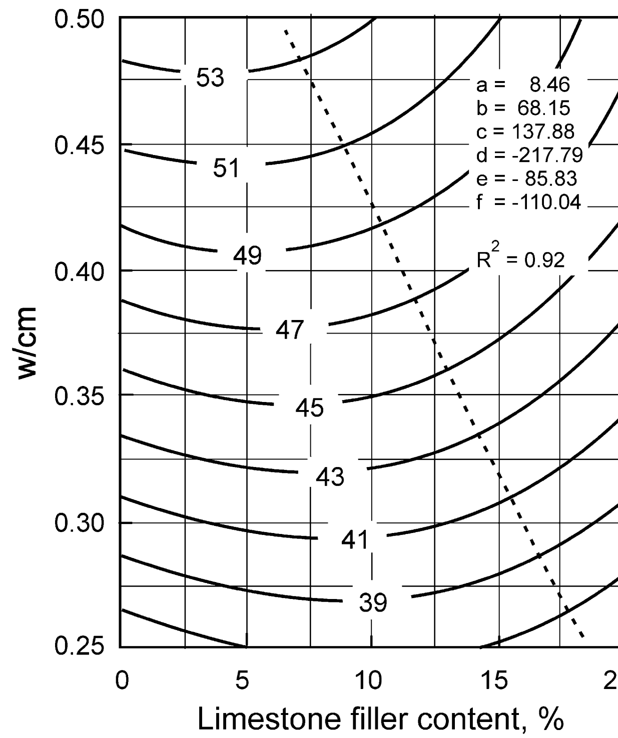

Fig. 2. Isoresponse curves of the volume of hydration products (in cm^3 by 100 g of cement) at 28 days as function of limestone filler content and w/cm used.

For w/cm of 0.35, the α of active grains increased up to 0.74 and 0.78 at 28 days for pastes containing C10 and C20 cements, respectively. In both cases, more than three-quarters of the active grains presented in cement react to produce cementing compounds.

The α of the C0 paste with a w/cm ratio ranging from 0.30 to 0.40 was 14% and 22% lower than that of the corresponding pastes containing C10 and C20 cement, respectively. Consequently, it can be observed that the α of the active grains increases whenever the replacing limestone filler that provides the space to locate the compounds is increased.

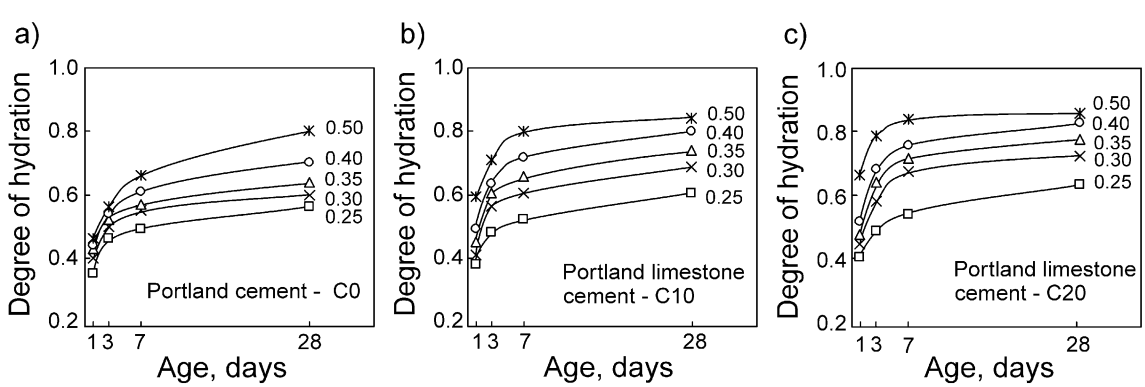

Fig. 1. Evolution of α up to 28 days for different w/cm used: (a) C0, (b) C10, and (c) C20 cements.

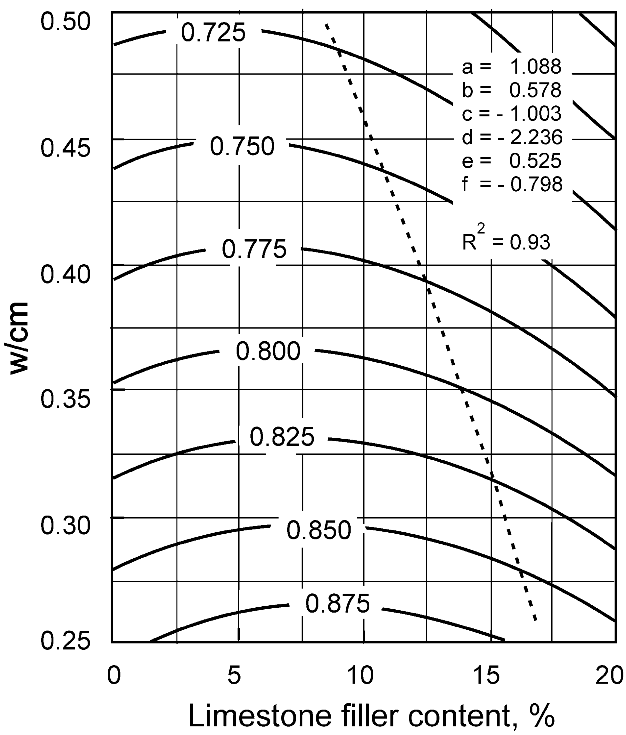

Fig. 3. Influence of limestone filler content and w/cm on the gel–space ratio of cement paste at 28 days.

For a conventional w/cm of 0.5, there was sufficient available space to locate the hydration compounds and, therefore, α in C0, C10, and C20 pastes yielded similar values at 28 days (0.80, 0.82, and 0.81, respectively).

Pastes with both PLCs present a high α at early ages; therefore, they present a little hydration progress from 7 to 28 days, while the C0 paste showed an increasing rate of α until 28 days. At early ages, the increase of α should also be attributed to the interaction between limestone with portland cement grains, and the replacement of coarse grains by smaller grains of clinker fraction in PLC. This situation is indicated by the retained material on the 75-μm sieve reported in Table 1.

The high value of α for clinker particles does not imply an improvement of the volume of hydration products (V_g), because the potential cementing material decreases when the particles of clinker are replaced by limestone filler grains causing the effect commonly called *dilution*. For this reason, the study of the variation of V_g for each paste is needed. According to Powers' model of cement, the volume of hydration products is proportional to α ($V_g = 0.694\alpha$) for a plain portland cement. For pastes containing limestone filler, the reduction of potential cementing material produced by addition is proportional to the filler content (V_f) in the cement. Then, this expression becomes $V_g = 0.694\alpha(1 - V_f)$ and it represents the numerator of the gel–space ratio, which takes into account the acceleration of hydration and the dilution effect caused by limestone filler. Thus, it is important to determine the proportion of limestone filler (V_f) that could be added without a reduction in the volume of hydration products (V_g). This proportion depends on the w/cm ratio used and it is important at 28 days, the typical age for concrete evaluation, when both effects produced by limestone filler are compensated.

To solve this question, a quadratic response surface model was used. The model is represented by the following expression: $V_g = a + bx_1 + cx_2 + dx_1^2 + ex_2^2 + fx_1x_2$, where V_g is the volume of hydration products at 28 days, x_1 is the percentage of limestone filler, and x_2 is the w/cm ratio. The coefficients (a, b, c, d, e, and f) were obtained after the best fit to the mathematical model by using the least square method. Complementary experimental data of pastes containing 5% and 15% of limestone filler (not reported here) were introduced in this calculation. Fig. 2 shows the isoresponse curves for this model of the volume of hydration products (V_g) at 28 days. The dashed curve on Fig. 2 shows the maximum level of limestone filler to obtain a large or similar volume of cementing compound for a given w/cm ratio. It can be observed that the percentage of limestone filler increases when the w/cm ratio in the paste decreases. The large volume of hydration products occurs for high w/cm pastes, which have a large space to be filled

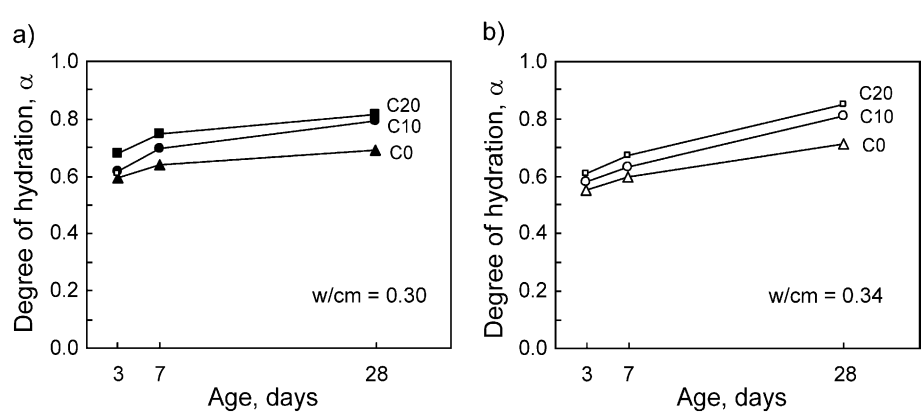

Fig. 4. Evolution of α for concrete: (a) w/cm = 0.30 and (b) w/cm = 0.34.

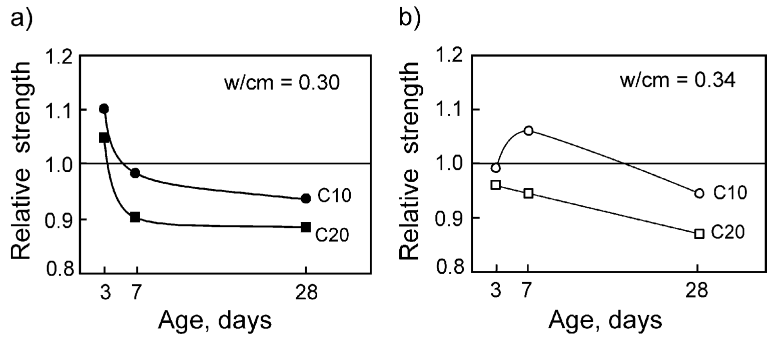

Fig. 5. Relative compressive strength of concrete: (a) w/cm = 0.30 and (b) w/cm = 0.34.

by these hydration products. The gel–space ratio concept measures this property of the paste.

Furthermore, the addition of limestone filler affects the denominator included in the gel–space ratio, because it produces a change in the *effective w/c ratio*; then its expression is $0.319\alpha+(w/cm)/(1-V_f)$. Fig. 3 shows the isoresponse curves obtained by using a quadratic model for the analyzed pastes. It can be observed that to obtain the same quality of paste, the percentage of limestone filler has to decrease when the w/cm ratio used in the system increases. Hence, for a typical w/cm ratio (0.30–0.35) in HPC, it is possible to incorporate around 15% of limestone filler in cement to obtain a similar or better gel–space ratio. However, for the w/cm ratio used in conventional concrete (0.50), around 5% of limestone filler could be added to cement without reduction in gel–space ratio at this age. These isoresponse curves depend on the type of clinker, the intergrinding process, and the age of evaluation.

3.2. Influence of limestone filler addition on concrete mixtures

To corroborate the results obtained in the paste system, the evolution of hydration and its relationship with the compressive strength of concrete (w/cm = 0.30 and 0.34) were evaluated. The development of α was similar to that of the pastes (see Fig. 4). Concretes with limestone filler cements presented a higher α than that of the corresponding plain concretes at all ages studied. At 28 days, the value of α is approximately 0.70 for both C0 concretes; while concretes with C10 and C20 cements developed an α ranged from 0.79 to 0.85. These values of α are higher than the corresponding values obtained in the paste system. This is due to the heterogeneity of the concrete (increase of voids by air and interfaces), but it can also be attributed to the accuracy of the method used.

Fig. 5 shows the evolution of the compressive strength for concretes containing C0, C10, and C20 cements for both w/cm ratios used. It can be observed that both concretes with C10 cement have a compressive strength similar to or higher than that of plain concrete up to 7 days; while the strength of concretes containing C20 cements was similar to that of plain concrete up to 3 days, thereafter a reduction of the relative strength was observed. The early strength can be attributed to the increase of α in C10 and C20 cements that compensate the reduction of active material. At 28 days, the dilution effect becomes more important, leading to a relative strength reduction when the limestone filler addition increases. For concretes with w/cm ratio of 0.30, this reduction was 6% and 13% for C10 and C20 cements, while these values were 10% and 12% in the concrete mixtures with w/cm ratio of 0.34. Experimental values reported here are comparable to the strength reduction projected by Bentz and Conway [16] in their computational model.

According to the gel–space ratio concept, the compressive strength of concrete depends on the *effective w/c ratio* and the degree of hydration of cement. For the same portland cement composition, the addition of filler creates changes in both gel–space ratio terms.

For a given w/cm ratio, the numerator of gel–space ratio predicts the amount of hydrated cementing material. In concrete mixtures, it can be calculated as $HCM = CUC(1-V_f)\alpha$, where CUC is the cement unit content, V_f is filler content, and α is the degree of hydration. For concretes containing PLC, the active cementing material is reduced from 450 to 418 and 368 kg/m^3 for C10 and C20 concretes,

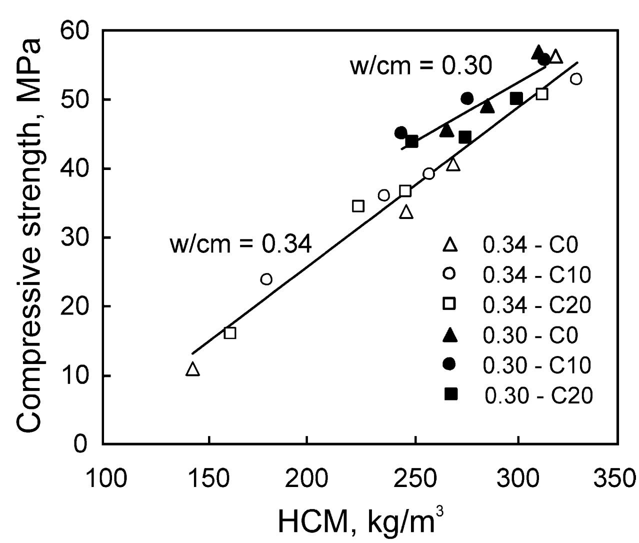

Fig. 6. Relationship between hydrated cementing material in concrete and the compressive strength.

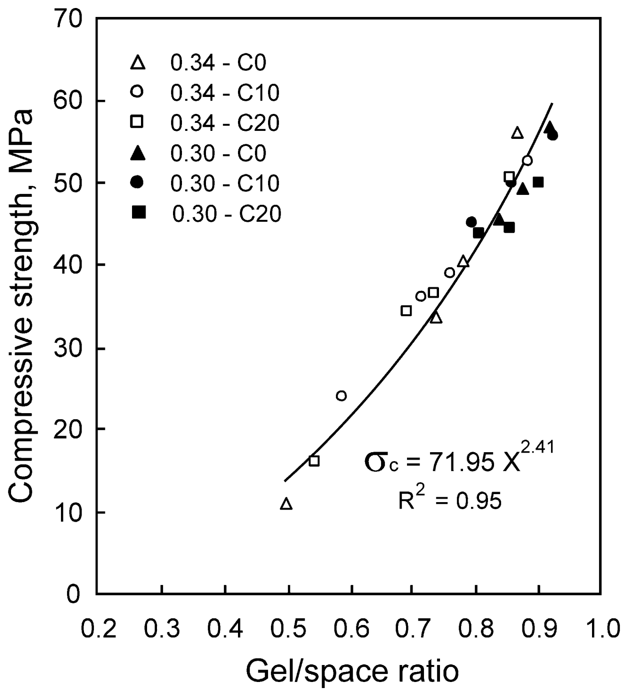

Fig. 7. Compressive strength of concrete as function of the gel–space ratio.

respectively. Consequently, only an increase of α of cement grains could produce a similar amount of HCM in concrete [7]. Fig. 6 shows a good relationship between the compressive strength and the HCM calculated for both concrete mixtures used. According to this figure, the results indicate that the same level of the compressive strength could be obtained for the same volume of cementing material for a given w/cm ratio. However, it can be observed that the experimental values are associated with two different curves depending on the w/cm ratio used.

The addition of limestone filler in cement produces an increase of the *effective w/c ratio*, because the filler is an inert addition and it could be computed as an ultrafine aggregate in concrete. The *effective w/c ratio* in concrete changes from 0.30 in concrete containing C0 cement to 0.37 in concrete containing C20 cement, while it changes from 0.34 to 0.415 for the other mixture. Then, the maximum percentage of limestone filler is also limited by the w/cm ratio used in the mixtures that increments the space to be filled by the hydration products. If the *effective w/c ratio* increases over 0.42, capillary pores should be presented in the full hydrated system.

Finally, the strength of concrete is related to the gel–space ratio, which measures all effects produced by the addition of limestone filler (acceleration of hydration, dilution, and increase of *effective w/c ratio*). Fig. 7 shows the compressive strength/gel–space ratio expression obtained from a curve fitting of experimental data. The close agreement of experimental values with this basic concept of concrete science confirms that the optimum level of limestone filler is a function of the mixture proportions. As energy requirements for pyroprocessing and gases emissions are reduced by the addition of limestone filler in cement, these type of cements contribute to achieve the environmental goals for concrete production.

4. Conclusions

For low w/c ratio concrete, a large proportion (more than 35%) of portland cement remains unhydrated acting as an expensive and energy-consuming filler. The use of limestone filler in this mixture is a more rational option from the energy consumption, emission reduction, and economic point of view. The optimum level of limestone addition depends on the concrete mixture proportions.

The compressive strength reduction for concrete containing up to 18.1% of limestone filler was in the range of 8–12% at 28 days. To obtain the same quality of paste, the percentage of limestone filler added has to increase when the w/cm ratio used in the system decreases. This optimum value, for a given clinker and intergrinding process, could be estimated by using the gel–space concept.

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