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Influence of limestone content, gypsum content and fineness on early age properties of Portland limestone cement produced by inter-grinding

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ABSTRACT

This paper examines the behavior of Portland limestone cements (PLCs) made by inter-grinding clinker, gypsum and limestone in a full size-cement plant, while varying the content of limestone filler (LF – 0% and 24%), content of gypsum (GC – 2.5% and 5.0%) and PLC fineness, measured as that fraction retained on a 45 μm sieve (R45 – 5% and 18%). The influence of the combined action of these variables on the particle size distribution (PSD) and early age properties of blended cement was studied using a 2^3 experimental design. Fineness evaluated by the parameters of the Rosin–Rammler–Springer–Bennett (RRSB) distribution function shows that the uniformity index (n-parameter) depends strongly on LF content; while the characteristic diameter (x'-parameter) depends on R45 and LF content. As for the inter-grinding process, water demand is reduced by incorporation of LF and increased by reduction of R45, producing a compensation. Setting time is mainly affected by R45; LF produces a few modifications and the influence of gypsum content and gypsum–limestone interaction are not as obvious. Calorimetry studies show that LF decreases the height of the main peak and the total heat released, while gypsum content modifies the time of acceleration and the post-peak hydration, specifically for fine cements. In accordance, chemical shrinkage decreases when R45, LF content and gypsum content increase. Up to 2 days, strength is mainly governed by the R45 and the LF in PLC, which act inversely. At early ages, the influence of gypsum content on early properties increases up to 48 h. XRD analysis shows its stimulation of calcium silicate hydration during the first hours and ettringite formation after 24 h.

1. Introduction

During the last decades, Portland limestone cement (PLC) has shown a rapid increase of production in the cement industry in order to achieve the goals of lowering consumption of natural raw materials, saving fuel energy for clinker production, and reducing CO_2 emissions [1,2]. Based on previous French experience, the European standard EN 197-1 identified two types of PLC containing 6–20% limestone and 21–35% limestone, respectively. According to the CEMBUREAU statistics [3], two-thirds of the market shares of cement in European countries correspond to CEM II cements, with PLC being the most frequently used.

PLC can be produced by two kinds of technology, either by inter-grinding of Portland cement clinker, limestone and gypsum, or by blending the separate grinding of Portland cement (clinker + gypsum) and limestone [4]. Indeed, both processes present advantages and disadvantages. Inter-grinding is easier and the mill acts as a grinding device and a homogenizer at the same time. This technique has good results when it is included in a closed milling system equipped with high efficiency separators. Clinker, gypsum and limestone have different grindabilities, and the individual particle size distribution (PSD) of each component influences the early hydration of interground blended cement [5]. Then, the milling operation requires that parameters can be set according to the proportions of the components in PLC to obtain an optimal efficiency at a given output fineness [6,7]. Separate grinding and mixing technology is more appropriate to design the PSD in a multicomponent cement and to produce a low quantity oriented to the market of tailor-made cement [4].

For a given PLC, the grinding system, the charge of the mill and the duration of the process determine the PSD of the cement [8]. PSD also depends on the fineness and on the amount of limestone used in the PLC [9]. PSD is vital for the rheology and the early-age hydration process that determines the early properties of cement, such as water demand, heat released, strength development and early-age volume change [10]. However, its influence on the cement hydration has been scarcely reported [11]. Also, the C_3A phase reacts with $CaCO_3$ in limestone to form monocarbonate and it influences ettringite stabilization [12–14]. This interaction between gypsum and limestone on the control of early hydration

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of C_3A can also interfere with the setting time and the early strength of PLC depending on the cement composition [15] and the particle sizes of reactants [16].

Since the incorporation of limestone produces changes in the PSD parameters and the optimum gypsum, this study is aimed at evaluating the behavior of PLC obtained from industrial production with controlled variables. The main objective is to understand the real influence of limestone on early age properties of PLC, considering its interactions with gypsum content and fineness. This paper examines the behavior of PLC produced by inter-grinding clinker, gypsum and limestone in a full size-cement plant varying the content of LF, gypsum and its fineness.

2. Materials and methods

2.1. Development of the factorial design approach

In this industrial experiment, a 2^k complete factorial design was used to give an efficient and structured approach to examining the composition and milling influences on the early age properties of PLC. After a screening analysis on variables that affect the behavior of PLC, three independent variables ($k = 3$) were selected: limestone content (LF), gypsum content (GC) and PLC fineness, measured as the residue on a 45 μm sieve (R45). This experimental design consists of eight (2^3) factorial points, where each variable is fixed at lower and upper levels of the region explored. The experimental region includes cement composition according to type CEM II/L (EN 197): LF is varied from 0 to 24%, GC from 2.5 to 5.0%, and R45 from 18% to 5%. Table 1 displays the absolute and coded values for the model.

The modeled responses are assumed to be linearly dependent on the level of each factor. To validate the linearity assumption, cement (P9) with a composition near to the experimental center point of the design was manufactured. The center point permits the control of the goodness-of-fit of the planar two-level factorial model. If a curvature of the response surface in the region of the design exists, the actual center point value will be either higher or lower than the one predicted by the factorial design points.

Using this approach, the linear mathematical model describing the influence of the main factors (LF, R45, CG) and their interactions on the relevant properties (response Y) are expressed as:

$$Y = \alpha_0 + \alpha_1\mathrm{LF} + \alpha_2\mathrm{R45} + \alpha_3\mathrm{GC} + \alpha_4\mathrm{LF}\cdot\mathrm{R45} + \alpha_5\mathrm{LF}\cdot\mathrm{CG} + \alpha_6\mathrm{R45}\cdot\mathrm{GC} + \varepsilon \quad (1)$$

where α_i are the coefficients that measured the contributions of the independent variables to a given property (Y) and ε is the random error term representing the effects of uncontrolled variables. In this equation, the third order interaction term was ignored.

Design-Expert® software (Stat Ease Inc., MN, USA) was used for the data processing and model evaluation. The coefficients of the model are calculated by a stepwise regression method.

Analysis of variance (ANOVA) is used to test the significance of each variable of the model. The model is considered statistically significant when the F-test, an evaluation of the term variance with the residual variance, is much larger than the critical value obtained from the table values for an F-distribution based on $\alpha = .05$ and the degrees of freedom of treatments and error. A probability less than .05 was considered as significant. Also, a graphical analysis of residuals was carried out to probe the adequacy of the model. Different types of plots were used to determine that the residuals are normally distributed, the values of the outlier t statistic are less than |3.5| and the Cook's distance is lower than 0.5. The R^2 coefficient is also calculated for model validation, but it usually provided less information than graphical methods. The ANOVA report also includes the significance of the curvature test evaluating the linearity of the model [17]; when the curvature test was statistically significant, the estimated value of the center point composition has a large distance from the value measured experimentally. Then, the model could be no linear and the response could be modeled better in a quadratic manner using a surface response method.

For each response (Y), the F-value for each individual variable is the test for comparing the variance associated with that variable with the residual variance. A variable of the model is significant when the probability is less than 0.05, indicating the contribution of the proposed variable on the measured response. When this probability has a value greater than 0.10, the variable is non-significant (NS). Then, it was eliminated from the model and the significance of each variable was calculated again.

2.2. Materials

All cements were manufactured using a clinker derived from the same raw materials and process with a lime saturation factor (LSF) of 0.97 ± 0.01, aluminates modulus of 1.06 ± 0.01 and silica modulus of 3.19 ± 0.02, gypsum with a purity grade of 92.2% and a quality limestone containing 88.6% $CaCO_3$ as calcite, without clay, and with quartz as the main impurity. The chemical analyses of these materials are provided in Table 2.

Clinker, limestone and gypsum were interground to two different fineness levels (18 and 5% of the material was retained on a 45 μm sieve) using an industrial ball mill with two-compartments (Unidan, FLSmidth) with a capacity of 95–115 Tph, which is integrated to a closed milling circuit equipped with a high efficiency separator (SEPAX, FLSmidth). With the purpose to limit the experimental program, a grinding aid admixture (CBA, Grace) was incorporated in the same proportions (0.3 l/tn) for all cements. In practice, Portland cements are often produced without grinding aids.

2.3. Testing procedures

The complete requirements for Portland limestone cements established in the IRAM 50000 standard (Materials Standard Insti-

Table 1
Experimental points of complete 2^3 factorial design used expressed in absolute variable value and coded value.

Cement	Absolute value			Coded		
	Limestone filler (LF)	Retained on 45 μm (R45)	Gypsum content (GC)	Limestone filler (LF)	Retained on 45 μm (R45)	Gypsum content (GC)
P1	0	5.0	2.50	−1	−1	−1
P2	0	5.0	5.00	−1	−1	1
P3	0	18.0	2.50	−1	1	−1
P4	0	18.0	5.00	−1	1	1
P5	24.0	5.0	2.50	1	−1	−1
P6	24.0	5.0	5.00	1	−1	1
P7	24.0	18.0	2.50	1	1	−1
P8	24.0	18.0	5.00	1	1	1
P9	12.0	11.5	3.75	0	0	0

Table 2
Chemical composition of Portland clinker, limestone and gypsum used.

	Chemical composition, (%)							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	LOI
Clinker	22.88	3.69	3.49	66.55	0.72	1.06	0.9	0.71
Gypsum	–	–	–	–	–	–	42.9	20.5
Limestone filler	7.02	0.94	0.40	51.35	0.34	0.39	0.03	39.5

tute in Argentine) were determined. Normal consistency and setting time were performed according to the IRAM 1619 standard (EN 196-3). The specific surface area was measured using Blaine's method (IRAM 1623–EN 196-6). At 7 and 28 days, compressive and flexural strengths were assessed on mortar bars 40 × 40 × 160 mm^3 in compliance with the IRAM 1622 standard (EN 196-1). To check the LF and gypsum content in each cement, LOI and SO_3 content were determined using the IRAM 1504 (EN 196-2) procedure. The residue on 75 and 45 μm sieves was determined by using a wet sieve procedure according to IRAM 1621 (ASTM C430). Additionally, the PSD of each cement was measured using laser granulometer equipment (CILAS 920L) and the results are reported via two parameters of the Rosin–Rammler–Springer–Bennett (RRSB) distribution function: the uniformity index (n) and the characteristic diameter (x'). Results of these tests are summarized in Table 3.

The heat release of the cements was measured on pastes ($w/b = 0.4$) using a semiadabiatic differential calorimeter operating at 20 °C. Temperature was recorded during the first 48 h of hydration and the heat released was calculated as the integral below the heat dissipation rate curve versus time using a similar procedure to EN 196-9.

Chemical shrinkage measurements were carried out using the volumetric method, similar to that presented in ASTM C1608. It consists of immersing a given mass (100 g) of cement paste ($w/b = 0.26$) in an Erlenmeyer flask filled with water. A rubber stopper containing a graded pipette of 0.01 ml was placed on top of the flask, establishing the initial height of water in the pipette. The recipient was placed in a water bath at 20 ± 1 °C and the position of the meniscus in the pipettes was measured at regular intervals (1 h) until 24 h. Decrease of the water column in ml is directly proportional to the total chemical shrinkage.

Early compressive and flexural strengths of cement were determined on mortar specimens (40 × 40 × 160 mm – Flow = 130 ± 10%) made of cement, sand and water (1:2:0.40), which were cured in a fog room at 20 ± 2 °C and demoulded before testing at 12, 24 and 48 h. Three specimens were tested for flexural strength and the six remaining half parts were tested for compressive strength. Reported values are the average, satisfying that the standard deviation is less than 5% of the average value.

Hydration compounds in cement paste were evaluated by X-ray diffraction (XRD) at 24 and 48 h. For this purpose, a new set of pastes ($w/b = 0.4$) was made at 20 °C and the hydration stopped by immersion in acetone. Then, the paste was dried at 40 °C and ground to a particle size less than 45 μm. XRD measurements were performed on a diffractometer (Philips X'Pert) equipped with a graphite monochromator using CuKα radiation and operating at 40 kV and 20 mA. Step scanning was made from 5 to 35° 2θ using a scan speed of 2°/min and a sampling interval of 0.02° 2θ.

3. Test results and discussions

3.1. Factorial models exploitation

The analyses of variance (ANOVA) for each 2^3 response model are presented in Table 4. Results on the significance of the model, the curvature test, correlation coefficient (R^2) and the accomplishment of graphical analysis for eight experimental points can be observed. In this table, the coefficients of the 2^3 model are also reported: the independent coefficient (α_0) represents the value of response for the center point (cement P9) and the variable coefficient (α_i) is the variation (+ or $-$) into the lower and upper levels of the factor. A negative coefficient shows that an increase of this variable results in a reduction of the measured response.

Subsequently, a brief analysis of the results and the significance of each variable on PSD parameters and early age properties are presented.

3.2. Fineness

Table 3 reports results for PSD parameters and Blaine fineness. Comparing results for the lower and upper levels of each variable, it can be observed that the n-parameter depends largely on LF content, while the x'-parameter depends on R45 and the LF content.

As regards the inter-grinding process of PLC, its components (limestone, gypsum and clinker) present a different grindability. There is a general assumption that gypsum and limestone are easier to grind than Portland clinker. But, new developments in the clinker process have increased the porosity of clinker, making a product that is easier to grind than limestone. In this experiment, the clinker has a lower Bond index than limestone. Therefore, the composition of fractions in the PSD curve is different for the same R45. Several researchers [4,7,18] have reported that the presence of limestone filler extends the width of the PSD (n-parameter in RSSB

Table 3
Results of standard requirements and fineness for Portland and Portland limestone cements.

	Cement	LOI (%)	SO_3 (%)	Retained on sieve		RRSB parameters		Blaine m^2/kg	Water demand (%)	Setting time (min)		Compressive strength (MPa)	
				75 μm	45 μm	x' (μm)	n			Initial	Final	7 days	28 days
P1	0-5-2.5	0.81	2.46	<0.1	5.2	17.9	0.93	362	28.0	140	200	44.2	55.2
P2	0-5-5.0	0.93	2.94	0.1	5.0	18.0	0.93	364	28.4	155	215	50.4	63.0
P3	0-8-2.5	0.64	2.21	4.0	17.2	24.7	0.95	261	27.0	170	240	38.3	54.7
P4	0-8-5.0	1.04	3.27	4.8	18.0	26.5	0.94	271	27.6	180	255	37.5	50.2
P5	24-5-2.5	10.05	1.77	0.1	6.5	12.4	0.85	450	27.0	150	225	41.7	51.6
P6	24-5-5.0	10.66	2.97	0.1	6.0	12.2	0.84	500	27.4	155	230	41.7	48.5
P7	24-18-2.5	10.39	1.78	4.1	19.4	19.6	0.88	357	26.2	165	235	34.7	46.9
P8	24-18-5.0	11.09	2.78	4.5	19.7	20.5	0.85	398	26.2	190	260	33.7	43.2
P9	12-11.5-3.75	5.67	2.50	2.6	15.3	21.7	0.93	318	26.8	195	265	40.7	52.4

Table 4
Results of 2^3 models for each response analyzed.

Response		Model		Curvature		Diagnostic plot			α_i-coefficients					R^2
		Prob > F	Significance	Prob > F	Significance	1	2	3	α_0	α_{LF}	α_{R45}	α_{GC}	α_{LFxR45}	
Parameter of RRSB	*n*-parameter	0.0002	S	0.0633	NS	✓	✓	✓	0.900	−0.041				0.921
	x′ parameter	<0.0001	S	0.0097	S	✓	✓	✓	19.0	−2.8	3.9			0.989
Water demand		0.0010	S	0.0644	NS	✓	✓	✓	27.23	−0.53	−0.48	0.18		0.977
Setting time	Initial	0.0016	S	0.0181	S	✓	✓	✓	166.2		16.2			0.833
	Final	0.0014	S	0.0134	S	✓	✓	✓	236.3	8.8	18.8			0.929
Heat released	At 12 h	0.0010	S	0.8642	NS	✓	✓	✓	91.7	−16.3	−5.5	2.1	3.9	0.998
	At 24 h	0.0016	S	0.1747	NS	✓	✓	×	148.8	−18.8	−4.3	3.9		0.970
	At 48 h	0.0018	S	0.1418	NS	✓	✓	✓	200.7	−24.6		9.0		0.920
Chemical shrinkage	At 12 h	0.0003	S	0.0548	NS	✓	×	×	1.39	−0.17	−0.19	−0.09		0.987
	At 24 h	<0.0001	S	0.0145	S	✓	✓	×	2.52	−0.01	−0.02	−0.03		0.993
Compressive strength	At 12 h	<0.0001	S	0.7886	NS	✓	×	×	10.53	−2.77	−3.09			0.978
	At 24 h	<0.0001	S	0.0579	NS	✓	✓	×	27.68	−4.25	−4.34			0.980
	At 48 h	0.0006	S	0.2103	NS	✓	×	×	40.26	−3.98	−3.75	2.37		0.983
Flexural strength	At 12 h	0.0003	S	0.2813	NS	✓	✓	✓	2.43	−0.69	−0.56		−0.16	0.987
	At 24 h	0.0003	S	0.0504	NS	✓	×	×	5.44	−0.53	−0.62			0.960
	At 48 h	0.0019	S	0.1705	NS	✓	✓	✓	7.40	−0.77	−0.53	0.18		0.992
Compressive strength	At 7 days	0.0002	S	0.4442	NS	✓	✓	✓	39.84	−1.91	−3.81			0.969
	At 28 days	0.0118	S	0.7013	NS	✓	✓	✓	51.29	−3.74	−2.54			0.831

Diagnostic plot: (1) Normal probability of studentized residuals; (2) Outlier t vs run order less than 3.5; (3) Cook‘s distance is less than 0.50. Evaluation: ✓:pass; ×:fail.

is lower than cement) indicating that clinker particles are in the larger sizes and limestone in the smaller ones. For the same R45, results have shown that the *n*-parameter was 0.94 ± 0.01 for Portland cement and it decreased to 0.86 ± 0.02 when 24% of limestone was added. Complementarily, there was a reduction of 5–6 μm in the *x*′-parameter when limestone was added. The increase of gypsum content from 2.5 to 5.0% produces no significant changes in either RRSB parameter.

From ANOVA (Table 4), the factorial model for the *n*-parameter is significant and LF content is the only significant variable. The *x*′-parameter model includes LF and R45 as significant variables and the curvature test is significant indicating that the model could be quadratic. Exploring this solution with the response surface method (RSM), it can be observed that LF is the quadratic term producing a great influence on *x*′ when it was greater than 6%.

Judging Blaine's test results, specific surface increased (from 89 to 136 m^2/kg) when LF was added in order to maintain the same R45; while the change in R45 from 18 to 5% produced an increase of the specific surface of around 100 m^2/kg. The gypsum content causes a low variation of specific surface (±13 m^2/kg). Blaine's value also depends on milling process factors (mill charge, air and material flow rates, material and air temperatures, pressure at the mill exit) and it is only an indicative parameter for production of PLC.

3.3. Water demand

Analyzing the results of water needed for normal consistency (Table 3), substitution of 24% of LF in cements produces a reduction of 1% in water demand and a reduction of R45 from 18% to 5% produces an increase of 1% in water demand. According to Schiller and Ellerbrock [18], water demand is composed of three fractions: low proportion of chemical water needed to form the initial hydration products, a second proportion needed to lubricate the initial hydration products, and a large amount of water to lubricate the surfaces of the cement grains. For the same size, limestone grains demand less water than reactive clinker grains because they only require the lubrication water. When clinker grains are substituted by LF, water demand needed for lubrication of a large specific surface is compensated or reduced due to the presence of less reactive grains that reduces the water related with hydration products. Basically, a wide PSD produces low space to fill with water, because finer particles of easy ground material fill the gaps between the coarse particles of hard material [19]. For this response, ANOVA (Table 4) shows that the main variables are LF (±0.53%) and R45 (±0.48%), while the gypsum content is significant, but its low proportion in cement composition produces a low change (±0.18%) in water demand. All interaction terms of the model are non-significant. Results are in accordance with several previous researches that use inter-grinding processes at a laboratory scale [7,18,20,21]. However, an inappropriate distribution of particles size when limestone is blended with cement could produce an increase in water demand [22].

3.4. Time of setting

In Table 3, results show that finer cements have a shorter initial or final setting time for the same level of limestone and gypsum added. Results on setting time obtained from earlier studies [7,20,21,23] are dissimilar, showing an increase or decrease of setting time. For a given clinker, the optimum gypsum content decreases when limestone content increases [24]. Results show that an increase of gypsum produces a shorter setting time (5–20 min) for PLC while it delays the setting time for Portland cement (10–15 min). According to Bentz [25], setting of cement occurs when isolated particles are weakly connected by the formation of initial hydration products. Then, he suggests that the influence of PSD on the setting time is not obvious at constant *w*/*c*; while coarse Portland cement may require more time to achieve the hydration degree due to its slow hydration rate, it can set at a lower hydration degree as fewer bridges are needed between particles. This situation is even more complex in PLC: incorporation of limestone causes an increase of *w*/*c* and the initial setting time could be delayed, but limestone particles may participate in shorter bridges of hydration products, causing no significant changes in the setting time (±10 min).

ANOVA showed that the influences of the selected variables on the initial and final times of setting are not as obvious, and the only variable that the models revealed as significant was the R45 (Table 4). Contrary to what is expected, gypsum, LF content and their interaction are statistically non-significant factors in the setting times, when they vary from their upper to lower levels for this inter-grinding process. The curvature test showed that the setting times of the P9 cement are significantly distant from their calculated values.

3.5. Calorimetric curves

Fig. 1 shows the calorimetric curves up to 48 h for cements with and without limestone filler, respectively. They represent a typical calorimetric curve for a Portland cement. Firstly, it shows a high rate of ΔT due to the dissolution process and very early hydration of aluminate phases. Then, the valley is the dormant period where the concentration of species in solution increases until promoting the C_3S reaction. The second peak is the acceleration of hydration reactions due to the silicate hydration with the initial precipitation of the CSH and CH, primarily from C_3S, and a shoulder may be observed at the descending branch of the second peaks, which is probably due to renewed ettringite (AFt) formation. A third peak due to the transformation of AFt to monosulfoaluminate (AFm) is absent or overlapping due to the low C_3A content of the cement (3.88%) [26]. Finally, hydration reactions slow down gradually and reach a very low rate after 2 days.

Comparing Fig. 1a and b, it can be observed that limestone filler tends to reduce both the peak rate and the amount of heat released, as reported by several authors for PLC when limestone was introduced by blending or inter-grinding [10,27–29].

For cement without limestone filler (Fig. 1a), the second peak is narrow, while the acceleration rate of the hydration (slope of curve) and its maximum value are high when decreasing the R45. For the range studied, gypsum content does not modify the acceleration rate for the same R45, but it produces a wide second peak for the maximum level (5%). The time of the dormant valley is close for all cements and the time for the maximum peak is delayed in coarse cements.

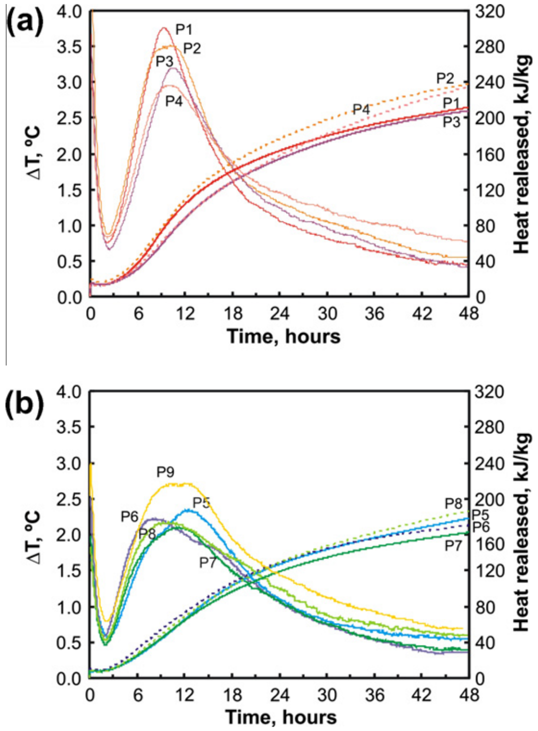

Fig. 1. Calorimetric curves: (a) Portland cements with different fineness and gypsum contents. (b) Portland limestone cements with different fineness and gypsum contents.

For cement with limestone filler (Fig. 1b), the second peak is lower and wider due to less reactive material and the possible coarser size of reactive particles. The acceleration rate is much lower than the corresponding cement without limestone and it decreases for the coarser cement. For PLC with 2.5% of gypsum (P5 and P7), the curve exhibits an obvious shoulder after the first peak attributable to AFt formation, as described by other authors [30]. This shoulder is smaller in PLC with 5% of gypsum (P6 and P8) and the maximum peak occurs at an earlier age. Barker and Matthews [27] reported that the timing of the peak depends on the method of the PLC preparation. For these cements, there is an acceleration of the maximum peak for PLC with high gypsum content and some retardation for PLC with low gypsum.

For the heat released at 12, 24 and 48 h, ANOVA (Table 4) showed that: LF variation affects this property at all ages, fineness had a marked effect at 12 and 24 h but it did not affect heat release at 48 h, and gypsum was statistically significant at 12 and 48 h. In the analysis of α_i-coefficients obtained for Q_{12}, Q_{24} and Q_{48}, it can be observed that variation of LF content produces a change in the heat released of 35, 25 and 24% at 12, 24 and 48 h, respectively. On the other hand, variation of R45 had a decreasing significance on these properties producing variations of 12% at 12 h, 8% at 24 h and less than 1% at 48 h. For gypsum, its influence on these properties is significant at 48 h; the effect of varying the gypsum content from 2.5 to 5.0% has an effect of 4.5%, 5.2% and 9% on the heat released at 12, 24 and 48 h, respectively.

3.6. Chemical volume shrinkage

Fig. 2 shows the evolution of chemical volume shrinkage for the studied cement. Chemical shrinkage presents a typical curve, characterized by low volume changes until the initial setting time, a large change due to hydration of silicates and the decelerating process after 12–18 h when hydration becomes controlled by diffusion processes.

For cements with and without limestone, chemical shrinkage decreases when cement is coarse or gypsum dosages increase indicating a slow rate of hydration at early hours. Incorporation of 24% limestone produces a reduction in chemical volume shrinkage (approximately 0.25 cm^3/100 g of cement at 24 h) due to a dilution effect. Considering models for chemical shrinkage at 12 and 24 h, ANOVA (Table 4) showed that the three studied variables are significant, but their influences (α_i-coefficients) decrease with time, as occurred in the analysis of heat release. An increase of chemical shrinkage was reported when w/c is constant or limestone filler is used as sand replacement [31] indicating its participation in stimulating cement hydration.

3.7. Early strength

Fig. 3 shows the evolution of compressive and flexural strength up to 48 h for mortar with and without limestone filler. The compressive and flexural strengths have a similar behavior at early ages yielding a very good correlation between both variables ($f'_f = 0.189\, f'_c; R^2 = 0.962$). Analyzing the results of the factorial models for both strengths (Table 4), significant factors for early strength are R45 and LF content of blended cements. Cements with a R45 = 5% (P1, P2, P5 and P6) presented higher compressive (4.8–9.4 MPa) and flexural (0.5–1.5 MPa) strength than those with R45 = 18% (P3, P4, P7 and P8). A review about the influence of PSD on early strength of cement shows that the 0–3 μm fraction dominates 1-day strength, the 3–8 μm fraction influences 2-day strength, and the 8–25 μm fraction dominates the strength development after this time [19]. On the other hand, incorporation of limestone produced a decrease of compressive (3.7–9.4 MPa) and flexural (0.5–2.0 MPa) strength at all test ages. The coefficients of

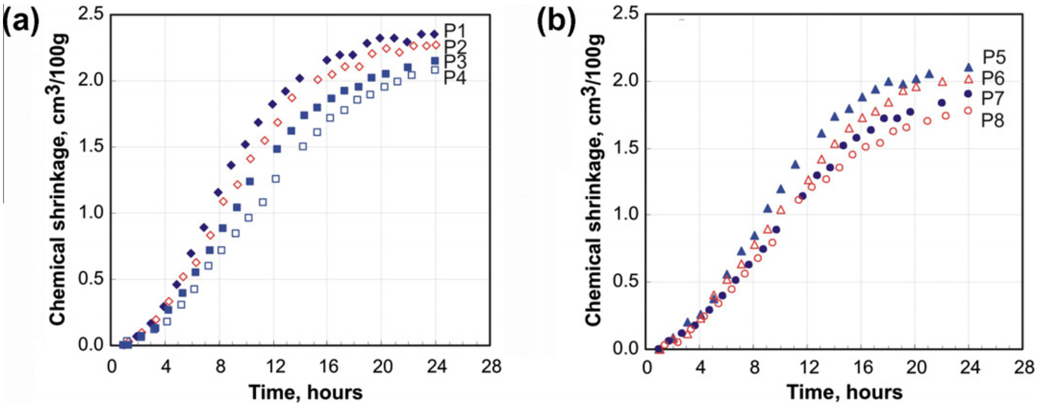

Fig. 2. Chemical volume shrinkage: (a) Portland cements with different fineness and gypsum contents. (b) Portland limestone cements with different fineness and gypsum contents.

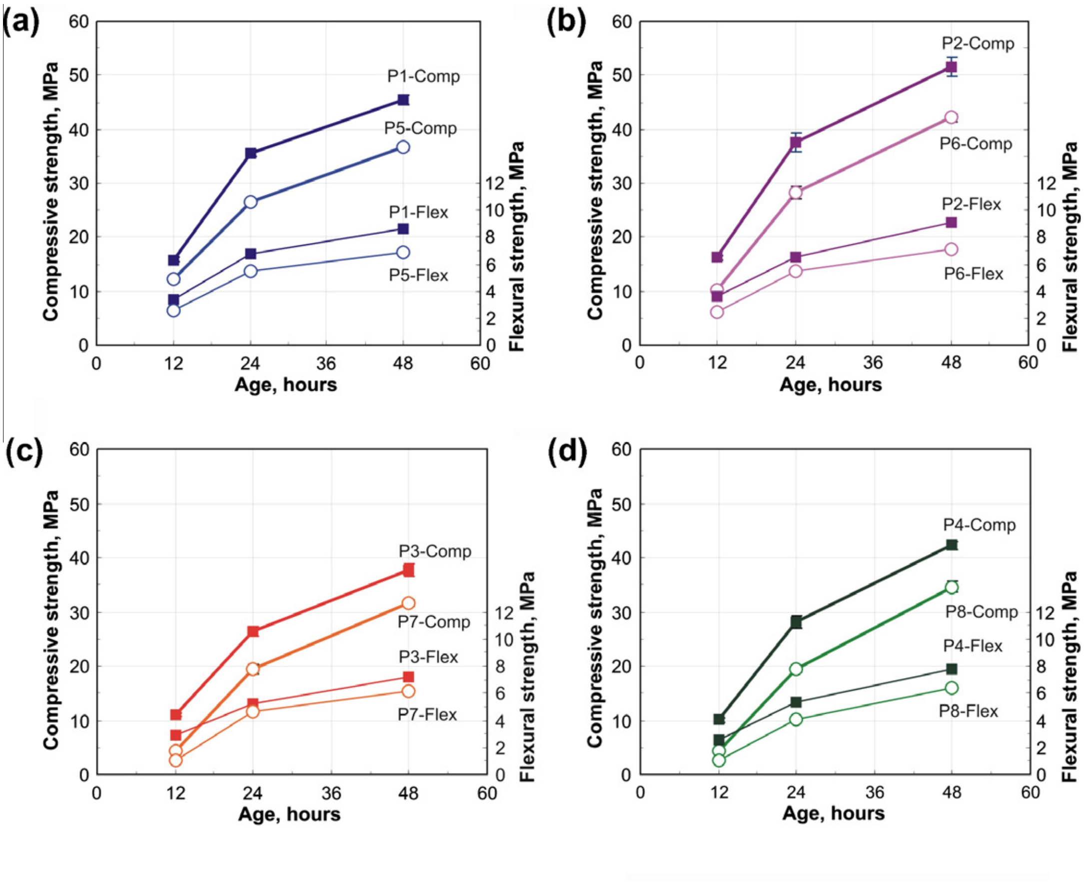

Fig. 3. Compressive and flexural strength of mortars (*w*/*c* = 0.40) at early ages.

the model (Table 4) indicate that both parameters have the same weight within the studied domain. At 24 h, the curvature of the model is significant (P9-strength cannot be estimated adequately by the model) and the exploration of the data using a response surface model indicates that limestone filler is the quadratic term. This can be attributed to the stimulation of cement hydration produced by finer limestone filler particles that disperse the cements grains and act as nucleation sites [11]. This process compensates for the dilution of cementing products produced by limestone, and it enhances the strength.

The influence of gypsum content depends on the test age. At 12 h, it is not a significant variable but it has a slight influence on the cement with limestone filler, while strength does not change significantly in cement without limestone filler. At 24 h, cements without limestone filler present an increase of strength when the gypsum content increases and it also occurs in finer limestone cements (P5 and P6). However, it was not a statistically significantly term in the model. Finally, gypsum content is a significant variable at 48 h producing an increase of compressive (3–5.3 MPa) and flexural (0.2–0.4 MPa) strength when it increases from 2.5 to 5.0%. This behavior can be attributed to the effects of gypsum content on the stimulation of calcium silicate hydration [11,28] and on ettringite formation [13,14].

Among the different interactions between factors of the model, the R45 and LF interaction was considered statistically significant for the flexural strength response at 12 h.

This experimental approach indicates that to obtain a determined early strength in limestone cements, the large addition of limestone can be compensated by a finer grinding and by optimizing the gypsum content in the blended cement.

3.8. Influence of variables on early age properties

To summarize the influence of studied variables on early age properties, Fig. 4 presents the influence of limestone filler, retained on 45 μm sieve and gypsum content on the percentage variation of compressive strength, flexural strength, heat released and chemical shrinkage. This variation of properties is referenced to the composition of the center point of the design (P9 – cement) and it was calculated as the α_i coefficient divided by the α_0 coefficient in percent for each response model.

For limestone filler content (Fig. 4a), the decrease or increase from the center point (12% LF) produces a significant variation of properties at 12 h. Then, the influence is reduced with the progress of time producing a variation of around ±10% at 48 h.

Fig. 4b shows that the R45 variable has a large influence on very early strength producing an increase of more than 20% at 12 h, but it exhibits a lower influence on the heat released. Later, its influence on strength declines producing a variation of less than 10%. At 48 h, this variable has no influence on heat released for the analyzed system. Between 2.5 and 5.0%, the gypsum content causes a variation of less than 10% on the early age properties of the cements analyzed (Fig. 4c). It exerts an influence at 12 h on the hydration rate (heat released and chemical shrinkage) but it does not cause significant changes in strength. At 48 h, the variation of the gypsum content exerts an influence of more than 5% on compressive strength.

3.9. Hydration products

Fig. 5 shows XRD-patterns for hydrated paste of coarse cements (R45 = 18%) with different gypsum contents, either with or without limestone filler. For cement without limestone filler (Fig. 5a), the major crystalline phases identified were calcium hydroxide (CH), ettringite and unreacted calcium silicates and ferroaluminates. From 24 to 48 h, the intensity of the CH peak grows significantly, with concurrent decreases of the main C_3S peak at 29.5 $2\theta°$. The increase of ettringite is the main change that occurs for both gypsum contents used in this cement. A difference between the P2 and P4 cements is a large peak for ettringite at 24 h for the P4 cement with a larger gypsum content and the slight peak around ($2\theta = 10.0°$) attributable to the monosulfoaluminate phase for the P2 cement at 48 h.

For cements with limestone filler (Fig. 5b), calcite ($2\theta = 29.4°$) and quartz ($2\theta = 26.5°$) introduced by limestone are clearly identified in the XRD-pattern. The intensity of CH and unhydrated cement peaks are less than in the corresponding P2 and P4 cements due to dilution effects. The main difference is the low intensity peaks of ettringite, absent at 24 h, and the presence of monocarboaluminate in the P7 cement after 48 h due to its high

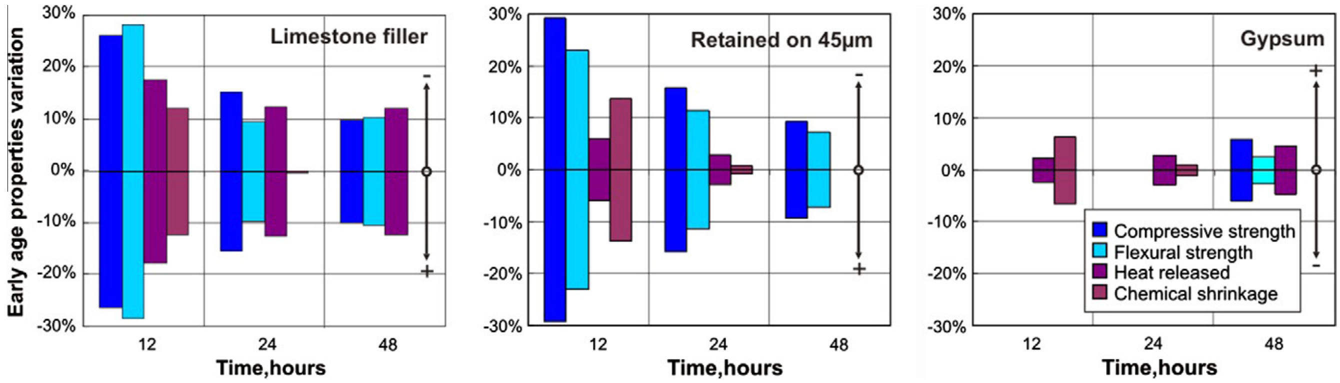

Fig. 4. Percent variation of early age properties of center point PLC (P9) when LF, R45 and GC variables are changed to high and low level.

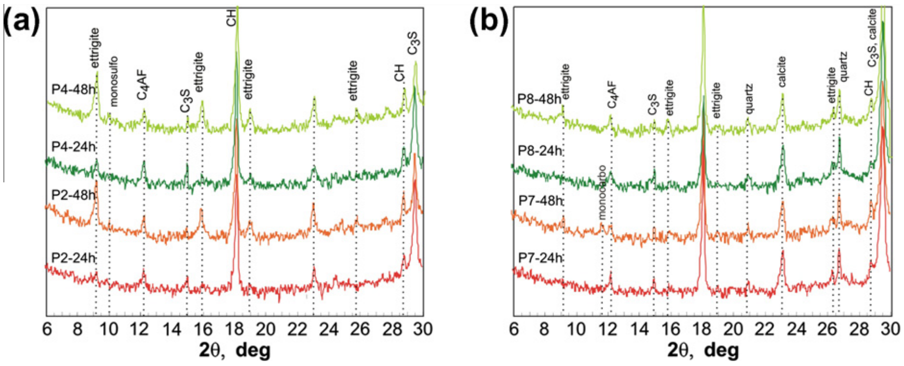

Fig. 5. XRD-patterns of hydrated cement pastes at 24 and 48 h: (a) Cements without limestone filler and low gypsum content (P2) or high gypsum content (P4). (b) Cements with 24% limestone filler and low gypsum content (P7) or high gypsum content (P8).

stability, compared to monosulfoaluminate [13,32]. The low intensity of ettringite can also be attributable to dilutions.

These changes in the assembly of the hydration products from 24 to 48 h justify the significance of gypsum content in the strength, heat released and chemical shrinkage, because they illustrate the formation of ettringite (AFt – phase) and the occurrence of the AFm phase at this time.

3.10. Standard strength

Results of standard compressive strength at 7 and 28 days indicate that the main factors are fineness and limestone filler content. Fineness is the dominant variable at 7 days producing a compressive strength variation of ±3.81 MPa, while limestone content has a moderate influence (±1.91 MPa). At 28 days, the importance of these factors is reversed; limestone content is the main variable (±3.74 MPa) and fineness is less influential (±2.54 MPa). The third variable analyzed, gypsum content, was not significant at later ages.

A simple analysis justifies this behavior: at 7 days the increase of the hydration degree in the finer clinker fraction of blended cement compensates for the reduction in cementing material, produced by the dilution effect when increasing the limestone filler content. Then, at later ages, the dilution effects largely affect the compressive strength as the complete hydration of the clinker fraction has occurred in both finer and coarse cements [33–35].

4. Conclusions

In this paper, the inter-grinding process based on an R45 objective was used to produce limestone filler cement. The influence of the main factors (fineness, gypsum and limestone content) varying from minimum to maximum levels on the PSD and the early behavior of PLC has been described and the following conclusions can be drawn:

- The PSD is wider for PLC compared with pure PC. When LF is added, the n-parameter decreases and the x'-parameter is reduced by 5–6 μm for the same R45 objective.
- Water demand for standard consistency of cement paste is slightly reduced by the incorporation of limestone and it is slightly increased when R45 decreases, producing a compensation.
- Setting time is mainly affected by R45, the limestone content produces a few modifications and the influence of gypsum content and gypsum–limestone interaction are not as obvious. Times of setting of PLC satisfy the standard and are similar to those observed in Portland cement.
- Calorimetry studies show that LF decreases the height of the main peak and the total heat released. Limestone and coarse cement decrease the acceleration rate during the maximum peak, which occurs earlier for high gypsum contents. At early ages, heat released is affected by LF, while R45 has an effect only until 24 h. Gypsum is statistically significant at 48 h.
- Chemical shrinkage is reduced when the cement is coarse; the effects of an increase of limestone filler content or gypsum content agree with calorimetric results.
- Early strength is mainly governed by the R45 and the LF in PLC, which act inversely. The influence of gypsum content depends on age: at 12 h it is not significant, at 24 it has a slight influence and it is significant at 48 h.
- Dilution, less reactive materials in cement, produced by incorporation of LF causes a reduction of chemical shrinkage, heat released and strength at early age. A low R45 objective for the grinding process produces finer clinker particles that react faster and finer limestone particles that cause the stimulation of cement hydration. R45 objective can compensate the dilution of cementing products produced by limestone, and it enhances the strength of PLC without increases of heat released during 48 h.
- Gypsum content governs the formation of ettringite and its transformation, which occurs after 24 h making this variable statistically significant for all studied properties at 48 h.

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