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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