Effect of the addition of calcined clay-limestone-gypsum in the hydration of Portland Cement pastes

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ABSTRACT

Currently, mineral additions are widely used as they favor not only the partial replacement of Portland cement, they reduces clinker production, but also provide certain chemical and physical properties that make concrete more durable. The variation of the water-cement ratio, the use of setting retarding additives and the addition of Cementitious Supplementary Materials (MCS) are factors that have a great influence on the hydration of the cement and the formation of the phases of a hydrated cement paste. That is why this research focuses on evaluating the effect of the active mineral addition of calcined clay, limestone and gypsum (LC2), in the cement hydration process. The work consists of several stages: first, a study is made of the variations that are made to the water to define the protocol and the amount of addition to study (30%); In a second stage, calorimetry and chemical shrinkage tests are carried out on cement pastes and a final stage where the influence of the addition on the hydration processes of the pastes is analyzed. This research provides a way of replacing Portland cement through the use of mineral additions, as is the case of LC2, which are in turn within the Construction Industry, to be a sustainable way of production of materials in Cuba.

Keywords: Pozzolanas, concrete, shrinkage, cement, paste

1. INTRODUCTION

The replacement of part of the clinker with other mineral constituents has long been investigated for economic and ecological reasons. The amount of clinker that can be replaced by supplementary cementitious materials (MCS) depends on the type of MCS used. MCSs traditionally used are wastes from industrial processes, such as fly ash, microsilica and blast furnace slag, as well as natural pozzolans such as zeolitized tuff and volcanic ash. (1)

Currently, in Cuba, work is being done on the production of concretes, where cements with active mineral additions are used, with the fundamental objective of improving the properties of the same and reducing the appearance of cracks due to changes in volume. These changes in the volume of the concrete elements, known as shrinkage, cause the appearance of cracks, which not only affect the aesthetics of the buildings, but also represent the malfunctioning of the same. These cracks can be explained as the result of a physical-chemical process that the cement paste undergoes, after being mixed with the aggregates, and which consists mainly of a variation in volume, which may depend on many factors, including the type of cement, the aggregates, the water-cement ratio, and fundamentally the humidity and temperature conditions during curing. (2,3)

In this context, it is of capital importance to identify and develop new sources of pozzolanic materials that allow the production of binders with high volumes of clinker substitution at an affordable cost from an economic, energy and environmental point of view. (4)

The Centre for Research and Development of Structures and Materials CIDEM has carried out a study on the evaluation of shrinkage in pastes and concretes of Portland P 35 cement with 30% active mineral additions (LC2), which is no more than a product of calcined clay, limestone and gypsum in suitable proportions that substitute cement in the manufacture of concretes. All this is done to know the influence of the hydration process on the volume changes of LC2 as an active mineral addition.

2. METHODOLOGY

It is important to define the influence of active mineral additions such as LC2 on the kinetics of hydration in Portland cement pastes from the characterization of materials.

For the microstructure analysis of the cement paste, 6 samples with cement P 35 were prepared as a reference, varying the water/cement ratio (0.40, 0.45 and 0.50) and the incorporation of Superplasticizer.

Then, under the same conditions, the paste samples are elaborated with cement P 35 and the mineral addition LC2 at 30%.

In the study of cement pastes, calorimetry techniques are used to study the hydration of cement with mineral addition LC2 according to NC:525, 2014 Hydraulic Cement (Test methods. Determination of the heat of hydration and chemical shrinkage) to measure volume changes that occur between 0 and 7 days; the standard NC: 504, 2013 (Cement Volume stability) was consulted.

2.1 Experimental design

For the development of the research, a dosage is defined for the tests on cement pastes, where the water/cement ratio is varied.

Table 1 Samples

Samples	Composition
P 40	P 35, Ra/c=0.40
PA 40	P 35, Ra/c=0.40, 0.5% SP
P 45	P 35, Ra/c=0.45
PA 45	P 35, Ra/c=0.45, 0.5% SP
LC2-40	70%P 35+30% LC^2, Ra/c=0.40
LC2(A)-40	70%P 35+30% LC^2, Ra/c=0.40, 0.5%SP
LC2-45	70%P 35+30% LC^2, Ra/c=0.45
LC2(A)-45	70%P 35+30% LC^2, Ra/c=0.45, 0.5%SP
LC2-50	70%P 35+30% LC^2, Ra/c=0.50
LC2(A)-50	70%P 35+30% LC^2, Ra/c=0.50, 0.5%ASP

The active mineral addition is formulated in the Faculty of Construction where the thermal activation of the clay is developed by calcination at 800°C, then proceeds to grinding in a ball mill MB 800, and mixes the clay with limestone in a 2:1 ratio with 7% gypsum total to grind.

Table 2 Raw materials for the production of LC^2

Raw Materials	Origin
Clay	Yaguajay
Limestone	Morejón Quarry, Sancti Spíritus
Gypsum	Punta Alegre

Table 3 Composition of the active mineral addition LC2

Materials	Quantity (Kg)	%
Clay	19.8	62
Limestone	9.6	31
Gypsum	0.6	7

The cement to be used is produced at a cement factory in Cienfuegos, according to NC: 95, 2011 Portland Cement - Specifications, classified as Portland P 35 cement.

3. DISCUSSION OF RESULTS

The hydration process of Portland cement with 30% LC2 mineral addition is slow compared to pure Portland cement(5). Previous studies have shown that these cements have greater chemical stability and a denser microstructure. The aim of this research is to evaluate the LC2 influence on the hydration of cement pastes with a 30% substitution.

3.1 Effect in the hydration of cement pastes.

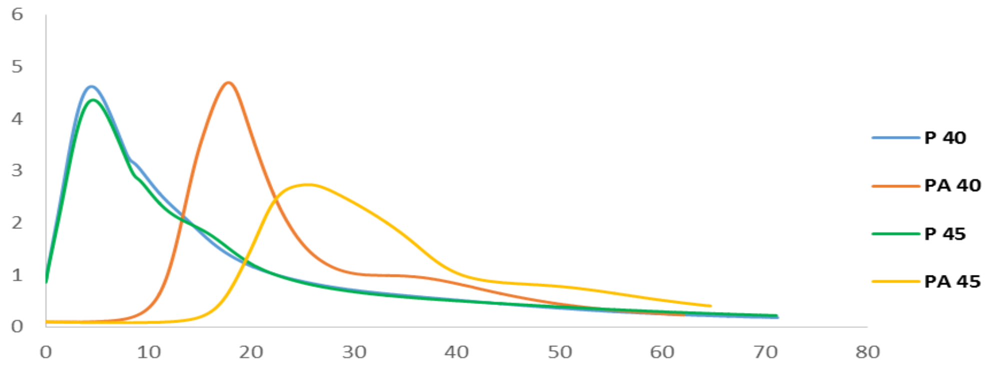

Fig. 1. Heat accumulated during hydration of the standard sample.

The use of the Superplasticizer favors the delay of the initial setting of the cement, thus prolonging the formation of the phases of a hydrated paste (5). Therefore, the comparison between the samples with and without additive is carried out in order to analyze the effect of this on the hydration of the cement pastes. the induction period of samples P 40 (Portland Cement, Ra/c 0.40, without additive) and P 45 (Portland Cement, Ra/c 0.45, without additive) which has an approximate duration of two hours. The curves of accumulated heat rise to a maximum point that coincides with the formation of hydrated calcium silicates (C-S-H) that occupy between 50% and 60% of the hydrated cement paste. In samples PA 40 (Portland Cement, Ra/c 0.40, with additive) and PA 45 (Portland Cement, Ra/c 0.45, with additive) a delay in the initial setting stage is observed, due to the effect of the Superplasticizer used. The paste is held in a plastic state for approximately 20 hours before moving on to the Acceleration Period, where the hydration rate reaches its maximum value at 36 hours, indicating that the initial setting has been completed and hardening of the paste begins.

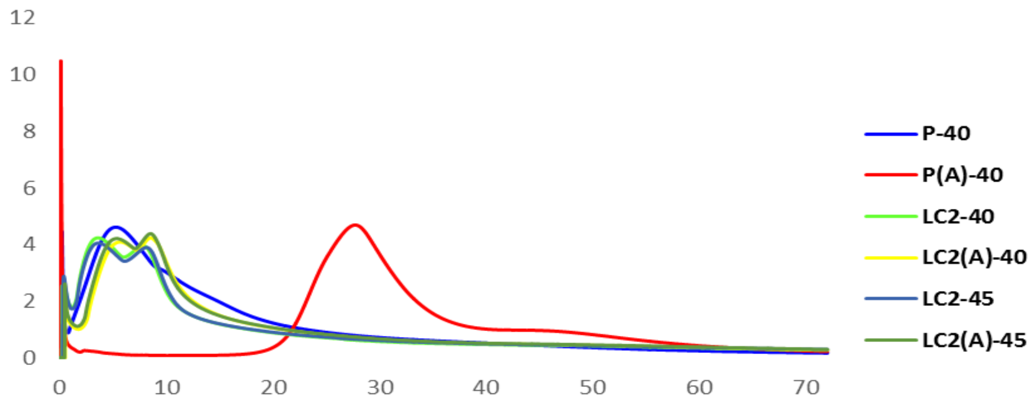

Fig. 2. Heat accumulated during hydration.

The behavior during hydration of samples with P 35 and mineral addition LC2, with variation of the water-cement ratio. As can be seen, the effect of the additive of delaying the initial setting of the paste is similar to that observed in the standard samples (See Annex I). In samples LC2(A)-4 (30% LC2, Ra/c 0.40, with additive) and LC2(A)-45 (30% LC2, Ra/c 0.45, with additive) the induction period is delayed approximately between five and seven hours; this is due to the fact that, within the composition of the paste, the mineral addition LC2 has a greater specific surface area, a part of the additive is absorbed by it and thus its retarding function is limited.

The samples LC2-40 (30% LC2, Ra/c 0.40, without additive) and LC2(A)-40 (30% LC2, Ra/c 0.40, with additive) in which the formation stage of the hydrated calcium silicate (C-S-H) (first peak of the curve) and the reaction stage of the tricalcium aluminate where ettringite is formed (second peak of the curve) are well defined. In the LC2(A)-40 sample (30% LC2, Ra/c 0.40, with additive) the ettringite formation stage has higher heat release values than LC2-40 (30% LC2, Ra/c 0.40, without additive).

For both samples, a longer induction period is evident with respect to the pattern, because the pozzolanic reaction occurs more slowly. After approximately ten hours, all samples, except PA 40 (Portland Cement, Ra/c 0.4, with additive), which is under the effect of the SikaPlast additive, begin to stabilize. The slopes of the curves decrease and coincide at 72 hours. It can be affirmed that, in the hydration of the components of the paste, both the standard and the samples with mineral addition LC2 behave in a similar way for the same water-cement ratio.

3.2 Effect in the volume changes

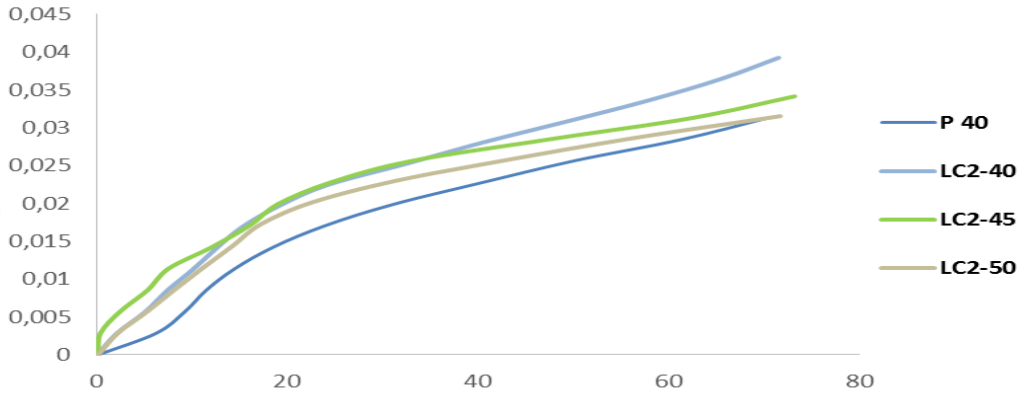

Fig. 3. Effect of variation in water-cement ratio on volume changes.

In samples LC2(A)-40 (30% LC2, Ra/c 0.40, with additive) and LC2(A)-45 (30% LC2, Ra/c 0.45, with additive) the effect of the additive is evident in the first 10 hours. The curves have a behavior similar to the samples that do not have additive, with the difference that in the latter there is an increase in volume variation of 0.005 ml/g. This shows that the additive influences the volume changes that occur in the pastes, which decrease by 40 percent.

An analysis is made of the variation in volume produced in the samples with mineral addition LC2, with respect to the standard samples, for different water-cement ratios.

The figure shows the influence of the mineral addition LC2 and the variation of the water/cement ratio on the chemical shrinkage of cement pastes. When comparing the pastes with mineral addition LC2, with the standard sample P 40 (Portland Cement, Ra/c 0.40, without additive) an increase of 0.005 ml/g cement is appreciated in the shrinkage during the first 72 hours. With respect to the water-cement variation, the samples with LC2 addition with lower water content present a greater variation in volume as a function of time. (See Fig. 3)

It is observed that the samples LC2-40 (30% LC2, Ra/c 0.40, without additive) and LC2-50 (30% LC2, Ra/c 0.50, without additive) are the best performing, although the sample LC2-45 (30% LC2, Ra/c 0.45, without additive) in the first 8 hours has variations in the deformations with respect to the other samples. After the 30 hours the samples are stabilized, where the LC2-50 (30% LC2, Ra/c 0.50, without additive) is the one with the lowest chemical shrinkage values and similar to the sample P 40 (Portland Cement, Ra/c 0.40, without additive).

3.3 Effect the shrinkage and calorimetry

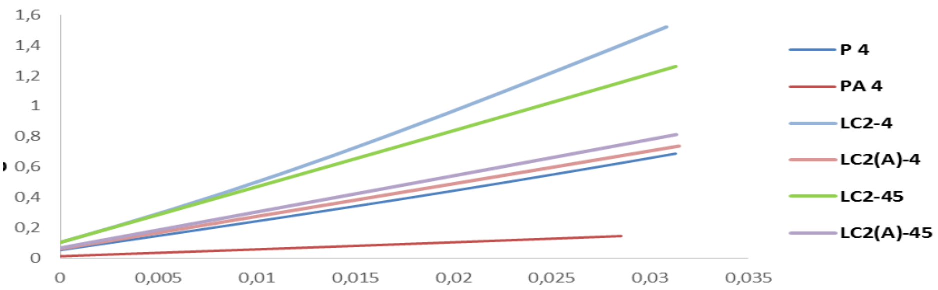

Fig. 4. Comparison of shrinkage values versus calorimetry.

Referring to the comparison between the shrinkage values (ml/g cement) and the calorimetry values (J/g cement) for the samples with P 35 and the samples with 30% addition of LC2 to Portland cement, it can be seen that there is a linear correlation between the values obtained by both methods, so it is feasible to use them in the analysis of the hydration processes of cement pastes.

It is observed that samples with Superlasticizer, when varying their volume during the three days, give off more heat in the hydration process than samples without additive. In the case of LC2 samples, the one with the best relationship between volume changes and heat release in the component formation process is presented by the LC2(A)-40 sample (30% LC2, Ra/c 0.40, with additive).

4. CONCLUSIONS

1. LC2 as an active mineral addition presents less variation in volume and heat release in the hydration process, for a given mass of paste, where the best substitution is with a water-cement ratio of 0.40.

2. The addition of clay + limestone + gypsum (LC2) can be used as a mitigation measure of the cracks produced by shrinkage, since these volume changes occur in the cement paste and with the substitution of 30%, this phenomenon is reduced.

3. The use of additives such as calcined clay and limestone not only favors the partial substitution of cement, reducing the production of clinker, but also provides certain properties that make concrete more durable**.**

5. REFERENCES

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