Volumetric Deformations at Early Age on Portland Cement Pastes with the Addition of Illitic Calcined Clay

Agustín Rossetti, Graciela Giaccio and Edgardo Fabián Irassar

Abstract With the aim of reducing the environmental impact associated with cement production, during the last decade, different percentages of clinkers have been replaced in cement by supplementary cementitious materials (SCMs). When new SCMs are incorporated in concrete, it is necessary to evaluate, not only the mechanical properties (as strength and stiffness) and the durability but also the deformations that can generate cracking and decrease the service life of the structures. This paper is focused on the study of volumetric changes at the early ages of pastes made with blended cements with the addition of illitic calcined clays from the Buenos Aires province, Argentina. The objective of this work is to present preliminary studies on the effect of illitic calcined clays on the autogenous and chemical shrinkage of pastes. The studies were made on pastes (water/cementitious material ratio equal to 0.275) using a Portland cement type II/A-L, with the incorporation of different percentages (10%, 20% and 30%) of illitic calcined clays. A device for direct deformation measurement was used to register linear dimensional changes; the general guidelines of ASTM C 1608 were applied for the determination of chemical and autogenous shrinkage. The volumetric changes measured with direct device are the sum of the chemical and autogenous shrinkage accompanied with the expansion due to the heat released during hydration. It was found that pastes incorporating calcined clays had early deformations similar to or lower than reference paste without clay.

Keywords Illitic calcined clays · Paste · Autogenous and chemical shrinkage

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A. Rossetti · G. Giaccio
LEMIT, CIC, Av 52 e/ 121y122, B1900AYB La Plata, Provincia de Buenos Aires, Argentina

E. F. Irassar (✉)
Facultad de Ingeniería, CIFICEN (UNCPBA-CICPBA-CONICET), B7400JWI Olavarría, Argentina
e-mail: firassar@fio.unicen.edu.ar

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1 Introduction

In the last years, in the cement industry, the tendency to use cementitious supplementary materials (SCMs) has grown. The most commonly used being blast furnace slag, calcareous filler and natural pozzolans. Its use is justified by economic and environmental issues. Studies have shown that the projections of cement consumption in the coming years will be very high and, on the other hand, the production of these SCMs will not be enough to cover the demands of the world market, mainly in the developing countries. In this circumstance, calcined clays with an adequate content of aluminum in their structure to react with the cement-like kaolinite, illite and montmorillonite appear as a promissory alternative. There are several studies on kaolinite calcined clays and their performance in concrete, but there are few references to illitic calcined clays.

Illitic clays are one of the most abundant clay minerals in the earth's crust. They come from the alteration of feldspars and micas in rocks due to weathering processes. The illitic clays acquire pozzolanic properties when they are thermally activated at 950 °C [1] causing dehydroxylation and the collapse of their structure to form an amorphous aluminosilicate compound [2]. Knowing the pozzolanic capacity of the addition, to prevent cracking, other technological aspects of the fine materials such as the volumetric stability in paste, mortar and concrete must be studied.

Autogenous shrinkage refers to an apparent volume or length reduction of hydrated cement under isothermal conditions and without interchange of water to the medium [3]. This phenomenon is caused by the continuous hydration of the cement after the formation of a resistant initial structure and can be explained by the theory of capillary pressure that is generated in pastes of low w/c ratio [4].

Generally, the autogenous shrinkage manifests itself at an early age within the first 24 h after the paste is mixed, but the matrix of the paste is more prone to cracking during the first 12 h [5]. During this period, the tensile strength of the paste is too low to resist the stresses caused by the volumetric deformation. The addition of supplementary cementitious materials modifies these behaviors. Mineral additions tend to produce densification and refinement of the internal structure of pores and then mechanical characteristics, durables and volumetric changes are modified [6]. To study the autogenous shrinkage, it can be measured as volumetric or length changes. Beyond the selected method, during the measuring of deformations, generally what is measured is a combination of autogenous, chemical, drying shrinkage and volumetric deformations by thermal processes that must be able to be identified separately [7].

Chemical shrinkage refers to volume changes the at early ages of hydration, which occur when the hydrated cement compounds are formed, as they have smaller volumes than the original compounds (cement and water) before being combined [8]. After the initial structure of the paste is formed during hydration, the continuous hydration generates the formation of voids in the matrix of the solid skeleton. At this point, the value of the autogenous shrinkage is lesser than the chemical, since the first one measures the apparent reduction of the volume, while the accumulated value of the vacuum is considered to be the chemistry. In the plastic state, the terms “chemical shrinkage” and “autogenous shrinkage” could be used interchangeably, but studies by Holt [9] have shown that autogenous shrinkage and chemistry are not equivalent in concretes with w/c ratio less than 0.30.

The objective of this work is to analyze the influence of illitic calcined clays incorporation on the autogenous and chemical shrinkage of pastes at an early age after casting. The studies were done on pastes (w/c = 0.275) using a Portland cement type II/A-L, with the incorporation of different percentages (10%, 20% and 30%) of an illitic calcined clay. A device for direct deformation measurement was implemented to register linear dimensional changes and the general guidelines of ASTM C 1608 were applied for the determination of chemical and autogenous shrinkage.

2 Materials and Methods

2.1 Materials and Mixtures

Portland cement type II/A-L 42.5 R (UNE-EN-197) with 10% of calcareous filler and an illitic calcined clay from a quarry of Olavarría (Argentina) identified as ICC was used. The clay stones were reduced to 5 mm particles and calcined in an oven. The temperature increased at 10.5 °C/min up to 950 °C and the maximum temperature was maintained for 90 min and then samples were cooled slowly in the oven according to previous test [1]. Finally, calcined clays were ground in a laboratory ball mill until obtaining 90% of the particles smaller than 45 μm. XRD analysis reveals low-intensity peaks of dehydroxylated illite and the associated minerals are quartz, hematite, oligoclase and spinel. Chemical composition of the cement and the clay determinate by XRF are reported in Table 1. The calcined clay meets the chemical requirements for Class N pozzolan (ASTM C 618): $S + A + F > 70\%$; $SO_3 < 4\%$ and $LOI < 10\%$. For this illitic calcined clay, the Frattini test was positive after 14 days, and also, the compressive strength development was reported in previous paper [1].

The physical characteristic of the materials, density (ASTM C 188), retained on 75 and 45 μm sieves (ASTM D 422 and C 618), the Blaine specific surface (ASTM C 204) and the particle size distribution (PSD) determined using the laser granulometer (Malvern Mastersizer 2000) are reported in Table 2.

This study was performed on pastes with 0.275 water/cement + ICC ratio; the pastes incorporated 0, 10, 20 and 30% of calcined clay as cement replacement (percentages by weight) and they are identified as PC, ICC10, ICC20 and ICC30, respectively.

Table 1 Chemical composition and loss on ignition of the cement and the ICC (%)

Material	CaO	SiO_2	Al_2O_3	Fe_2O	MgO	SO_3	K_2O	Na_2O	TiO_2	P_2O_5	LOI
Cement	60.92	16.58	4.21	1.80	2.16	1.77	0.67	0.28	0.29	0.19	2.05
ICC	1.13	63.43	18.32	7.89	2.71	0.04	4.29	1.52	0.90	0.06	0.19

Table 2 Physical characteristics of ICC and cement

Property/material		ICC	Cement
Density		2.65	3.05
Retained on sieve, %	75 μm	4.02	–
	45 μm	5.68	–
Particle size distribution	d10, μm	1.29	2.39
	d50, μm	7.34	15.7
	d90, μm	36.95	48.0
Specific surface Blaine, m^2/kg		724	
Specific surface BET, m^2/g			1.88

2.2 *Direct Linear Deformations*

Linear deformations were measured using a device that automatically recorded length changes of the pastes after casting ($t = 0$). The device used (Fig. 1) consists of steel mold of 40 × 40 × 160 mm (Fig. 1a) with a mobile end in contact with a LVDT (Fig. 1b) that measures the longitudinal deformation.

This device can measure the longitudinal deformations in both directions, as a screw of ~4 cm long was incorporated into the mobile part so the paste can drag the head. To avoid friction and adhesion of the paste with the faces of the mold, this was covered with a layer of Teflon and oil. After filling and compaction, the test paste was covered with a waterproof film and a thermocouple was introduced to measure the temperature inside the paste (Fig. 1c). The device was placed in a container with water in the base and was covered with a lid to control the temperature (22 °C) and humidity (>95%) (Fig. 1d). During the test, data acquisition (LVDT and thermocouple) occurred every 2 min until 48–72 h.

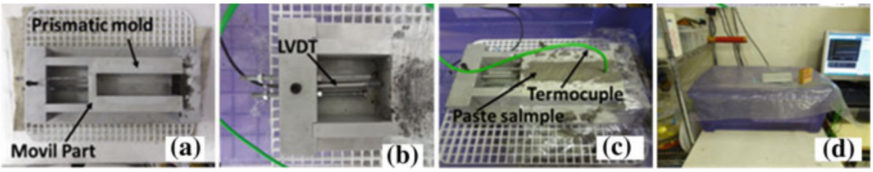

Fig. 1 **a** Device used to measure longitudinal deformations; **b** LVDT; **c** molded paste with thermocouple ready to measure internal temperature; **d** device in the container ready to start the test

2.3 Volumetric Determination of Chemical and Autogenous Shrinkage

Chemical shrinkage was determined based on the methodology proposed by ASTM C 1608; it was placed approximately 100 g of paste (w/cm = 0.275) in a glass cylindrical container, then it was carefully filled with water, and finally, a plug with a capillary tube to ensure a tight seal was placed, as shown in Fig. 2a. Then the container was introduced in isothermal medium, and in half-hour intervals, measurements of the water level in the capillary tube were made.

The autogenous shrinkage was studied with the same methodology described in the previous paragraph but with the main difference that the paste was isolated to avoid water interchange and moisture variations (condition of the autogenous shrinkage). To isolate the paste, it was placed and consolidated inside a latex membrane, and then, it was introduced in the glass container (Fig. 2b) ensuring that no air bubbles remain inside. Then the plug and graduated tube were placed and proceed to measure in the same way as the chemical shrinkage. In order to make continuous measurements, webcams programmed to monitor the whole experience filming the capillary tubes were implemented (Fig. 2c).

In addition, with these pastes, rings (2 cm thick) were cast to determine the times of cracking using the method of restrained contraction (Fig. 3). After 24 h of casting the pastes, the external part of the mold was removed and the rings were kept in laboratory environment (temperature 20 °C and relative humidity of 70%). The idea of this study was to determine qualitatively if the addition of the calcined clays increases the contraction which would mean that the fissures occur earlier.

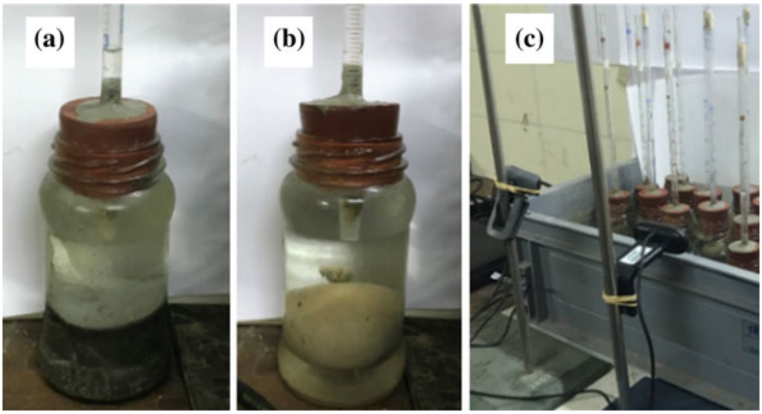

Fig. 2 **a** Chemical shrinkage; **b** autogenous shrinkage; **c** monitoring cameras

Fig. 3 Determination of restrained shrinkage in paste rings with the addition of illitic calcined clay

3 Results and Discussion

3.1 Longitudinal Deformations

The results of Direct Linear Deformation Experiment were analyzed taking into account the results from Holt thesis [10]. According to Holt, the curve of the longitudinal variation at early age is the sum of several processes: reabsorption of the bleeding water, growth of the ettringite crystals, growth of the portlandite crystals, topochemical reaction produced by the hydration of the C_3S, thermal expansion product of the exothermic reactions of the hydration of the cement, among others.

Figure 4 shows the results of the longitudinal deformations and the temperature for the reference pastes made only with cement (PC) and the pastes with the incorporation of the different percentages of illitic calcined clays (ICC10, ICC20, ICC30).

Analyzing the curve corresponding deformation to the PC control: from the beginning of the measurement (time 0) and up to ~90 min, shrinkage is observed reaching a maximum of 320 μm/m as a result of the chemical contraction while the temperature decreased slightly. After 90 min, both curves (deformation and temperature) present an inflection point that occurs in correspondence with the initial setting time, the rate of hydration heat increases and the solid skeleton of high connectivity develops where the water moves freely through the interior of the paste. This process generates an expansion of ~170 μm/m until 4 h (final setting) and it is attributed to the heat of hydration. Between 4 and 6 h after the formation of the solid skeleton by the setting process, capillary pressures begin because the continuous hydration makes a structure of pores that inhibit the free movement of water in the hardened paste.

From this point, a competition between capillary pressure and temperature starts, winning pressure and making small shrinkage until it stabilizes. Between 6 and 10 h, there is volumetric and thermal stability and the paste reaches the maximum temperature (~10 h). Then the curve deformation shows shrinkage lower than 60 μm/m attributed to the deceleration of the heat released by hydration and begins the cooling of the paste. Between 14 and 24 h, an expansion lower than 90 μm/m is developed, although the thermal curve indicates a continuous cooling of the paste until it stabilizes at room temperature for 36 h. In other words, the expansion process that takes

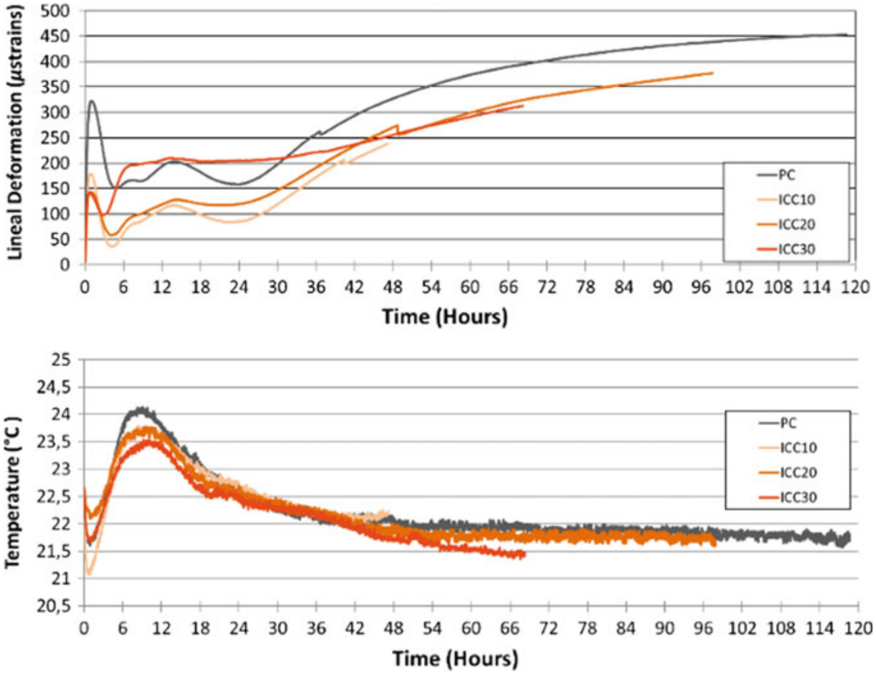

Fig. 4 Linear deformations and temperature variation measured in Portland cement paste with illitic calcined clays

place between 10 and 24 is independent of temperature. After 24 h, a combination of thermal, chemical and autogenous shrinkage is developed. After 36 h, the temperature stabilizes and only the autogenous and chemical shrinkage develops, reaching 300 μm/m at 120 h.

Analyzing the deformation curves corresponding to the cement with the addition of illitic calcined clays: at the beginning, the initial shrinkage is less than that one measured for the control cement. Then at the start of the setting time (90 min), the solid skeleton formation begins producing an expansion by the reabsorption of the free water and thermal expansion for the ICC10 and ICC20 pastes. This expansion is lower for the ICC30. The shrinkage by capillary pressure appears ~at 4 h and it is compensated by the thermal expansion until the system stabilizes at 14 h. At this time, there is no variation in volume due to the balance between the chemical–autogenous shrinkage and the cooling. From 14 to ~24 h, ICC10 and ICC20 samples have a slight expansion, where is more pronounced in the ICC10 which can be attributed to a lower effective ratio of water to cement (effective w/c = 0.34) making a high confined space where the free water wants to move. The paste ICC30 shows higher shrinkage between 4 and 7 h, and after that, the shrinkage remains constant until 36 h where the shrinkage increases (autogenous and chemical) without thermal influence since the paste has reached equilibrium with the environment. At 48 h, final shrinkage of the pastes is less than that corresponding to the reference paste with a similar value (250 μm/m) for the three replacement percentages studied.

3.2 Volumetric Deformations. Chemical and Autogenous Shrinkage

Figure 5 shows the results of the chemical (Q) and autogenous (A) shrinkage measured following the guidelines of ASTM C 1608 of pastes PC, 10ICC, 20ICC and 30ICC with 0, 10, 20 and 30% of clay replacement, respectively. It can be seen that for all calcined clay replacements, both autogenous and chemical shrinkage are slightly lower than for the control paste. The differences in volume changes are not significant and there was not a clear effect produced by the clay content. Analyzing the chemical shrinkage curve at the age of 60 h, the values are practically the same reaching 3 $cm^3/100$ g. It is important to highlight that addition of different percentages of calcined clays did not increase the chemical or autogenous shrinkage.

During the restricted shrinkage ring test, it was possible to observe that the cracking occurred between 20 and 48 h after casting. It should be noted that the control paste PC was the first to crack, and as the percentage of addition increased the cracking took place in later time, this behavior is consistent with the deformations measured using the other methods described above.

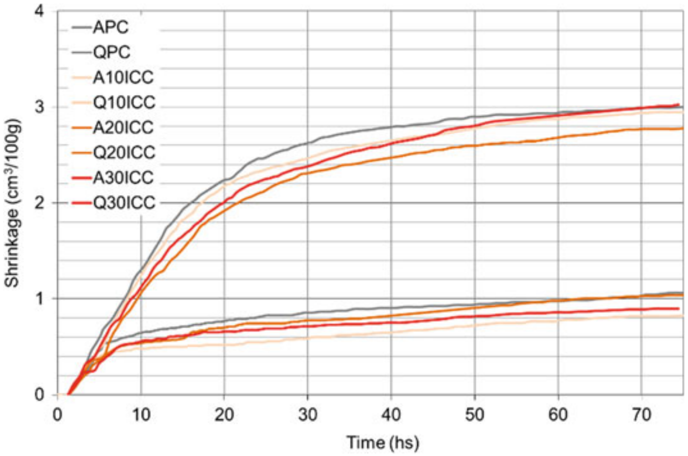

Fig. 5 Chemical and autogenous shrinkage curves with the addition of 10, 20 and 30% of illicit calcined clay according to ASTM C 1608

4 Conclusions

In the present work, first measurements of deformations were made in Portland cement pastes with the incorporation of different percentages of illitic calcined clays using a direct measurement method (linear deformations) and a modification of the ASTM C 1608 standard (volumetric deformations). The main conclusions are:

- The volumetric changes determined by an experimental device of direct measurement provide information on the different states of the paste as well as the thermal gradients in cements mixed with calcined clays.
- The deformation curve (direct measurement method) corresponding to the control cement presents a higher number of inflection points than those corresponding to the different percentages of illitic calcined clays pastes. The first explanation to this is that as the additional content grows, the effective water–cement ratio increases and this causes a less confined and less restrictive internal system.
- For all replacements of illicit calcined clay, volumetric deformations, both in terms of autogenous and chemical shrinkage, yield final values that are less than the control paste. This situation is also reflected when the pastes are analyzed with the direct measurement method.

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