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Influence of initial curing on the properties of concrete containing limestone blended cement

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Abstract

This paper describes the effect of duration of initial curing on the mechanical properties (compressive strength, tensile strength, and modulus of elasticity) and the chloride penetration of concretes containing limestone blended cements. Three concrete mixtures (water/cementitious = 0.5) containing a portland and two limestone blended cements were subjected to three different initial curing regimens (full, wet, and air curing). Results show that mechanical properties of concrete containing limestone blended cement are less affected by the cessation of moist curing at early ages. This is attributed to the hydration acceleration owing to limestone presence and the increase of fineness in the clinker fraction of the blended cement. A prolonged initial moist curing reduces this advantage of limestone blended cements and the dilution effect produced by limestone addition impairs the potential mechanical properties. For concretes cured for an initial 7 days, there was no substantial difference in mechanical properties and chloride penetration resistance of cements with and without limestone filler.

Keywords: Curing; Blended cement; Filler; Mechanical properties; Diffusion

1. Introduction

The continuation of hydration reactions in portland cement is essential to improve the potential strength and durability of concrete. This continuation depends on the type and fineness of cement, the type and the amount of supplementary material present, the water–cement ratio and the curing conditions, especially at early ages [1]. The objective of curing is to provide an appropriate environmental condition within a concrete structure (temperature and humidity) to ensure the progress of hydration reactions causing the filling and segmentation of capillary voids by hydrated compounds.

For a given condition, curing duration to achieve an adequate hydration of portland cement concrete depends mainly on the type (chemical and mineralogical composition) and the fineness of cement. ACI 308 Recommended Practice [2] suggests 7 days of moist curing for most structural concretes. However, the curing period should be extended to 14 days when the cement contains supplementary cementitious materials, such as slag, natural pozzolan, and fly ash, owing to the slow hydration reactions between supplementary cementitious materials and the calcium hydroxide. This reaction requires the presence of water to produce the cementing compounds that contribute to filling the capillary voids.

Limestone filler is largely used in cement production, but it does not have pozzolanic properties and consequently, it does not produce C-S-H [3]. Several compounds are formed by the reaction of limestone and cement, such as carboaluminates, but they have little or no contribution to filling the capillary voids [4]. Limestone filler addition produces mainly physical effects in the cement paste, which can be summarized as the proper filler effect, hydration acceleration, and the dilution effect. Limestone filler fills the voids between clinker particles improving the grain packing of cement and dispersing the clinker particles [5]. It also acts as nucleation sites of calcium hydroxide crystals at early hydration ages [6,7] accelerating the hydration of clinker particles, especially the C_3S [8,9], and consequently improves the early strength. Finally, an associated effect of

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limestone addition is the reduction of potential cementing material, which is commonly known as dilution.

From a durability point of view, curing is essential to improve the quality of cover concrete blocking the ingress of aggressive substance into the concrete structure. Chloride ion induced corrosion of reinforcing steel is an extensive problem. Among the causes, the lack of attention give to durability criteria other than strength requirements and the change of cement composition producing an early strength with a high water–cement ratio can be enumerated. For this reason, the depth of chloride penetration is an important parameter to evaluate the influence of cement composition and curing regimes as durability criteria.

Several publications [10–16] report the strength and durability properties of mortar or concrete with limestone subjected to continuous water curing. However, a few bibliographic references were found about the influence of interruption of curing in concretes containing limestone blended cements.

This article describes a study on the mechanical properties and chloride penetration of concrete containing limestone blended cements subjected to different periods of initial moist curing.

2. Experimental program

2.1. Materials

A normal portland cement (C0) and two limestone blended cements (C10 and C20) obtained from the same portland clinker by an intergrinding process in the cement plant were used. The clinker contains 65% of C_3S and 5.3% of C_3A, and the limestone content by mass was 0%, 9.3%, and 18.1% according to the data supplied by the cement producer. Cements have the same strength class (45 MPa at 28 days) leading to a large specific surface of limestone blended cements (317, 372, and 420 m^2/kg for 0%, 9.3%, and 18.1% of filler content, respectively). For these cements, an increase of fineness is not directly related to an increase of fineness of clinker particles. Considering that limestone has a higher grindability degree than that of clinker, then clinker particles are in the coarse fraction of cement and the limestone particles occupy the fine fraction [17].

Coarse aggregate was crushed granite stone with a maximum size of 19 mm for mechanical test specimens and 12.5 mm for chloride penetration test specimens. For all concretes, fine aggregate was a natural sand with a fineness modulus of 2.35.

2.2. Mixtures and specimens

Concrete mixtures were formulated with a water–cementitious ratio of 0.50 and a total cementitious content of 350 kg/m^3. A ratio between the weight of the sand and the total weight of the aggregate was approximately 0.42 and the water content was adjusted to obtain a slump of 70 mm. Concrete mixture details are presented in Table 1. For each mixture, forty 100 × 200 mm cylinders, forty 150 × 300 mm cylinders and three beams were cast. After casting, the molds containing the specimens were stored in laboratory environment for 24 h.

2.3. Curing regimes

After removal from the molds, concrete specimens were cured under the following conditions:

Full cured: specimens immersed in water saturated with lime until the test age.
Wet cured: specimens immersed in water saturated with lime for 6 days and then air curing in normal laboratory environment.
Air cured: specimens air cured in normal laboratory environment.

2.4. Mechanical properties

Compressive strength and the static modulus of elasticity were determined on 100 × 200 mm specimens. Tensile strength was determined on 150 × 300 mm cylinders using the ASTM C 496 splitting test. In all cases, the mean of three test values is reported. Mechanical properties of concrete were obtained at 1, 3, 7 and 28 days. The moisture content of specimens at the test was the result of humidity interchange between specimens and the environment. Hence, full cured specimens were only tested in the same moisture condition at all ages.

2.5. Hydration degree

At each age, fragments of concrete tensile specimen were used to determine the amount of non-evaporable water and

Table 1
Mixture proportions and properties of fresh concrete

	Mixture proportions, (kg/m^3)						Bleeding	
Mixture	Water	Cement	Fine aggregate	Coarse aggregate	Slump (mm)	Unit weight (kg/m^3)	Type	Capacity (%)
C0	175	350	770	1050	75	2428	Uniform	12.0
C10	175	350	760	1050	65	2390	Uniform	1.4
C20	175	350	755	1050	65	2358	Uniform	1.2

the hydration degree (α). The non-evaporable water was obtained according to the procedure proposed by Powers [18]. This value was used as a means of estimating the hydration degree supposing that the filler is a chemically non-active addition and the water needed for the full hydration of cement used was taken as 0.23. Results provided by this method are not accurate, but they are sufficiently indicative of hydration reaction progress [19].

2.6. Chloride ion penetration

Concrete specimens (100 × 150 × 530 mm) were cured in wet and air regimens. The surfaces of the specimens were epoxy-coated with the exception of one surface perpendicular to molding and then immersed in water during 24 h for saturation of specimens. Thereafter, the specimens were exposed to a 3% sodium chloride solution.

After 45 days of immersion in solution, a 70-mm thick slice was sawed from the top of each prism and the specimens were newly epoxy-coated and immersed in solution again for future determination. The depth of chloride penetration was measured by splitting the slice and the resulting surfaces were sprayed with $AgNO_3$ (0.1N) to register the stained zone as chloride penetration front.

3. Results and discussion

3.1. Properties of fresh concrete

Table 1 shows that the water demand of the concrete remains constant in spite of the increase in the specific surface of limestone blended cements. However, both concretes with limestone showed an adequate workability, a good finish, and they were very cohesive. Previous studies carried out on mortars and paste demonstrated that the addition of very fine limestone filler does not significantly increase the water demand [5,20]. Fresh density of concrete shows a slight decrease when limestone filler content increases.

The increase of filler content in cement drastically reduces the bleeding capacity of fresh concrete as shown in Table 1. The reduction of bleeding capacity is due to the large specific surface of limestone blended cement and the blocking of capillary pores by the filler particles obstructing the water movement through the fresh concrete [21].

3.2. Compressive strength

The effect of different curing conditions on the compressive strength of concretes with and without limestone filler is reported in Table 2. For the full curing regime, the compressive strength was 40.2, 38.1, and 36.3 MPa for C0, C10, and C20 concretes, respectively. At 1 day, limestone filler concretes (C10 and C20) exhibit a higher value of compressive strength (11.06 and 9.03 MPa) than to the corresponding reference concrete (3.72 MPa). A similar trend was observed at 3 days, but the difference between reference concrete and limestone filler concretes was minimal. At 7 days, all concretes attain a similar level of compressive strength (30.0, 29.6, and 30.3 MPa for C0, C10, and C20, respectively). After 28 days of wet curing, test results exhibit the highest compressive strength for the reference concrete (40.2 MPa) while limestone filler concretes attain a 5% to 10% lower strength value. For this curing condition, at 7 days, all concretes have reached at 75% to 80% of potential 28-days' strength that is recommended by concrete codes as curing time. Cessation of moist curing at 7 days causes a higher 28-days' compressive strength (43.8, 42.0, and 42.6 MPa) than that observed for full cured specimens in all concretes studied. A possible explication for this is that the rate of strength gain is not affected by the lack of curing and the lower moisture content of specimens at the test age causes a higher 28-days' compressive strength.

Table 2
Compressive strength and modulus of elasticity related with the corresponding value of reference concrete full curing

	Full curing			Wet curing			Air curing		
Age (days)	C0	C10	C20	C0	C10	C20	C0	C10	C20
Compressive strength									
1	1.00	3.12	2.43	–	–	–	–	–	–
3	1.00	1.25	1.23	–	–	–	0.83	1.02	1.05
7	1.00	0.99	1.01	–	–	–	0.67	0.77	0.86
28	1.00	0.95	0.90	1.09	1.06	1.06	0.68	0.74	0.78
Modulus of elasticity									
3	1.00	1.11	1.14	–	–	–	0.95	1.08	1.09
7	1.00	1.07	1.09	–	–	–	0.88	0.94	0.97
28	1.00	0.97	0.93	0.91	0.89	0.88	0.75	0.80	0.84

For the air curing regime, the early cessation of moist curing causes a severe decrease of strength gain for all concretes. However, reference concrete suffers the highest decrease of compressive strength at 28 days (32% compared to 28 days, the full curing strength), while both concretes containing limestone filler cement show less strength decrease (22% and 14% for C10 and C20, respectively). Best results obtained for limestone filler concretes are due to the acceleration of hydration at the early age.

3.3. Tensile strength

Results show the same general trend as for compressive strength under different curing regimes. Fig. 1 shows the relation between tensile and compressive strength. At 1 day, limestone blended cements exhibit the best results (0.46, 1.33, and 1.14 MPa for C0, C10, and C20 concretes, respectively). At 7 days of wet curing, limestone concretes show an equivalent tensile strength to that of the reference concrete (3.05 MPa). After 28 days of full curing, the reference concrete has a higher tensile

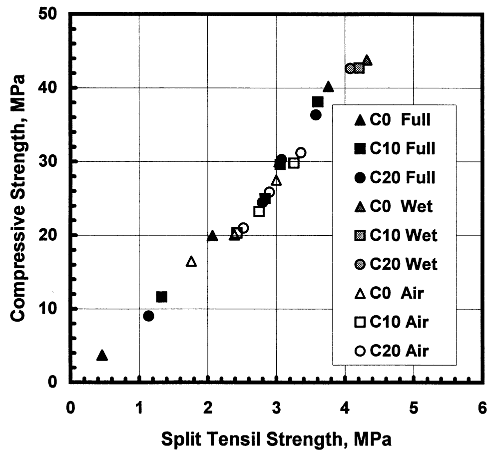

Fig. 1. Compressive and tensile strength relationship.

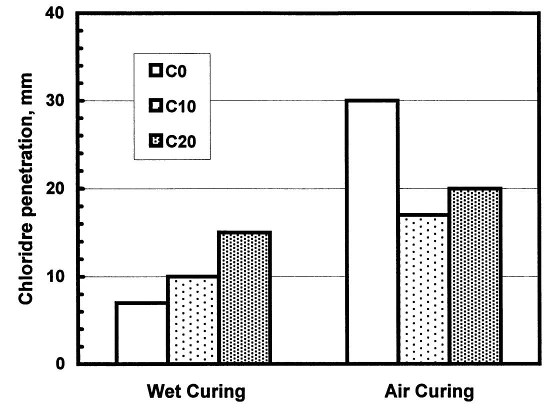

Fig. 2. Chloride ion penetration for concretes' air and wet curing after 45 days' immersion in 3% NaCl solution.

strength than that corresponding to limestone concretes (3.76, 3.61, and 3.58 MPa).

The lack of curing on the 28 days' tensile strength produces a similar effect to that of compressive strength. Air curing leads to a high strength of limestone concretes while wet curing produces an equivalent tensile strength of concretes with and without limestone.

3.4. Modulus of elasticity

Results are presented in Table 2. For full curing, reference concrete showed a lower E-value at early age (3 days). This difference between the reference and limestone concretes is also presented at 7 days. Then, limestone concretes (38.6 and 37.0 GPa) have a lower E-value than the corresponding reference concrete (39.8 GPa).

For all concretes, wet curing produces a reduction in the 28-days' E-value compared to full curing. It is assumed that all factors that increase the strength also increase the modulus of elasticity except for moisture saturation. Contrary to compressive strength, the modulus of elasticity decreases with the lack of moisture in the specimen [22].

In air curing regime, limestone concretes showed the best results at all ages. At 28 days, E-values of limestone concretes are 8% and 13% higher than the corresponding reference concrete. Then, the difference between 28 days' E-value full curing and 28 days' E-value air curing was significantly small for limestone concretes.

3.5. Chloride ion penetration

Fig. 2 shows the depth of the stained zone by $AgNO_3$ after 45 days of immersion in chloride solution. As expected, air curing produces the deepest chloride penetration in all concretes. However, both limestone concretes exhibit a lower penetration of chloride ion front than the corresponding reference concrete. For wet curing regime, these concretes have a deeper chloride ion penetration. The lack of curing significantly aggravates the chloride ion penetration of reference concrete increasing the depth from 7 to 30 mm, while for limestone concrete this was from 10–15 mm to 17–20 mm. These results indicate that chloride penetration is also affected by curing regimens according to the change in hydration kinetics of cements and the hydration development at the curing cessation time.

3.6. Hydration degree (α) and hydrated cementing materials

The evolution of mechanical properties and the chloride penetration of concrete subject to the different curing regimes described above are basically associated with the hydration kinetics of the cements, especially with the hydration degree developed at the time moist curing ceased.

Fig. 3 shows the evolution of hydration degree of clinker particles for all concretes. A reduction 28 days' α-value occurred when the moist curing was reduced. The reduction of α was ranged from 7% to 18% in concretes with limestone filler while ranging from 20% to 28% in the reference

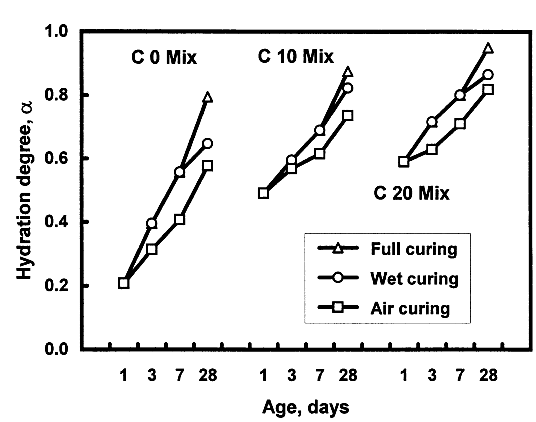

Fig. 3. Hydration degree of clinker fraction in concretes subjected to different curing regimes.

concrete. However, limestone blended cements contain a low clinker mass per ton of cement. Then, the mechanical properties of limestone blended concrete will be similar to the reference concrete when it reaches the same volume of hydrating cementing materials as in cement not containing limestone addition.

For a given chemical and mineralogical composition of clinker, the hydrating cement material (HCM) is controlled by hydration degree (α), the volume of limestone addition (V_f) and the unit cement content (UCC) of concrete. It can be written as:

$$HCM = \alpha * UCC(1 - V_f).$$

The HCM in limestone blended cements at a given age is the result of three main factors. First, limestone addition causes the acceleration of hydration process of cement grains, especially the C_3S, due to CH nucleation. This effect is more pronounced at early age. Bonavetti [7] has demonstrated that the hydration degree of the clinker portion in cement paste (w/c = 0.40) containing limestone filler (5% to 20% by cement mass) increases from 5% to 25% during the first 7 days. In this study, the size distribution and reactivity of clinker grain was the same in cement with and without addition because limestone addition was incorporated as weight replacement of a manufactured portland cement. Second, a large specific surface of clinker particles in limestone blended cements lead to a high hydration degree at early age. This high fineness of clinker fraction is required to reach an equivalent standard strength class of cements. Third, limestone addition decreases the cementing material per ton of cement due to the dilution of clinker fraction, because limestone grains do not produce cementing materials. These effects increase with the increase of limestone replacement level.

Fig. 4 shows a scheme of HCM for full curing cements with different filler contents. Analyzing this scheme and the time of curing cessation, results described above can be justified.

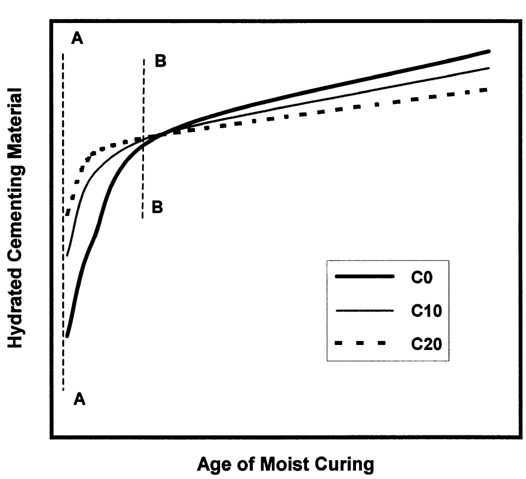

Fig. 4. Schematic representation of hydrated cementing materials (HCM) in concretes subjected to full curing.

3.6.1. Full curing

At 1 and 3 days, both concretes with limestone filler present a higher HCM than the corresponding reference concrete. In this case, the acceleration of hydration compensates the dilution of clinker fraction and then limestone concretes have a high strength and modulus of elasticity. At 7 days, these effects reach equivalent value and then mechanical properties are similar. At 28 days, the hydration degree of clinker fraction limestone concretes is higher than the corresponding reference concretes, but the dilution effect causes a low HCM. Then, the loss of mechanical properties of limestone concretes is more important when there is increase in the proportions of limestone in blended cements [5].

3.6.2. Wet curing

When curing was ceased at 7 days, a similar volume of HCM was developed in all concretes: the acceleration of hydration at early ages compensates the dilution effect. This case is presented by B–B line in Fig. 4. Then, similar mechanical properties were obtained. However, the penetration of chloride in both limestone filler concretes was slightly deeper than the corresponding plain concrete instead of the same maturity degree of all concretes. The acceleration of hydration of limestone cements produce a higher volume of large pores than in plain cement [14] which can induce some changes in the connectivity and tortuosity of the capillary pore structure which governs the chloride diffusion.

3.6.3. Air curing

For lack of curing, the acceleration of hydration process at early ages is more important than the dilution of clinker fraction leading to a high volume of HCM at the time of curing cessation. At 1 day, HCM estimates were 75, 140, and 150 kg/m^3 for C0, C10, and C20 concretes, respectively. In Fig. 4, this case is represented by the A–A line. Thereafter, both concretes with limestone filler have a high strength and elasticity modulus and a less penetration of chloride ions.

4. Conclusions

For the materials used in this study, the following conclusions can be drawn.

(1) Mechanical properties (compressive strength, tensile strength, and modulus of elasticity) of concretes with limestone blended cements are less sensitive to an early interruption of the moist curing. Curing cessation at 1 day results in a 14% to 22% of potential strength loss by these cements while this curing condition increases the loss of potential strength for plain concrete by about 32%.

(2) This study suggests that the changes in the hydration development at early ages and the dilution effect produced by limestone addition are the cause of concrete behavior. At early curing ages, the increase of hydration produces a greater volume of cementing material, then concrete is less sensitive to curing cessation. At prolonged curing time, the progress of hydration compensates this acceleration and the dilution effect causes a less HCM. For concretes cured for an initial period of 7 days, an equilibrium between these factors is achieved and the potential mechanical strength is not affected by the cessation of curing.

(3) The chloride penetration was found less sensitive to the lack of curing in concretes containing limestone blended cements. The resistance to chloride penetration was considerably enhanced by 7 days moist curing and the depth of penetration increases with the increase of limestone content due to the predominance of the dilution effect over the hydration acceleration.

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