Cement & Concrete Composites 46 (2014) 32–40

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Effects of portland cement replacement with limestone on the properties of hardened concrete

Federica Lollini *, Elena Redaelli, Luca Bertolini

Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Piazza Leonardo da Vinci 32, 20133 Milan, Italy

ARTICLE INFO

Article history:
Received 6 September 2012
Received in revised form 25 October 2013
Accepted 30 October 2013
Available online 8 November 2013

Keywords:
Blended cement
Compressive strength
Durability
Carbonation
Diffusion

ABSTRACT

Limestone portland cement has a lower environmental impact during the production phase in comparison with portland cement. However, the environmental advantages initially gained should be correlated to the long-term performance of concrete structures. Hence, the knowledge of the long-term properties, and in particular durability performance, is essential to assess the actual environmental impact of limestone replacement. In the literature, there is disagreement on durability behaviour and the contribution of limestone to the resistance to chloride and carbonation penetration is controversial. In this paper, the effect of the percentage of replacement of portland cement with ground limestone, water/binder ratio and cement content on compressive strength, electrical resistivity, sorptivity and resistance to carbonation and chloride penetration was evaluated. Results showed that both mechanical properties and resistance to penetration of aggressive agents decreased by replacing 15% of portland cement with limestone; a further decrease occurred with 30% limestone.

1. Introduction

During the last decades, portland limestone cement (*PLC*) has shown a rapid increase of production in the cement industry. According to the CEMBUREAU statistics [1], in Europe the CEM II cements correspond to two thirds of the market and, among them, in some countries such as Italy, portland limestone cement is the most frequently used [2]. This type of cement is produced by blending ordinary portland cement (*OPC*) with limestone or inter-grinding portland cement clinker and limestone. The European Standard EN 197-1 allows CEM II portland limestone cements to contain up to 35% limestone.

The constant growth of the use of *PLC* is mainly due to the lower consumption of natural raw materials, the saving of fuel energy for clinker production, and the reduction of CO_2 emissions [3–6]. This is supported by some studies which showed that in concrete with low water/binder ratio (i.e. lower than 0.4) a large volume of cement remains unhydrated, since there is not enough space to locate the hydration compounds, and part of portland cement can be replaced with more economical particles, such as limestone [7–9]. However there is the need to assess the performance of *PLC* concrete and its long term behaviour, especially for concrete with higher water/binder ratio.

Several studies were carried out since the late 1970s on the properties of limestone portland cement paste, mortar and concrete. Concrete performance is affected by the quality of limestone, whether the limestone was interground or blended and the particles size distribution [10–13], and, hence, the comparison among results of different studies is often rather difficult. However, some considerations, especially on compressive strength and durability issues, can be made.

Several authors claim that compressive strength is relatively unaffected by limestone replacement up to 15% of the total mass of binder [14–16], whilst when the percentage of limestone increases, the strength is reduced compared to *OPC* concrete, indicating that limestone behaves somewhat as an inert addition [15]. According to some authors an increase of early-age strength occurs with limestone additions (in the range 5–20%) due to the improvement in particle packing [17], increase of cement hydration rate [18–24], early production of calcium carbo-aluminates [25] and formation of nucleation sites of calcium hydroxide crystals [10,26].

As far as the carbonation resistance is concerned, several authors state that the use of *PLC* concrete, in comparison to *OPC* concrete, leads to an increase in the carbonation rate for concrete with the same water/binder ratio, however the carbonation resistance is similar in concrete with equal compressive strength [14–16,27]. On the contrary, according to [28], even the replacement of portland cement with up to 35% interground limestone seems not to lead to a decrease in the carbonation resistance.

As far as the resistance to chloride penetration is concerned, some authors report that in concrete with addition of limestone

* Corresponding author. Tel.: +39 02 2399 3144; fax: +39 02 2399 3180.
E-mail addresses: federica.lollini@polimi.it (F. Lollini), elena.redaelli@polimi.it (E. Redaelli), luca.bertolini@polimi.it (L. Bertolini).

0958-9465/$ - see front matter
http://dx.doi.org/10.1016/j.cemconcomp.2013.10.016

filler the diffusion coefficient of chloride is reduced compared to portland cement concrete, due to the filler effect of limestone [29], whilst other authors state that increased chloride ion penetration occurs in *PLC* concrete in comparison to *OPC* concrete [8,9,30,31]. The increase in the rate of chloride ingress has been attributed to the reaction between the limestone filler and aluminates (C_3A and C_4AF) and the formation of compounds with lower binding capacity for chloride in comparison to reaction products of aluminates in portland cement [32]. For other authors, a limited substitution of portland cement with limestone (up to 15%) does not significantly affect the resistance to chloride penetration [15,16,28,33]. Even studies on gas, water and oxygen permeability as well as sorptivity and porosity, that can be useful to depict the *PLC* concrete behaviour with respect to the resistance to the movement or penetration of fluids and ionic species, are controversial and available results on these parameters are affected by the amount of replaced portland cement [15–19,28,34–38].

Although a lot of work has been done in the last decades to investigate the performances of limestone portland cement and the knowledge level is continuously extending, there is still disagreement on durability issues. In order to contribute to this discussion, an experimental study was carried out to assess the effect of the partial replacement of portland cement with ground limestone in proportions of 15% and 30% on the properties of concretes with various water/binder ratios, binder contents and curing times. In particular, compressive strength, electrical resistivity, sorptivity coefficient, carbonation rate and chloride diffusion coefficient were evaluated.

2. Materials and methods

A portland cement CEM I 52.5R (*OPC*), according to EN 197-1 standard, was used to produce blended portland limestone cements (*PLC*). The portland cement was partially replaced, in a cement factory, with 15% (15% *LI*) and 30% (30% *LI*) ground limestone, in order to simulate cements of type CEM II/A-L and CEM II/B-L according to EN 197-1 standard. The chemical compositions are reported in Table 1. The particle size analyses of *OPC* and ground limestone are given in Fig. 1a, showing a maximum size of 30 μm for portland cement and about 100 μm for ground limestone, and a median particle size (i.e. the particle sizes corresponding to 50% cumulative passing) of about 7.5 μm for both portland cement and limestone. These binders were used to make concrete with three different water/binder ratios, equal to 0.42, 0.46 and 0.61, and different binder dosages, ranging from 250 to 400 kg/m^3. Crushed limestone aggregates, divided in five different classes (sand and calc1-calc4), with maximum size of 12.5 mm were used;

Table 1
Chemical composition and surface area of the cement and limestone used.

Chemical analysis (%)	Portland	Limestone
CaO	63.46	43.76
SiO_2	20.45	15.78
Al_2O_3	5.28	1.98
SO_3	3.29	0.27
Fe_2O_3	2.84	0.80
MgO	1.53	1.10
K_2O	1.02	0.57
Na_2O	0.29	0.06
Mn_2O_3	0.07	0.05
TiO_2	0.24	0.11
P_2O_5	0.10	0.06
Cl	0.01	–
Ignition loss (%)	1.4	35.82
Blaine surface area (cm^2/g)	5340	6102

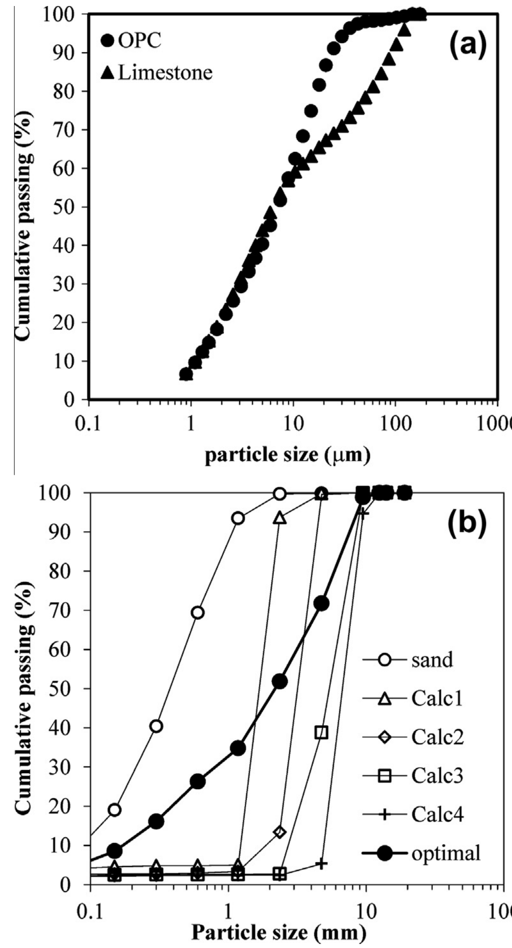

Fig. 1. Grain size analyses of *OPC* and limestone (a) and aggregate size distribution (b).

the combination was chosen in order to fit the Fuller's grading curve (Fig. 1b). An acrylic high range water reducing superplasticizer (according to EN 934-2 standard) was added to the mixes in order to achieve a class of consistency *S*4 according to EN 206-1 standard. Table 2 summarizes the concrete mixtures and results of the slump test.

After mixing, concretes were cast into moulds of various geometries (see later), covered with a plastic sheet and stored in laboratory at 20 °C. After 24 h, the specimens were demoulded and cured at 20 °C and 95% relative humidity (only electrical resistivity specimens were immersed in water).

Different tests were carried out after several curing times. Compressive tests were carried out, according to EN 12390-3 standard, on two replicate 100 mm cubes after 1, 7, 28, 90 and 180 days of curing. Electrical bulk resistivity was measured, during a period of about 500 days, on two replicate 50 mm × 50 mm × 100 mm prism specimens, cured and kept under water. A couple of stainless steel wires was embedded in the specimens and the electrical conductance between them was measured; the electrical conductance was then converted in electrical resistivity by means of a cell constant evaluated through a finite element model.

For sorptivity testing, cylindrical specimens, cured 28 days, with diameter of 100 mm and height of 50 mm, were used. According to EN 13057 standard, the specimens were dried in an oven at approximately 100 °C until constant mass (approximately for 48 h) and, after this, the lateral surface of the specimens was masked with epoxy. Then specimens were placed in a tray such that their bottom surfaces up to a height of 2 mm were in contact with water.