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

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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

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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/m³. Crushed limestone aggregates, divided in five different classes (sand and calc1-calc4), with maximum size of 12.5 mm were used;
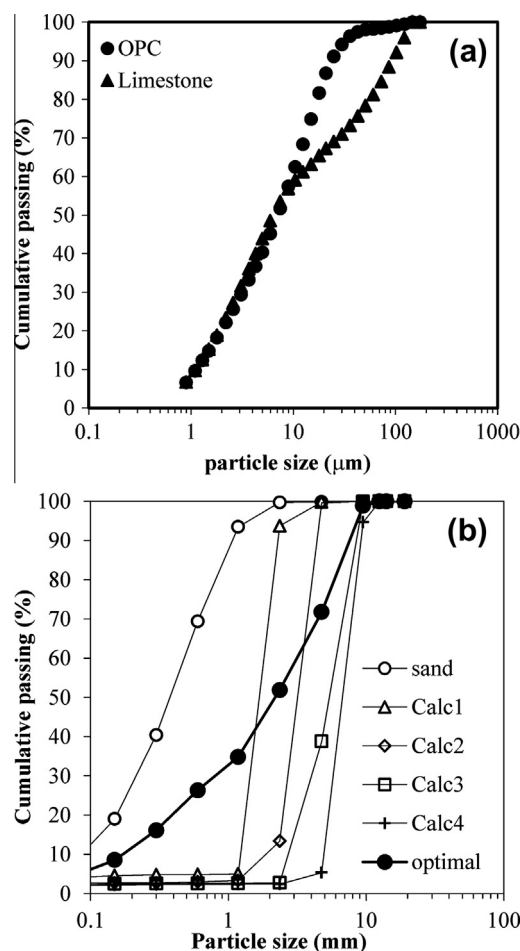

Fig. 1. Grain size analyses of *OPC* and limestone (a) and aggregate size distribution (b).

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.

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$_2$O$_3$	5.28	1.98
SO$_3$	3.29	0.27
Fe$_2$O$_3$	2.84	0.80
MgO	1.53	1.10
K$_2$O	1.02	0.57
Na$_2$O	0.29	0.06
Mn$_2$O$_3$	0.07	0.05
TiO$_2$	0.24	0.11
P$_2$O$_5$	0.10	0.06
Cl	0.01	–
Ignition loss (%)	1.4	35.82
Blaine surface area (cm^2/g)	5340	6102

Table 2
Mixture proportions of the concretes and results of the slump test.

Series	OPC[*] (%)	Limestone[*] (%)	w/b	Water (kg/m^3)	Binder (kg/m^3)	Aggregates (kg/m^3)	Admixture[**] (kg/m^3)	Slump (mm)
OPC	100	–	0.61	183	300	1857	2.5	200
			0.46	138	300	1979	6.8	185
			0.46	161	350	1868	3.5	190
			0.42	147	350	1913	9.2	180
15% LI	85	15	0.61	152	250	1983	4	190
			0.61	183	300	1857	2.5	180
			0.46	138	300	1979	6.4	170
			0.46	161	350	1868	3.5	205
			0.42	147	350	1913	5.4	175
			0.42	168	400	1815	5.5	215
30% LI	70	30	0.61	183	300	1857	2.5	210
			0.46	138	300	1979	7	170
			0.46	161	350	1868	5	165
			0.42	147	350	1913	5.4	165

[*] Percentage of the total mass of binder.
[**] Acrylic superplasticizer.

The specimens were removed from the tray and weighed at different time intervals up to 24 h to evaluate mass gain. The water absorption per unit surface was then plotted versus the square root of time and the slope of the best-fit line was defined as the sorptivity coefficient of concrete.

In order to evaluate the resistance to the penetration of carbonation, 100 mm cube specimens, cured 1, 7 and 28 days, were masked with epoxy, so that carbonation was allowed to penetrate only from two opposite faces, and exposed, after 28 days (for specimens cured 1 and 7 days) and 30 days (for 28-day cured specimens) from casting, to an environment with 20 °C, 65% R.H. and a constant flux of 2% CO_2 (accelerated carbonation). After different times of exposure, the minimum and the maximum carbonation depths were measured with the phenolphthalein test on 20 mm diameter cores taken perpendicularly to the mould surface, and the average value between the two was determined. The accelerated carbonation coefficient K_{ACC} was evaluated according to the relationship:

$$d = K_{ACC} \cdot \sqrt{t} \tag{1}$$

where d is the average carbonation depth at time t.

Resistance to penetration of chloride ions was tested, after 28 days of curing at $T = 20$ °C and 95% R.H., on cylindrical specimens by means of the so-called Rapid Chloride Migration (RCM) test, according to NT-BUILT 492 standard. Specimens, laid on an inclined plastic support, were placed in a container with a 10% NaCl solution, whilst a chloride free solution was poured inside a plastic tube mounted coaxially to them. A potential difference of 30 V was applied, the initial current was measured and, according to its value, the applied voltage was adjusted and the duration of the test determined (6–96 h). At the end of the test, the specimen was split axially, and on its fracture surface a colorimetric indicator (0.1 M $AgNO_3$) solution was sprayed. The average chloride penetration depth x_m (m) was measured and the chloride diffusion coefficient D_{RCM} was calculated as:

$$D_{RCM} = \frac{RT}{zFE} \cdot \frac{x_m - \alpha\sqrt{x_m}}{t} \tag{2}$$

where R is the gas constant (J/K mol), T the average temperature in the anodic solution (K), z the absolute value of charge number, F Faraday's constant (96500 C/mol), t time (s); $E = (U-2)/L$ (U is the applied voltage in V, L the thickness of the specimen in m) and α is defined as:

$$\alpha = 2\sqrt{\frac{RT}{zFE}} erf^{-1}\left(1 - \frac{2c_d}{c_0}\right) \tag{3}$$

where c_d is the chloride concentration at which the colour change is observed (assumed equal to 0.07 N) and c_0 the chloride concentration of the test solution (2 N).

3. Results

3.1. Compressive strength

Fig. 2 shows, for each type of concrete, the average values of compressive strength at different curing times. Results on concrete with different binders are grouped on the basis of w/b ratio and binder dosage (e.g. 0.46/300 means concrete with w/b = 0.46 and b = 300 kg/m^3); different patterns in the bars show the compressive strength reached after various times of curing. For all the concretes, the expected increase in compressive strength due to the decrease in water/binder ratio and to the increase in curing time can be observed. For instance, compressive strength of 15% LI concrete, cured 7 days and with a binder dosage of 300 kg/m^3, increased from 38 to 60 MPa when water/binder ratio decreased from 0.61 to 0.46; increasing the curing time to 28 days, the strength of these mixes further increased, approaching values of about 45 and 75 MPa respectively.

It should however be observed that also the cement content showed some influence on the strength of concrete; for a given
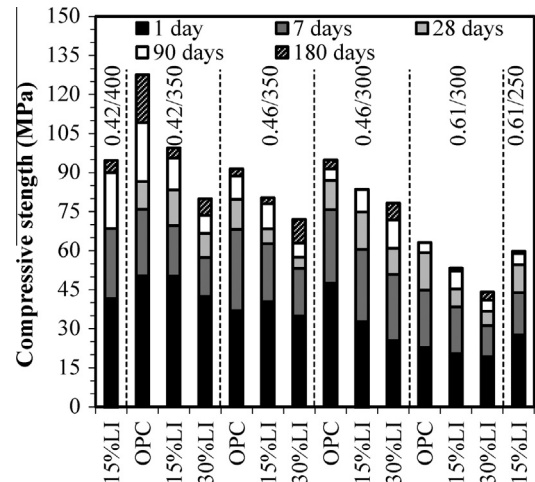

Fig. 2. Compressive strength of concrete as a function of curing time, water/binder ratio, type of binder and binder dosage (e.g. 0.42/400 means w/b = 0.42 and b = 400 kg/m^3).

w/b ratio, a slight decrease in the strength was observed as the binder content increased. For instance the 15% *LI* concrete with w/b ratio of 0.46 and cured 28 days, had a strength of 75 and 68 MPa with binder content of respectively 300 and 350 kg/m^3. Fig. 2 also shows the influence of the partial replacement of portland cement with ground limestone. With the same curing time and water/binder ratio, 15% *LI* and 30% *LI* concretes showed lower compressive strengths compared to *OPC* concrete. For instance specimens with w/b of 0.61 and binder content of 300 kg/m^3, cured 28 days, had a strength that decreased from about 60 MPa when portland cement was used to 45 and 37 MPa when 15% and 30% of portland cement was replaced with limestone.

3.2. Electrical resistivity

Electrical resistivity of concrete was measured on saturated specimens to avoid the effect of moisture content and focus on the microstructure of the material and its evolution in time due to the hydration of the binder. For all the specimens, the electrical resistivity showed a sharp increase in the first days of curing, approaching then almost steady values after about 200/250 days for *PLC* concrete and 250/300 days for *OPC* concrete. Fig. 3 summarizes the electrical resistivity values in the first periods of curing (1, 7 and 28 days) and when the hydration process was almost ended (360 days).

For the same curing time, resistivity decreased when the water/binder ratio increased: for instance, after 28 days of curing, a resistivity of 40 Ω m was measured on 15% *LI* concrete with $w/b = 0.46$ and $b = 300$ kg/m^3 and of about 29 Ω m for the concrete with $w/b = 0.61$ and $b = 300$ kg/m^3. Lower values of electrical resistivity were observed for concretes with higher binder content. For instance, after 28 days of curing, on *OPC* concretes with $w/b = 0.46$, resistivities of 55 and 45 Ω m were evaluated with binder contents of 300 and 350 kg/m^3 respectively. In Fig. 3 the influence, after different curing times, of the partial replacement of portland cement with limestone on the electrical resistivity can also be observed. After 1 day of curing, for some water/binder ratios, a slightly higher electrical resistivity was observed on *PLC* concrete in comparison with *OPC* concrete, whilst after higher curing times, the resistivity of *PLC* concrete was strongly reduced in comparison with *OPC* concrete. For instance, after 360 days of curing, the *OPC* concrete with binder content of 300 kg/m^3 and w/b ratio of 0.61 showed a resistivity of 110 Ω m, which decreased to 70 and 60 Ω m for 15% *LI* and 30% *LI* concretes, respectively.

Fig. 4. Water sorptivity coefficient as a function of water/binder ratio, type of binder and binder dosage on concretes cured 28 days (e.g. 0.42/350 means $w/b = 0.42$ and $b = 350$ kg/m^3).

3.3. Sorption

The sorptivity coefficient of concrete cured 28 days is shown in Fig. 4. On concretes with *OPC* cement, sorptivity tests were performed only on specimen with w/b ratio of 0.42. For all the types of concrete the sorptivity coefficient decreased when the water/binder ratio and the binder content decreased. For instance, a sorptivity coefficient of 1.29 kg/(m^2 h$^{0.5}$) was measured on 15% *LI* concrete, $w/b = 0.61$ and $b = 300$ kg/m^3 and of 0.56 kg/(m^2 h$^{0.5}$) for concrete with the same binder content and a w/b ratio of 0.46. With regard to 15% *LI* concrete, with w/b ratio of 0.46, the sorptivity coefficient increased to 0.69 kg/(m^2 h$^{0.5}$) when the binder content increased to 350 kg/m^3. An increase in the amount of the portland cement replaced with limestone led to an increase of the sorptivity coefficient. For instance, for the water/binder ratio of 0.42, the sorptivity coefficients were of 0.34, 0.46 and 0.67 kg/(m^2 h$^{0.5}$) respectively for *OPC*, 15% *LI* and 30% *LI* concretes.

3.4. Resistance to carbonation

Fig. 5 shows the role of curing and concrete composition, i.e. limestone content, water/binder ratio and cement content on the
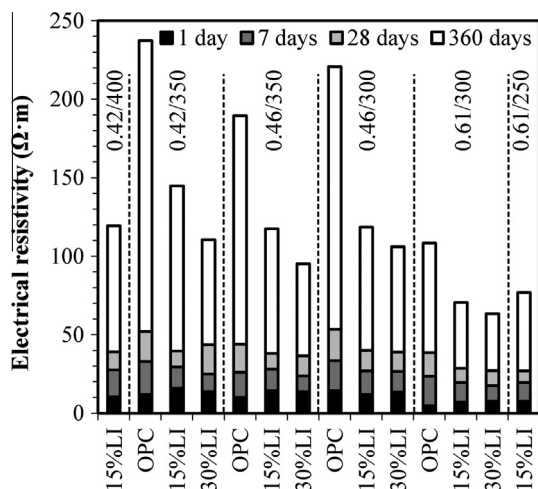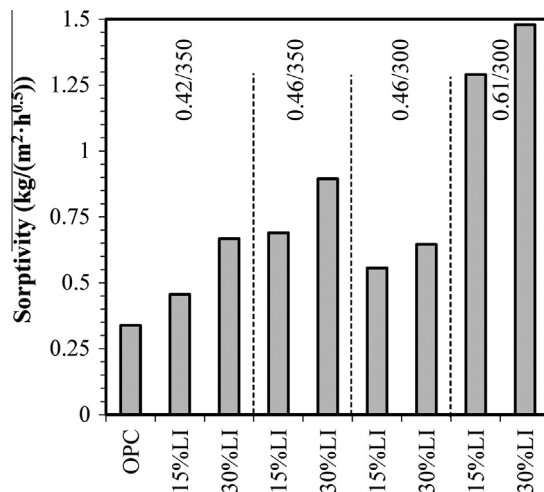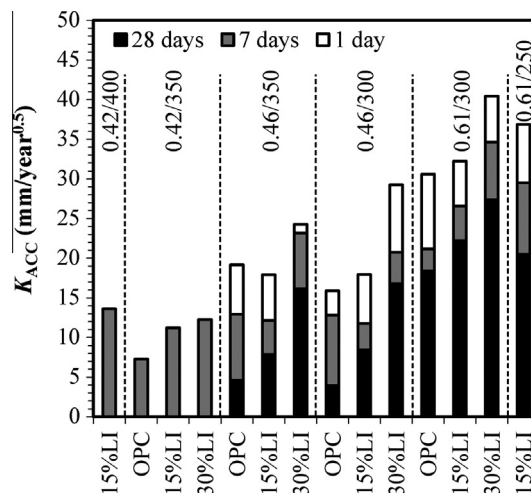

Fig. 3. Electrical resistivity of water-saturated concrete specimens as a function of curing time, water/binder ratio, type of binder and binder dosage (e.g. 0.42/400 means $w/b = 0.42$ and $b = 400$ kg/m^3).

Fig. 5. Accelerated carbonation coefficient of concrete, K_{ACC}, as a function of curing time, water/binder ratio, type of binder and binder dosage (e.g. 0.42/400 means $w/b = 0.42$ and $b = 400$ kg/m^3).

carbonation coefficient, K_{ACC}. On concretes with w/b ratio of 0.42, carbonation tests were performed only on specimens cured 7 days.

At all curing times, a significant influence of the water/binder ratio, whose decrease led to a reduction in the accelerated carbonation coefficient, can be observed, while the binder content did not show any significant influence. Comparing concretes with the same composition, a decrease in the carbonation coefficient can be observed when curing increased from 1 to 28 days. For instance in concrete with 15% limestone, 350 kg/m^3 of binder and w/b ratio of 0.46, values of accelerated carbonation coefficient of 17.9, 12.1 and 7.8 mm/year$^{0.5}$ were evaluated respectively on specimens cured 1, 7 and 28 days.

Only slight differences in the carbonation coefficient were observed between 15% LI and OPC concretes, cured 1 and 7 days. For instance, for 1-day cured concretes with $w/b = 0.61$ and $b = 300$ kg/m^3, the accelerated carbonation coefficient was about 31 and 32 mm/year$^{0.5}$ respectively for OPC and 15% LI concrete. However increasing the curing time up to 28 days, OPC concretes performed better than 15% LI since they showed a lower carbonation coefficient. For instance, K_{ACC} increased from 18 to 22 mm/year$^{0.5}$ for 28-day cured concrete with $w/b = 0.61$ and $b = 300$ kg/m^3, when 15% of cement was replaced with limestone. Regardless of the curing time, 30% LI concrete showed a higher carbonation coefficient compared to OPC concrete, and the carbonation coefficient was more than doubled for 28-day cured specimens. For instance, 7-day cured specimens with w/b ratio of 0.61 and binder content of 300 kg/m^3 had an accelerated carbonation coefficient that increased from about 21 mm/year$^{0.5}$ with OPC concrete to 35 mm/year$^{0.5}$ with 30% LI concrete.

3.5. Resistance to chloride penetration

The resistance to chloride penetration was investigated by means of the Rapid Chloride Migration test on specimens cured 28 days. Fig. 6 shows the diffusion coefficient D_{RCM} as a function of concrete composition. The role of w/b ratio clearly appears, while the binder content showed a negligible effect. For instance for 15% LI concrete, the diffusion coefficient decreased from about 19×10^{-12} to 15×10^{-12} m^2/s, when the water/binder ratio decreased from 0.61 to 0.46.

A remarkable influence of the limestone content was observed; for 15% LI concrete the diffusion coefficient was almost doubled compared to OPC concrete. For instance, specimens with w/b ratio of 0.61 and binder content of 300 kg/m^3 had a diffusion coefficient that increased from 12×10^{-12} m^2/s for OPC concrete to 19×10^{-12} m^2/s for 15% LI concrete. The D_{RCM} further increased in 30% LI concrete and it approached a value of about 38×10^{-12} m^2/s.

4. Discussion

In order to evaluate the role of the replacement of portland cement with limestone, the effect of the other parameters should be first considered. Initially the role of water/binder ratio, curing and binder content and subsequently the effect of limestone replacement will be investigated.

4.1. Mixture proportions and curing

Results presented in the previous section reflect the well-known effects of the water/binder ratio and the curing time on the properties of hardened OPC and PLC concretes. Both the decrease of w/b ratio and the increase of curing time lead to a refinement of the pore structure, as highlighted by increased electrical resistivity, with beneficial effects on mechanical strength and resistance to aggressive agents, i.e. water, carbon dioxide and chloride ions.

Even an effect of the binder content can be observed. This is of particular concern, since in the specifications for concrete durability (e.g. European standard EN 206-1 and ACI 365.1R-00) a minimum cement content is required and only little information is available in the literature on the effects of binder dosage [39–41]. The effect of binder content can be studied considering 15% LI concrete, since for this blend the three water/binder ratios and two different binder contents were studied (Table 2). Fig. 7 shows the effect of binder content on several properties (28-day compressive strength, 360-day electrical resistivity, sorptivity, 7-day accelerated carbonation coefficient and chloride diffusion coefficient). For the generic property, P, the effect of binder content reduction was evaluated as the ratio between P' (measured, for each w/b ratio, on 15% LI concrete with the lower binder content b') and P'' (measured, for each w/b ratio, on 15% LI concrete with the higher binder content b'') multiplied by 100. Values above 100% show an increase in the considered property when the binder content is reduced, whilst values below 100% show a decrease.
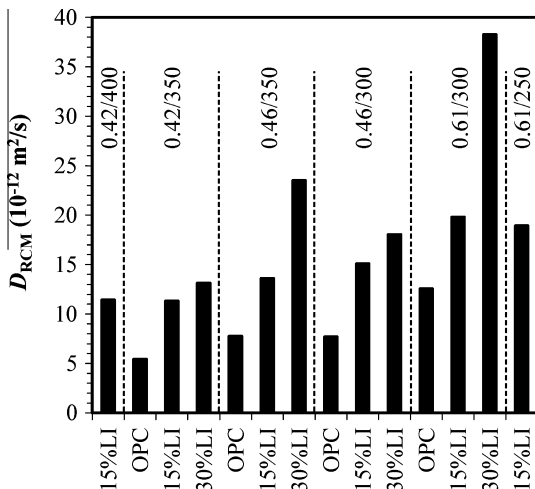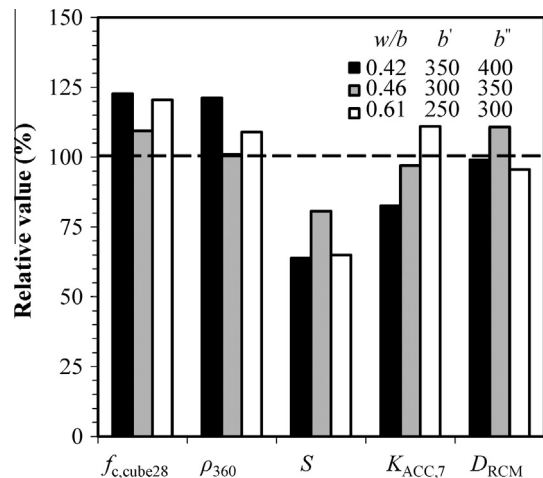

Fig. 6. D_{RCM} coefficients as a function of water/binder ratio, type of binder and binder dosage on concretes cured 28 days (e.g. 0.42/400 means $w/b = 0.42$ and $b = 400$ kg/m^3).

Fig. 7. Effect of the decrease of binder content (b' = lowest binder content; b'' = highest binder content) for different w/b ratios, on the relative values of 28-day compressive strenght ($f_{c,cube28}$), 360-day electrical resistivity (ρ_{360}), sorptivity (S), accelerated carbonation coefficient on 7-day cured specimens ($K_{ACC,7}$) and chloride diffusion coefficient (D_{RCM}) for 15% LI concrete.

Sorption, defined as the absorption of water in the capillary pores due to the capillary action, was clearly affected by the binder content: for all the w/b ratios, a sharp decrease of sorptivity coefficient was observed when the binder content was reduced. As a matter of fact, the decrease of the binder content, leading to a decrease of the amount of cement paste in concrete with the same w/b ratio, leads to a decrease of the total concrete porosity and, hence, of the sorption, whilst it does not affect the porosity of the cement paste component, which is mainly related to the water/binder ratio and degree of hydration (i.e. time of curing). For the same reason, electrical resistivity experienced an increase due to the reduction of the binder dosage, due to a reduction of the volume of cement paste available for ionic transport.

A systematic effect of the binder dosage on carbonation coefficient was not observed. The decrease in the amount of cement paste due to a decrease of the binder dosage leads to two opposing effects: on one hand the total porosity of concrete is lower; on the other hand the amount of portlandite is also lower, due to the lower amount of hydrated cement. The former hinders carbonation, the latter promotes it. Hence, these two effects could be compensated and none of them could be prevalent. Even for the diffusion coefficient, evaluated from the average chloride penetration depth x_m, an effect of the binder content was not detected. As far as compressive strength is concerned, a slight and systematic positive effect was observed when decreasing the binder dosage, in agreement with the decrease of the total concrete porosity.

4.2. Portland cement replacement with limestone

In this work, the effect of a limestone coarser than the accompanying cement, being ground to a maximum size of about 100 μm (Fig. 1a), was studied. Fig. 8 summarizes the effect of replacement of portland cement with 15% (Fig. 8a) and 30% (Fig. 8b) limestone on compressive strength, electrical resistivity, sorptivity, carbonation and chloride diffusion coefficient. The effect was evaluated as the percentage ratio between the value measured on PLC concrete and on the corresponding OPC concrete.

It is evident that the properties of the hardened concrete were significantly affected by the partial replacement of portland cement with limestone, especially when the amount of replaced cement was 30% (Fig. 8b). In general, the replacement of portland cement with ground limestone led to a decrease in the compressive strength ($f_{c,cube,28}$) and electrical resistivity (ρ) and an increase in sorptivity (S), carbonation ($K_{ACC,7}$) and chloride diffusion (D_{RCM}) coefficients, with the exception of the relative $K_{ACC,7}$ between OPC and 15% LI concrete with w/b ratio of 0.46.

To investigate the effect on compressive strength, Fig. 9 shows the relationship between 28-day compressive strength and the water/binder ratio for concrete with OPC, 15% LI and 30% LI. Neglecting the influence of binder dosage (§4.1), experimental data of each type of binder were fitted through an exponential relationship, according to Abram's law [42]. Each type of binder clearly showed a different relationship, underlying that at equal w/b ratio OPC concrete had a higher strength than PLC concrete. Supposing limestone acts as an inert material, the water/cement ratio, w/c, was evaluated from the water/binder ratio as:

$$\left(\frac{w}{c}\right) = \frac{w}{(b - LI)} = \frac{w}{b} \cdot \frac{100}{100 - \%LI} \tag{4}$$

where $\%LI$ is the limestone percentage content with respect to the total binder.

Fig. 10a shows the relationship between compressive strength and the water/cement ratio for OPC, 15% LI and 30% LI concretes, for different curing times of 1, 7 and 28 days. At 28-day curing, a good exponential relationship (indicated by the black continuous
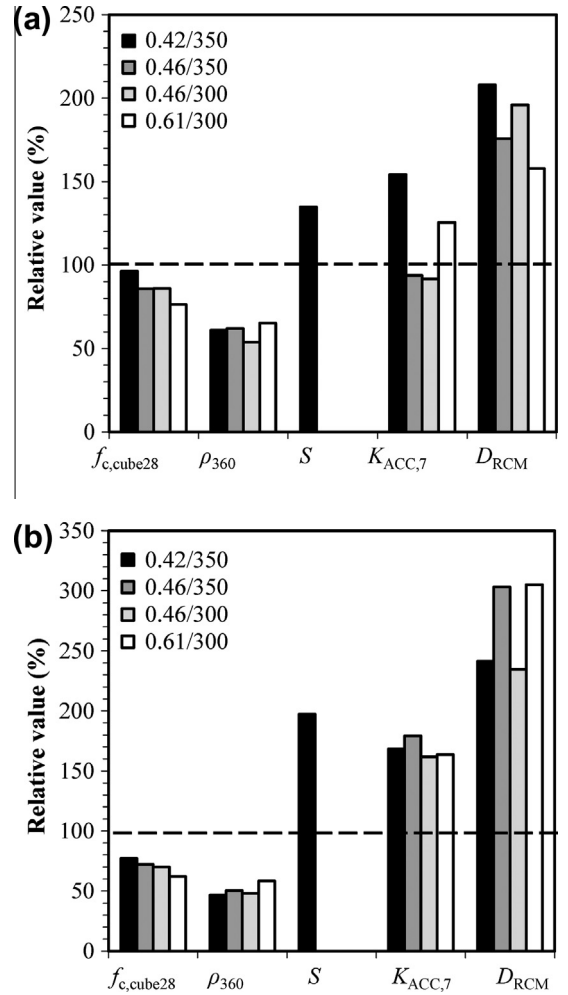

Fig. 8. Effect of the replacement of portland cement with 15% (a) and 30% (b) limestone relative to OPC on the relative values of 28-day compressive strength ($f_{c,cube28}$), 360-day electrical resistivity (ρ_{360}), sorptivity (S), accelerated carbonation coefficient on 7-day cured specimens ($K_{ACC,7}$), chloride diffusion coefficient (D_{RCM}) for different water/binder ratios.
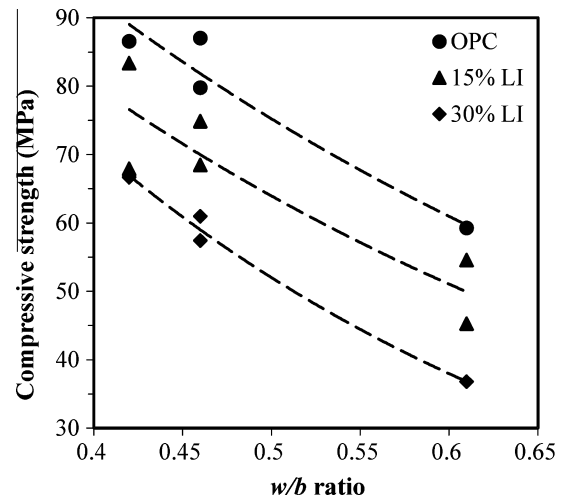

Fig. 9. Compressive strength as a function of the water/binder ratio and exponential fitting lines for OPC, 15% LI and 30% LI concretes after 28 days of curing.

line), similar to that of OPC concrete (indicated by the black dashed line), can be found, supporting the assumption that limestone acts essentially as a dilution of portland cement in the systems
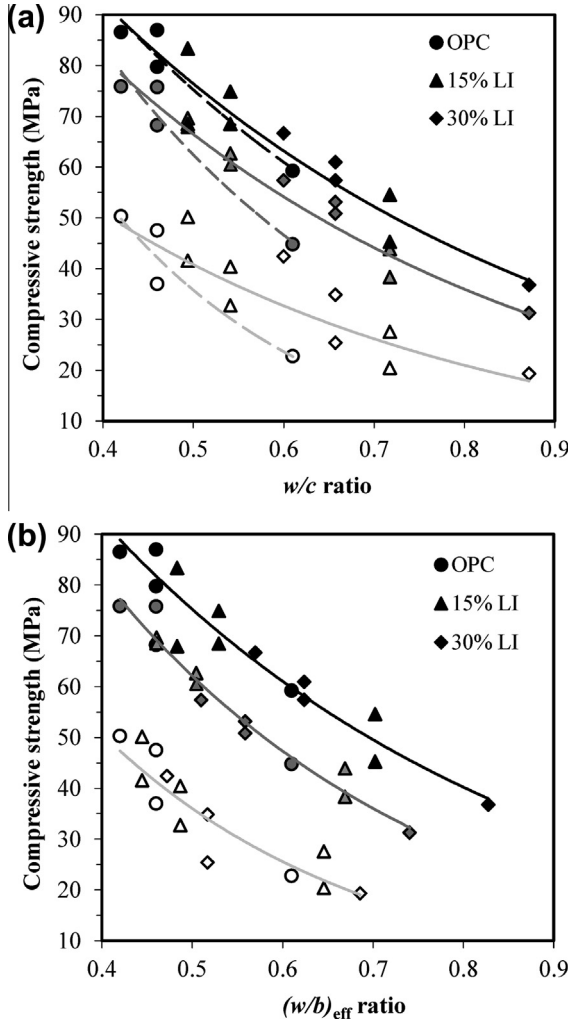
Fig. 10. Compressive strength as a function of the water/cement ratio, w/c (a) and the effective water/binder ratio, $(w/b)_{eff}$ (b), for *OPC*, 15% *LI* and 30% *LI* concretes after 1 (white symbols), 7 (grey symbols) and 28 days (black symbols) of curing (continuous lines: interpolation of all data; dashed lines: interpolation of *OPC* data).

investigated here. This means that when limestone portland cement is used the compressive strength can be estimated using the correlation of the "pure" portland cement, provided that the water/cement ratio is considered instead of w/b ratio. A reasonable correlation between strength and w/c ratio was observed also after 1 and 7 days of curing, although at these ages, the compressive strength of *PLC* concrete was slightly higher than the strength of *OPC* concrete, suggesting that, at early ages, limestone, although inert, has beneficial effects on compressive strength.

The beneficial effects of limestone can be quantified through the "efficiency factor", k, which expresses the fraction of portland cement that can be replaced by a given amount of a mineral addition at unchanged compressive strength. k-value equal to 1 means that the addition can be considered equivalent to portland cement, conversely k-value of 0 means that the addition has no effect. For each curing time, the "efficiency factor" k was evaluated by interpolating (with the least squares method) Abram's law for *OPC* concrete, shown in Fig. 10a, replacing w/b with the $(w/b)_{eff}$, defined as:

$$\left(\frac{w}{b}\right)_{eff} = \frac{w}{c_{eq}} = \frac{w}{c + k \cdot LI} \tag{5}$$

where c_{eq}, is the equivalent cement content, which is defined as the sum between the portland cement content and the limestone content in the mix multiplied by the k-value.

Results in terms of relationship between compressive strength and the effective water/binder ratio, $(w/b)_{eff}$, are shown in Fig. 10b. k-values of 0.63, 0.41 and 0.12 were respectively determined for curing times of 1, 7 and 28 days. The relatively high values of the efficiency factors estimated at low curing times confirm that limestone has some beneficial consequences, which may be ascribed to the formation of nucleation sites of calcium hydroxide crystals [10,26], to an acceleration of the clinker hydration [12,13,18–24] or to a beneficial filler effect of the fine limestone particles, as suggested by various authors. The acceleration of the clinker hydration in *PLC* concrete may lead to a higher degree of hydration in comparison to *OPC* concrete, after the same curing time. Hence, comparing a *PLC* and an *OPC* concrete with the same w/c ratio the higher degree of hydration of *PLC* concrete brings about a lower capillary porosity and higher compressive strength. This effect could be considered limited at early ages, conversely the filler effect may occur after any times of curing, however it seems to be not much effective with the extension of curing time, as indicated by the relatively low k-value after 28 days of curing. The k-value evaluated in this work may be affected by the fineness of the ground limestone, which may be supposed to be slightly coarser than that of limestone interground with portland cement [21–30], as well as by its quality (e.g. limestone chemical composition). As far as the role of fineness is concerned, several studies on limestone [12,13,35,43] as well as other mineral and inert addition [44,45] showed that when the addition was finer, concrete properties improved. However in some studies the effect was significant only at early age [12,13] and in the range of limestone addition from 5% to 10% [43]. Hence, further studies are needed to evaluate whether strength performance deficiencies of *PLC* in comparison to *OPC* concrete may be actually compensated by an increase in fineness or if the effect of fineness may be marginal.

As far as the role of limestone on the resistance to carbonation is concerned, the accelerated carbonation coefficient, measured on 7-day cured specimens, experienced an increase between 60% (evaluated on concrete with $w/b = 0.46$ and $b = 300$ kg/m^3) and 80% (on concrete with $w/b = 0.46$ and $b = 350$ kg/m^3) with the replacement of 30% limestone. Conversely, a systematic effect was not observed in the presence of 15% of limestone. The effect was further investigated, analyzing the relationship between the accelerated carbonation coefficient and the w/c ratio on concretes cured 1, 7 and 28 days (Fig. 11a). As for compressive strength after 1 and 7 days of curing, the carbonation coefficient of *PLC* concrete was slightly lower than the carbonation coefficient of *OPC* concrete. These results suggest that limestone acts similarly in determining compressive and carbonation resistance and, hence, the correlation between carbonation coefficient and $(w/b)_{eff}$ ratio, determined by fitting compressive strength results, was investigated (Fig. 11b). The good relationship between these parameters, even at low curing time, confirms that limestone contributes to the carbonation resistance of the concrete by accelerating the hydration processes at early ages and later it acts essentially as a dilution. Furthermore, the fact that k-values evaluated through compressive strength were valid also for the carbonation coefficient suggested that these properties are mainly related to the same parameters. This is confirmed by the good relationship, for different curing times, between K_{ACC} and compressive strength, shown in Fig. 11c. The rate of carbonation is similar in concretes with equal strength, regardless of the quantity of limestone that replaces portland cement. From a practical point of view, it means that, provided that a certain compressive strength is assured, concrete will behave in relation to carbonation resistance in a similar way, regardless of the amount of portland cement replaced with limestone. However, to achieve the same strength, the water/binder ratio should be decreased, increasing the amount of replaced cement in accordance to results shown in Fig. 9.
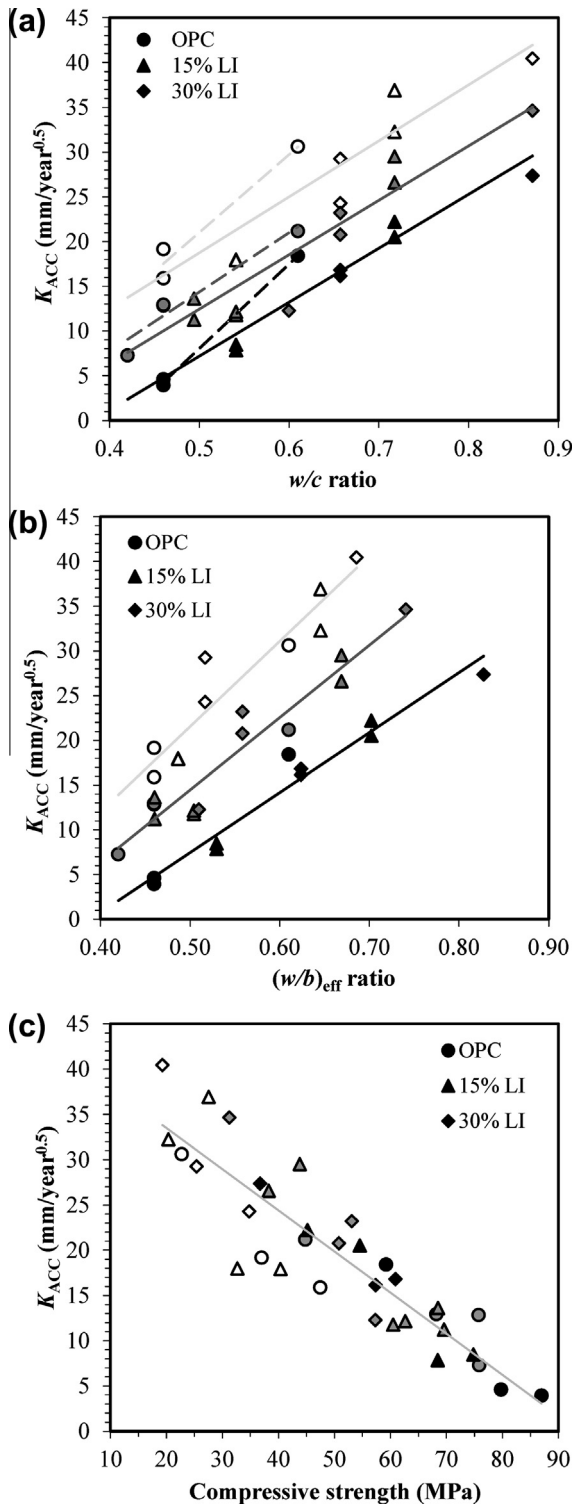
Fig. 11. Accelerated carbonation coefficient, K_{ACC}, as a function of the water/cement ratio, w/c (a), the effective water/binder ratio, $(w/b)_{eff}$ (b), and compressive strength (c) for *OPC*, 15% *LI* and 30% *LI* concretes after 1 (white symbols), 7 (grey symbols) and 28 days (black symbols) of curing (continuous lines: interpolation of all data; dashed lines: interpolation of OPC data).

As far as the resistance to chloride penetration is concerned, D_{RCM} significantly increased when the portland cement was replaced with limestone, clearly indicating that portland limestone cement does not hinder chloride penetration to the same degree. With the replacement of 15% limestone, an increase of D_{RCM} between 60% and 100% (evaluated respectively on concrete with w/

$b = 0.61$ and $w/b = 0.42$) was observed; whilst with the replacement of 30% limestone, D_{RCM} further increased up to 200% (Fig. 8). Although a linear correlation between D_{RCM} and w/c ratio can be observed in Fig. 12a, an even higher D_{RCM} in comparison to the correlation which could be expected by considering only the water/cement ratio was obtained, suggesting that limestone might have a detrimental effect in hindering chloride penetration; such an effect has been explained considering that the reaction compounds of C_3A in *PLC* concrete have a lower binding capacity for chloride in comparison to the hydration products of aluminates in *OPC* concrete [32]. Therefore, to compensate for the detrimental effect of limestone, in order that the D_{RCM} obtained with *PLC* and *OPC* concretes are equal, the $(w/b)_{eff}$ ratio of the *PLC* concrete should be equal to the w/c ratio of the OPC concrete, and hence the effective binder content, c_{eq}, content should be increased. This effect is also reflected in the relationship between compressive strength and diffusion coefficient: concretes with the same compressive strength do not have similar resistance to chloride penetration (Fig. 12b). High D_{RCM} can be obtained with binders simulating limestone portland cement (15% *LI* and 30% *LI*), in spite of the high values reached by compressive strength. As a consequence, when limestone cements are used, a higher compressive strength should be guaranteed to also assure an adequate resistance to chloride penetration.
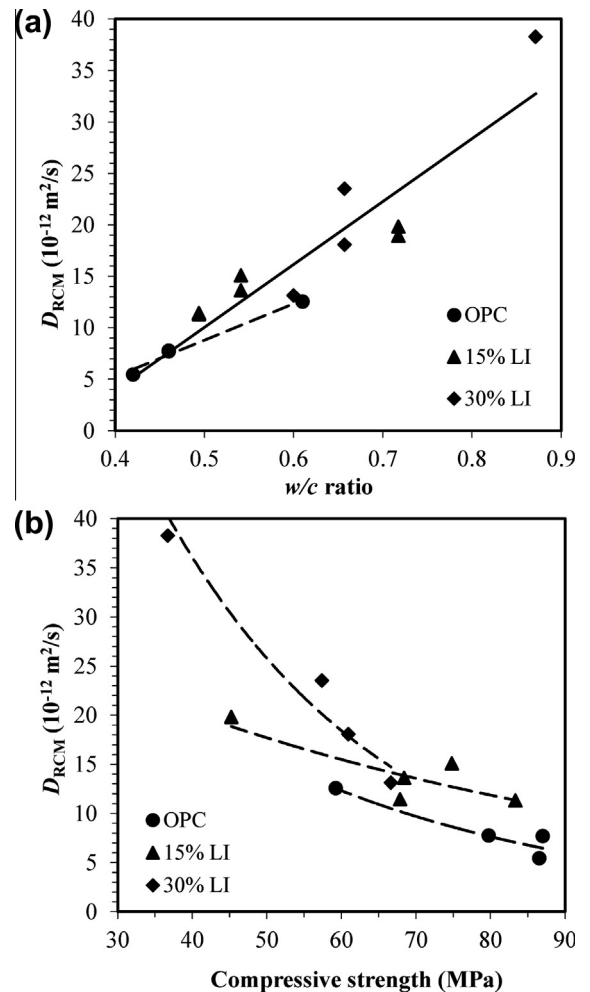
5. Conclusions

Fig. 12. Rapid Chloride Migration coefficient, D_{RCM}, as a function of the water/cement ratio, w/c (a) and compressive strength (b) (continuous lines: interpolation of all data; dashed lines: interpolation of OPC data).

The effect of limestone was studied by replacing portland cement with a ground limestone in concrete with different limestone replacement (15–30% by mass of binder), water/binder ratio (0.42–0.61) and binder content (250–400 kg/m^3). On the basis of results of experimental tests for the materials employed in this study, the following conclusions can be drawn.

1. Besides the well-known beneficial effects on the properties of hardened concrete of decreasing the water/binder ratio and increasing the curing time, the binder dosage showed some influence on sorption, strength and resistivity, whilst no effects on carbonation and chloride diffusion were observed.
2. The replacement of portland cement with 15% limestone led to a reduction in 28-day compressive strength and to an increase of chloride diffusion coefficient, whilst a clear effect was not detected on the accelerated carbonation. The replacement of 30% limestone led to a remarkable worsening of all the studied properties.
3. Compressive strength and accelerated carbonation coefficient of concrete showed a good correlation with the water/cement ratio, i.e. assuming limestone acts as inert filler after quite long curing time; whilst at early ages a positive effect of limestone was detected. As a matter of fact relatively high values of the efficiency factors were estimated at low curing times, which however decreased with the extension of curing time.
4. The diffusion coefficient of chloride increased in the presence of limestone and this effect was even more than expected by considering an inert behaviour of limestone.
5. Concretes with equal compressive strength experienced the same resistance to carbonation independently from the amount of portland cement replaced with limestone, indicating that, provided the compressive strength requirement is guaranteed, also the resistance to carbonation penetration is achieved. Conversely, concretes with equal compressive strength experienced a lower resistance to chloride penetration when made with limestone.

Acknowledgments

References

[1] Cembureau. World statistical review 1996–2006. CEMBUREAU (European Cement Association); 2008.
[2] AITEC. Annual relation; 2010 [in Italian].
[3] Baron J, Dourve C. Technical and economical aspects of the use of limestone filler additions in cement. World Cem 1987;18(4):100–4.
[4] Kenai S, Soboyelo W, Soboyelo A. Some engineering properties of limestone concrete. Mater Manuf Process 2004;19(5):949–61.
[5] Damtoft JS, Lukasik J, Herfort D, Sorrentino D, Gartner EM. Sustainable development and climate change initiatives. Cem Concr Res 2008;38(2):115–27.
[6] Thomas MDA, Hooton D, Cail K, Smith BA, de Wal J, Kazanis KG. Field trials of concretes produced with portland limestone cement. Concr Int 2010;32:35–41.
[7] Bonavetti V, Donza H, Menendez G, Cabrera O, Irassar EF. Limestone filler cement in low w/c concrete: a rational use of energy. Cem Concr Res 2003;33(6):865–71.
[8] Bentz DP, Irassar EF, Bucher BE, Weiss WJ. Limestone fillers conserve cement. Concr Int 2009;31(11):35–46.
[9] Bentz DP. Modeling the influence of limestone filler on cement hydration using CEMHYD3D. Cem Concr Comp 2006;28(2):124–9.
[10] Soroka I, Setter N. The effect of fillers on strength of cement mortars. Cem Concr Res 1977;7(4):449–56.
[11] Tennis PD, Thomas MDA, Weiss WJ. State-of-the-art report on use of limestone in cements at levels of up to 15%. Cem Assoc Canada 2011.
[12] Sun H, Hohl B, Handwerker C, Rushing TS, Cummins TK, Weiss J. Jet mill grinding of portland cement, limestone, and fly ash: Impact on particle size, hydration rate, and strength. Cement Concr Comp; 2013. <http://dx.doi.org/10.1016/j.cemconcomp.2013.03.023>.
[13] Kumar A, Oey T, Kim S, Thomas D, Badran S, Li J, et al. Simple methods to estimate the influence of limestone fillers on reaction and property evolution in cementitious materials. Cement Concr Comp 2013;42:20–9.
[14] Livesey P. Performances of limestone-filled cements. In: Swamy RN, editor. Blended cements in construction. London: Elsevier; 1991. p. 1–15.
[15] Matthews JD. Performance of limestone filler cement concrete. In: Dhir RK, Jones MR, editors. Euro-cements, impact of ENV 197 on concrete construction. London: E & FN Spon; 1994. p. 113–47.
[16] Dhir RK, Limbachiya MC, McCharthy MJ, Chaipanich A. Evaluation of Portland limestone cements for use in concrete construction. Mater Struct 2007;40(5):459–73.
[17] Ranc R, Moranville-Regourd M, Cochet G, Chaudouard G. Durability of cements with fillers. ACI SP 1991;126:1239–58.
[18] Heikal M, El-Didamony H, Morsy MS. Limestone-filled pozzolanic cement. Cem Concr Res 2000;30(11):1827–34.
[19] Zelić J, Krstulović R, Tkalčec E, Krolo P. The properties of Portland cement–limestone–silica fume mortars. Cem Concr Res 2000;30(1):145–52.
[20] Ramachandran VS, Zhang CM. Influence of CaCO$_3$ on hydration and microstructure characteristic of C$_3$S. Il Cem 1986;83:129–52.
[21] Pera J, Husson S, Guilhot B. Influence of finely ground limestone on cement hydration. Cem Concr Compos 1999;21(2):99–105.
[22] Vuk T, Tinta V, Gabrovšek R, Kaučič V. The effects of limestone addition, clinker type and fineness on properties of Portland cement. Cem Concr Res 2001;31(1):135–9.
[23] Lothenbach B, Le Saout G, Gallucci E, Scrivener K. Influence of limestone on the hydration of Portland cements. Cem Concr Res 2008;38(6):848–60.
[24] Bonavetti V, Donza H, Menéndez G, Cabrera O, Irassar EF. Limestone filler cement in low w/c concrete: a rational use of energy. Cem Concr Res 2003;33(6):865–71.
[25] Voglis N, Kakali G, Chaniotakis E, Tsivilis S. Portland-limestone cements. Their properties and hydration compared to those of other composite cements. Cem Concr Comp 2005;27(2):191–6.
[26] Tsivilis S, Batis G, Chaniotakis E, Grigoriadis Gr, Theodossis D. Properties and behavior of limestone cement concrete and mortar. Cem Concr Res 2000;30(10):1679–83.
[27] Barker AP, Matthews JD. Concrete durability specification by water/cement or compressive strength for European cement types. In: Proceeding 3rd Int Conf on the Durability of Concrete. Detroit. ACI SP-145; 1994. p. 1135–1164.
[28] Tsivilis S, Chanitakis E, Kakali G, Batis G. An analysis of the properties of Portland limestone cements and concrete. Cem Concr Comp 2002;24(3–4):371–8.
[29] Hornain H, Marchand J, Duhot V, Regourd M. Diffusion of chloride ions in limestone filler. Cem Concr Res 1995;25(8):1667–78.
[30] Irassar EF, Bonavetti VL, Menhdez G, Donza H, Cabrera O. Mechanical properties and durability of concrete made with portland limeston cement. In: Proceeding 3rd Int. Symp. on Sustainable Development of Concrete. Detroit. ACI SP-202; 2001. p. 431–450.
[31] Ghrici M, Katsioti S, Said-Mansour M. Mechanical properties and durability of mortar and concrete containing natural pozzolana and limestone blended cement. Cem Concr Comp 2007;29(7):542–9.
[32] Fagerlund G. Imaginable effects of limestone filler on chloride transport. Lund Institute of Technology Lund University. Report TVBM-7187; 2005.
[33] Güneyisi E, Gesoglu M, Özturan T, Mermerdas K, Özbay E. Properties of mortars with natural pozzolana and limestone-based blended cements. Aci Mater J 2011;108(5):493–500.
[34] Pandey SP, Sharma RL. The influence of mineral additives on the strength and porosity of OPC mortar. Cem Concr Res 2000;30(1):19–23.
[35] Tsivilis S, Chaniotakis E, Batis G, Meletiou C, Kasselouri V, Kakali G, et al. The effect of clinker and limestone quality on the gas permeability, water absorption and pore structure of limestone cement concrete. Cem Concr Comp 1999;21(2):139–46.
[36] Bonavetti V, Donza H, Rahhal V, Irassar E. Influence of initial curing on the properties of concrete containing limestone blended cement. Cem Concr Res 2000;30(5):703–8.
[37] Helal MA. Effect of curing on the physico-mechanical characteristic of the hardened cement pastes containing limestone. Cem Concr Res 2002;32(3):447–50.
[38] Tsivilis S, Tsantilas J, Kakali G, Chaniotakis E, Sakellariou A. The permeability of Portland limestone cement concrete. Cem Concr Res 2003;33(9):1465–71.
[39] Wassermann R, Katz A, Bentur A. Minimum cement content requirements: a must or a myth? Mater Struct 2009;42(7):973–82.
[40] Dhir RK, McCarthy MJ, Zhou S, Tittle PAJ. Role of cement content in specifications for concrete durability: cement type influences. P I Civil Eng – Str. B 2004;157(2):113–27.
[41] Buenfeld NR, Okundi E. Effect of cement content on transport in concrete. Mag Concr Res 1998;50(4):339–51.
[42] Neville AM. Properties of concrete. New York: John Wiley & Sons; 1973.
[43] Tsivilis S, Chaniotakis E, Badogiannis E, Pahoulas G, Ilias A. A study on the parameters affecting the properties of Portland limestone cements. Cem Concr Comp 1999;21(2):107–16.
[44] Bertolini L, Carsana M, Frassoni M, Gelli M. Pozzolanic additions for durability of concrete structures. Proc Inst Civ Eng – Construction Mater 2011;164(6):283–91.
[45] Carsana M, Frassoni M, Bertolini L. Comparison of ground-waste-glass with other supplementary cementitious materials. Cem Concr Comp 2014;45(1):39–45.