The Effect of Ground Limestone Addition on Carbonation and Chloride Resistance of Concrete

Luca Bertolini¹ Federica Lollini² Elena Redaelli³

ABSTRACT

In Italy, as in many other European countries, a growing diffusion of limestone cements has been observed in the recent years. Several studies were carried out since the late 1970s in order to evaluate the role of limestone in the hydration reactions of the clinker and the effect of limestone on concrete performance, in terms of mechanical properties and durability. Although the knowledge level has continuously extended, there is a partial disagreement on some topics, especially related to the durability issues. In particular the available information on the contribution of limestone to the resistance to chloride and carbonation penetration are limited and controversial. This paper presents a study aimed at the evaluation of the effects of the partial replacement of portland clinker with ground limestone, as a function of the water/cement ratio and the cement content. In particular hardened concrete was characterised by means of measurements of compressive strength, electrical resistivity and resistance to chloride and carbonation penetration. Results showed that both mechanical properties and resistance to penetration of aggressive agents, i.e. of carbonation and chloride, decreased by increasing the limestone content.

KEYWORDS

Ground limestone, Chloride, Carbonation, Reinforced concrete.

¹ Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milano, ITALY, luca.bertolini@polimi.it

²Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milano, ITALY, federica.lollini@polimi.it

³Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Milano, ITALY, elena.redaelli@polimi.it

1 INTRODUCTION

Recently an increase in the use of limestone cements has been observed in Italy as well as in many other European countries. Limestone cement is obtained by replacing portland clinker with ground limestone (up to 35% in accordance with the standard EN 197-1).

Due to the increment of limestone cement production and of its utilization, several studies were carried out since the late 1970s in order to evaluate the participation of limestone to the hydration reactions of the clinker and the effect of limestone on concrete performances, related to mechanical properties and resistance to penetration of aggressive agents [Dhir et al. 2007, Hornain et al. 1995, Liversey 1991, Matthews 1994, Tsivilis et al. 2002, Zelić et al. 2000]. Regarding the carbonation resistance, according to Tsivilis et al. [2002] after 1 year of exposure lower carbonation depths were measured in portland limestone concrete with limestone content up to 35% compared to portland cement, while for Dhir et al. [2007] for cement with up to 15% of limestone there was no significant influence on carbonation resistance, while higher limestone content showed a lower resistance to carbonation. As far as the resistance to chloride penetration is concerned, some authors reported that the addition of limestone filler reduces the diffusion coefficient of chloride ions, due to the filler effect of limestone [Hornain et al. 1995], whilst other authors reported that differences in diffusion coefficient, measured by means of an accelerated test, of concrete with up to 15% of limestone substitution, were relatively minor and they increased slightly with water/cement ratio compared to OPC concrete [Dhir et al. 2007]. Hence, although the knowledge level has continuously extended, the available information on limestone contribution to the resistance to chloride and carbonation penetration are limited and controversial.

This paper presents a study aimed at the evaluation of the effect of ground limestone, as a function of water/cement ratio, cement content and curing time, on various performances of the hardened concrete (e.g. compressive strength, carbonation rate and chloride diffusion coefficient evaluated by means of accelerated tests).

2 EXPERIMENTAL PROCEDURES

In order to investigate the effects of the partial replacement of portland cement with ground limestone on performances of hardened concrete, different types of concrete were cast. A portland cement CEM I 52.5R (OPC), according to EN 197-1 standard, was used for the reference concrete mix. Part of this cement was replaced with 15% (15%LI) and 30% (30%LI) of ground limestone, in order to simulate cements CEM II/A-L and CEM II/B-L. The particle size analysis of both OPC and limestone is given in Figure 1. Each type of binder (OPC, 15%LI and 30%LI) was used to produce concrete with three different water/binder ratios (*w/b*), equal to 0.42, 0.46 and 0.61, and different binder dosages (*b*), ranging from 250 kg/m³ to 400 kg/m³.



Figure 1. Grain size analysis of OPC and cement limestone.

Crushed limestone aggregates with maximum size of 16 mm were used, and an acrylic superplasticiser was added to the mixes in order to achieve a class of consistence *S4* according to EN 206-1 standard, i.e. a slump of 160-200 mm. Table 1 summarizes the concrete mixes.

After the mixing, concretes were cast into moulds with different shapes, covered with a plastic sheet and stored in laboratory at 20°C for 24 h, until demoulding. 100 mm cubes were cured at 20°C and 95% relative humidity for 7, 28, 90 and 180 days. At the end of the curing, as well as after demoulding, compressive tests were carried out, according to EN 12390-3 standard. Electrical resistivity was measured as a function of time on $50 \times 50 \times 100$ mm specimens cured under water. In order to evaluate the resistance to the penetration of carbonation, 100 mm cube specimens were cast and cured 1, 7 and 28 days at T = 20°C and R.H. = 95%. After 28 days from casting specimens were masked with epoxy, so that carbonation was allowed only from two opposite faces, and exposed to an environment with 20°C, 65% R.H. and a constant flux of 2%CO₂ (accelerated carbonation). Carbonation depth was measured with the phenolphthalein test on 20 mm diameter cores, after different times of exposure (i.e. 28 days, approximately 3 and 6 months). Carbonation depths, *d*, measured after different time, *t*, were fitted through the relationship:

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

and the carbonation coefficient K_{acc} was evaluated according to the minimum square methods.

Resistance to penetration of chloride ions was tested on cylindrical specimens, cured 28 days at T = 20°C and R.H. = 95%, by means of the so-called Rapid Chloride Migration (RCM) test, according to NT-BUILT 492 standard [1999]. A plastic tube was mounted coaxially to a 50 mm thick concrete cylinder, and a chloride-free solution was poured inside. The specimen, laid on an inclined plastic support, was placed in a container with a 10% NaCl solution. 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 hours). At the end of the test, the specimen was split axially, and on its fracture surface a 0.1 M AgNO₃ solution was sprayed. The average chloride penetration depth x_m (m) was measured and the chloride diffusion coefficient D_{RCM} was calculated as:

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

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 (=1), 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:

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

where c_d is the 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) [NT-Built 492 1999]. Further details on experimental procedures, concrete compositions and results of other experimental tests are given elsewhere [Bertolini *et al.* 2007 and Bertolini *et al.* 2008].

3. RESULTS AND DISCUSSION

Mechanical properties of hardened concrete were evaluated after different curing times. Table 1 summarizes results of compressive test and electrical resistivity measurements, evaluated as the average value of two replicated specimens, after 28 and 180 days of curing.

Figure 2 shows the influence of partial replacement of portland cement with ground limestone, of water/binder ratio and binder content on compressive strength of specimens cured 28 and 180 days. Regardless of the days of curing, the replacement with 15 and 30% of limestone led to a decrease in the compressive strength. For instance specimens with w/b 0.61 and cement content of 300 kg/m³, 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 cement was replaced with limestone 'Fig 2a'. The decrease in the compressive strength of concrete could indicate the inert behaviour of limestone, i.e. limestone does not react and, substantially, acts as a dilution of cement, increasing the effective water/cement ratio.

Series	w/b	binder	δ	$R_{ m c}$	ρ		
		(kg/m^3)	(kg/m^3)	(MPa)	$(\Omega \cdot m)$		
Curing [*]			28	28	180	28	180
OPC	0.61	300	2489	59.2	63.1	38	79
	0.46	300	2544	87	94.9	53	153
	0.46	350	2461	70.7	91.5	44	115
	0.42	350	2525	86.6	127.6	52	140
15%LI	0.61	250	2474	54.5	59.8	27	63
	0.61	300	2431	45.2	53.3	29	59
	0.46	300	2571	47.8	83.0	40	92
	0.46	350	2461	67.3	80.4	38	101
	0.42	350	2511	83.3	99.4	40	112
	0.42	400	2470	63.7	94.1	39	101
30%LI	0.61	300	2472	36.7	44.1	27	59
	0.46	300	2492	62	78.3	39	95
	0.46	350	2461	57.4	72.1	36	86
	0.42	350	2490	66.6	79.9	43	103

Table 1. Composition and mechanical properties of the tested concretes (average values of two samples): w/b = water/binder ratio; δ = density; R_c = compressive strength and ρ = electrical resistivity.

^(*) Days of wet curing at 20°C and 95% R.H.

Moreover it was observed that both water/binder ratio and binder content influenced the compressive strength: not only the water/binder ratio led to the well known decrease in compressive strength, but also a strength decrease was observed when the binder content increased.

Figure 3 shows the effect of limestone on the electrical resistivity measured after 28 and 180 days of curing. The electrical resistivity is an important parameter used to measure the resistance of a material to ion penetration. It is strongly influenced by the moisture content of concrete; nevertheless in a saturated material the effect of the humidity can be avoided thus enabling the resistivity to be related mainly to the microstructure of the material (assuming that the composition of the pore solution does not significantly change in the different concrete).



Figure 2. Effect of the partial replacement of portland cement with limestone, of water/binder ratio and binder dosage (white symbols = 250 kg/m^3 , black symbols = 300 kg/m^3 , grey symbols = 350 kg/m^3 and dark grey symbols = 400 kg/m^3) on compressive strength after 28 (*a*) and 180 (*b*) days of curing.



Figure 3. Effect of the partial replacement of portland cement with limestone, of water/binder ratio and binder dosage (white symbols = 250 kg/m^3 , black symbols = 300 kg/m^3 , grey symbols = 350 kg/m^3 and dark grey symbols = 400 kg/m^3) on electrical resistivity after 28 (*a*) and 180 (*b*) days of curing.

Therefore a concrete electrical resistivity, in a water saturated specimen, is an indirect measure of the concrete porosity and it can be used to follow the evolution in time of the hydration. For each water/binder ratio and curing, the replacement of ground limestone led to a decrease in electrical resistivity of hardened cement paste. For instance, on 28-day cured specimens with water/binder ratio of 0.46 and binder dosage of 350 kg/m³ electrical resistivities of 53, 40 e 38 Ω ·m were measured on portland, 15 and 30% of limestone concrete 'Fig. 3*a*'. The electrical resistivity decrease in saturated concrete with the increase of the limestone percentage shows that, for the same curing time and water/binder ratio, the replacement of portland cement with limestone leads to an increase of the capillary porosity of cement paste.

Series	w/b	binder	$K_{\rm acc,1}$	$K_{ m acc,7}$	$K_{\rm acc,28}$	$D_{\rm RCM}$
		(kg/m^3)	$(mm/year^{0.5})$	$(mm/year^{0.5})$	(mm/year ^{0.5})	$(10^{-12} \text{ m}^2/\text{s})$
Curing			1^*	$\overline{7}^*$	$\overline{28}$	28
OPC	0.61	300	30.6	21.2	18.4	12.55
	0.46	300	15.9	12.8	3.9	7.69
	0.46	350	19.2	12.9	4.6	7.75
	0.42	350	-	7.3	-	5.43
15%LI	0.61	250	36.9	29.5	20.5	18.92
	0.61	300	32.2	26.6	22.2	19.81
	0.46	300	17.9	11.8	8.4	15.08
	0.46	350	17.9	12.1	7.8	13.62
	0.42	350	-	11.2	-	11.30
	0.42	400	-	13.6	-	11.42
30%LI	0.61	300	40.4	34.6	27.4	38.27
	0.46	300	29.2	20.7	16.8	18.05
	0.46	350	22.5	23.2	16.1	23.51
	0.42	350	-	12.2	-	13.12

Table 2. Carbonation coefficient, K_{acc} , from accelerated test and diffusion coefficient, D_{RCM} , fromrapid chloride migration test (average value of two replicate samples).

^(*)Tests started 28 days after casting (after wet curing specimens were exposed in the laboratory at 20°C and about 65% R.H.).



Figure 4. Effect of the partial replacement of portland cement with limestone, of water/binder ratio and binder dosage (white symbols = 250 kg/m^3 , black symbols = 300 kg/m^3 , grey symbols = 350 kg/m^3 and dark grey symbols = 400 kg/m^3) on accelerated carbonation coefficient, K_{acc} , on specimens cured 1 (*a*), 7 (*b*) and 28 (*c*) days.

The penetration of carbonation was evaluated on specimens exposed under accelerated conditions. After different exposure times the carbonation depth was measured and the carbonation coefficient, $K_{\rm acc}$, was calculated through the relationship (1) [Table 2]. Figure 4 shows the influence of limestone replacement on carbonation coefficient, K_{acc} , measured on concrete cured 1, 7 and 28 days. When part of portland cement was replaced with 15% of limestone and specimens were cured 1 and 7 days, compared to a porland cement only slight differences in the carbonation coefficient were observed 'Figs 4a and 4b'. For instance, for 1-day cured concretes with w/b = 0.61 and b = 300 kg/m³, the accelerated carbonation coefficient was 30.6 and 32.3 mm/year^{0.5} respectively for OPC and 15% LI. However increasing the curing time up to 28 days OPC concretes performed better than 15% LI since they showed a lower carbonation coefficient, i.e. a higher resistance to the penetration of carbonation 'Fig. 4c'. For instance K_{acc} increased from 4 to 8.4 mm/year^{0.5} for 28-day cured concrete with w/b =0.46 and $b = 300 \text{ kg/m}^3$, when 15% of cement was replaced with limestone. Regardless the curing time, the replacement of part of portland cement with 30% of limestone led to a higher carbonation coefficient, which was more than doubled for 28-day cured specimens. For instance, 7-day cured specimens with w/b ratio of 0.42 and binder content of 350 kg/m³ had an accelerated carbonation coefficient that increased from about 7.3 mm/years^{0.5} when portland cement was used to 12.2 mm/years^{0.5} when 30% of cement was replaced with ground limestone.

At any time of curing, 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 strongly influence the accelerated carbonation coefficient. Comparing concretes with the same composition at different curing times, a strong decrease in the carbonation coefficient, which led to a more impervious material, can be observed when curing increased from 1 to 7 or 28 days. For instance in concrete with 15% limestone, 350 kg/m³ 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 measured respectively on specimens cured 1, 7 and 28 days.

The resistance to chloride penetration was investigated by means of the Rapid Chloride Migration test on specimens cured 28 days [Table 2]. Figure 5 shows the diffusion coefficient D_{RCM} , calculated through equations 2 and 3, as a function of concrete composition (limestone content, water/binder ratio and binder content). A remarkable influence of the limestone content was observed; with the replacement of 15% of cement with limestone the diffusion coefficient was doubled. For instance specimens with *w/b* ratio of 0.46 and binder content of 300 kg/m³ had a diffusion coefficient that increased from 7.69·10⁻¹² m²/s when portland cement was used to 15.08·10⁻¹² m²/s when 15% of cement was replaced with ground limestone. The D_{RCM} further increased with 30% of limestone and, in this case, a higher sensitivity to the water/binder ratio was observed, which led to a rather high value of D_{RCM} in concrete with *w/b* ratio of 0.61. For instance taking into account a water/binder ratio of 0.42 the diffusion coefficient was 5.43·10⁻¹² and 13.12·10⁻¹² m²/s respectively for OPC cement and 30% limestone. For any binder the significant role of reducing the *w/b* ratio clearly appears in 'Fig. 5', while the binder content showed a negligible effect. For instance for OPC concrete the diffusion coefficient decreased from 12.55·10⁻¹² to 5.43·10⁻¹² m²/s, when the water/binder ratio decreased from 0.61 to 0.42.



Figure 5. Effect of the partial replacement of portland cement with limestone, of water/binder ratio and binder dosage (white symbols = 250 kg/m^3 , black symbols = 300 kg/m^3 , grey symbols = 350 kg/m^3 and dark grey symbols = 400 kg/m^3) on the rapid chloride migration coefficient, D_{RCM} , on 28-day cured specimens.

4 CONCLUSIONS

The influence of limestone content as well as other parameters such as water/binder ratio, binder content and curing, on the properties of hardened concrete was studied with particular regard to the resistance to carbonation and chloride penetration, measured by means of accelerated tests. The effect of limestone content was studied by replacing part of the portland cement with 15 and 30% of ground limestone in concretes with different values of water/binder ratio and binder content. Results showed that both compressive strength and electrical resistivity decreased by increasing the limestone content.

The replacement of 15% of limestone only slightly influences the carbonation resistance compared to a portland cement, while increasing the substitution content the resistance to carbonation is drastically reduced.

A remarkable increase in the chloride diffusion coefficient was observed even replacing in concrete with 15% limestone, showing that limestone cements are not suitable in chloride bearing environments.

The beneficial effect related to the decrease in the water/binder ratio and the increase in curing time was estimated and some influence of the dosage of binder was observed in the compressive resistance.

ACKNOWLEDGMENTS

This research was financed by the Italian Ministry of University and Research (MIUR), Holcim Italia S.p.A. and Sismic.

REFERENCES

Bertolini, L., Lollini, F., Redaelli, E. 2007, 'Influence of concrete composition on parameters related to the durability of reinforced concrete structures', Proc. of the International RILEM Workshop: Integral Service Life Modelling of Concrete Structures, Guimarães, Portugal, 5 6 November 2007, pp. 71–78.

Bertolini, L., Lollini, F., Redaelli, E. 2008, 'Concrete composition and service life of reinforced concrete structures exposed to chloride bearing environments', Proc. 1st International Symposium on Life-Cycle civil Engineering, IALCCE'08, Varenna, Italy, pp. 113–118.

Dhir, R.K., Limbachiya, M.C., McCharthy, M.J., Chaipanich, A. 2007, 'Evaluation of Portland limestone cements for use in concrete construction', *Materials and Structures*, **40**[5], 459–473.

Heikal, M., El-Didamony, H., Morsy, M.S. 2000, 'Limestone-filled pozzolanic cement', *Cement and Concrete Research*, **30**[11], 1827–1834.

Hornain, H., Marchand, J., Duhot, V., Regourd, M. 1995, 'Diffusion of chloride ions in limestone filler', *Cement and Concrete Research*, **25**[8], pp. 1667–1678.

Livesey, P. 1991, 'Performances of limestone-filled cements', in: *Blended Cements in Construction*, ed R.N. Swamy, Elsevier, London, pp. 1–15.

Matthews, J.D. 1994, 'Performance of limestone filler cement concrete', in: *Euro-cements, impact of ENV 197 on concrete construction*', eds R.K. Dhir, M.R. Jones, E & FN Spon, London, pp. 113–147.

NT BUILD 492, 1999, 'Concrete, mortar and cement-based repair materials: chloride migration coefficient from non-steady state migration experiment', NORDTEST.

Sersale, K. 1999, 'Advances in portland and blended cement', Proc. 9th International Congress of the Chemistry of Cement, New Delhi, India, vol 1, pp. 109–115.

Tsivilis, S., Chanitakis, E., Kakali, G., Batis, G. 2002, 'An analysis of the properties of Portland limestone cements and concrete', *Cement and Concrete Composities*, **24**[3-4], pp. 371–378.

Zelić, J., Krstulović, R., Tkalčec, E., Krolo, P. 2000, 'The properties of Portland cement-limestonesilica fume mortars', *Cement and Concrete Research*, **30**[1], 145–152.