Carbonation resistance of concrete: limestone addition effect

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Systematic analysis and evaluation of experimental results on carbonation and carbonation-induced corrosion resistance of concrete made with Portland limestone cement (PLC) are presented; these results have been extracted from 143 globally published studies in the literature since 1986, by 274 researchers from 131 institutions and 34 countries, and yielding a 19 000 data matrix are presented. It is shown that the carbonation of concrete increases with increasing limestone content, within the range permitted by standard BS EN 197-1:2011. This effect, however, is less marked for concrete designed on an equal strength basis to the corresponding Portland cement (PC) concrete than concrete designed on an equal water/cement (*w/c*) basis. Eurocode 2 standard specifications for XC3 carbonation exposure for characteristic cube strength of concrete (or its *w/c* ratio) may need to be reviewed for the addition of limestone. Other influencing factors: curing, limestone fineness, total cement content, were also studied. A comparison has been conducted for the carbonation performance of concrete made with PLC and cement containing fly ash and ground granulated blast-furnace slag. Procedures to reduce the carbonation of PLC concrete are proposed. Response to accelerated carbonation, at 3–5% carbon dioxide concentration, of PLC concrete is similar to natural indoor exposure. A conversion factor of 1 week accelerated carbonation equal to 0.75 year natural indoor exposure was determined.

Introduction

Although historically the use of limestone (LS) as a construction material dates back to ancient times, when calcined LS or gypsum was used to make mortar (Mayfield, 1990) and when LS became one of the main constituents of the raw feed used to manufacture Portland cement clinker in 1824, it is the acceptance of LS as an addition to cement with Portland clinker (EN 197-1, 2000 (BSI, 2011)), to reduce the carbon footprint of concrete, that is offering new potential for the use of this material in concrete.

The first attempt at using LS as a component of cement was in 1965 in Germany, and later in 1979 the French Cement Standards allowed its use as an addition; this was followed by its adoption by various standards: the Canadian Standards in 1983 at 5% addition, British Standards in 1992 up to 20% addition and European Standard EN 197-1 in 2000 as Portland LS cements CEM II/A-L and CEM II/B-L with LS content 6–20% and 21–35%, respectively. Indeed, now the use of Portland limestone cement (PLC) has been adopted worldwide. This use is increasing on grounds of sustainability, enforcing reduction in energy and carbon dioxide emission

associated with Portland cement (PC) manufacture (Tennis *et al.*, 2011). In addition, among all cement addition materials, such as ground granulated blast-furnace slag (GGBS) and fly ash (FA), LS is the most widely available natural material, with calcium carbonate (CaCO_3) occupying 5% of the earth's crust (Thenepalli *et al.*, 2015).

When LS is added to PC, it influences its properties both in the fresh and hardened states, as well the durability. Although the performance of PLC has been investigated widely in the past in terms of durability, the available information has remained fragmented and often unhelpful in further developing the use of PLC in concrete construction. Moreover, delivering sustainability in a meaningful manner demands compliance with required durability specifications in a cost-effective way.

The main aim of this paper, which is the third and the final in a series of papers, is to establish the potential resistance of PLC to carbonation and carbonation-induced corrosion of concrete and how this performance compares with the use of FA (Lye *et al.*, 2015) and GGBS (Lye *et al.*, 2016). To facilitate a meaningful performance comparison of the

three additions, the paper has been formatted similarly to the two papers previously published in the *Magazine of Concrete Research* (Lye *et al.*, 2015, 2016).

Methodology adopted

An extensive search of the published literature in English has been undertaken, using different databases and citation indices in order to ascertain the extent and nature of related research that has been undertaken and to obtain the available test data, arising from 34 countries and dating back to 1986. It was noted that the major contribution in this field has come from Europe (Figure 1).

The sourced literature was examined and divided into four major categories and other subcategories, as shown in Figure 2 and further explained below.

- (a) Narrative review papers: these summarise the findings of the selected few studies and give conclusions. Although useful, such publications do not necessarily give the test information in any detail.
- (b) Experimental results papers: these present and discuss the experimental data obtained from the dedicated projects undertaken.
- (c) In situ measurement papers: these are studies undertaken on existing structures (new or old), which report the results of the tests undertaken on structural members in situ or the specimens cored from them.

- (d) Modelling papers: these represent theoretical work. The study presented in this paper does not include the results arising from modelling work.
- (e) Portland composite cement mixtures: these consisted of additional cementitious materials to LS, such as GGBS, FA, silica fume (SF) and metakaolin (MK). Although these studies investigated carbonation of concrete with LS in conjunction with other additions, the results obtained made it difficult to clearly appreciate the role of LS addition and such data have been excluded from further consideration.

For the studies concerning carbonation depth/rate of PLC concrete, an additional breakdown was made, where some papers did not provide the results of the reference concrete mixes made with PC, and a few publications had duplicated data and were not considered further. The analyses of the data have been undertaken considering the type of carbonation exposure (accelerated or natural) and the type of cementitious mixture (paste and mortar/concrete). It should also be noted that in expressing water/cement ratio (*w/c*), the word ‘cement’ refers to the whole combination of Portland cement clinker and LS.

Overview of the literature

Although limited in number, and without detailed analysis of the data, both the individual and organisation reviews (Table 1) suggest that there is consensus among these

Figure 1. Country distribution for authors of the collected publications

^a: Some references may be counted in more than one category.

^b: Shaded categories are not taken into consideration in this study.

Figure 2. Flow chart showing the type of references found in the literature regarding the carbonation of PLC

reviewers that the carbonation resistance of concrete is not significantly altered with the addition of up to 15–20% LS (i.e. cements such as Portland–LS cement, CEM II/A in BS EN 197-1 (BSI, 2011)). However, the reviews provided by the national cement/concrete organisations in Canada, Sweden, UK and USA concluded that, at a given w/c ratio, the use of LS addition as a cement component (i.e. the use of PLC as per BS EN 197-1 (BSI, 2011)) can potentially be expected to increase its carbonation, albeit in some cases, and up to a certain level of LS addition it may not be significant in the context of overall concrete mix variations. However, the mixes designed on an equal strength basis with PLC can be expected to carbonate at a similar rate to PC concrete.

On the other hand, the overview of the reported data relating to the effect of LS addition to PC on the carbonation of concrete (PLC concrete) subjected to both natural and accelerated exposures, as presented in Table 2, revealed that the vast majority of the results of the tested mixes (76%) show that the inclusion of LS leads to a higher rate of concrete carbonation. In contrast, only 9% of the reported data suggest that the carbonation of PLC concrete can be lower than the corresponding PC concrete, with 3% indicating no change, and 4% showing a variable trend; for 8% of the reported results there were no

corresponding PC concrete mixes tested, and therefore the PLC data could not be compared with the corresponding PC concrete mixes.

Analysis of published data

Variation in the testing procedures used

The test conditions employed in the reported studies to measure the effect of LS on the resistance of concrete to carbonation, using both accelerated and natural exposures, are summarised in Table 3. While the first impression can be that widely varying conditions have been applied to measure the carbonation resistance of both PC and PLC test concrete mixes, in reality the majority of the test parameters in general have been kept within an acceptable range. The main points emerging from Table 3 are listed below.

- Carbonation exposure. Surprisingly, natural exposure was adopted more than accelerated exposure in the testing of concrete for carbonation, in a ratio of 3 to 2, and within this indoor exposure had been used the most.
- Specimen. Although the choice of test specimens in the form of cylinders, prisms and cubes appeared to be

Reference	No. of cited references	Main observation
(a) Individual		
Ayub <i>et al.</i> (2013)	1	LS addition increases the carbonation rate in concrete, except when the amount of cement replacement is 15% or less
Müller (2012)	1	The use of LS addition up to 20% could slightly increase the carbonation depth
Torgal <i>et al.</i> (2012)	3	No considerable influence on carbonation resistance with LS content up to 15%
(b) Organisation		
Hooton <i>et al.</i> (2007); Cement Association of Canada	6	LS has the potential to increase the carbonation of concrete
Lagerblad (2005); Swedish Cement and Concrete Research Institute CBI, Sweden	1	PLC concrete will carbonate somewhat faster, as the amount of Portland clinker cement paste and the buffering capacity is less than in the corresponding PC concrete
Detwiler and Tennis (1996); Hawkins <i>et al.</i> (2003); Portland Cement Association, USA	9	The literature review shows mixed results for PLC when compared to PC. The differences are of limited practical significance in the context of overall concrete mix variations
Tennis <i>et al.</i> (2011); Portland Cement Association, USA	6	PLC concrete will carbonate at a similar rate to PC concrete, provided the concretes are designed for the same target strength
CSWP (2011); Concrete Society, UK	2	PLC increases the rate of carbonation when concretes are produced at a constant w/c; whereas PLC has similar carbonation to PC when both concretes are designed to meet an equal strength

Table 1. Summary of the findings of the narrative reviews in the literature regarding the carbonation of the PLC concrete

influenced by the relevant standard specifications adopted in a specific study, a large number of tests have been carried out using prisms. Moreover, in most cases information on how the specimens have been prepared for testing has not been provided. However, where declared, the majority of specimens were in the sealed form to allow for uniaxial directional carbonation.

- (c) Curing. With the exception of some studies, and to a certain extent influenced by the local standard specifications, moist curing with relative humidity of 80–100%, temperature of 20–30°C and duration of up to 28 d have generally been adopted.
- (d) Pre-conditioning. Although this information was lacking in the majority of studies, where declared the commonly adopted treatment was carried out at a temperature of 20–30°C, relative humidity of 45–85% and a duration of 14–28 d.
- (e) Accelerated and natural exposure conditions. The commonly used accelerated exposure consisted of a carbon dioxide concentration of up to 5%, duration of ≤30 d, temperature of 20–30°C and humidity of 61–80%, whereas the natural indoor exposure was of a period of up to 5 years' duration.

- (f) Measurement. The vast majority of the studies utilised a phenolphthalein indicator to measure the depth of carbonation; the remainder did not declare the measurement method employed.

Limestone effect

Given the large number of test parameters involved, as can be seen from Table 3, the effect of LS addition on the carbonation resistance of PLC concrete has been analysed in relative terms to the corresponding PC concrete (used as reference) and the results thus obtained are shown plotted in Figure 3, with the majority of the data population being within the 5–35% LS replacement band. The scatter in the data is understandably high as their source is global and the variables involved are high. In developing Figure 3, some of the data were excluded from further consideration, as follows

- outliers at each LS replacement level using box and whiskers plots
- where the corresponding value for reference PC concrete was not available
- excessively high relative values (greater than 200%) resulting from low carbonation measurement were considered to be unrealistic

Observation ^a of carbonation depth of LS mixes	Main suggested causes	Number of tested mixes		
		Accelerated	Natural	Total
Higher (455)	Cement			
Accelerated (155)	Reduction of Portland cement clinker	32	49	81
Natural (300)	Limestone plays the role of a nucleation site for calcium carbonate precipitation	4	0	4
	Design			
	Low cement content	8	11	19
	Higher w/c ratio	10	12	22
	Insufficient curing	17	29	46
	High carbon dioxide concentration	2	0	2
	Hardened properties			
	Reduction of calcium hydroxide	12	19	31
	Higher porosity/Coarser pore structure	24	35	59
	Higher permeability	0	12	12
	Low strength	6	9	15
	Reduction of alkalinity	6	0	6
	Not given	53	105	158
Lower (51)	Cement			
Accelerated (21)	Higher specific area of LS	0	5	5
Natural (30)	Design			
	Lower w/c ratio	2	2	4
	Sufficient curing	2	3	5
	Higher strength	1	2	3
	Hardened properties			
	Lower porosity	0	5	5
	Not given	10	19	29
No change (16)	Equal strength	0	4	4
Accelerated (8)	Low w/c	1	0	1
Natural (8)	Not given	7	4	11
Variable (25)				
Accelerated (1)	Not given	1	24	25
Natural (24)				
No reference mixture (47)				
Accelerated (34)	Not applicable	34	13	47
Natural (13)				

^aHigher/lower/no change/variable carbonation depth of LS mixture with respect to corresponding reference PC mixture

Table 2. Suggested causes of carbonation phenomenon of PLC concrete from the literature

- results showing full carbonation of test specimens, as in such cases it was not possible to calculate the actual depth of carbonation.

The best-fit relationship presenting the effect of using LS on the carbonation of concrete for the mean values is also plotted in Figure 3, having a coefficient of correlation $R^2 = 0.9335$. The trend line shows that, as the addition of LS

increases, the relative carbonation of concrete increases at an increasing rate. For simplicity of reference, the range of BS EN 197-1:2011 (BSI, 2011) common cements with LS addition has also been shown. It can be seen that, at 35% of LS addition (the maximum limit permitted in BS EN 197-1:2011 (BSI, 2011)), the carbonation of PLC concrete could be about 62% higher than the corresponding PC concrete, whereas at 5% LS inclusion carbonation of PLC

	Parameter	Variable	No.		Parameter	Variable	No.	
1. Carbonation	Accelerated (219)	—	219	2. Specimen	Specimen (594)	Cylinder	143	
	Natural (375)	Indoor	200			Prism	307	
		Outdoor, sheltered	132			Cube	128	
		Outdoor, unsheltered	18			Not given	16	
	3. Curing	Exposure (594)	Outdoor, not given		10	Preparation (594)	Sealed	116
			Not given		15		Unsealed	22
			Moist		499		Unspecified	456
4. Pre-conditioning		Air	45	Preparation (594)	Omitted	12		
			Not given		50	Applied	226	
			Not given		50	Not given	356	
	Duration: d (594)	1–14	327		Duration: d (226) ^a	1–7	39	
		15–28	166	14–28		115		
		56–91	40	76–351		45		
		>91	7	Not given		27		
5 (a). Accelerated exposure conditions	Not given	54	Temperature: °C (226) ^a	20–30	169			
		20–30		522	35–80	43		
		>30		3	Not given	14		
	Temperature: °C (594)	Not given	69	Humidity: % (226) ^a	45–85	186		
		80–100	485		Not given	40		
		40–80	37					
5 (b). Natural exposure conditions	Humidity: % (594)	Not given	72	Humidity: % (200)	40–65	189		
		Not given	72		Not given	11		
		Not given	72		Not given	11		
	Carbon dioxide: % (219)	<3	48	Indoor	Duration: years (200)	<1	92	
		3–5	90		1–5	108		
		6–10	10		Temperature: °C (200)	20–25	192	
		20–100	68		Not given	8		
		Not given	3					
	Duration: d (219)	≤30	131	Outdoor	Humidity: % (200)	40–65	189	
		31–90	53		Not given	11		
		91–180	13		Sheltered, duration: years (132)	<1	48	
		>180	21		1–3	47		
		Not given	1		4–9	37		
	Temperature: °C (219)	<20	1	Not given	Unsheltered, duration: years (18)	<1	12	
		20–30	203		1–4	6		
>30		10						
Not given		5	Unspecified, duration: years (10)		≤1	10		
Humidity: % (219)		<50	6					
6. Measurement: Method (594): Phenolphthalein (554 ^b), Not given (40)	50–60	49	Not given	Duration: years (15)	≤1	15		
	61–80	159						
	Not given	5						

Note: Number in parenthesis is the sum of tested mixes in each individual parameter

^aData compiled from studies where pre-conditioning is applied

^bPhenolphthalein concentration: 1% phenolphthalein (17) and not given (537)

Table 3. Compilation of test parameters of carbonation measurement in the literature

Figure 3. Limestone addition effect on carbonation resistance of concrete. Data of Figure 3 taken from: Abualgasem *et al.* (2014); Ali and Dunster (1998); Alunno-Rosetti and Curcio (1997); Balayssac *et al.* (1995); Balcu *et al.* (2012); Barker and Matthews (1994); Baron (1986); Batic *et al.* (2013); Bertolini *et al.* (2007, 2009); Bertrand and Poitevin (1991); Cangiano and Princigallo (2010); Catinaud *et al.* (2000); Chowanec and Scrivener (1992); Collepardi *et al.* (2004a); Courard *et al.* (2005); Courard and Michel (2014); Dhir *et al.* (2004, 2007); Drouet *et al.* (2010); El-Hassan and Shao (2015); Galan *et al.* (2010a, 2010b, 2012); Holt *et al.* (2009, 2010); Hussain *et al.* (2013); Ingram and Daugherty (1992); Kaewmanee and Tangtermsirikul (2014); Kargol *et al.* (2013); Kjellsen *et al.* (2005); Kuosa *et al.* (2008,

2012, 2014); Krell (1989); Leemann *et al.* (2015); Livesey (1991); Lollini *et al.* (2014); Manns *et al.* (2001); Marques *et al.* (2013); Meddah *et al.* (2014); Moir and Kelham (1993, 1999); Matthews (1994); Neves *et al.* (2015); Pomeroy (1993); Müller and Lang (2006); Müller *et al.* (2014); Mwaluwinga *et al.* (1997); Nielsen *et al.* (2014); Parrott (1994, 1996); Phung *et al.* (2015); Proske *et al.* (2013, 2014); Rabehi *et al.* (2013); Ranc *et al.* (1991); Rozière and Loukili (2011); Schmidt (1992a, 1992b); Schmidt *et al.* (1993); Shi *et al.* (2015); Silva and de Brito (2016); Sprung and Siebel (1991); Rostami *et al.* (2012); Shao *et al.* (2014); Tezuka *et al.* (1992); Thomas and Hooton (2010); Thomas *et al.* (2013); Tsvilis *et al.* (2000, 2002); Vandanjon *et al.* (2003).

concrete could easily be assumed to be comparable to that of PC concrete.

Influence of strength and w/c ratio

The results plotted in Figure 3 are separated in terms of 28 d strength and w/c ratio within natural and accelerated exposures and are shown plotted on the basis of

- equal strength, in Figures 4(a) and 4(b).
- equal w/c ratio, in Figures 5(a) and 5(b).

These figures show the following points.

- The effect of PLC on the carbonation of concrete at equal strength, as to be expected, is less marked than at equal w/c ratio, showing at 35% LS content for natural exposure an increase of 32% (Figure 4(a)) and 75% (Figure 5(a)), respectively.
- Accelerated carbonation gives rise to higher carbonation compared with natural exposure up to 58% on equal concrete strength basis (Figures 4(a) and 4(b)) and 85%

Figure 4. Influence of LS on carbonation resistance of concrete at equal 28 d strength for (a) natural and (b) accelerated carbonation exposures

Figure 5. Influence of LS on carbonation resistance of concrete at equal w/c ratio for (a) natural and (b) accelerated carbonation exposures

on the basis of equal concrete w/c ratio (Figures 5(a) and 5(b)).

- When concrete mixes are designed on an equal strength basis, an addition of up to 10% of LS can be absorbed without giving rise to an increase in the carbonation of concrete. This facility is not available when the mixes are designed on an equal w/c ratio basis.

Influence of limestone fineness

The effect of LS fineness on the carbonation resistance of PLC concrete, although of interest, has not been widely

reported. The tests reported by Kaewmanee and Tangtermsirikul (2014) using mortar mixes containing only 10% LS of Blaine fineness essentially similar to that of PC (3320 and 3430 cm^2/g , respectively) showed an increase in carbonation depth of 30%, and increasing the fineness of LS from 3320 to 9260 m^2/g reduced the difference to 25% only, suggesting that increasing the fineness of LS more than that of PC is not a viable solution for controlling the carbonation of PLC concrete.

Influence of cement content

Although not exhaustively, the effect of cement content on the carbonation of concrete has been examined over the cement range of 240–390 kg/m³, with LS content of 15–30% and constant *w/c* ratios of 0.46–0.65, using accelerated carbonation exposure under the following conditions: moist curing for 28 d; temperature of 20°C; relative humidity of 55–65%; carbon dioxide concentration of 2–5%; exposure duration up to 140 d (Dhir *et al.*, 2004; Lollini *et al.*, 2014; Marques *et al.*, 2013).

The results obtained are shown plotted in Figure 6. Although the data are few, and at times appear to be conflicting, there is sufficient evidence to suggest that the carbonation of both concretes decreases at a slow rate with increasing cement content, PC or PLC.

Influence of curing

Curing conditions

The study of the effect of curing on the carbonation of PLC concrete with *w/c* ratio varying from 0.45 to 0.76, LS content up to 35%, has been limited to moist and air curing for a period of 28 d. Two types of exposure conditions employed were accelerated with temperature 20/30°C, relative humidity 60/65% and carbon dioxide concentration 50/4% with test duration of 28/91 d, respectively, by Rabehi *et al.* (2013) and Hussain *et al.* (2013) and natural indoor and outdoor shelter for a duration of 1, 4 and 9 years, respectively, by Baron

(1986), Ranc *et al.* (1991) and Ali and Dunster (1998). These studies showed, in general terms, that although the carbonation of both sets of concrete increased with the air curing of the test specimens, the PLC concrete relative to PC concrete did so at an increased rate that increased with LS content. The accelerated exposure produced higher carbonation than natural exposure, with the difference between the two widening with LS content.

Curing duration

The influence of curing duration on the carbonation resistance of PLC concrete has been studied with LS contents of 0–35%, for a duration of 1–365 d and at a temperature of 20 and 30°C, under both accelerated (2, 5 and 50% carbon dioxide concentration) by Lollini *et al.* (2014), Rabehi *et al.* (2013) and Marques *et al.* (2013), and natural exposure conditions (indoor and outdoor sheltered) by Balayssac *et al.* (1995), Barker and Matthews (1994), Matthews (1994), Moir and Kelham (1993, 1999), Parrott (1996) and Thomas *et al.* (2013). The carbonation resistance of concrete, measured both in accelerated and natural exposures, improves with moist curing duration, particularly with initial moist curing. Although PLC concrete mixes give higher carbonation values than PC concrete, the difference between the two decreases with time, and does so more when the LS content is less than 15% and the mixes are designed on an equal strength basis.

Carbonation depth with strength grade of concrete

To envisage the provision of adequate concrete cover to reinforcement of PLC concretes, the obtained results are analysed in terms of carbonation depth and compressive strength. Taking 50 years as the design working life, category 4 for building structures and other common structures as specified in Eurocode 0 (BS EN 1990:2002+A1:2005 (BSI, 2002)), the expected carbonation depth data of concrete are shown plotted against 28 d characteristic cube strength for different natural exposure conditions, namely, (a) indoor, (b) outdoor sheltered and (c) outdoor unsheltered, in Figure 7.

Figure 7 has been established as outlined below.

- The data used are taken from Figure 3 and in addition the carbonation data of those PLC mixes for which PC control mixes were not adopted by the authors (Assie *et al.*, 2006, 2007; Bertolini *et al.*, 2008; Bolzoni *et al.*, 2006, 2014; Corinaldesi and Moriconi, 2004; Diamanti *et al.*, 2013; Figueiras *et al.*, 2009; Franzoni *et al.*, 2013; Frazão *et al.*, 2015a, 2015b; McNally and Sheils, 2012; Meira *et al.*, 2014; Nieuwoudt *et al.*, 2012; Owsiak and Grzmil, 2015; Perlot *et al.*, 2013; Redaelli and Bertolini, 2011a, 2011b, 2014; Révay and Gável, 2003; Rio *et al.*, 2015; Segura *et al.*, 2013; Sistonen *et al.*, 2008; Thienel and Beuntner, 2012; Tschegg *et al.*, 2011;

Figure 6. Influence of cement content on carbonation depth of PLC concrete exposed to accelerated carbonation

Figure 7. Extrapolated carbonation depth at 50 years of PC and PLC concretes subjected to natural carbonation exposures: (a) indoor; (b) outdoor sheltered; (c) outdoor unsheltered, at different characteristic cube strengths

Ylmen and Jäglid, 2013) have also been incorporated for this exercise.

- Where the ultimate figure for carbonation was given as zero by the authors, such studies have been ruled out from the analysis in this case.
- The predictable carbonation depth data at 50 years (D_{50}) were determined based on Fick's law, $D_{50} = K \times t^{0.5}$, where K is the rate of carbonation (mm/year^{0.5}) and $t = 50$ years. The value of K used was as provided by the authors or alternatively calculated by employing the final carbonation depth data given by the authors.
- Characteristic cube strength has been determined using a variation coefficient of 6% given in ACI 301:2005 (ACI, 2005) for fair laboratory control class.
- The data provided by the authors where the test mixes did not comply with the BS EN 206:2013 (BSI, 2013) mix limitations for the carbonation class XC were also not considered in this case.

As seen from Figure 7, the highest carbonation depths were for the indoor exposure and the lowest for the outdoor unsheltered exposure, with carbonation depth increasing with decreasing compressive strength and increasing LS content. Additionally, and important to this study, the following observations can be noted.

- For the indoor exposure, the 50 year estimated carbonation depths of both PC and PLC concretes surpass the minimum concrete cover specified in Eurocode 2 (BS EN 1992-1-1:2004+A1:2014 (BSI, 2004)) for the minimum cube compressive strength of 37 MPa for exposure class XC3 (Figure 7(a)).
- For the outdoor sheltered exposure, the 50 year expected carbonation depths of PC and PLC (CEM II/A) concretes are below 25 mm, whereas concrete with PLC (CEM II/B) has a carbonation depth greater than the minimum cover requirement (Figure 7(b)).

- In the case of the outdoor unsheltered exposure, although the amount of data is comparatively small, the 50 year carbonation depths of both PC and PLC (CEM II/A) concretes are below 25 mm, with the latter being higher than the former (Figure 7(c)).

Figure 7 also proposes how to obtain a carbonation of PLC concrete comparable to that of PC concrete. Using the carbonation of PC concrete at 37 MPa, as an example, subjected to indoor and outdoor sheltered conditions, to attain a similar carbonation to PC concrete, the compressive strength of PLC concrete would have to be increased on average by about 5.5 MPa and 10.5 MPa for CEM II/A (6–20% LS) and CEM II/B (21–35% LS) cements, respectively (Table 4).

In addition, Table 4 columns (a) and (b) summarises, for the indoor and outdoor sheltered exposures

- (a) estimated carbonation depth corresponding to 37 MPa
- (b) characteristic cube strength corresponding to 25 mm cover of concrete made with combinations of PC and different LS contents, such as those covered by BS EN 197-1:2011 (BSI, 2011).

The accelerated carbonation data pertaining to 3–5% carbon dioxide exposure were analysed in a similar way to the natural indoor exposure conditions shown plotted in Figure 7(a). This showed that 1 week of accelerated carbonation exposure for concrete made with PC, CEM II/A (6–20% LS) and CEM II/B (21–35% LS) is equivalent to about 0.58, 0.69 and 0.92 years of natural indoor carbonation exposure, respectively. These values are dissimilar to that suggested by Ho and Lewis (1987), who proposed a factor of 1.0 with accelerated carbonation at 4% carbon dioxide concentration. Figure 8 was prepared using these conversion factors and shows trend lines that are similar to the natural indoor carbonation exposure shown in Figure 7(a).

Cement	(a) At 37 MPa		(b) At 25 mm cover		(c) At w/c = 0.55		(d) At 25 mm cover	
	Carbonation depth: mm		Characteristic strength: MPa		Carbonation depth: mm		w/c ratio	
	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered	Indoor	Outdoor sheltered
CEM I	30	18	42	20	27	17	0.54	0.67
CEM II/A (6–20% LS)	33	23	44	34	32	24	0.49	0.56
CEM II/B (21–35% LS)	39	35	48	45	44	29	0.42	0.51

Table 4. Fifty-year extrapolated carbonation depth, characteristic cube strength and w/c ratio of PC and PLC concretes for different design parameters

Figure 8. Extrapolated carbonation depth at 50 years of PC and PLC concretes based on accelerated carbonation exposure (3–5% carbon dioxide concentration) at different characteristic cube strengths

Carbonation depth at specified w/c ratio

The 50-year expected carbonation depths of concrete with respect to w/c ratio for natural exposure of indoor, outdoor sheltered and outdoor unsheltered conditions are presented in Figures 9(a), 9(b) and 9(c) respectively. The suggested maximum w/c ratio of 0.55 for XC3 exposure provided by BS EN 206:2013 (BSI, 2013) and the conforming minimum concrete cover of 25 mm as specified in Eurocode 2 (BS EN 1992-1-1:2004+A1:2014 (BSI, 2004)) are also shown in Figure 9. This figure has been developed based on the results used in Figure 3, and in addition the carbonation data of those PLC mixes for which PC control mixes were not adopted by the authors, after they were subject to the selection criterion based on mix limitations for the carbonation exposure.

The relative resistance to carbonation of PC and PLC concretes shown in Figure 9 are similar to that in Figure 7 (with respect to characteristic strength). For comparable carbonation to PC concrete at 0.55 w/c ratio, as an example, subjected to natural indoor and outdoor sheltered exposures, Figure 9 suggests that the w/c ratio of PLC concrete made with CEM

II/A (6–20% LS) and CEM II/B (24–35% LS) need to be reduced by about of 0.06 and 0.13, respectively.

Taking a w/c ratio of 0.55 and a concrete cover of 25 mm, the corresponding carbonation depths and w/c ratios of concrete made with PC and PLC as provided in BS EN 197-1:2011 (BSI, 2011) were obtained and are given in Table 4 columns (c) and (d).

The 50-year carbonation depths derived for the accelerated exposure measurements at 3–5% carbon dioxide concentration, using the established conversion factors of 0.59, 0.79 and 0.90 for PC, CEM II/A (6–20% LS) and CEM II/B (21–35% LS), respectively, are shown plotted in Figure 10. Although, similarly to Figure 9, there is considerable scatter within the results, an average conversion factor of 1 week accelerated carbonation is equivalent to 0.75 years of natural indoor exposure and may be adopted for practical convenience.

In situ carbonation measurements

Guiglia and Taliano (2013) reported the results of an extensive study undertaken involving Italian highway infrastructure. The testing programme covered structures along 135 km on such different members as piers, abutments, tunnels and walls with the following testing parameters: overall range of age at field measurement 1–5 years; LS content up to 25%; outdoor sheltered exposure for abutments, piers and tunnels; outdoor unsheltered exposure for walls; range of mean relative humidity, $RH = 64$ –75%; range of mean in situ core compressive strength 27–45 MPa; mean carbonation depth range for a duration of 1 to 5 years, for sheltered and unsheltered exposures, were 3–19 mm and 2–13 mm, respectively. Although the duration exposure for which the results are reported is short, the majority of the results show that PLC concrete had higher carbonation rates than the PC concrete for both type of exposures.

However, contrary to the Italian project, in another set of in situ carbonation measurements of concrete road pavements constructed in Canada during 2008–2009, with the carbonation measurements taken at an age of 3–4 years, PC concrete was found to carbonate at a faster rate than PLC concrete (Hossack *et al.*, 2014). Some of the details provided are LS content, 12%; w/c ratio, 0.37–0.44; in situ core strength, 43–59 MPa; outdoor sheltered exposure; measured carbonation within the range of 0.5–5.0 mm. Clearly some important information is missing and this, together with the early age for which carbonation data is only available, makes the assessment of PLC concrete difficult, if not impossible.

Influence of limestone on carbonation-induced reinforcement corrosion

The effect of LS addition on carbonation-induced corrosion of reinforcement is an important topic, yet only a few studies

Figure 9. Extrapolated carbonation depth at 50 years of PC and PLC concretes subjected to natural carbonation exposures: (a) indoor; (b) outdoor sheltered; (c) outdoor unsheltered, at different w/c ratios

Figure 10. Extrapolated carbonation depth at 50 years of PC and PLC concretes based on accelerated carbonation exposure (3–5% carbon dioxide concentration) at different w/c ratios

have been found to have reported on the subject. Moreover, based on the expectation that use of LS as a component of cement is likely to increase, and the obvious susceptibility of PLC concrete to carbonation as identified in the previous sections, the effect of LS use on the reinforcement corrosion of concrete can give rise to concern. However, given the limited number of studies (Bolzoni *et al.*, 2006, 2014; Matthews, 1994; Parrott, 1994, 1996; Redaelli and Bertolini, 2011a, 2011b, 2014; Sistonen *et al.*, 2008) reporting on reinforcement corrosion after cover has fully carbonated, and the complexity of the test methodology and the measurements used, the information available in the literature can at present only be examined in a qualitative manner, as summarised in Table 5.

Table 5 shows that, in general, the test specimens were made with cement blends of 0–25% LS content with w/c ratios of 0.55–0.71 and subjected to natural carbonation exposure for up to 5 years or accelerated carbonation conditions for up to 25 weeks. The corrosion of steel reinforcement was measured in different terms as weight loss of reinforcement (g/m^2), corrosion current (mA/m^2) and corrosion rate ($\mu\text{m/year}$). For the studies that have been undertaken, PLC concrete has been

found to show a higher rate of reinforcement corrosion than the corresponding PC concrete. The rate of corrosion has been found to be not significantly affected by w/c ratio or the period of moist curing (Parrott, 1994), although some studies have produced conflicting results, showing that the corrosion rate of PLC increases with a rise in the w/c ratio (Redaelli and Bertolini, 2011a, 2011b).

Measures to minimise carbonation effect of PLC concrete

The effect of LS addition on the carbonation of concrete can be minimised by a number of means. Although increasing the moist curing will certainly help to enhance the resistance of PLC concrete against carbonation by developing a less porous and less permeable concrete, to achieve this in practice can be difficult, owing to present construction practices. Other possible options for improving the carbonation resistance of PLC concrete are listed below.

- Restricting the LS addition content to a smaller proportion, namely, to a maximum of 20%. Such a cement will be in compliance with PLC of type CEM II/A (6–20% LS) as in BS EN 197 (BSI, 2011). Although this option may be used without greatly reducing the carbonation resistance of concrete, it would be less effective in minimising the embodied carbon of the cement industry.
- Increasing the specified characteristic strength of concrete by a significant reduction in its w/c ratio using a high-range water-reducing admixture. This option should enhance the durability and sustainability characteristics of concrete (Dhir *et al.*, 2000, 2004, 2006).
- Increasing the thickness of concrete cover could be considered as an additional obvious choice. Nevertheless, this will impact structural design and sustainability aspects, and is unlikely to be preferred by the design engineer.

Comparison of carbonation resistance of concrete made with PLC, FA and GGBS

This is the third paper in the series of studies planned to assess the effect of cement additions on the resistance to carbonation of concrete, where the first two have dealt with the effect of FA (Lye *et al.*, 2015) and GGBS (Lye *et al.*, 2016). To facilitate a meaningful comparison in the performance of the three major additions, all adopted by EN 197-1 (BSI, 2011) for use in concrete as a component of cement, as mentioned before, the same methodology and formatting have been adopted for each of the studies in the series. Figure 11 and Figure 12 and Tables 6 and 7 summarise their relative performance, as discussed below.

Replacement effect

At the same replacement level, and in a concrete of the same composition, FA can be expected to give the highest

References	Main points emerging
(a) Studies where PLC concrete is assessed alongside PC reference concrete	
Matthews (1994)	Corrosion rate of PLC concrete was higher than that of PC concrete Reinforcement corrosion measurement: percentage rebar weight loss; range of PC results: 0.14–0.19; range of PLC (5% LS) results: 0.15–0.21; range of PLC (25% LS) results: 0.32–0.45 Prism specimen: 100 × 100 × 300 mm; concrete cover: 10 mm; LS contents: 0, 5 and 25%; w/c ratio: 0.60; moist curing: 28 d; exposure: natural outdoor unsheltered; duration: 5 years; equal w/c mix
Parrott (1994)	Corrosion rate of PLC concrete was slightly higher than that of PC concrete and was not significantly affected by w/c ratio and curing duration Reinforcement corrosion measurement: rebar weight loss (g/m ²); range of PC results: 9–17 g/m ² ; range of PLC (5% LS) results: 11–19 g/m ² Cube specimen: 100 × 100 × 100 mm; concrete cover: 4 mm; LS contents: 0 and 5%; w/c ratio: 0.59–0.71; moist curing: 3 and 545 d; exposure: natural indoor, outdoor sheltered and outdoor unsheltered; duration: 4 years; equal w/c mix
Parrott (1996)	Corrosion rate of PLC concrete was higher than that of PC concrete Reinforcement corrosion measurement: rebar weight loss (g/m ²); range of PC results: 7–11 g/m ² ; range of PLC (15% LS) results: 8–15 g/m ² ; range of PLC (19% LS) results: 15–26 g/m ² ; range of PLC (25% LS) results: 21–30 g/m ² Cube specimen: 100 × 100 × 100 mm; concrete cover: 4 mm; LS contents: 0, 15, 19 and 25%; w/c ratio: 0.60; moist curing: 1–28 d; exposure: natural indoor; duration, 1.5 years; equal w/c mix
(b) Studies where only PLC concrete has been assessed	
Bolzoni <i>et al.</i> , (2006, 2014)	The steel rebar of PLC concrete exhibited a high corrosion rate Reinforcement corrosion measurement: corrosion rate through linear polarisation resistance method (µm/year), PLC result: 12 µm/year Prism specimen: 200 × 250 × 50 mm; concrete cover: 20 mm; LS content: 14%; w/c ratio: 0.60; moist curing: 28 d; carbon dioxide: 10%; temperature: 25°C; RH: 65%, duration: 25 weeks
Redaelli and Bertolini (2014)	The corrosion rate of PLC concrete was considered to be on the moderate level Reinforcement corrosion measurement: corrosion current (mA/m ²), PLC result: 4 mA/m ² Prism specimen: 40 × 40 × 160 mm; concrete cover: 15 mm; LS content: 13%; w/c ratio: 0.65; moist curing: 7 d; carbon dioxide: 2%; temperature: 21°C; RH: 65%, duration: 6 weeks
Redaelli and Bertolini (2011a, 2011b)	The corrosion rate results of PLC concrete reflected high activity and increased with increasing w/c ratio Reinforcement corrosion measurement: corrosion current (mA/m ²), range of PLC results: 15–18 mA/m ² Cylinder specimen: 60 × 300 mm; concrete cover: 25 mm; LS content: 15%; w/c ratio: 0.55–0.70; moist curing: 7 d; carbon dioxide: 6%; temperature: 20°C; RH: 60%, duration: 18 weeks
Sistonen <i>et al.</i> (2008)	The corrosion rate results for PLC concrete indicated active corrosion Reinforcement corrosion measurement: corrosion current (mA/m ²), PLC result: 16 mA/m ² Cylinder specimen: 44 × 200 mm; concrete cover: 15–19 mm; LS content: 13%; w/c ratio: 0.70; air curing: 21 d; carbon dioxide: 7%; temperature: 22°C; RH: 75%, duration: 10 weeks

Table 5. Summary of influence of LS addition on carbonation induced corrosion

rate of carbonation followed by LS and GGBS, see Figure 11. This can be explained in terms of the reactivity of each of the three additions and the consumption of calcium hydroxide (Ca(OH)₂). However, given that GGBS is usually used at a

much higher replacement level, depending upon the actual replacement level, in practice the carbonation of concrete with the use of GGBS may be higher than that with LS and FA.

Figure 11. Comparison of LS, FA and GGBS concretes; effect of replacement

Fifty-year extrapolated carbonation depth

The estimated 50-year carbonation depth of PLC, FA and GGBS concretes designed on an equal strength basis (Figures 12(a) and 12(b)) is lower than that of concretes based on an equal w/c ratio basis (Figures 12(c) and 12(d)). Taking the minimum concrete cover of 25 mm and w/c ratio of 0.55 or characteristic cube strength of 37 MPa as per BS EN 206 (BSI, 2013), for indoor exposure conditions, all concretes (reference PC, PLC, FA and GGBS) are likely to surpass the adopted cover before the time period of 50 years (Figures 12(a) and 12(c)). Nevertheless, for outdoor sheltered exposure conditions, this minimum concrete cover is

- (a) adequate for concrete made with
 - (i) CEM I,
 - (ii) CEM II/A (6–20% LS),
 - (iii) CEM II/A (6–20% FA)
 - (iv) CEM II/B-S (21–35% GGBS)
- (b) not adequate for concrete made with:
 - (i) CEM II/B (21–35% LS)
 - (ii) CEM II/B (21–35% FA)
 - (iii) CEM IV/B (36–55% FA)
 - (iv) CEM III/A (36–65% GGBS)
 - (v) CEM III/B (66–80% GGBS).

Mix design adjustment for similar carbonation

In order to obtain comparable carbonation to PC concrete, the concrete mix design adjustment made in terms of reduction in

w/c ratio or increase in compressive strength for PLC and FA concretes will be more than for GGBS concrete at the same replacement level (Table 6).

Accelerated and natural indoor carbonation relationship

Although the relationship for the natural indoor and accelerated carbonation of concrete developed for PLC in this study and for FA and GGBS by (Lye *et al.*, 2015, 2016) are dissimilar (Table 7), for practical purposes, a conversion factor of 1 week of accelerated carbonation (at 3–5% carbon dioxide concentration) can be assumed to be equivalent to 0.65 years of natural indoor carbonation.

Conclusions

- (a) In general, combinations of LS with PC, similar to the range in BS EN 197-1 (BSI, 2011), lead to increased carbonation. The degree of this increase depends on the composition of concrete in terms of its w/c ratio and strength, maturity and pore structure as it is subjected to carbonation.
- (b) Carbonation measurements relative to the corresponding PC concrete suggest that the depth of carbonation increases with LS content, giving an increase of the order of 50% with 30% LS content, which is similar to PLC type CEM II/B in BS EN 197:2011 (BSI, 2011).
- (c) For PLC concrete designed in terms of equal strength or equal w/c ratio to PC concrete, the carbonation of PLC concrete designed on the basis of equal w/c ratio is higher than that designed on an equal strength basis, for both natural and accelerated carbonation exposures. This difference in the performance of the two sets of PLC mixes can be narrowed with the use of finer LS and/or extended moist curing of concrete mixes designed on the equal w/c ratio basis. PLC mixes designed on an equal strength basis and exposed to a prolonged moist curing can attain a carbonation resistance near to that of PC concrete.
- (d) In studying the estimated 50 years' carbonation of concrete with respect to its strength, w/c ratio and cover, in compliance with the mix limits of BS EN 206-1:2013 (BSI, 2013) for the carbonation exposure classes, outdoor unsheltered exposure was found to cause the lowest carbonation and indoor the highest. Additionally, the results showed that, for a certain exposure class and specified strength and w/c ratio, the required thickness of concrete cover increases as the LS content of the cement is increased. On the other hand, for a particular cover, the required strength increases and w/c ratio decreases with the LS content of the cement.
- (e) One week of accelerated carbonation of PLC concrete, at 3–5% carbon dioxide concentration, was found to be

Figure 12. Comparison of 50-year estimated carbonation depth for LS, FA and GGBS concretes. Note: Data normalised so that the 50-year estimated carbonation of PC reference in PLC, FA and GGBS results is similar under the same carbonation exposure and

data for CEM I/A (6–20% GGBS) and CEM I/B (81–95% GGBS) under outdoor carbonation not available: (a) at 37 MPa, indoor; (b) at 37 MPa, outdoor sheltered; (c) at $w/c = 0.55$, indoor; (d) at $w/c = 0.55$, outdoor sheltered

Cement	Mix adjustment for similar carbonation	
	Additional strength, MPa ^a	w/c reduction ^b
CEM I	0.0	0.0
CEM II/A (6–20% LS)	5.5	0.06
CEM II/A (6–20% FA)	5.0	0.05
CEM II/A-S (6–20% GGBS)	n/a	n/a
CEM II/B (21–35% LS)	10.5	0.13
CEM II/B (21–35% FA)	7.5	0.15
CEM II/B-S (21–35% GGBS)	5.5	0.10
CEM IV/B (36–55% FA)	10.0	0.25
CEM III/A (36–65% GGBS)	9.5	0.20
CEM III/B (66–80% GGBS)	13.0	0.22

^aPC at 37 MPa

^bPC at 0.55 w/c

Table 6. Comparison of PLC, FA and GGBS concretes, mix adjustment for similar carbonation

Cement type	Duration equivalent to 1 week accelerated exposure: years
PLC	0.58–0.92
FA	0.38–0.54
GGBS	0.60–0.65

Table 7. Relationship between accelerated and indoor carbonation for PLC, FA and GGBS concretes

about equivalent to 0.75 years of natural indoor exposure.

- (f) The rate of corrosion in PLC concrete, upon carbonation reaching the reinforcement, was found to be higher than that in PC concrete.
- (g) In-situ carbonation measurements of 1–5 years of concrete structures made with PC and PLC showed that although the carbonation varies with exposure conditions, PLC concrete is likely to carbonate at a faster rate than the corresponding PC concrete.
- (h) In order to lower the carbonation influence of PLC on structural concrete, consideration should be given to restricting the addition of LS, and increasing the target strength and/or the thickness of concrete cover. Nonetheless, these measures must be assessed alongside the other design requirements of durability and sustainability.
- (i) Comparing the carbonation performance of concrete made with PLC with concrete made with cement

containing FA (Lye *et al.*, 2015) and GGBS (Lye *et al.*, 2016), the main points to note are given below.

Similarities: Concrete made with cement containing PLC, FA and GGBS carbonates at a higher rate than concrete made with PC, and this increase is higher for concrete designed on an equal w/c ratio basis than on an equal strength basis. The minimum concrete cover suggested for a characteristic cube strength of 37 MPa or w/c ratio of 0.55 as stated in Eurocode 2 for XC3 exposure needs to be reviewed for concrete containing LS, FA and GGBS.

Differences: As in practice GGBS is generally used in structural concrete at a considerably higher level than FA or LS, it can be expected to be at a higher risk than PLC and FA concretes. The accelerated indoor carbonation relationship of concrete differs for LS, FA and GGBS materials, but even so, for ease of use, a figure of 1 week of accelerated carbonation equals 0.65 years of natural indoor exposure has been proposed.

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