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Chloride ingress in concrete: limestone addition effects

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Chloride ingress in concrete: limestone addition effects

This paper presents analysis and evaluation of experimental results of chloride ingress and chloride-induced corrosion resistance of concrete made with Portland limestone cement (PLC). The results were mined from 169 globally published studies from 32 countries since 1989, yielding a matrix of 20 500 data points. This review showed that chloride ingress in concrete increases with increasing limestone (LS) content, within the range permitted in BS EN 197-1:2011. However, this effect is less for PLC concrete mixes designed for strength equal to corresponding Portland cement (PC) concrete mixes than those designed on an equal water/cement (w/c) basis. The results also showed that Eurocode 2 specifications for chloride exposure, in terms of characteristic cube strength of concrete or w/c ratio, may need to be reviewed for the use of LS with PC. This study also investigated other influencing factors such as cement content, LS fineness, the method of producing PLC, aggregate volume content and particle size, combined chloride and sulfate environment, curing and exposure temperature. A comparison was made for the performance of PLC concrete in terms of pore structure and related properties, strength, carbonation and chloride ingress. Procedures to improve the resistance of PLC to chloride ingress in concrete are proposed.

Introduction

The use of limestone (LS) as a building material dates back to ancient times, when calcined LS or gypsum was used to make mortar (Mayfield, 1990). LS has been used as a main raw material in the production of Portland cement (PC) clinker since 1824 and, over the last few decades, has also been used in ground form as a filler aggregate as well as an addition to PC to obtain cement combinations and Portland limestone cements (PLCs) and Portland composite cements as per BS EN 197-1:2000 (BSI, 2000).

The earliest attempt at the use of LS addition with PC was in 1965 in Germany. In 1979, French cement standards permitted its use as an addition. This was followed by its recognition in various other standards, such as the Canadian standard in 1983 (at 5% addition), the British standard in 1992 (up to 20% addition) and European standard EN 197-1 in 2000 as PLCs CEM II/A-L and CEM II/B-L with LS contents of 6–20% and 21–35%, respectively, as well as potential for its use in combination with other cementitious materials. The highest permissible LS addition tends to vary according to national and international standards, ranging from 10% to 35% (Table 1).

The use of PLC has been increasing steadily worldwide, with sustainable construction focus enforcing reductions in energy consumption and carbon dioxide emissions associated with PC manufacture. It is generally accepted that 15% PC replacement by LS can reduce the carbon dioxide footprint of concrete by approximately 12% (Schmidt *et al.*, 2010). In addition, about 1.4 t of primary raw materials are required to produce 1 t of

PC, while the production of PLC requires nearly 10% less primary raw resources (TCC, 2010). Moreover, among all the cement addition materials (e.g. ground granulated blast-furnace slag (GGBS), fly ash (FA), silica fume (SF) and metakaolin (MK)), LS is the most widely available natural material as calcium carbonate (Thenepalli *et al.*, 2015), and it is also typically available in large amounts near PC manufacturing plants.

Consequently, a thorough understanding of the behaviour of LS used in combination with PC for concrete production is important, not only in terms of the general performance of PLC as per BS EN 197-1:2011 (BSI, 2011), but also in terms of the durability of concrete made with PLC. Resistance to chloride ingress is crucial for the durability of reinforced concrete subjected to marine environments or de-icing salts. If chloride penetrates concrete, it can cause severe corrosion of the reinforcement. This threatens safety, reduces performance and distorts the appearance of the concrete. Although PLC has been commonly studied with respect to the durability of concrete, the information available is disjointed and often unhelpful in further understanding and developing the usage of PLC in concrete construction.

A series of studies was undertaken by the authors to examine the effect of LS use in combination with PC on the durability of concrete. The first study in this series addressed the effect of PLC on properties related to pore structure (Elgalhud *et al.*, 2016) and the second dealt with carbonation resistance (Elgalhud *et al.*, 2017). This study deals with chloride ingress and chloride-induced corrosion in concrete made with PLC.

Table 1. LS contents permitted in PLC in some national and international standards

Country	LS content: %	Standard/source
Standards adopting maximum LS addition level of 35%		
UK and Europe	CEM II/A: 6 to 20 CEM II/B: 21 to 35	BS EN 197-1:2011 (BSI, 2011), EN 197-1:2011 (CEN, 2011)
South Africa	CEM II/A: 6 to 20 CEM II/B: 21 to 35	SANS 50197-1:2013 (SABS, 2013) (based on EN 197-1:2011 (CEN, 2011))
Singapore	CEM II/A: 6 to 20 CEM II/B: 21 to 35	SS EN 197-1:2014 (SSC, 2014)
Mexico	6 to 35	NMX-C-414-ONNCCCE-2014 (MS, 2014)
Standards adopting maximum LS addition level below 35%		
USA	>5 to 15	ASTM C 595-M-2016 (ASTM, 2016)
	>5 to 15	Aashto M240-2016 (Aashto, 2016)
Canada	>5 to 15	CSA A3001-2013 (CSA, 2013)
Australia	8 to 20	AS 3972-2010 (SA, 2010)
New Zealand	Up to 15	SNZ 3125:1991 (SNZ, 1991) (amended in 1996)
China	Up to 15	Hooton (2015)
Iran	6 to 20	Ramezaniapour <i>et al.</i> (2009)
Former USSR	Up to 10	Tennis <i>et al.</i> (2011)
Argentina	≤20	Tennis <i>et al.</i> (2011)
Brazil	6 to 10	Tennis <i>et al.</i> (2011)
Costa Rica	≤10	Tennis <i>et al.</i> (2011)
Peru	≤15	Tennis <i>et al.</i> (2011)

Aim and objectives

The aim of this study was to analyse, evaluate and synthesise, in a systematic manner, globally published experimental data on chloride ingress and chloride-induced corrosion in concrete made with PC and LS. For practical reasons, comparisons with PC concrete were used to assess the potential effects of LS addition on concrete performance.

Methodology

Extensive sourcing of published experimental results on the subject was undertaken using different databases and citation indices in order to ascertain the extent and quality of research that has been undertaken and to obtain the available published material. The total number of sourced publications, in the English medium, was 169, originating from 32 countries worldwide between 1989 and 2016 (Figure 1), with the most significant contributions coming, in descending order, from Italy, the USA, Canada, UK, China and France (Figure 2).

The sourced publications were categorised as shown in Figure 3, and explained in more detail as follows.

- Narrative reviews summarise different studies, from which conclusions may be drawn in general terms, contributed by the reviewers' own experience, and where the outcomes are very much qualitative rather than quantitative. Ten of the sourced publications were narrative reviews (ACI, 2015; Benn *et al.*, 2012; CSWP, 2011; Hawkins *et al.*, 2003; Hooton *et al.*, 2007; Hooton, 2010; Kaur *et al.*, 2012; Detwiler and Tennis, 1996; Müller, 2012; Van Dam *et al.*, 2010).
- Experimental results deal with laboratory testing work undertaken using standard specimens (cubes, cylinders or

prisms) under controlled conditions (e.g. specified temperature and duration).

- In situ measurements comprise studies undertaken on concrete structures (new or old), where the concrete has been subjected to site conditions and usually the tested specimens are in the form of extracted cores. Only one study dealt with in situ measurements (Hossack *et al.*, 2014).
- Modelling studies involve theoretical work to simulate experimental conditions. Modelling work relating to chloride ingress in PLC was undertaken in nine studies (Aguayo *et al.*, 2014; Attari *et al.*, 2012, 2016; Climent *et al.*, 2002; Demis and Papadakis, 2011, 2012; Demis *et al.*, 2014; Faustino *et al.*, 2014; McNally and Sheils, 2012). However, such work is outside the scope of the present study.

The experimental works were further divided into Portland composite cement mixes and PLC.

- Portland composite cement mixes consisted of ternary or quaternary blends of PC, LS and other supplementary cementitious materials, such as GGBS, FA, SF and MK. In total, 31 studies using composite cement mixtures were sourced (Abd-El-Aziz and Heikal, 2009; Alonso *et al.*, 2012; Attari *et al.*, 2012; Badogiannis *et al.*, 2015; Bentz *et al.*, 2013; Bjegovic *et al.*, 2012; Chaussadent *et al.*, 1997; Dave *et al.*, 2016; Dogan and Ozkul, 2015; Ekelu and Murugan, 2012; Güneysisi *et al.*, 2005, 2006, 2007; Holt *et al.*, 2009, 2010; Hu and Li, 2014; Kathirvel *et al.*, 2013; Katsioti *et al.*, 2008; Lang, 2005; Li *et al.*, 2013, 2014; Lotfy and Al-Fayez, 2015; Mohammadi and South, 2016;

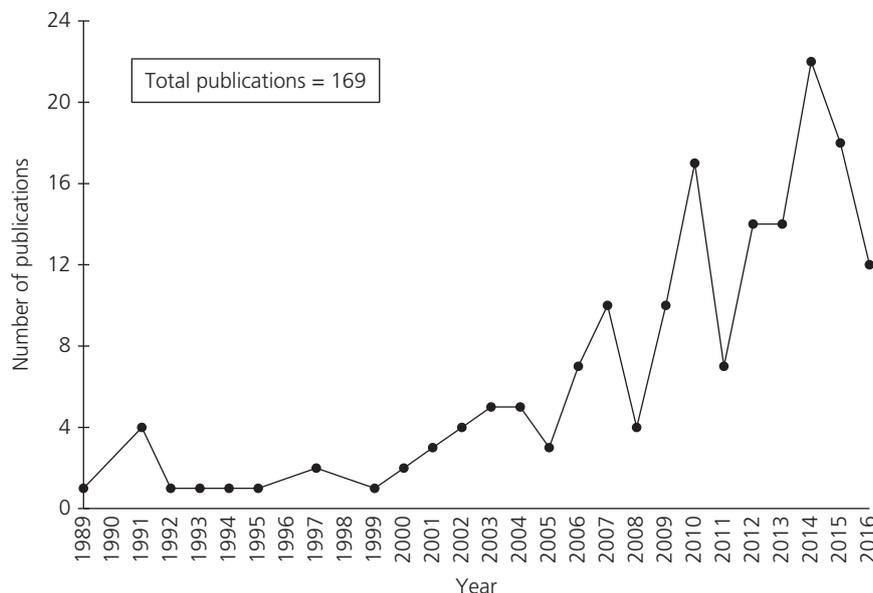


Figure 1. Annual distribution of collected publications

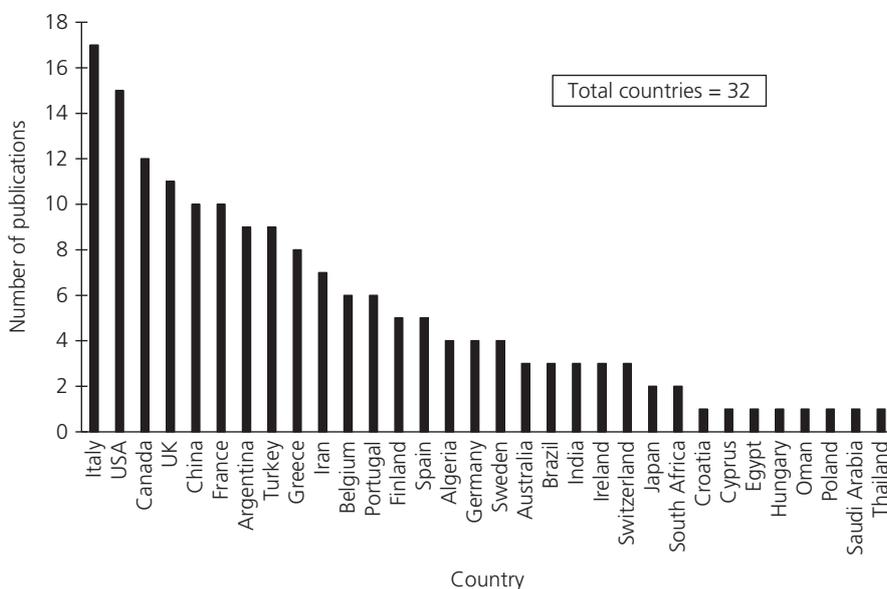


Figure 2. Country distribution for first author of the collected publications

Pipilikaki and Katsioti, 2009; Shao-li *et al.*, 2015; Siad *et al.*, 2015; Sideris and Anagnostopoulos, 2013; Tanesi *et al.*, 2013; Thomas *et al.*, 2012; Villagrán Zaccardi *et al.*, 2010, 2013). However, the results of these works could not be used in this study because the sole effect of LS could not be clearly identified.

- The publications that studied the behaviour of PLC in chloride-bearing exposure were divided into chloride ingress measurements and chloride-induced corrosion

(Figure 3). Some of the studies did not provide results for corresponding PC mixtures (Ahmad *et al.*, 2014; Assie *et al.*, 2006; Audenaert and De Schutter, 2009; Audenaert *et al.*, 2007, 2010; Beigi *et al.*, 2013; Bertolini and Gastaldi, 2011; Bertolini *et al.*, 2002, 2004a; Bolzoni *et al.*, 2006, 2014; Brenna *et al.*, 2013; Carsana *et al.*, 2016; Chiker *et al.*, 2016; Climent *et al.*, 2006; Corinaldesi and Moriconi, 2004; Figueiras *et al.*, 2009; Franzoni *et al.*, 2013; Frazão *et al.*, 2015; Kenai *et al.*, 2008; Matos *et al.*,

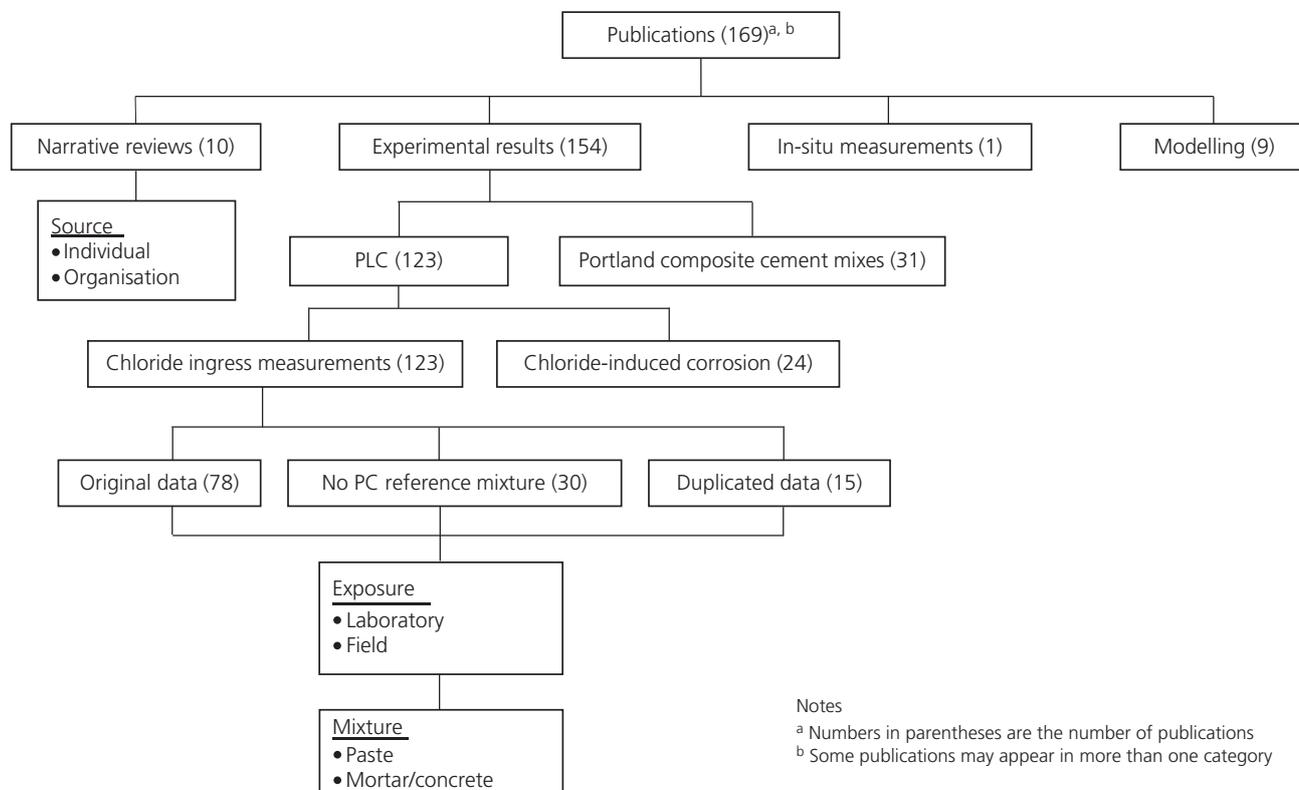


Figure 3. Distribution of publication data from the literature search

2016; Meira *et al.*, 2014; Ramezani pour and Afzali, 2015; Romano *et al.*, 2013; Sánchez *et al.*, 2008; Sfikas *et al.*, 2013; Sistonen *et al.*, 2008; Tittarelli and Moriconi, 2011; Yüksel *et al.*, 2016; Zhang *et al.*, 2016). Some publications contained duplicated data. Additionally, some analyses were undertaken considering the type of exposure (laboratory or field as marine environment) and finally the type of cementitious mixture (paste and mortar/concrete).

It is important to note that wherever the term water/cement (w/c) ratio is used in this paper, 'cement' refers to the combination (binder) of PC clinker and LS addition.

Overview of the literature

Although limited in number and lacking in detailed analysis of the data, the narrative reviews from both organisations and individual researchers (Table 2) suggest that there is some agreement among the studies in that chloride ingress in concrete is not significantly affected with the addition of LS up to 15–20% (i.e. the use of PLC such as a CEM II/A cement of BS EN 197-1:2011 (BSI, 2011)). However, some reviews suggest that there are differences in opinion due to differences in the concrete mixes tested and the test methods used to determine the rate of chloride ingress.

A review of the experimental data in the literature, consisting of 123 studies summarised in Table 3, revealed that most results (57%) showed that the use of LS with PC leads to a higher rate of chloride ingress. A variety of reasons have been suggested for this increase in chloride ingress in PLC concrete. In contrast, 17% of the results suggest that chloride ingress in PLC concrete can be lower than that in corresponding PC concrete, with 2% of the results indicating no change and 9% showing a variable trend; there were no corresponding PC concrete mixes tested in 15% of the data and therefore the PLC data could not be compared with corresponding PC concrete mixes.

Analysis of published data

Test methods and procedures employed

The test conditions employed to measure the effect of LS on chloride ingress in concrete in the published studies are summarised in Table 4. The main points to be noted are as follows.

- Chloride exposure. The vast majority of the studies measured chloride ingress using a non-natural exposure, with specimens tested in a laboratory using different accelerated methods.
- Material. The majority of the investigations adopted the use of mortar and concrete as test specimens.
- Specimen. The choice of test specimens in the form of cylinders, prisms or cubes appeared to be influenced by the

Table 2. Summary of the findings of narrative reviews regarding the performance of the PLC under chloride ingress

Published work	Number of cited references	Main observation
Organisations		
ACI Committee 211, USA (ACI, 2015)	2	Rapid chloride permeability of PLC with 10–15% LS is equivalent to PC, while other studies showed that PLC with 20% LS reduced the chloride ion diffusion coefficient by about 20% compared with PC
Concrete Society, UK (CSWP, 2011)	3	LS will not produce any significant improvement in resistance to chloride diffusion and may even reduce it slightly
Hawkins <i>et al.</i> (2003), Portland Cement Association, USA	7	Mixed results of PLC when compared with PC
Hooton <i>et al.</i> (2007), Cement Association of Canada, Canada	9	PLC (with LS up to 20%) and PC have similar durability to chloride ingress
Detwiler and Tennis (1996), Portland Cement Association, Canada	2	PLC containing 15% LS and PC have equivalent performance with respect to chloride permeability and chloride diffusion
Individual studies		
Benn <i>et al.</i> (2012)	7	There appear to be differences of opinion in the published data that are related to differences in the concrete mixes tested and the test methods used to determine the rate of chloride ingress
Hooton (2010)	1	PLC (with LS up to 20%) and PC have similar durability to chloride ingress
Kaur <i>et al.</i> (2012)	1	Differences in diffusivity coefficient of concrete up to 15% LS, compared with PC concrete, were relatively minor and increased slightly with w/c ratio
Müller (2012)	3	PLC has a comparable performance to PC under chloride ingress
Van Dam <i>et al.</i> (2010)	1	PLC (with 10% LS) and PC show similar rapid chloride permeability

Table 3. Suggested causes of the behaviour of PLC concrete under chloride ingress

Observation of chloride ingress in PLC mixes ^a	Main suggested causes	Number of tested mixes		
		Laboratory	Field	Total
Higher (156) (laboratory, 154; field, 2)	Cement			
	Reduction of PC	14	0	14
	Reduced production of calcium silicate hydrate	2	0	2
	Compounds of C3A in PLC concrete have a lower binding capacity	5	1	6
	Higher level of OH ⁻ ions presents in the pore fluid of the concrete made with LS	8	0	8
	Design			
	Higher w/c ratio	18	0	18
	Hardened properties			
	Higher porosity/coarser pore structure	42	1	43
	Higher permeability	15	0	15
	Not given	50	0	50
Lower (49) (laboratory, 48; field, 1)	Cement			
	Higher specific area of LS	1	0	1
	Design			
	Lower w/c ratio	1	0	1
	Sufficient curing	1	0	1
	Higher strength	6	0	6
	Hardened properties			
	Lower porosity	6	0	6
	Not given	33	1	34
No change (5) (laboratory, 5)	Equal strength	1	0	1
	Not given	4	0	4
Variable (26) (laboratory, 23; field, 3)	Cement			
	Decreases with improved particle size distribution until optimum level (10–15% LS) and then increases due to dilution of PC	11	2	13
	Not given	12	1	13
No reference mixture (44) (laboratory, 44)	Not applicable	44	0	44

^aHigher/lower/no change/variable chloride ingress in PLC mixture with respect to corresponding reference PC mixture

Table 4. Test parameters of PLC chloride ingress measurements in the published literature

Parameter	Variable	Number ^a	Parameter	Variable	Number ^a			
1. Chloride exposure	Laboratory	275	2. Material	Cement paste	3			
	Field	5		Mortar/concrete	277			
3.1 Specimen type	Cylinder/disc	161	3.2 Specimen preparation	Sealed	68			
	Prism	46		Unsealed	14			
	Cube	49		Unspecified	198			
	Column/slab	4						
	Not given	20						
4. Test method	Electrical indication (RCPT)	120	5. Standard/reference	ASTM C 1202 (ASTM, 2012b)	100			
				ASSHTO T277 (ASSHTO, 2015)	14			
				Not given	6			
	Steady-state migration	25		Dhir <i>et al.</i> (1990)	4			
				Page <i>et al.</i> (1981)	2			
				Truc <i>et al.</i> (2000)	3			
				Not given	16			
	Non-steady-state migration	106		NT Build 492 (Nordtest, 1999)	49			
				Luping and Nilsson (1993)	1			
				Nanukuttan <i>et al.</i> (2006)	3			
		SIA 262/1; SS, 2003	4					
		Gehlen and Ludwig (1999)	2					
		BAW, 2004	6					
Chloride profile	25	Not given	41					
		UNI 7928 (UNI, 1978)	8					
		ASTM C 1218 (ASTM, 2015)	2					
		ASTM C 1152 (ASTM, 2012a)	3					
Chloride conductivity	4	ASTM C 1152 (ASTM, 2012a)	3					
	2	Aashto T260 (Aashto, 2009)	2					
	1	NT Build 443 (Nordtest, 1995)	6					
6. Curing	Non-steady-state immersion	1	7. Pre-conditioning	Ait-Mokhtar <i>et al.</i> (2004)	1			
						Chronoamperometry		
6.1 Exposure	Moist	210	7.1 Preparation	Omitted	27			
				Air	5			
				Applied	201			
6.2 Duration: d	Not given	65	7.2 Duration: d ^b	Not given	52			
				1–14	32			
				15–28	112			
				56–91	66			
				>91	22			
				Not given	48			
6.3 Temperature: °C	20–30	218	7.3 Temperature: °C ^b	20–30	138			
				>30	4			
				Not given	58			
6.4 Humidity: %	80–100	215	7.4 Humidity: % ^b	45–85	68			
				40–80	5			
				Not given	60			
8. Laboratory conditions	Not given	60	9. Field conditions					
8.1 Chloride solution: %	<3	11	9.1 Exposure	Submerged in sea	1			
				3–5	152	Tidal exposure site	4	
				10–15	60	Marine aerosol	1	
				>15	8	9.2 Chloride solution: %	3–4	1
				Not given	44	Not given	5	
8.2 Duration: d	≤1	150	9.3 Duration: years	2	4			
				2–30	16			
				31–90	11			
				91–180	10			
				>180	33			
				Not given	55			
8.3 Temperature: °C	<20	2	9.4 Temperature: °C	2–20	1			
				20–30	194	Not given	5	
				>30	1	9.5 Humidity: %	>95	4
				Not given	78	Not given	2	

^aNumber is the sum of tested mixes^bData compiled from studies where pre-conditioning is applied

relevant specifications of the standard adopted in each specific study. The largest number of tests was carried out on cylinder/disc specimens.

- Test method. While various test methods have been used to measure chloride ingress, the two most commonly used methods were electrical indication based as on ASTM C1202 (ASTM, 2012b)/Aashto T277 (Aashto, 2015) (commonly referred to as the rapid chloride permeability test (RCPT) method) and non-steady-state migration, NT Build 492 test method (Nordtest, 1999).
- Curing. With few exceptions, and with the impact of the local standard specifications, most specimens were moist-cured at a relative humidity of 80–100% and temperature of 20–30°C for up to 28 d.
- Pre-conditioning. Although this information was generally lacking, in the studies that did provide this information the commonly adopted treatment was carried out at a temperature of 20–30°C and relative humidity of 45–85% for 1–7 d duration.
- Laboratory and field exposure conditions. The most commonly used laboratory exposure consisted of a chloride solution concentration of up to 5% for a duration of ≤ 30 d and temperature of 20–30°C, while field exposure (e.g. submerged in the sea or tidal exposure site) was generally for up to 3 years.

LS effect

Given that a large number of test parameters were involved in the test results (Table 4), the effect of LS inclusion on chloride ingress can best be analysed and evaluated in relation to the corresponding PC used as reference in the study. The reported results are plotted collectively in Figure 4. To visualise the data distribution and identify outliers, box and whisker plots are used. In developing Figure 4, the data points were dispersed slightly to prevent overlapping in order to provide a better view of the results. However, some of the data were not considered further. The excluded data were those

- with outliers at each LS replacement level using box and whisker plots
- where the corresponding value for reference PC concrete was not available to calculate the relative chloride ingress results required for the plot
- with excessively high relative values (greater than 200%) resulting from low chloride ingress measurements that were considered to be unrealistic
- where chloride ingress data were reported for paste specimens.

In addition, the same data reported in more than one publication were considered once only.

The best-fit relationship, showing the effect of LS on chloride ingress in concrete, using the mean values, is shown as a

solid line up to 50% LS content having a coefficient of correlation $R^2 = 0.84$, with another best-fit curve plotted as a broken line covering the results up to 35% LS content (the maximum limit permitted in BS EN 197-1:2011 (BSI, 2011) for structural concrete), having a coefficient of correlation $R^2 = 0.72$. Although the latter curve has a lower coefficient of correlation, it is considered to present a more realistic performance of PLC up to the upper limit permitted for structural concrete.

For convenience of reference, the range of BS EN 197-1:2011 (BSI, 2011) common cements with LS addition is also shown in Figure 4. It can be seen that, at 35% LS addition, chloride ingress in PLC concrete could be about 60% higher than that in the corresponding PC concrete, with performance comparable to that of PC at 5% LS content.

The results plotted in Figure 4 were separated in terms of strength and w/c ratio, and these are shown in Figures 5(a) and 5(b). The effect of LS addition for the mixes of equal strength (Figure 5(a)) shows that, although the results available are limited (compared with the equal w/c ratio results in Figure 5(b)), 10% LS addition may be used without adversely affecting the chloride ingress resistance of concrete; thereafter it starts to increase gently with further increases in LS content. An increase of 12% was found for 35% LS content. The mixes with equal w/c ratio (Figure 5(b)) show a similar trend (two trend lines are shown – the solid line for results up to 50% LS content and the broken line for results up to 35% LS content) to that for the overall results plotted in Figure 4, suggesting that, at 35% LS content, chloride ingress can be expected to increase by about 65%.

Curing effects

The influence of moist curing duration has been studied with LS contents of 0–35%, for durations of 1–360 d. The results are shown in Figures 6(a) and 6(b) for mixes with equal strength and equal w/c ratio. Recognising that the coefficients of correlation are generally low, the trend lines observed can only be considered qualitative. However, the following points of practical relevance can be noted.

- On an equal strength basis, the results are limited but show that PLC concrete with up to 15% LS (CEM II/A cement) can be expected to develop resistance to chloride ingress similar to a corresponding PC concrete.
- On an equal w/c ratio basis, the results show that the resistance to chloride ingress of PLC concrete in comparison to PC concrete can be expected to improve with moist curing duration, particularly with initial moist curing. While higher chloride ingress values were obtained, the difference between the two concretes decreases with time.

In addition, studies on the effect of curing on chloride ingress in PLC concrete (w/c ratio of 0.5, cement content of 350 kg/m³, LS contents of 0%, 9% and 18%, 28 d of moist

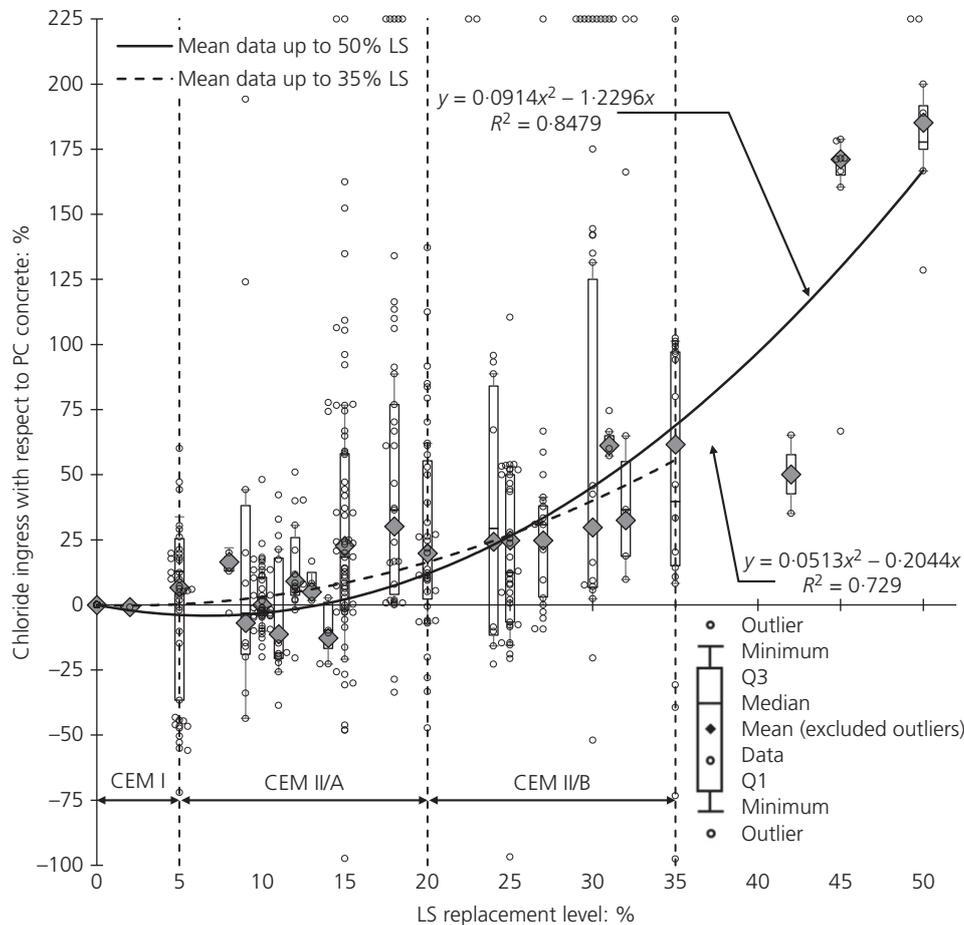


Figure 4. LS addition effect on chloride ingress in concrete. Data taken from Aguayo *et al.* (2014), Alunno-Rosetti and Curcio (1997), Assie *et al.* (2007), Barrett *et al.* (2014), Batic *et al.* (2010, 2013), Bentz *et al.* (2015), Bertolini *et al.* (2004b, 2007, 2011), Bonavetti *et al.* (2000), Bonneau *et al.* (2007), Boubitsas (2004, 2001), Calado *et al.* (2015), Cam and Neithalath (2010, 2012), Celik *et al.* (2014a, 2014b, 2015), Cochet and Jesus (1991), Cost *et al.* (2013), Courard and Michel (2014), Courard *et al.* (2005), Deja *et al.* (1991), Dhir *et al.* (2004, 2007), Fornasier *et al.* (2003), Gesoğlu *et al.* (2012), Ghiasvand *et al.* (2015), Ghrici *et al.* (2007), Githachuri and Alexander (2013), Güneysi *et al.* (2011), Hooton *et al.* (2010), Hornain *et al.* (1995), Hossack *et al.* (2014), Howard *et al.* (2015), Irassar *et al.* (2006, 2001), Juel and Herfort (2002), Kaewmanee and Tangtermsirikul (2014), Kobayashi *et al.* (2016), Kuosa *et al.* (2008, 2014), Leemann *et al.* (2010), Lemieux *et al.* (2012), Li and Kwan (2015), Livesey (1991), Lollini *et al.* (2014, 2015, 2016), Loser and Leemann (2007), Loser *et al.* (2010), Meddah *et al.* (2014), Menadi and Kenai (2011), Menéndez *et al.* (2007), Moir and Kelham (1993, 1999), Matthews (1994), Moukwa (1989), Müller and Lang (2006), Palm *et al.* (2016), Pavoine *et al.* (2014), Persson (2001, 2004), Pourkhorshidi *et al.* (2010), Ramezaniyanpour *et al.* (2009, 2010, 2014), Ranc *et al.* (1991), Selih *et al.* (2003), Shaikh and Supit (2014), Shi *et al.* (2015), Siad *et al.* (2014), Silva and de Brito (2016), Sonebi and Nanukuttan (2009), Sonebi *et al.* (2009), Sotiriadis *et al.* (2014), Tezuka *et al.* (1992), Thomas *et al.* (2010a, 2010b, 2010c), Thomas and Hooton (2010), Tsvilis and Asprogerakas (2010), Tsvilis *et al.* (2000), Uysal *et al.* (2012), Van Dam *et al.* (2010), Wu *et al.* (2016), Xiao *et al.* (2009), Yamada *et al.* (2006), Younsi *et al.* (2015) and Zhu and Bartos (2003)

and air curing, specimens immersed in 3% sodium chloride (NaCl) solution for up to 1 year (Bonavetti *et al.*, 2000; Irassar *et al.*, 2006) showed that chloride ingress increases with air curing and also that the rate of chloride ingress is greater for PLC concrete relative to PC concrete.

Exposure temperature

Studies investigating how the temperature of the chloride-bearing environment may affect the penetration of chlorides into PLC concrete relative to PC concrete are limited. The data available

from the two studies, with different test conditions (Moukwa, 1989; Yamada *et al.*, 2006), came to similar conclusions, namely that (a) at lower temperatures, chloride ingress in concrete is adversely affected with the inclusion of PLC and that (b) this is due to increased dissolution of calcium hydroxide ($\text{Ca}(\text{OH})_2$).

LS fineness and type of PLC (inter-grinding or blending)

The effects of LS fineness on chloride ingress in PLC concrete have been investigated over a range of fineness values

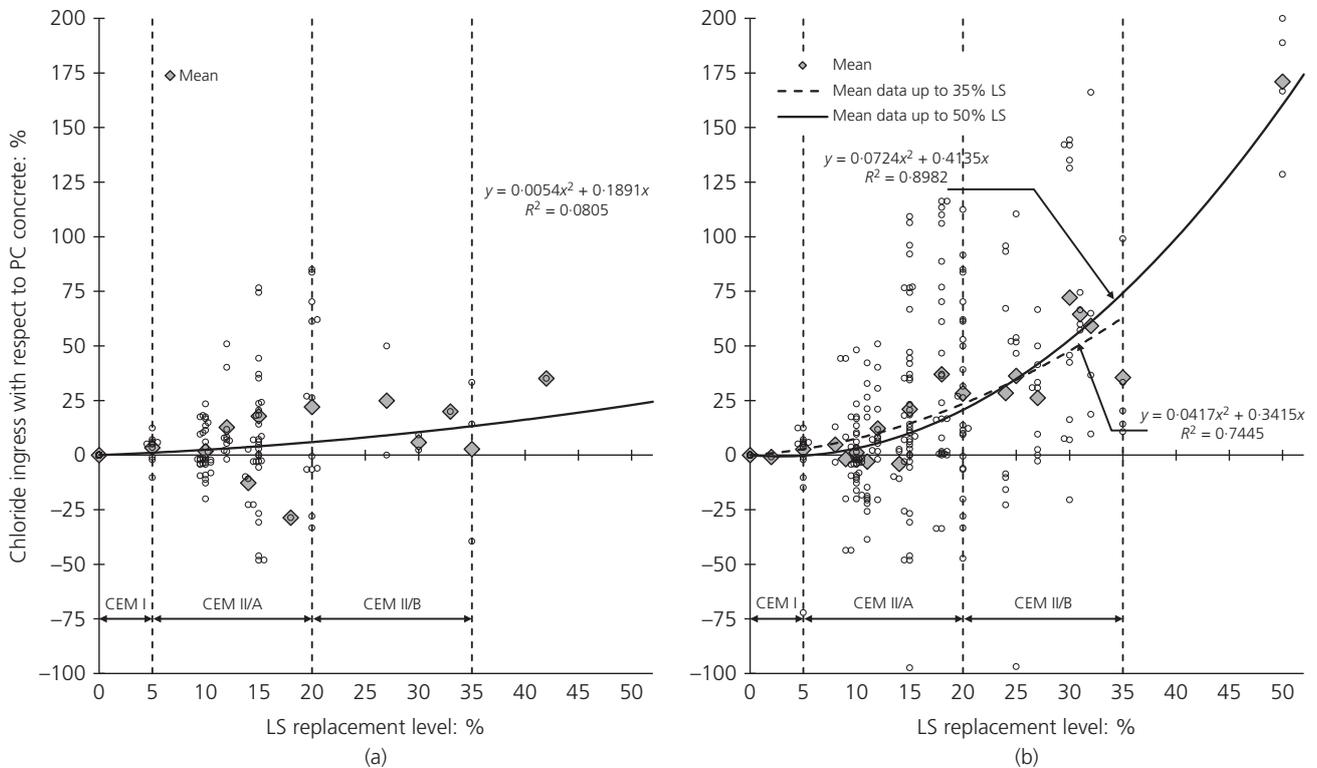


Figure 5. Influence of LS on chloride ingress in concretes of (a) equal 28 d strength and (b) equal w/c ratio. Data taken from Figure 4

(200–1500 m²/kg), LS contents (8.4–50%), w/c ratios (0.40–0.50), cement contents (292–500 kg/m³) and moist curing durations (28–90 d). The results obtained were analysed and are plotted separately in terms of equal 28 d strength and equal w/c ratio of the concrete in Figures 7(a) and 7(b), respectively.

Figure 7 shows that, in general terms, regardless of whether the mixes were designed in terms of equal strength or equal w/c ratio, the effect of LS fineness on chloride ingress is insignificant up to 35% LS content. The influence of fineness can be observed to be consistent with the compressive strength results, with finer LS resulting in slightly improved strength.

For the concretes of equal strength (Figure 7(a)), the LS contents used ranged from 8.4 to 13%, which although relatively low, shows that the relative chloride ingress in PLC is close to that in PC and there is a slight enhancement in chloride ingress resistance of concrete due increased LS fineness. On the other hand, although the equal w/c ratio results (Figure 7(b)) at times appear to be conflicting, and in contrast to the equal strength results, there is some evidence to suggest that chloride ingress in PLC concrete decreases to some extent with increasing LS fineness.

In addition, Ghiasvand *et al.* (2015) examined PLC produced by two different methods (inter-grinding and blending) with

10% LS content. The fineness of the PLC varied from 3640 to 5980 cm²/g and the results suggested that, for this difference in LS fineness, chloride ingress resistance was not significantly different, irrespective of whether the PLC was produced by inter-grinding or blending.

Cement content

The effect of total cement content on chloride ingress in PLC concrete was studied by Bertolini *et al.* (2007) and Lollini *et al.* (2014, 2016) using LS up to 30%, a w/c ratio of 0.46, cement contents of 300–350 kg/m³ and moist curing for 28 d. The chloride diffusion results for PLC concrete (13.6–23.5 × 10⁻¹² m²/s) were considerably higher than those for PC concrete (7.0–8.0 × 10⁻¹² m²/s) for all the mixtures studied. As expected, due to the narrow range of cement content employed, its effect on chloride ingress was found to be negligible in both PC and PLC mixes.

Combined chloride and sulfate environment

Sotiriadis *et al.* (2014) and Yamada *et al.* (2006) studied chloride ingress in PC and PLC mixtures exposed to a combined chloride- and sulfate-bearing environment. The experimental conditions were LS content of 0–35%, w/c ratio of 0.50–0.52, moist curing for 7 d, exposure temperature of 5–20°C and immersion for 6–18 months. The test solutions were (a) artificial seawater with 0.28% SO₄²⁻ and 1.89–2.11% Cl⁻ and

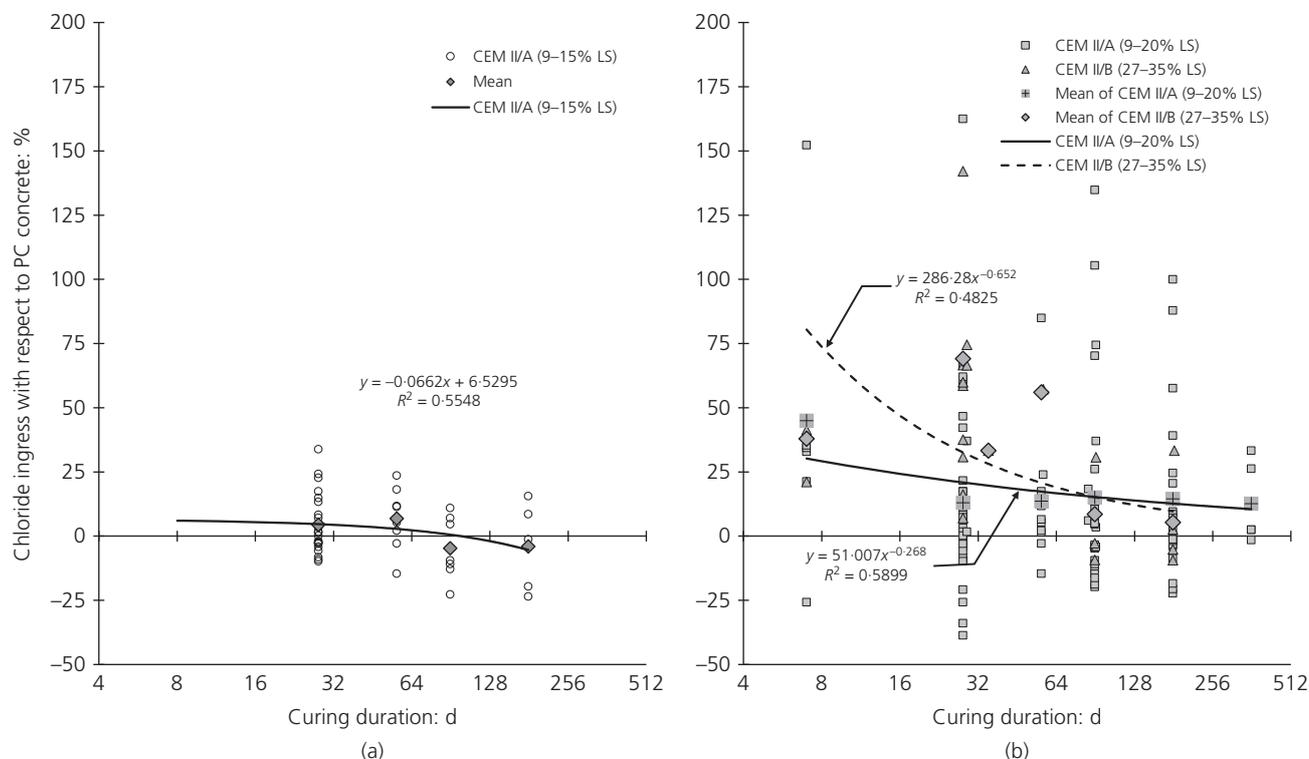


Figure 6. Influence of moist curing duration on chloride ingress in PLC concretes of (a) equal strength design and (b) equal w/c ratio with respect to PC concrete. Data taken from Aguayo *et al.* (2014), Bertolini *et al.* (2011), Cam and Neithalath (2010, 2012), Ghiasvand *et al.* (2015), Ghrici *et al.* (2007), Githachuri and Alexander (2013), Güneşli *et al.* (2011), Hooton *et al.* (2010), Hossack *et al.* (2014), Howard *et al.* (2015), Irassar *et al.* (2006), Lollini *et al.* (2015), Palm *et al.* (2016), Pavoine *et al.* (2014), Persson (2001), Pourkhorshidi *et al.* (2010), Ramezani-pour *et al.* (2009, 2010), Silva and de Brito (2016), Thomas *et al.* (2010a, 2010b) and Xiao *et al.* (2009)

(b) a solution containing 0.00–0.10% SO_4^{2-} and 1.89–2.11% Cl^- . The following results were obtained.

- The chloride measurements of PC and PLC with LS contents up to 15% were comparable.
- The PLC with 35% LS content had the highest chloride ingress.
- In the presence of lower sulfate contents, high chloride contents were recorded due to the greater amount of dissolved calcium hydroxide in comparison with seawater, with the sulfate ions suppressing the dissolution of calcium hydroxide.

Aggregate content and particle size

The effects of aggregate content and particle size were examined by Wu *et al.* (2016). The variables in this study were LS contents of 0, 5 and 10%, w/c ratio of 0.45, standard curing for 56 d, with samples with varying aggregate content (0–1468 kg/m^3) and mean aggregate size (0.00–2.88 mm). In general, the chloride ingress results of the PC and PLC mixes showed similar trends. In comparison with PC, the inclusion of 5% LS resulted in a minor reduction in chloride migration (by 5–9%), and, although hard to justify and possibly due to

experimental error, chloride migration increased noticeably (by 40–45%) with 10% LS. Increases in aggregate volume content and particle size led to slight increases in chloride ingress in both the PC and PLC mixtures, due to a coarser pore structure and the sizeable presence of an aggregate–matrix interface.

Chloride ingress: effect of concrete strength

To study the relationship between compressive strength and chloride ingress in PLC concrete, the results used in Figures 4 and 5 are plotted in terms of chloride ingress of PLC concrete as a percentage of the corresponding PC concrete against characteristic cube strength in Figure 8. This figure was developed in the following way.

- Characteristic cube strengths were calculated from the measured strengths using a variation coefficient of 6% given in ACI 301-05 (ACI, 2005) for fair laboratory control class.
- The reported results where the test mixes did not comply with the mix limitations of BS EN 206:2013 (BSI, 2013) for chloride exposure class XS1 were not considered further in developing the figure.
- For convenience, linear regression was applied in the analysis of the data. As the coefficients of correlation were

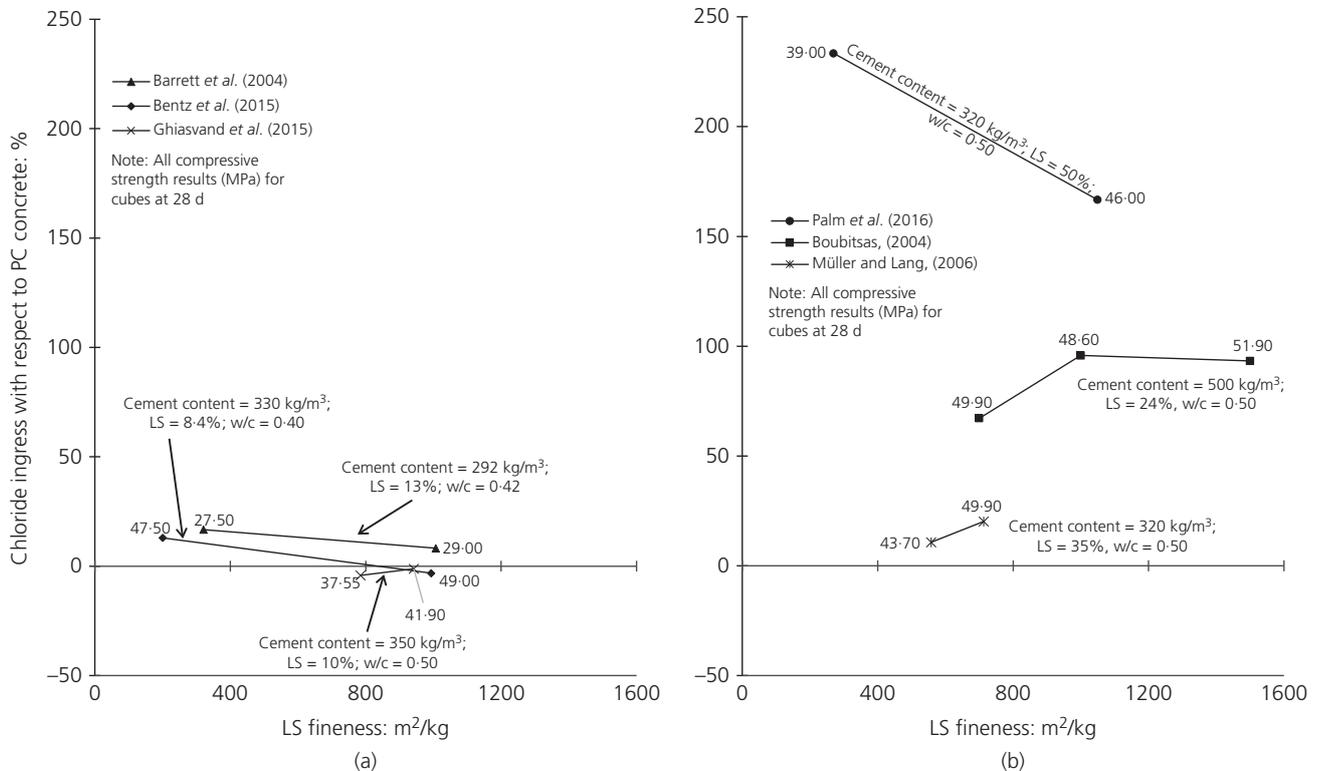


Figure 7. Influence of LS fineness on chloride ingress in PLC concretes of (a) equal strength design and (b) equal w/c ratio with respect to PC concrete

generally poor, the trend lines obtained can only be considered of qualitative value.

- For comparison purposes, the minimum characteristic strength of 37 MPa for XS1 exposure class recommended in Eurocode 2 (BSI, 2004) was chosen. This is shown by the dotted vertical line.

Figure 8 reveals the following important points.

- Chloride ingress increases with decreasing compressive strength and increasing LS content. The relative chloride ingress for both CEM II/A (6–20% LS) and CEM II/B (21–35% LS) concretes can exceed the minimum cover of 35 mm specified in Eurocode 2 at the minimum characteristic strength of 37 MPa for exposure class XS1 (considering the design working life is 50 years) (BSI, 2004).
- For chloride ingress similar to that of PC concrete at 37 MPa, the compressive strength of PLC concrete may have to be increased from 37 MPa to 50 MPa and 60 MPa for cements such as CEM II/A (6–20% LS content) and CEM II/B (21–35% LS content), respectively. Alternatively, the required minimum cover for PLC concrete at 37 MPa would have to be increased for concrete made with CEM II/A (6–20% LS) and CEM II/B (21–35% LS) cements.

Chloride ingress in concrete specified in terms of w/c ratio

Looking from another perspective, chloride ingress in PLC concrete specified in terms of w/c ratio is shown in Figure 9. The base data used in this figure are those used in Figures 4 and 5 and were subjected to the same screening process as adopted for Figure 8. The recommended maximum w/c ratio of 0.50 for XS1 exposure class given in BS EN 206:2013 (BSI, 2013) was selected and is shown as the vertical dotted line.

Figure 9 shows that, for a given w/c ratio, chloride ingress increases with LS content and the chloride ingress behaviour of concrete is similar to that in Figure 8, but at a slightly greater rate. Additionally, for a similar chloride ingress to CEM I concrete at w/c = 0.50, mixes made with CEM II/A and CEM II/B with LS addition would need to be designed with a reduced w/c ratio, of about 0.40 and 0.35, respectively. Alternatively, the required minimum cover (i.e. 35 mm) of PLC concrete at w/c = 0.50 would need to be increased for both CEM II/A (6–20% LS) and CEM II/B (21–35% LS) cements.

In situ chloride ingress measurements

Published research on situ chloride ingress is limited. Hossack et al. (2014) studied the in situ chloride content of concrete pavements constructed in two different locations in Canada

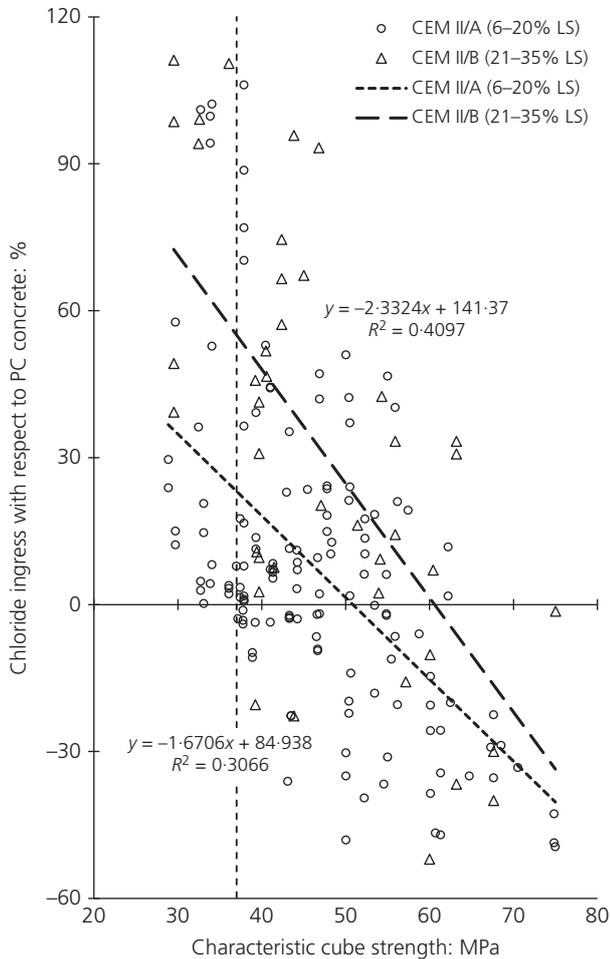


Figure 8. Chloride ingress in PLC concrete with respect to PC concrete at different characteristic cube strengths. Data taken from Figures 4 and 5

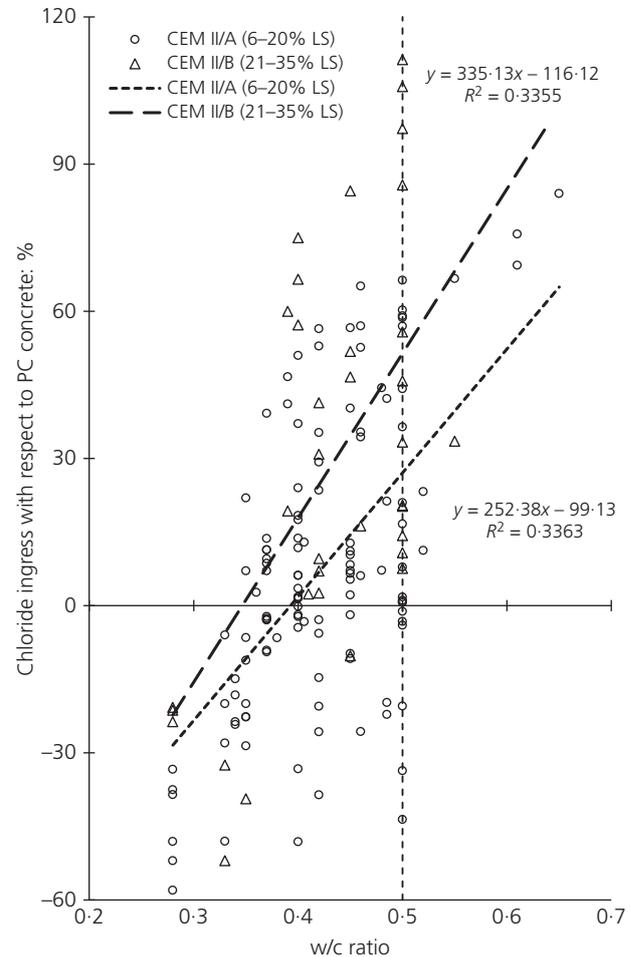


Figure 9. Chloride ingress in PLC concrete with respect to PC concrete at different w/c ratios. Data taken from Figures 4 and 5

during 2008 and 2009. The test conditions were as follows: age at the time of measurements, 3 and 4 years; LS content, 0% and 12%; w/c ratio, 0.37 and 0.44; in situ core strength 43–59 MPa. Although the effect of LS on the strength varied, chloride measurements at both locations showed, in general, that PLC concretes had on average 20% higher chloride penetration than PC concrete. This was attributed to the lower alumina content of PLC due to the dilution of C_3A and C_4AF with the addition of LS, which reduces the capacity for chloride binding.

Influence of LS on chloride-induced corrosion of reinforcement

The effect of LS addition on chloride-induced corrosion, although important, is not widely reported. However, as the use of LS is known to increase the susceptibility of concrete to chloride ingress, it is necessary to determine how this may influence the corrosion of steel reinforcement in PLC concrete. Only 13 studies have reported on the chloride-induced

corrosion of PLC concrete. The results showed that chlorides can reach the steel reinforcement in sufficient concentrations (i.e. higher than 0.4% by cement mass, BS EN 206 (BSI, 2013)) and consequently the corrosion process could, in principle, be considered to have initiated. Additionally, due to the complexity of the test methodology and the nature of measurements, the data obtained could only be examined in a qualitative manner, as presented in Table 5.

The reported research suggests that, in general, the test specimens used had cement blends of 0–35% LS, with w/c ratios of 0.42–0.72, and were subjected to chloride exposure for up to 5 years. The corrosion of steel reinforcement was measured using different methods, such as corrosion potential (mV), weight loss of reinforcement (g/m^2), corrosion current/density (mA/m^2) and corrosion rate ($\mu m/year$).

In the studies that assessed PLC concretes with respect to reference PC concretes, the rate of corrosion in PLC concrete was generally higher than that of the corresponding PC concrete.

Table 5. Summary of influence of LS addition on chloride-induced corrosion

Reference	Main points
Batic <i>et al.</i> (2010)	<ul style="list-style-type: none"> ■ Corrosion rate of PLC mixture higher than that of PC mixture and increase in w/c ratio minimised the differences between the corrosion results of the two mixtures ■ Reinforcement corrosion unit: corrosion rate i ($\mu\text{A}/\text{cm}^2$) ■ Cylinder specimen, 50 × 100 mm; concrete cover, 22 mm; LS contents, 0 and 22%; w/c ratios, 0.50 and 0.65; moist curing, 28 d; exposure, immersion in a 3% sodium chloride solution; duration, 9 months; equal w/c mixes
Batic <i>et al.</i> (2013)	<ul style="list-style-type: none"> ■ Concrete made with PLC showed greater corrosion rate than PC concrete and increase in w/c ratio reduced the differences between the two mixtures. Moreover, the type of curing did not introduce significant change except for mixture with the higher w/c and cured in lime water ■ Reinforcement corrosion unit: corrosion rate i ($\mu\text{A}/\text{cm}^2$) ■ Cylinder specimen, 50 × 100 mm; concrete cover, 22 mm; LS contents, 0 and 35%; w/c ratios, 0.50 and 0.65; air and wet (lime water) curing, 28 d; exposure, immersion in a 3% sodium chloride solution; duration, 9 months; equal w/c mixes
Bertolini <i>et al.</i> (2011), Lollini <i>et al.</i> (2015)	<ul style="list-style-type: none"> ■ Corrosion activity of PLC concrete is higher than that of PC concrete ■ Reinforcement corrosion unit: rebar corrosion potential (mV) ■ Prism specimen, 60 × 250 × 150 mm; concrete cover, 15 mm; LS contents, 0, 15 and 30%; w/c ratio, 0.61; moist curing, 28 d; exposure, ponding using 3.5% sodium chloride solution; duration, 2 years; equal w/c mixes
Deja <i>et al.</i> (1991)	<ul style="list-style-type: none"> ■ Rate of reinforcement corrosion of PLC concrete lower than that of PC concrete ■ Reinforcement corrosion unit: rebar weight loss (g/m^2) ■ Prism specimen, 40 × 40 × 160 mm; concrete cover, 22 mm; LS contents, 0 and 5%; w/c ratio, 0.50; moist curing, 56 d; exposure, immersed in 23% sodium chloride solution; duration, 12 months; equal 28 d strength mixes
Diab <i>et al.</i> (2015), Diab <i>et al.</i> (2016)	<ul style="list-style-type: none"> ■ In general, corrosion rate of PLC concrete higher than that of PC concrete until a certain level of LS replacement (15%); after that started to decrease until it became similar or lower than that of PC concrete at 20% and 25% LS additions. Furthermore, corrosion activity of PLC concrete principally depended on the cement content, w/c ratio of the mix and LS fineness ■ Reinforcement corrosion unit: corrosion rate (mm/year) ■ Cylinder specimen, 75 × 150 mm; concrete cover, 31 mm; LS contents, 0, 10, 15, 20 and 25%; w/c ratios, 0.48, 0.55 and 0.65; curing, lime water for 6 d then in air for 21 d; exposure, immersion in 5% sodium chloride solution; duration, 9 months; equal 28 d strength only for 10% LS mixtures
Moir and Kelham (1993), Matthews (1994), Livesey (1991)	<ul style="list-style-type: none"> ■ Corrosion rate of PLC (5% LS) concrete similar to PC concrete. Corrosion results of PLC (25% LS) concrete varied over time compared to PC concrete ■ Reinforcement corrosion unit: percentage rebar weight loss (%) ■ 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, tidal zone; duration, up to 5 years; equal w/c mixes
Pavoine <i>et al.</i> (2014)	<ul style="list-style-type: none"> ■ Corrosion rate of PLC concrete higher than that of PC concrete ■ Reinforcement corrosion unit: corrosion current (mA) ■ Specimen, four concrete elements 1 m long, 100 mm thick and 200 mm high sealed together to form a closed container; concrete cover, 25 mm; LS contents, 0 and 10%; w/c ratios, 0.40 and 0.55; moist curing, 6 weeks; exposure, container subjected to 5% sodium chloride solution; duration, up to 3 months; equal 28 d strength mixes
Tsivilis <i>et al.</i> (2000), Tsivilis <i>et al.</i> (2002)	<ul style="list-style-type: none"> ■ Corrosion rate of PLC concrete lower than that of PC concrete ■ Reinforcement corrosion unit: rebar weight loss (g/m^2) ■ Prism specimen, 80 × 80 × 100 mm; concrete cover, 20 mm; LS contents, 0, 10, 15, 20 and 35%; w/c ratios, 0.62 and 0.72; moist curing, 28 d; exposure, partially immersion in a 3% sodium chloride solution; duration, 12 months; equal w/c only for 35% LS mixture

It has also been reported that an increase in w/c ratio reduced the difference between the corrosion results of the two mixtures and that the type of curing did not produce a significant change except for mixtures with a higher w/c ratio and in specimens cured with lime water (Batic *et al.*, 2010, 2013). It has also been suggested that the corrosion of reinforcement in PLC concrete principally depends on the cement content, w/c ratio and LS fineness (Diab *et al.*, 2015, 2016).

In addition, some researchers have assessed the corrosion behaviour of PLC concrete without testing PC concrete. These studies involved LS contents of 10–20%, w/c ratios of 0.46–0.65, exposure durations of up to 8 years and chloride concentrations of 3.5–10.0% (Bertolini *et al.*, 2002, 2004a; Bolzoni *et al.*, 2006, 2014; Brenna *et al.*, 2013; Fayala *et al.*, 2013; Garcés *et al.*, 2006; Meira *et al.*, 2014; Ormellese *et al.*, 2006; Romano *et al.*, 2013; Sistonen *et al.*, 2008;

Zacharopoulou *et al.*, 2013). The overall outcome of these studies suggests that the use of PLC concrete leads to moderate to high increases in the corrosion rate.

PLC performance in terms of pore structure and related properties, strength, carbonation rate and chloride ingress

To facilitate a meaningful comparison of the durability performance of PLC concrete, Figure 10 was constructed to collectively analyse the effect of LS content on porosity and related properties (i.e. water absorption and sorptivity), strength, carbonation rate and chloride ingress relative to corresponding PC concretes.

In developing Figure 10, to make it easier for the research to be adopted in practice, some simple modifications were carried out to the trend lines observed in the studies reported previously in this paper (Figure 4) and two previous studies of the current authors (Elgalhud *et al.*, 2016, 2017). These modifications were based on the concept that the physical and chemical effects of the inclusion of LS are mainly as a filler (better packing of the pore matrix), heterogeneous nucleation (improving early strength) and dilution (increasing the effective w/c), as suggested by Irassar (2009), although these effects rely on the amount and fineness of LS used in a mix (Sezer, 2012). The main change adopted was the use of simple linear regression as opposed to polynomial

regression. Although a degree of accuracy may have been lost in this process, the outcome has been to produce a useful tool that should allow estimation of the changes that may be expected with the use of LS on the pore structure of hardened concrete, its strength, carbonation and chloride ingress resistance.

Figure 10 suggests that, for practical purposes, it is feasible to accept that

- up to 15% LS content, its effect may be considered constant and almost neutral
- beyond 15% LS content, an increase in LS content gives rise to a progressive reduction in all the properties of concrete and, in this case, pore structure (in the form of porosity, water absorption and sorptivity) strength and durability (as carbonation and chloride ingress).

Table 6 shows that the trends of sorptivity and water absorption are mainly the same and are influenced by LS slightly more than the porosity, which reflects the variance in the working mechanism of each. In addition, the sensitivity of PLC to carbonation exposure is higher than that of chloride ingress. This could be attributed to the pH of LS/calcium carbonate (CaCO_3), which is between 8.5 and 10 (Chen *et al.*, 2009; Hua and Laleg, 2009; Phung *et al.*, 2015) and is lower than the pH of PC (i.e. 12.5–12.8), and this is considered to decrease the pH of the resultant PLC (particularly at high LS contents such as 35%).

In summary, it is proposed that although the use of LS generally has some impact on the properties of concrete, this can be insignificant up to a maximum of 15% LS content, which is below the maximum limit of 20% for CEM II/A PLC (BSI, 2011) and which thus may need to be revised.

Improving PLC performance in practice

The effect of LS addition on chloride ingress in concrete can be lessened in a number of ways. Although extending the moist curing duration will certainly help greatly to improve the resistance of PLC concrete against chloride ingress by developing a less porous and less permeable concrete, accomplishing this in practice can be difficult due to present construction practices. The other options for enhancing the resistance of PLC concrete to chloride ingress could be realised by the following.

- (a) Restricting LS addition to a smaller proportion (i.e. a maximum of 15%). Such a cement would be in part compliance with PLC of type CEM II/A (6–20% LS) in BS EN 197-1:2011 (BSI, 2011). Although this option may be used, because it limits the replacement of PC content in cement, it would negatively impact on the carbon dioxide footprint of the cement industry.

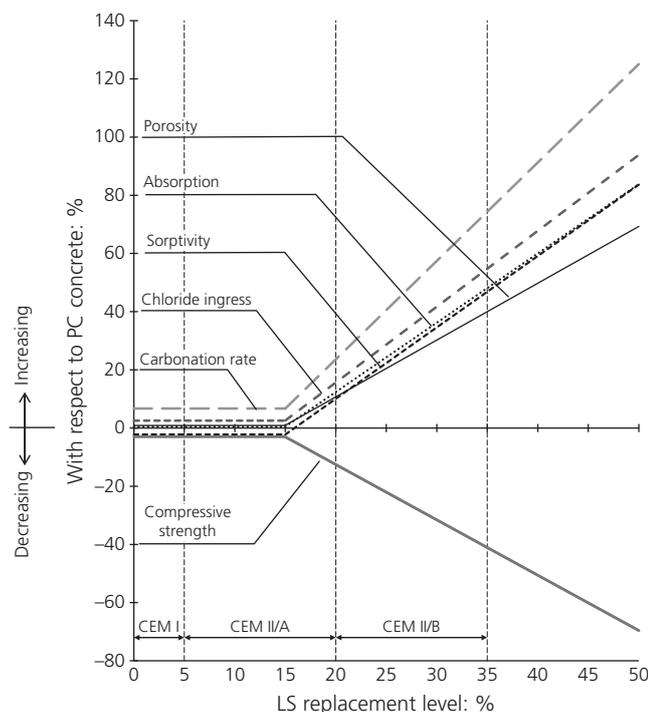


Figure 10. Mode of PLC performance in terms of pore structure and related properties, strength, carbonation rate and chloride ingress

Table 6. Mode of PLC performance in terms of pore structure and related properties, strength, carbonation rate and chloride ingress

Cement type	LS content: %	With respect to PC: %					
		Porosity	Water absorption	Sorptivity	Compressive strength	Carbonation rate	Chloride ingress
CEM I	1–5	0.9	0.5	–2.0	–3.0	6.7	2.6
CEM II/A-L	6–15	0.9	0.5	–2.0	–3.0	6.7	2.6
	20	10.6	12.4	10.1	–12.5	23.6	15.6
CEM II/B-L	21	12.6	14.8	12.5	–14.4	27.0	18.2
	25	20.5	24.3	22.3	–22.0	40.5	28.6
	30	30.2	36.2	34.6	–31.6	57.4	41.5
	35	40.0	48.1	46.9	–41.1	74.3	54.7
	40	49.7	60.0	59.1	–50.6	91.2	67.6
—	45	59.5	71.9	71.3	–60.1	108.1	80.8
	50	69.3	83.8	83.6	–69.6	125.1	93.9

- (b) Enhancing the porosity of the concrete by
- (i) optimising particle packing by revising the proportions of coarse and fine aggregates and/or introducing the use of fillers (Dhir and Hewlett, 2008)
 - (ii) developing more effective use of LS by adopting other additions such as small proportions of SF and MK (Elgalhud *et al.*, 2016).
- (c) Increasing the specified characteristic strength of concrete by reducing its w/c ratio through the use of a high-range water reducing admixture. This option should enhance the durability and sustainability of concrete (Dhir *et al.*, 2000, 2004, 2006).
- (d) Increasing the thickness of concrete cover could be considered as an additional obvious option. However, this will influence structural design and sustainability aspects and this solution is unlikely to be chosen by design engineers.

Conclusions

For combinations of LS and PC within the bands of CEM II/A (6–20% LS) and CEM II/B (21–35% LS) cements specified in BS EN 197-1:2011 (BSI, 2011), the results show that, in general, the chloride ingress of concrete increases at an increasing rate as the LS content is increased and that the rate of this increase and the significance thereof can vary depending on whether the PLC mixes are designed on the basis of equal strength or equal w/c ratio, with the latter showing a greater effect than the former. Likewise, the duration and type of curing (in terms of relative humidity and temperature), exposure conditions and LS fineness also tend to affect the magnitude and rate of the LS effect on chloride ingress.

Accordingly, these effects have been found to be more sensitive and significant with CEM II/B PLC than with CEM II/A PLC. This appears to support the approach adopted in BS 8500-1:2006+A1:2012 (BSI, 2006), in which CEM II/B does not appear to be suggested for use in conditions subject to chloride exposure. Additionally, compliance with mix

limitations for chloride exposures as per BS EN 206-1:2013 (BSI, 2013) may have to be revised upwards for PLC.

The limited in situ chloride ingress measurements of concrete structures made with PC and PLC (12% LS) over a period of 3–4 years showed that PLC concrete had a higher chloride ingress rate than the corresponding PC concrete. Additionally, the results showed that, due to depassivation of reinforcement, the rate of corrosion in PLC concrete, upon chlorides reaching the reinforcement, was generally higher than that in PC concrete.

The results of this study considered together with two previous studies (Elgalhud *et al.*, 2016, 2017) show that the effects of LS addition on concrete pore structure (in terms of porosity, absorption and sorptivity), strength and resistance to carbonation and chloride ingress are similar, but their magnitudes may be different.

For practical purposes, and in view of the findings of two previous studies in this series (Elgalhud *et al.*, 2016, 2017), it is proposed that the effect of LS up to a content of 15% on concrete performance may be assumed to be negligible but increases thereafter at a constant rate with increasing LS content. In light of this, the maximum limit on LS content of CEM II/A may be considered for revision from 20% down to 15%.

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