

A software-assisted comparative assessment of the effect of cement type on concrete carbonation and chloride ingress

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Abstract. Utilization of supplementary cementing materials (SCM) by the cement industry, as a highly promising solution of sustainable cement development aiming to reduce carbon dioxide emissions, necessitates a more thorough evaluation of these types of materials on concrete durability. In this study a comparative assessment of the effect of SCM on concrete durability, of every cement type as defined in the European Standard EN 197-1 is taking place, using a software tool, based on proven predictive models (according to performance-related methods for assessing durability) developed and wide-validated for the estimation of concrete service life when designing for durability under harsh environments. The effect of Type II additives (fly ash, silica fume) on CEM I type of cement, as well as the effect of every Portland-composite type of cement (and others) are evaluated in terms of their performance in carbonation and chloride exposure, for a service life of 50 years. The main aim is to portray a unified and comprehensive evaluation of the efficiency of SCM in order to create the basis for future consideration of more types of cement to enter the production line in industry.

Keywords: carbonation; cement type; chloride penetration; concrete technology; corrosion; model prediction; service life; software.

1. Introduction

Today, despite the high level of research and the significant advances achieved in concrete technology leading to a plethora of available construction materials, issues of unsatisfactory durability of structures still appear on a frequent basis. A correct selection of the raw building materials, combined with a thorough durability design process utilizing proven predictive models of concrete service life, where the influence of the harmful environmental agents is identified and mitigated in advance during the design stage of the project, is the way forward for tackling durability problems and ensuring the desirable concrete service life of any type of structure. Keeping in mind that any set of construction materials entails certain aspects of environmental cost (from its production stage to its end-use) a sustainable solution to the previously mentioned problem should also be investigated. It is well known (CEMBUREAU 2009) that the footprint of each structural element on the environment is estimated based on the emissions of gases produced during their manufacturing stage. In concrete

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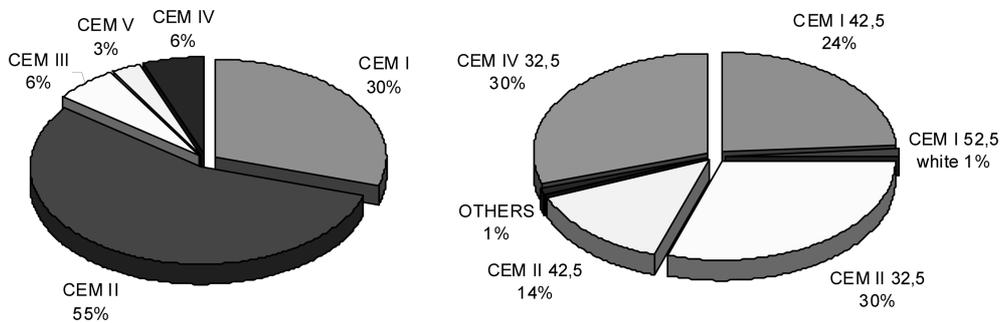


Fig. 1 European (left) and Greek (right) cement production (CEMBUREAU 2009, Tsakalakis 2010, WBCSD 2009)

production for example (CEMBUREAU 2009), the main emissions to air are associated with the cement-making process, where during the stage of clinker formation, CO₂ gasses and other greenhouse emissions are emitted to the atmosphere (0.873 tonnes of CO₂ gasses are emitted per 1 tonne of cement produced). A lower CO₂ emission can be achieved through the utilisation of supplementary cementing materials (SCM).

Incorporation of SCM by-products, like fly ash, silica fume or ground granulated blast furnace ash, as cement replacement materials, either in the form of blended cements (Portland composites or blast-furnace cements), or as additives/admixtures, besides the effect they entail on early concrete strength and volume stability (Papadakis 2000), they improve to a great extent the overall environmental contribution (CEMBUREAU 2009, WBCSD 2009), since they can replace clinker to a significant percentage (18% replacement of Portland cement results in a 17% reduction of the CO₂ emissions). In the European standard for cement (CEN EN 197-1 2000) a range of 27 different cement types incorporating SCM is clearly defined. Although there is a shift on European level (WBCSD 2009) in producing such types of cements (55.5% production of CEM II, according to Fig. 1) their utilization is not uniform across Europe (possibly due to the availability of raw materials or due to issues of economical nature). In Italy for example (AITEC 2009), where production of Portland composite cements (CEM II) constitutes 73% of the total national production, 66% of that is Portland limestone composite, the remaining being Portland cements incorporating blast furnace slag and natural pozzolanic materials. In Poland (Obetkon 2009), fly ash and blast-furnace slag CEM II type of cements are mainly produced, while in Greece (Tsakalakis 2010) natural pozzolan, fly ash, blast furnace slag and limestone are the main constituents of CEM II type of cements produced. Furthermore, production of blast furnace cements (CEM III) is at a very low level (6.2%).

Given the need for a sustainable and durable solution on the corrosion problem of reinforced concrete, emphasis should be placed on investigating the durability of concrete incorporating these types of materials. Due to the, previously mentioned, variability in cement production across Europe it is difficult to have an overall assessment of the effects of SCM incorporation on concrete durability. Efforts in the direction of a fundamental approach of SCM effect on concrete durability are very limited.

On this note, a comparative assessment of the effect of SCM on concrete durability, of every cement type as defined in the European Standard (CEN EN 197-1 2000) is taking place in this study. The evaluation was made using a software tool (EUCON), based on proven predictive models (according to performance-related methods for assessing durability) developed and validated

by Papadakis *et al.* (1991, 2007, 2011), for the estimation of concrete service life when designing for durability under harsh environments. Such a method considers each relevant deterioration mechanism, the service life of the structure, and the criteria which define the end of this service life, in a quantitative way. Concrete service life is reliably predicted using fundamental mathematical models that simulate the physicochemical processes leading to concrete carbonation and chloride diffusion (the most common deterioration mechanisms of reinforced concrete).

The effect of Type II additives (fly ash, silica fume) on CEM I type of cement, as well as the effect of every Portland-composite type of cement (and others) are evaluated in terms of their performance in carbonation and chloride exposure, for a service life of 50 years. The main aim is to portray a unified and comprehensive evaluation of the efficiency of SCM in order to create the basis for future consideration of more types of cement to enter the production line.

2. Estimation of service life

Principles of chemical and material engineering have been applied to simulate the physicochemical processes leading to concrete deterioration for carbonation and chloride exposure. In terms of carbonation exposure, based on reaction engineering principles, a system of non-linear differential equations, developed by Papadakis *et al.* (1991, 1996) models in a quantitative way the physicochemical processes leading to concrete carbonation. These include the diffusion of CO₂ in the gas-phase of pores, its dissolution in the aqueous film of these pores, the dissolution of solid Ca(OH)₂ in pore water, its ultimate reaction with the dissolved CO₂ and the reaction of CO₂ with CSH. The solution of the set of differential equations permits the calculation of the carbonation depth x_c , at a given time t , as well as the estimation of the critical time, $t_{cr,carb}$, required for the carbonation front to reach the reinforcement located at a distance c (concrete cover to reinforcement), for both Portland and blended cements, as well as when additions of SCM are used separately in concrete, according to the following equation

$$x_c = \sqrt{\frac{2D_{e,CO_2}(CO_2/100)t}{0.33CH+0.214CSH}}, \quad t_{cr,carb} = \frac{(0.33CH+0.214CSH)c^2}{2D_{e,CO_2}(CO_2/100)} \quad (1)$$

$$D_{e,CO_2} = 6.1 \cdot 10^{-6} \left(\frac{\varepsilon_c - \varepsilon_{air}}{1 - \frac{A}{d_A} - \varepsilon_{air}} \right)^3 (1 - RH/100)^{2.2} \quad (2)$$

where, CO₂ is the CO₂-content in the ambient air at the concrete surface (%), CH and CSH are the contents of calcium hydroxide and calcium-silicate-hydrate in concrete volume (kg/m³), D_{e,CO_2} the effective diffusivity of CO₂ in carbonated concrete (m²/s), RH the ambient relative humidity (%), ε_c the porosity of the carbonated concrete, ε_{air} the content of concrete in entrapped or entrained air, A the aggregate content in concrete volume (kg/m³) and d_A the aggregate density (kg/m³).

Considering the fact that once the onset of the carbonation front reaches the embedded bar, corrosion takes place with the known consequences (losses of bond between concrete/reinforcement, mass loss of the reinforcement and concrete cracking and spalling). The time required to crack the concrete cover is equal to the time required for the carbonation front to reach the bar (initiation period of corrosion, $t_{cr,carb}$, estimated as mentioned above) plus the time necessary for the layer of rust to build up around the bar and split the cover (corrosion propagation period, $t_{pr,carb}$, also estimated by the

models utilised in the software package). However, in certain cases (Papadakis *et al.* 1996, 2007) the corrosion rate in carbonated concrete at high relative humidity values can be of such magnitude, that the arrival of the carbonation front at the bar is followed shortly by splitting of the concrete cover. Therefore, the service life of a concrete structure, regarding corrosion of reinforcement induced by carbonation, can be safely assumed to be at least $t_{cr,carb}$.

As far as chloride transport in concrete is concerned, in many studies it is modelled using Fick's second law of diffusion, neglecting the chloride interaction with the solid phase. However, the latter process is very important including binding of chlorides by cement hydration products, ionic interaction, lagging motion of cations and formation of an electrical double layer on the solid surface, etc. On that note, the physicochemical processes of diffusion of Cl^- in the aqueous phase, their adsorption and binding in the solid phase of concrete, and their desorption, are described (Papadakis *et al.* 1996) by a non-linear partial differential equation (Eq. 3) for the concentration of Cl^- in the aqueous phase [$Cl^-(aq)$], the solution of which allows the calculation of the Cl^- bound in the solid phase [$Cl^-(s)$] and the estimation of the critical time for chloride-induced corrosion required for the total chloride concentration surrounding the reinforcement (located at a distance c from surface) to increase over the threshold for depassivation.

$$\frac{\partial[Cl^-(aq)]}{\partial t} = \frac{D_{e,Cl^-}(1+K_{eq}[Cl^-(aq)])^2}{K_{eq}[Cl^-(s)]_{sat} + \varepsilon(1+K_{eq}[Cl^-(aq)])^2} - \frac{\partial^2[Cl^-(aq)]}{\partial x^2},$$

$$[Cl^-(s)] = \frac{K_{eq}[Cl^-(aq)]}{1+K_{eq}[Cl^-(aq)]} [Cl^-(s)]_{sat} \quad (3)$$

$$D_{e,Cl^-} = \frac{2.4 \cdot 10^{-10}}{\left(\frac{K+CS+\sum(kP_{ACT})}{d_c} + \frac{W}{d_w}\right)^2} (\varepsilon_{eff})^{3.5}, \quad \varepsilon_{eff} = W/d_w - 0.226 \cdot 10^{-3} \{K+CS+\sum(kP_{ACT})\} \quad (4)$$

Where, x is the distance from the concrete surface (m), t is the time (s), K_{eq} the equilibrium constant for Cl^- binding (m^3 of pore volume/kg), $[Cl^-(s)]_{sat}$ the saturation concentration of Cl^- in the solid phase (kg/m^3 concrete), $[Cl^-(aq)]$ the concentration of Cl^- in the aqueous phase, D_{e,Cl^-} is the intrinsic effective diffusivity of Cl^- in concrete (m^2/s), ε_{eff} the effective (for diffusion) concrete porosity (m^3 pore volume/ m^3 concrete), K the clinker content in concrete (kg/m^3 of concrete), C cement content (kg cement/ m^3 of concrete), S , silica fume content (kg silica fume/ m^3 of concrete), P_{ACT} the active content of each SCM added either as cement constituent or as concrete addition, having an efficiency factor k , d_c , d_w , cement and water densities (kg/m^3).

The solution of the above system allows estimation of, the time (critical time for chloride-induced corrosion, $t_{cr,chlor}$) required for the total chloride concentration surrounding the reinforcement (located at a distance c from surface) to increase over the threshold for depassivation, as well as the adequate (minimum) concrete cover needed in order to sustain a chloride-induced corrosion free structure for a given service life.

In the case of an RC structure where the concrete cover is not crack free, the model can be adjusted accordingly. It is widely understood that cracks increase the transport properties of concrete, creating perfect pathways for gas and liquid transportation, thus, facilitating the ingress of deleterious species such as CO_2 or chlorides into concrete and accelerating the initiation time for the

corrosion of the steel reinforcement. The estimation of the life span of reinforced concrete structures having cracks is influenced by characteristics, such as crack width and length, in addition to the concrete properties and the environmental exposure conditions. The models developed by the authors to estimate the service life of reinforced concrete structures (as far as chloride ingress and the action of carbon dioxide from the atmosphere is concerned), presented briefly in the current study, take under consideration parameters influenced by the appearance of cracks on the concrete cover. Research has shown that the presence of cracks increases the diffusion coefficient of both chloride ions and carbon dioxide. A comparison of chloride diffusion coefficients for cracked and uncracked concrete showed an increase in the diffusion coefficient for cracked concrete by one or two orders of magnitude (Raharinaivo *et al.* 1986, Sahmaran *et al.* 2007), while a crack width of 0.2 mm was found to increase the carbon dioxide diffusion coefficient about three orders of magnitude compared to an average quality crack-free concrete (Aleksiev and Rosenthal 1976). In the model, by adjusting the values of the effective chloride and/or carbon dioxide diffusion coefficients and by taking under consideration the initial conditions (Cl^- concentration of the surface, environmental exposure, etc.), an initial profile corresponding to a cracked concrete surface is created, which will be used by the model as a starting point on the calculation of the service life estimation parameters.

The calculation of the carbonation depth (for a period of 50 years and for a 30 mm concrete cover) and the estimation of the adequate concrete cover needed to sustain a service life of 50 years (for the case of chloride ingress) were used as durability indicators in this study.

3. Effect of SCM and cement type on durability

3.1 Effect of type II additives on concrete durability

Supplementary cementing materials (SCM) were incorporated either as aggregates or as cement replacements (Table 1). A constant volume unit (1 m^3) of concrete was chosen as a common basis. When an SCM was added to this unit, then an equal volume of another component, either cement or aggregate, was removed in order to keep the same total volume and the common comparison basis. A typical CEM I 42.5 mix, water cured for 28 days (as it is assumed by the predictive model used) was selected as the reference type of cement (w/c 0.5, cement content 300 kg/m^3 , 31.5 mm crushed aggregates, no additives, no admixtures). In the case of fly ash 10, 20 and 30% replacement levels of the control cement mass were chosen, while in the case of silica fume, since it is a more intense pozzolanic material than fly ash (and hence the rate of pozzolanic reactions drops below one for lesser quantities than fly ash) 5, 10 and 15% replacement levels were used. The water content (kg/m^3) was kept constant for all specimens.

It should be noted at this point, that although complete pozzolanic activity (and complete cement hydration) is achieved at a considerably longer curing time than the 28 days assumed by the model, the model compensates for that supposition, through the utilization of SCM efficiency factors. Cement hydration is a long-term process that starts immediately upon contact of cement with water and continuous at a very high pace during the first 24 hours, but after a certain period of time it slows down, pending on the rate of hydration of the individual cement components. Considering the above and bearing in mind that concrete hardens at a very adequate level at 28 days (according to EN 206 hardened concrete is classified in respect to its 28 days compressive strength), the model based on research by Papadakis *et al.* (2002a, 2002b), utilizes the concept of the SCM efficiency

Table 1 Mix design configurations

SCM	Specimen	SCM (%)	C (kg/m ³)	W (kg/m ³)	w/c	A (kg/m ³)	FA (kg/m ³)	SF (kg/m ³)
-	Control	0	300	150	0.5	1925	-	-
S-FA Aggregate repl.	sfa-1-a	10	300	150	0.50	1890	30	-
	sfa-2-a	20	300	150	0.50	1856	60	-
	sfa-3-a	30	300	150	0.50	1821	90	-
Cement repl.	sfa-1-c	-10	270	150	0.56	1915	30	-
	sfa-2-c	-20	240	150	0.63	1905	60	-
	sfa-3-c	-30	210	150	0.71	1895	90	-
C-FA Aggregate repl.	cfa-1-a	10	300	150	0.50	1896	30	-
	cfa-2-a	20	300	150	0.50	1866	60	-
	cfa-3-a	30	300	150	0.50	1837	90	-
Cement repl.	cfa-1-c	-10	270	150	0.56	1920	30	-
	cfa-2-c	-20	240	150	0.63	1916	60	-
	cfa-3-c	-30	210	150	0.71	1911	90	-
SF Aggregate repl.	sf-1-a	5	300	150	0.50	1908	-	15
	sf-2-a	10	300	150	0.50	1890	-	30
	sf-3-a	15	300	150	0.50	1873	-	45
Cement repl.	sf-1-c	-5	285	150	0.53	1920	-	15
	sf-2-c	-10	270	150	0.56	1915	-	30
	sf-3-c	-15	255	150	0.59	1910	-	45

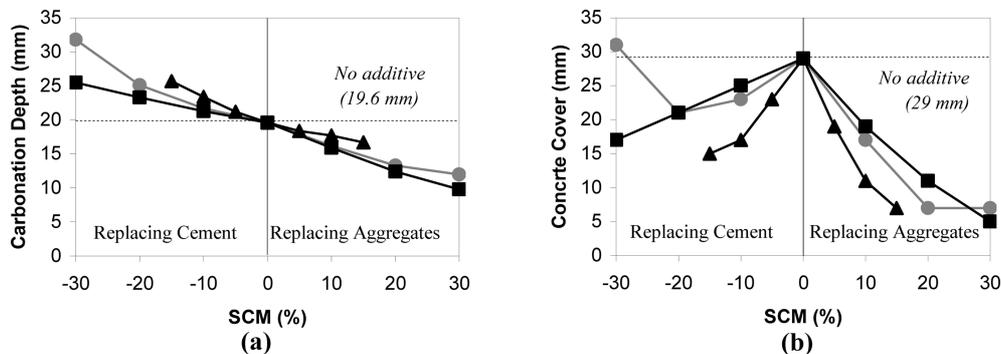


Fig. 2 Carbonation depth and sufficient concrete cover for chloride exposure of CEM I with Type II additives (▲ silica fume, ● siliceous fly ash, ■ calcareous fly ash)

factors (k -values) for strength and durability (chloride and carbonation exposure) to account for the effect of SCM, assuming a curing period of 28 days (or 91 days and 1 year in certain applications if necessary).

Overall it was seen that when SCM were used for aggregate replacement, the carbonation depth was decreased compared to the control mix (Fig. 2a and Table 2). Incorporation of calcareous fly ash (C-FA) in CEM I type of cement, produced a better performance for carbonation exposure than

Table 2 Durability indicators

SCM type	SCM (%)	f_c (MPa)	x_c (mm)	Δx_c (%)	$t_{cr,co2}$ (years)	Δt_{cr} (%)	$D_{e,co2}$ (m ² /s)	$\Delta D_{e,co2}$ (%)	C_{50} (mm)	ΔC_{50} (%)	$D_{e,Cl}$ (m ² /s)	$\Delta D_{e,Cl}$ (%)
Control	0	44.6	19.6	-	116,9	-	0,927	-	29	-	0.149	-
S-FA	10	47.4	16.2	-17.3	172	47,1	0,598	-35,5	17	-41.4	0.047	-68,7
Aggr.	20	50.3	13.3	-32.1	200	71,1	0,380	-59,0	7	-75.9	0,011	-93,0
Repl.	30	50.4	12.0	-38.8	200	71,1	0,311	-66,4	7	-75.9	0.009	-94,0
Cem. Repl.	-10	41.8	21.7	-	95.4	-18,4	0,965	4,1	23	-20.7	0,071	-52,1
	-20	38.0	25.1	-	71,3	-39,0	1,089	17,4	21	-27.6	0,046	-68,9
	-30	31.7	31.8	-	44,6	-61,8	1,522	64,2	31	-	0,086	-42,2
C-FA	10	51.4	15.9	-18.9	177,2	51,6	0,615	-33,7	19	-34.5	0,067	-54,9
Aggr.	20	58.0	12.4	-36.7	200	71,1	0,376	-59,4	11	-62.1	0,025	-83,2
Repl.	30	64.4	9.8	-50.0	200	71,1	0.235	-74,6	5	-82.8	0,073	-95,1
Cem. Repl.	-10	45.8	21.3	-	99,3	-15,1	0,988	6,5	25	-13.8	0,096	-35,7
	-20	46.9	23.3	-	83,2	-28,8	1,055	13,8	21	-27.6	0,060	-60,1
	-30	48.0	25.5	-	69,2	-40,8	1,119	20,7	17	-41.4	0,033	-77,6
SF	5	50.8	18.4	-6.1	132,2	13,2	0,819	-11,6	19	-34.5	0,057	-62,0
Aggr.	10	56.9	17.7	-9.7	143,5	22,8	0.755	-18,6	11	-62.1	0,019	-87,5
Repl.	15	62.0	16.7	-14.8	161,8	38,4	0.670	-27,8	7	-75.9	0,005	-96,7
Cem. Repl.	-5	48.0	21.2	-	99,9	-14,5	1.031	11,2	23	-20.7	0,072	-52,0
	-10	51.4	23.4	-	82,2	-29,7	1,187	28,0	17	-41.4	0,029	-80,5
	-15	51.4	25.7	-	67,9	-41,9	1,355	46,2	15	-48.3	0,022	-85,4

siliceous fly ash (S-FA) (Fig. 2a). Addition of 30% of C-FA reduced the carbonation depth by 50%, compared to a 38.8% reduction, when S-FA was used. Silica fume (SF) did not prove to be as effective as fly ash (FA), in inhibiting carbonation exposure. To draw a comparison between results, 10% addition of SF reduced the carbonation depth by 9.7%, compared to the 17.3% and 18.7% reductions observed when 10% of siliceous and calcareous fly ash was added. In the case where SCM were used as cement replacement materials, the carbonation depth was increased, with the increasing content of every type of SCM used.

Under chloride exposure (Fig. 2b), specimens incorporating SCM as either aggregate or cement replacement, produced smaller adequate concrete cover values (needed to sustain chloride exposure for a service life of 50 years), compared to control. Silica fume proved to inhibit chloride diffusion more efficiently than FA. A 62.1% reduction of the adequate concrete cover was noticed, compared to 41.1 and 34.5% reductions when siliceous or calcareous fly ash were respectively used (for 10% content of SCM). At higher concentration of SCM, calcareous fly ash proved to be more effective than siliceous one (82.8% reduction of the former, compared to a 75.9% reduction of the latter). Considerable reductions of the chloride ions intrinsic diffusivity, were also noticed (Fig. 3). Again, silica fume proved to be the most efficient SCM in that regard (10% of silica fume reduced the chloride diffusivity by 87.5%). Overall, a common observation of every type of SCM investigated, longer reductions of the adequate concrete cover (by 20.7%, for 10% of silica fume) and of the effective diffusivity (up to 19.2%) were noticed when SCM replaced aggregates compared to when

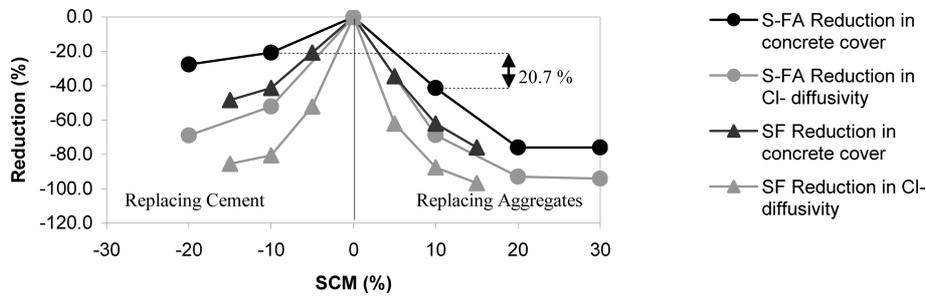


Fig. 3 Reduction of chloride diffusion coefficient and of adequate concrete cover needed to sustain chloride exposure for 50 years on silica fume and siliceous fly ash mixes

Table 3 Differences for 10% of SCM between aggregate and cement replacement

SCM (10%)	Reduction of adequate concrete cover (%)			Reduction of effective chloride diffusivity (%)		
	Replacing cement	Replacing aggregates	Difference	Replacing cement	Replacing aggregates	Difference
Silica fume	41.4	62.1	20.7	80.5	87.5	7.0
Siliceous fly ash	20.7	41.4	20.7	52.1	68.7	16.6
Calcareous fly ash	13.8	34.5	20.7	35.7	54.9	19.2

cement was replaced (Table 3).

3.2 Effect of CEM II type of cement on concrete durability

The service life of every CEM II type of cement, according to its composition and categorization under the EN 197-1 Standard, was evaluated for carbonation and chloride exposure. A standard CEM I mix of 0.45 water-cement ratio was selected as the reference type of cement (cement content

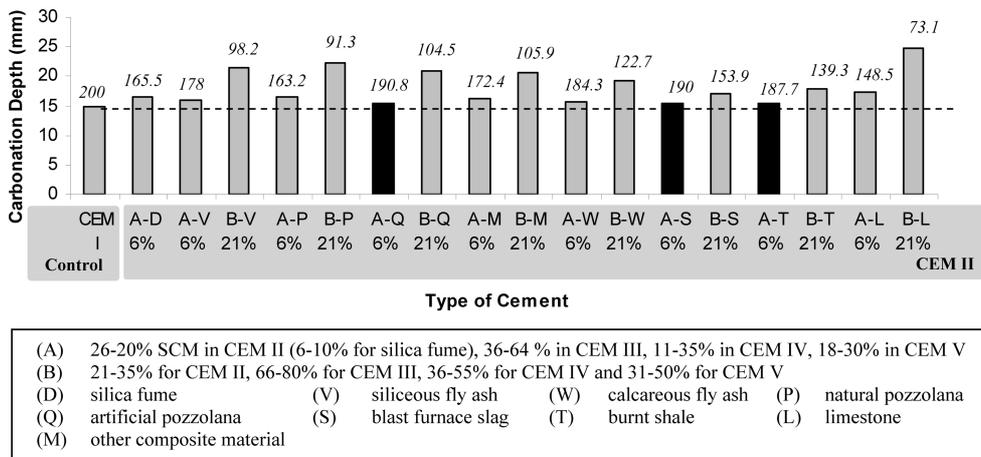


Fig. 4 Best carbonation depth values for a service life of 50 years of CEM II cement types

300 kg/m³, 31.5 mm crushed aggregates, no additives, no admixtures). On each type of SCM used, three different content levels were considered (minimum, medium and high).

An initial observation is that carbonation depth was increased (Fig. 4) and the critical time for initiation of corrosion (for a 30 mm concrete cover, indicated with *italics* in Fig. 4) was reduced, compared to the control values, for every type of CEM II cement. However, closer inspection reveals that certain types of cements, with low content of SCM (6%) produced a more suitable behavior. More specific:

- Portland-composite cements incorporating 6% artificial pozzolana (*Q*) and/or blast furnace slag (*S*), gave the most tolerable behavior in carbonation (4.1% increase of carbonation depth) followed by cement incorporating 6% burnt shale (*T*, 4.7% increase of carbonation depth).
- Cements incorporating pozzolanic materials with hydraulic properties (*W*, *S*, *T*), behaved much better (4.7% deviation from control) than those containing normal pozzolanic materials (*V*, *P*, *Q*, *M*, 8.3% deviation from control).
- Cements incorporating silica fume (*D*) produced a steady performance, regardless the SCM increase (11.5% increase of the carbonation depth).
- The lowest performance in carbonation exposure was produced by cements incorporating limestone.

Under chloride exposure every different type of Portland-composite cement used (except the one with limestone, CEM II/B-LL) behaved in an extraordinary way (Fig. 5). Cement incorporating 15% artificial pozzolana (CEM II/A-Q) produced the best performance (reductions of up to 62.2% on the concrete cover and 92.9% reduction of the chloride ions diffusivity, as shown in Fig. 6)

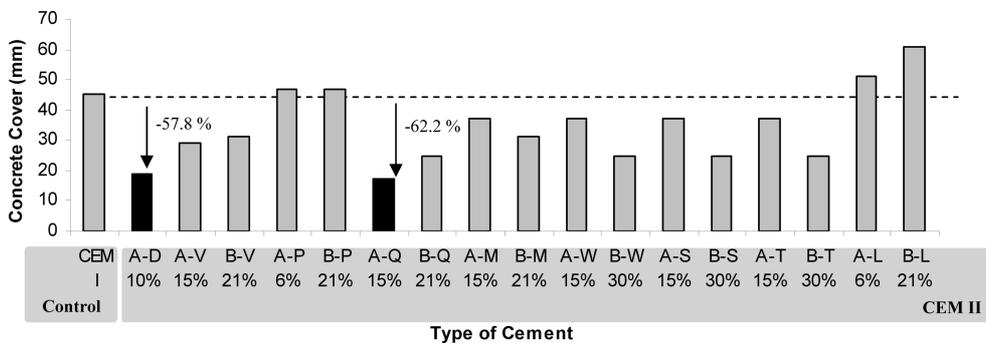


Fig. 5 Best adequate concrete cover values calculated to sustain for a service life of 50 years under chloride exposure, for every type of CEM II cements

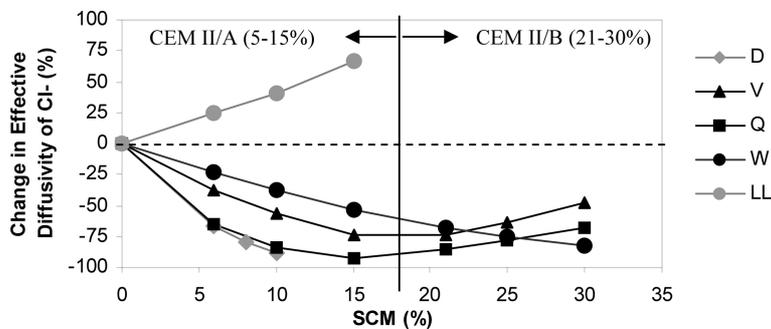


Fig. 6 Change of chloride ions diffusivity with SCM type and content

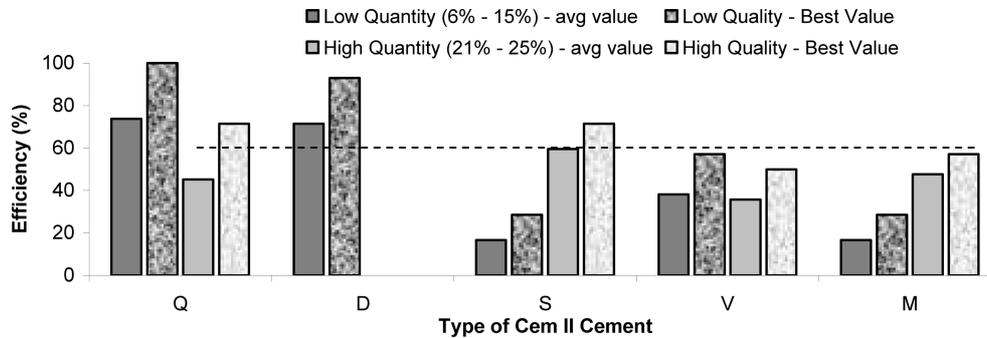


Fig. 7 Comparative performance of SCMs in chloride diffusion

followed by cements incorporating silica fume (CEM II/A-D, 57.8% decrease).

Overall the following observations were made:

- Cements containing pozzolanic materials with hydraulic properties, calcareous silica fume (*W*), blast furnace slag (*S*) and burnt shale (*T*), behaved in a similar manner, producing the best performance, overall, at low (6%-15%) and high (21%-30%) quantities of SCMs. The concrete cover values kept reducing with the increasing SCM content (up to 44.4% for 30% SCM).
- Cements containing siliceous fly ash (*V*) and other composite materials (*M*) produced reduced concrete cover values (35.6% reduction) up to a certain SCM percentage (15% and 21% respectively). At larger SCM quantities an increase in the concrete cover was noted.
- Incorporation of natural pozzolana (CEM II/A, B-P) gave increased concrete cover values (up to 22%).
- Addition of 15% of limestone increased the concrete cover by 26.7% (compared to control) but most important the chloride diffusivity by 67% (Fig. 6).

Based on the performance of the CEM II type of cements for chloride exposure, a scale of effectiveness was created, where by setting the control values (CEM I) as the reference/starting point of the scale and the performance of the 15% CEM II/A-Q (best performance) in chloride exposure, as the top (best) value, the behavior of each other type of CEM II cement was benchmarked against those values. Overall, the performance of the different types of SCMs in chloride exposure can be summarized as it is illustrated in Fig. 7.

3.3 Effect of other types of cement (CEM III, IV, V) on concrete durability

The steady performance of the increasing slag content on CEM II/S type of cement (previously mentioned), was further investigated, by evaluating cements with higher quantities of slag (CEM

Table 4 Performance of CEM III, IV, V type of cements

	CEM I (control)	CEM III/A			CEM III/B			CEM IV/A			CEM IV/B		CEM V/A
SCM (%)	0	36	43	51	66	11	20	30	36	40	45		
x_c (mm)	14.8	18.4	19.1	22.3	42.2	17.7	20.3	25.6	26.4	30.1	34.0		
t_{cr} (years)	200	133.4	123.1	90.3	25.3	144.3	109.4	68.6	64.6	49.7	38.8		
c_{50} (mm)	45	21	15	17	75	39	33	41	43	53	63		
c_{50} (%)	-	-53.3	-66.7	-62.2	8.9	-13.3	-26.7	-8.9	-4.4	17.8	40.0		

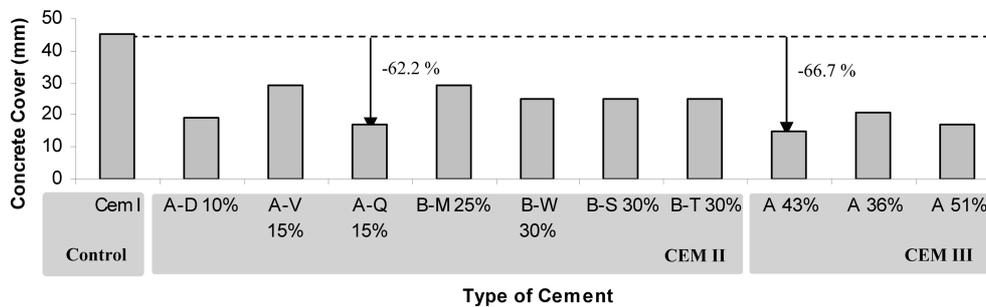


Fig. 8 Comparative performance of SCMs in chloride diffusion

III), where at 43% of SCM a 66.7% reduction of the adequate concrete cover needed to sustain a chloride free reinforced concrete structure for 50 years was noticed (Table 4). Overall blast furnace cements (CEM III) performed extremely well under chloride exposure (in contrast to their carbonation behaviour).

Comparing the best behavior of CEM II and CEM III type of cements it can be seen that a 43% blast furnace cement (CEM III) produced the best performance in designing for chloride exposure (at 50 years) than any other CEM II type of cement (Fig. 8).

As far as CEM IV type of cements is concerned, carbonation depth kept increasing with an increasing percentage of SCM. However, smaller values compared to CEM III type of cements were noticed. Up to 20% of SCM, the concrete covers (for chloride exposure) reduced by 26.7%. Increasing the content of slag, up to 40%, the concrete cover values started to increase but they still remained 4.4% below the control value. Finally, Composite cements (CEM V) gave considerable increases in carbonation depth, in addition to a very poor performance in chloride diffusion.

4. Discussion

The results of this study, as far as the concrete service life estimation of the effect of Type II additives on CEM I cement is concerned, showed that silica fume and fly ash reduced the carbonation depth values considerably (compared to the control) when used as aggregate replacements, an observation also reached by other researchers (Khunthongkeaw *et al.* 2006, Valcuende and Parra 2010). However, when these materials replaced cement, increased carbonation depths were observed. The explanation for such behaviour lays in the way these materials were incorporated into the mix. For aggregate replacement by an SCM the total amount of carbonatable materials remains almost the same and moreover the porosity decreases (and the diffusivity of carbon dioxide, see Table 2) resulting in lower carbonation rates (Papadakis 2000). In the case of cement replacement by SCM, by reducing the cement and clinker content, the amount of carbonatable materials is also reduced (due to the decrease in total CaO), resulting in higher carbonation rates (Valcuende and Parra 2010). In general SCM materials (as cement replacements) proved to be less resistant to carbonation, mainly due to their low binding capacity of CO₂, caused by their smaller concentrations of Ca(OH)₂, compared to control (due to the consumption by pozzolanic reaction and lower cement content). However, considering that for reasons of comparison certain parameters were kept unchanged (*w/c* ratio, cement content) better performances in carbonation exposure (than control) can be achieved by altering

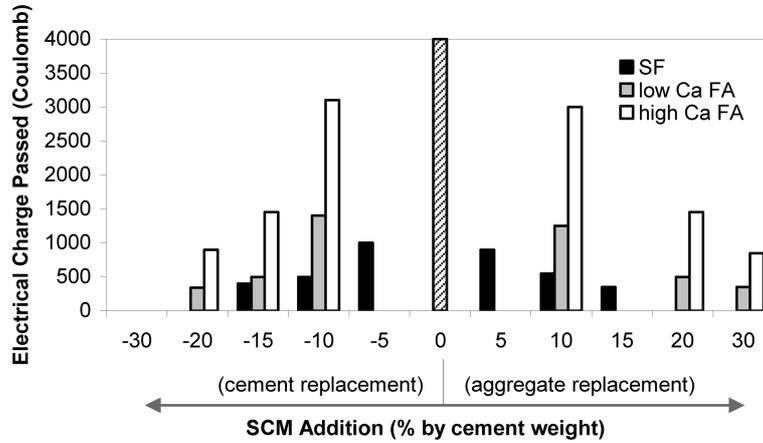


Fig. 9 Rapid chloride permeability on samples incorporating SCM (Papadakis 2000)

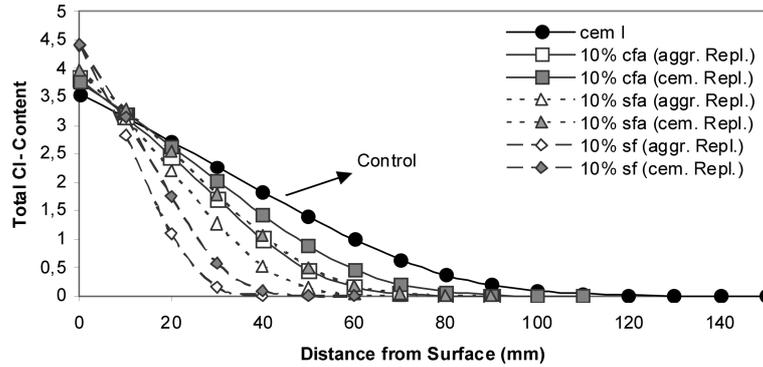


Fig. 10 Estimated total chloride profiles of SCM incorporating samples

these parameters.

Under chloride exposure every SCM behaved much better than control. It has been noticed that specimens incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface (Antiohos and Tsimas 2003, Chalee *et al.* 2010, Hosam *et al.* 2010). Rapid chloride permeability results, undertaken by the authors at a previous time (Papadakis 2000) on samples incorporating SCM, indicated that they all exhibited lower electrical charge than the control sample (OPC), with silica fume producing the best performance (Fig. 9). Such a trend was clearly visible on this study (Fig. 10). Silica fume, when used as additive, proved to be most efficient in inhibiting chloride ingress, followed by calcareous and siliceous fly ash.

Silica fume, composed by very small spherical particles, due to its ultra fineness and activity led to the formation of intense pozzolanic reaction products (with increased chloride ion binding capacity than fly ash) within the capillary pore spaces and as a consequence, a finer and more segmented pore system was produced (Hosam *et al.* 2010, Nochaiya *et al.* 2010). SEM analysis of a 14 days hydrated silica fume-cement paste sample (Fig. 11), indicates that, a fine network of pozzolanic product (CSH) has been created in the middle of a capillary pore, acting as a trap for chlorides.

Calcareous fly ash, apart of being pozzolonic active, reacting faster than the silicious one, it

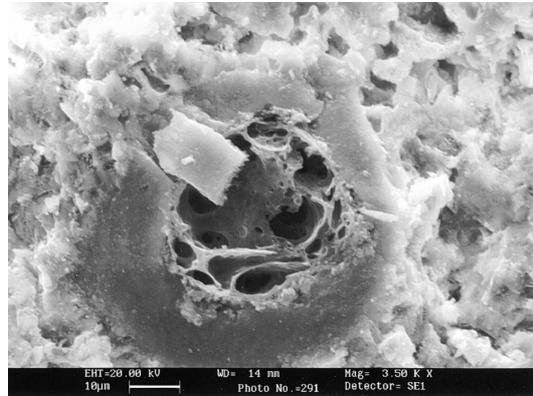


Fig. 11 SEM of 10% silica fume-cement paste after 14 days of hydration

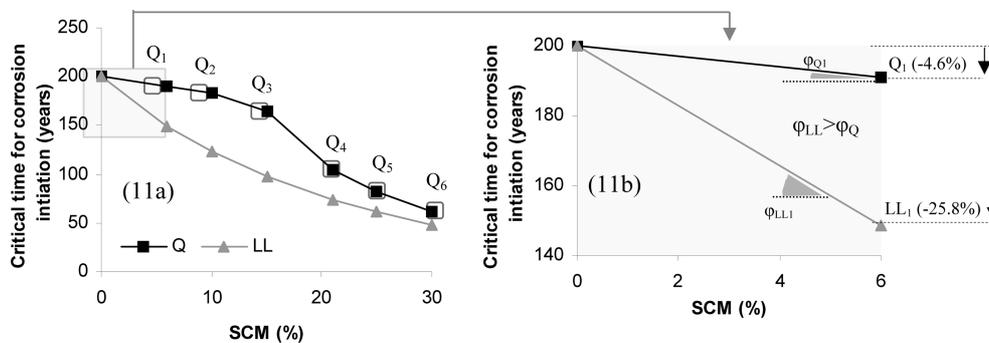


Fig. 12 Critical time for initiation of corrosion

contains higher amounts of aluminate-cementing compounds (C_3A , C_4AF), leading to more increased chloride ion binding capacity and Friedel's salt formation (Antiohos and Tsimas 2003) resulting in considerable decreases of the chloride ions diffusion coefficient (Table 2) and to an improved resistance of concrete to chloride penetration (Byung and Jang 2007).

On the service life evaluation of CEM II type of cements, larger carbonation depths than control were noticed. This is a general remark observed by other researchers (Kaid *et al.* 2009, Lo *et al.* 2009, Sisomphon and Franke 2007), mainly attributed to their low portlandite content and the subsequent reduction of $Ca(OH)_2$ from the pozzolanic activity. However, certain types of cement (6% artificial pozzolana, 6% fly ash, 6% blast furnace slag) produced a more tolerable behaviour. Trying to investigate the reasons, it is worth looking at the rate that these reductions took place. Considering the slope (angle) of the decrease of the critical time with the increasing SCM content, it can be seen (Fig. 12) that limestone Portland cements (which gave the worst performance in carbonation) produced the biggest rate of reduction (a slope of 83.4° , Table 5), which remained almost constant with increasing SCM content, in contrast to artificial pozzolana cement (which gave the most tolerable behaviour) where the reduction took place at a lesser pace (a slope of 56.9°) at small SCM quantities.

In general, although it is not the scope of this study to elaborate on this subject, the degree (slope) of the reduction of the critical time for initiation of corrosion is a factor of the rate of calcium hydroxide consumption by the pozzolanic reaction of the incorporated SCM (hence the available

Table 5 Ratio of reduction of the critical time for initiation of corrosion expressed as the slope of the change of that critical time with step by step increment of SCM

	SCM increment (%)	Slope (°)								
		V	Q	P	M	W	S	T	L	D
1	0-6	74,7	56,9	80,7	77,7	69,1	59,0	64,0	83,4	80,1
2	6-10	81,8	60,6	79,9	80,5	80,8	72,0	73,7	81,0	-
3	10-15	75,5	76,0	79,5	77,4	72,0	31,8	70,2	79,2	-
4	15-21	79,6	84,2	75,1	73,5	74,5	73,8	73,9	75,9	-
5	21-25	79,1	80,0	76,0	75,0	69,8	27,7	68,6	70,8	-
6	25-30	75,3	76,4	72,7	77,7	65,9	63,4	63,2	70,2	-

Table 6 Factors influencing the rate of decrease of the critical time for initiation of corrosion

	Effective diffusivity of CO ₂ (m ² /s)			Ca(OH) ₂ content (kg/m ³)			Degree of pozzolanic reaction			Carbonated concrete porosity		
	Q	S	L	Q	S	L	Q	S	L	Q	S	L
0		0.5307			69.2						0.068	
1	0.4937	0.5529	0.6851	38.9	60.5	64.8	1	1	1	0.067	0.069	0.073
2	0.4611	0.5784	0.7891	18.7	54.7	61.8	1	1	1	0.066	0.070	0.076
3	0.4566	0.5727	0.9452	0	47.5	58.1	0.9	1	1	0.066	0.070	0.080
4	0.6617	0.628	1.1632	0	38.8	53.7	0.59	1	1	0.073	0.072	0.085
5	0.8003	0.6219	1.3063	0	33.0	50.7	0.47	1	1	0.077	0.072	0.088
6	0.9951	0.5529	1.5702	0	25.7	47.0	0.37	1	1	0.082	0.073	0.093

Ca(OH)₂ content), the effective diffusivity of carbon dioxide in concrete and of the porosity of the carbonated concrete. Even though in both cases the level of the carbonatable materials is reduced (quantity of Ca(OH)₂, Table 6) in the case of artificial pozzolana cement the porosity was reduced, leading to a decreased diffusivity of CO₂, up to 15% of SCM, in contrast to limestone incorporating cements, where an increase in porosity and in CO₂ diffusivity were noticed. Hence, it can be said that in certain cases at low SCM concentration, the pozzolanic action and the filling properties of the SCM afford certain changes in porosity which predominate over the reduction in carbonatable materials leading to a less severe carbonation effect, an explanation which is further reinforced with results from other researchers (Khunthongkeaw *et al.* 2006, Valcuende and Parra 2010).

A significant number of researchers have dealt with the resistance of concrete that incorporate SCM, on chloride ingress. They all seem to agree that the ability of concrete to resist such an attack is mainly related to its microstructures and the chloride binding capacity of the formed hydration products. In this particular study, every type of CEM II cement (apart of CEM II/LL) produced reduced adequate concrete covers needed to sustain that exposure for 50 years, than control, with cements incorporating artificial pozzolana, silica fume and blast furnace slag to be the most efficient. The “not efficient” behavior of cements containing limestone, observed in this study (based on the simple mix design used, *w/c* 0.5, cement content 300 kg/m³), is not surprising due to its very low aluminum concentration (hence reduced ability to form Friedel’s salt). In general CEM II/A-L type of cements have the lowest chloride resistance (Loser *et al.* 2010) leading to increased penetration of chloride ions at quantities of limestone above 15% (Ramezaniapur *et al.* 2009) and increased

risk of corrosion (Lang 2005). Recent results indicate that very good resistance to chloride penetration and considerable decreases of the diffusion coefficients were noticed on cements containing pozzolans (Hosam *et al.* 2010), blast furnace slag (Guneyisi *et al.* 2009, Kaid *et al.* 2009, Tamimi *et al.* 2008) and silica fume (incorporation of 7.5% of silica fume reduced the diffusion coefficient of chlorides three times compared to a simple OPC mix, Elahi *et al.* 2010).

CEM III type of cement proved to be the most effective in inhibiting chloride ingress (a decrease of 66.7% on adequate concrete cover values was noticed for a 43% CEM III type of cement). Slag replacements of up to 40% have been known to reduce drastically the chloride penetrability of concrete (Tamimi *et al.* 2008), mainly due to the binding characteristics of the SCM. CEM III type of cement have a very high Al_2O_3/SO_3 ratio, leading to the formation of more AFm phases (and less AFt phases), increasing in this way the formation of Friedel's salt and the chemical binding of chloride ions (Selih *et al.* 2003).

A scale of effectiveness was created to be able to provide a unified numerical benchmarking of their effectiveness. Overall, considering the results of CEM II and CEM III type of cements overall, although several types of SCM performed extremely well at quantities up to 30%, blast furnace slag proved to be the most beneficiary SCM at large quantities (and overall) in inhibiting chloride ingress.

4. Conclusions

A comparative assessment of all the SCM incorporated cement types, categorized according to the European standard EN 197-1 for Cement, took place in this study, based on proven predictive models for the estimation of service life under harsh environments (briefly presented in principle). It was shown that

- Mixtures incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface.
- Under carbonation exposure even though CEM II type of cements produced larger carbonation depths compared to control, certain types of CEM II cement produced a "less severe" behaviour, at low quantities of SCM. A possible explanation is that at these low quantities the pore structure refinement predominates over the reduction of the carbonatable materials.
- Overall the CEM II type of cements produced an effective performance in terms of chloride exposure. Utilization of blastfurnace slag, artificial pozzolana and silica fume proved to be the most effective SCMs.
- The effect of slag proved to be beneficial even at larger quantities (40%, CEM III).

Taking into account the reduction in clinker achieved when an SCM is utilized and the overall performance of these materials presented in this study, utilization of these types of cement not only can guarantee a durable solution (under harmful environmental agents) but they also provide a sustainable solution, by reducing the CO_2 emissions associated with the clinker burning process during cement manufacturing.

Overall, it is hoped that the results of this study will pave the way for more thorough research attempts on the durability of SCM aiding in this way on the future utilization, in large scale, of these types of materials from cement manufacturing companies.

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