Supplementary cementing materials in concrete
Part I: efficiency and design

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Abstract

Many solid industrial by-products such as siliceous and aluminous materials (fly ash, silica fume, slags, etc.) as well as some natural pozzolanic materials (volcanic tuffs, diatomaceous earth, etc.) may be characterized as supplementary cementing materials (SCM) as they exhibit cementitious and/or pozzolanic properties. Due to plenty of these materials and their large variations on physical and chemical composition, the development of a general design for their use in concrete is required. In this work, the concept of an efficiency factor is applied as a measure of the relative performance of SCM compared with Portland cement. Artificial materials of various compositions and some natural pozzolans were studied. Compressive strength and accelerated chloride penetration tests were performed. With regard to these characteristics, efficiency factors for these materials were calculated. A mix design strategy to fulfil any requirements for concrete strength and service lifetime was developed and it enables concrete performance to be accurately predicted.
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1. Introduction

Supplementary cementing materials (SCM) may be divided into natural materials and artificial ones. To the former belong true pozzolans and volcanic tuffs. To the second category belong siliceous by-products, such as fly ashes, condensed silica fume and metallurgical slags (blast furnace slag, steel slag and nonferrous slags). Fly ash is the combustion residue (coal mineral impurities) in coal-burning electric power plants, which flies out with the flue gas stream and is collected by mechanical separators, electrostatic precipitators or bag filters. Condensed silica fume, sometimes known simply as silica fume or microsilica, is produced by electric arc furnaces as a by-product of the production of metallic silicon or ferrosilicon alloys. Slags are by-products of metallurgical furnaces producing pig iron, steel, copper, nickel and lead. According to ASTM C 595, a pozzolan is defined as "a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form compounds possessing cementitious properties (pozzolanic activity)." Thus, a pozzolanic material requires $Ca(OH)_2$ in order to form strength products, whereas a cementitious material itself contains quantities of CaO and can exhibit a self-cementitious (hydraulic) activity. Usually, the CaO content of the latter material is insufficient to react with all the pozzolanic compounds. Thus, it also exhibits pozzolanic activity (pozzolanic and cementitious materials). However, all these materials are often used in combination with Portland cement, which contains the essential for their activation, $Ca(OH)_2$ from its hydration.

It is generally accepted [1,2] that sustainable development of the cement and construction industries can be achieved by maximization of the use of cementitious and pozzolanic by-products. Besides the effect on usual structural properties, such as strength and volume stability, the durability of concrete incorporating SCM should be taken into account. As the majority of concrete deterioration cases is mainly connected to corrosion of reinforcement due to carbonation- or chloride-induced depassivation of steel bars

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[3,4], the effect of SCM on these deterioration mechanisms has to be studied.

In previous publications [5–7], a simplified scheme describing the activity of silica fume and fly ash in terms of chemical reactions is proposed, yielding quantitative expressions for the estimation of the final chemical and volumetric composition of SCM concrete. In the present work, a practical approach to the effect of SCM on the strength of Portland cement systems and on their resistance against carbonation and chloride penetration is presented using the concept of the SCM efficiency factor. The efficiency factor (or k-value) is defined as the part of the SCM in a pozzolanic concrete, which can be considered as equivalent to Portland cement, having the same properties as the concrete without SCM (obviously $k = 1$ for Portland cement). The quantity of the SCM in the mixture can be multiplied by the k-value to estimate the equivalent cement content, which can be added to the cement content for the determination of the water/cement (W/C) ratio, minimum required cement content, etc. The compressive strength was so far used as the property for the estimation of k-values [8,9]. In this work, durability properties are also used, such as resistance against carbonation and chloride penetration, and relative k-values are calculated. By applying the concept of the SCM efficiency factor, a concrete design strategy is presented which fulfils the standard specifications and strength expectations, and it ensures the required service lifetime.

2. Experimental section

2.1. Materials and specimen preparation

Six typical Greek SCMs were used: two natural materials and four industrial by-products. The natural materials were a volcanic tuff from Milos Island (Milos earth, defined as ME) and a diatomaceous earth from Samos Island (defined as DE). Three different fly ashes from Greek power plants (produced by Puplic Power) were used, i.e., a fly ash of relatively lower calcium content than the other fly ashes (fly

ash from Megalopolis plant, defined as FL), a high-calcium fly ash of normal sulfur content (fly ash from Ptolemais plant, defined as FH) and a high-calcium fly ash of high sulfur content (fly ash from Ptolemais plant, defined as FHS). Finally, a nickel slag (SL) produced by LARKO was used (defined as SL). All these SCMs were ground prior to use up to a fineness of 400 ± 20 m^2/kg according to Blaine's test [10]. Grinding of SCM reduced the particle size, broke up cenospheres and released smaller particles contained in pleroshperes, resulting in a significant increase of surface area available for pozzolanic reactions [2].

A rapid setting Portland cement was used (CEM I 52.5R according to European Standard EN 197) of the same fineness. Oxide analyses for all materials are presented in Table 1. The fraction of SiO_2, which is active for pozzolanic reactions, is also given (active silica). Normal graded limestone aggregates, including fine (37%), medium (21%) and coarse (42%) aggregates, were used. The coarse aggregate maximum size was 31.5 mm, the medium one was 8 mm and the fine one was 4 mm. Tap water at 20 °C was used. A common superplasticizer was used at a content of 0.5% of the total cementitious materials in order to retain the slump of the fresh concrete between 80 and 120 mm. The air content of the concrete mixtures was approximately 1%.

A constant volume unit (1 m^3) of concrete was chosen as a common comparison basis. When an SCM was added to this unit, then an equal mass of another component, either cement or aggregate, was removed in order to keep a similar total volume. Because of the similar density of SCM with that of aggregates (about 2600 kg/m^3 both), a mass substitution is equivalent with a volume one in the case of aggregates. In the case of cement substitution by an SCM, there is a little deviation due to the higher density of cement (about 3100 kg/m^3). The water content for all specimens was kept constant (175 kg/m^3). The mixture proportions of all concrete specimens are summarized in Table 2. For the control specimen, the W/C ratio was 0.5 and the aggregate/cement ratio (A/C) was 5.4. The dry materials were mixed for 2 min. Then, the water was added, containing the plasticizer and the mixing was continued for a further 2 min.

Table 1
Chemical analyses (%) of the materials used[a]

	Cement	FL	FH	FHS	SL	ME	DE
SiO_2	20.73	44.92	33.37	31.33	36.22	58.23	22.33
Al_2O_3	4.78	18.47	17.35	15.89	10.34	14.22	0.96
Fe_2O_3	3.87	7.90	5.57	5.37	40.19	4.31	1.00
CaO	64.73	14.87	25.21	27.38	5.08	7.40	45.89
MgO	2.05	2.22	3.05	3.02	3.12	1.43	1.54
K_2O	0.50	1.71	1.20	1.07	0.47	2.24	0.10
Na_2O	0.10	0.77	0.75	0.53	0.28	1.30	0.32
SO_3	2.47	3.89	5.57	7.90	0.23	1.16	1.24
Active SiO_2	–	70	75	73	5	50	50

[a] The methods specified by EN-450, EN-196 and EN-451 were followed.
[b] The fraction of SiO_2, which is soluble after treatment with HCl and with boiling KOH solution (European Standard EN 197-1).

Table 2
Mixture proportions for concrete specimens[a]

Specimen	C	W	P	A
Control	350	175	0	1900
P(+10)	350	175	35	1865
P(+20)	350	175	70	1830
P(−10)	315	175	35	1900
P(−20)	280	175	70	1900

[a] C, W, P and A: kg of cement, water, SCM (FL, FH, FHS, SL, ME, or DE) and aggregate, respectively, per m³ of total concrete volume (for zero air content). P(+): the SCM replaces aggregates, P(−): the SCM replaces cement, by weight of the control cement content.

2.2. Measurements

The specimens for strength measurements were cast in cubes of 150 mm, vibrated for 20 s on a vibration table and then covered to minimize water evaporation. The molds were stripped after 24 h and the specimens were immersed in lime-saturated water at 20 °C until testing. The testing age was after 2, 7, 28 and 90 days. For each age, three specimens of each mixture were tested for compressive strength and the mean value of these measurements is reported.

The specimens for rapid chloride permeability tests were cast in steel cylinders of 100 mm diameter and 200 mm height. The molds were stripped after 24 h and the specimens were placed under lime-saturated water at 20 °C for 90 days. This long-term curing period under water ensures an advanced degree of both Portland cement hydration and pozzolanic activity. The AASHTO T277 rapid test method was followed to rank the chloride penetration resistance of concrete by applying a potential of 60 V DC and measuring the charge passed through the specimen. The tested concrete cores were slices 51 mm thick, cut from the middle of the initially 200-mm specimens and coated with watertight tape on the cylindrical surface. Two specimens of each mixture were tested and the mean value is reported.

3. Results and modeling

3.1. Compressive strength

The experimental results are summarized in Fig. 1a–d for the two natural materials (ME and DE) and the three fly ashes (FL, FH and FHS). It is generally observed that when SCMs substitute aggregates, strengths higher than the controls are succeeded. The strength increase is due to the higher content of calcium silicate hydrate (CSH) (the main carrier of
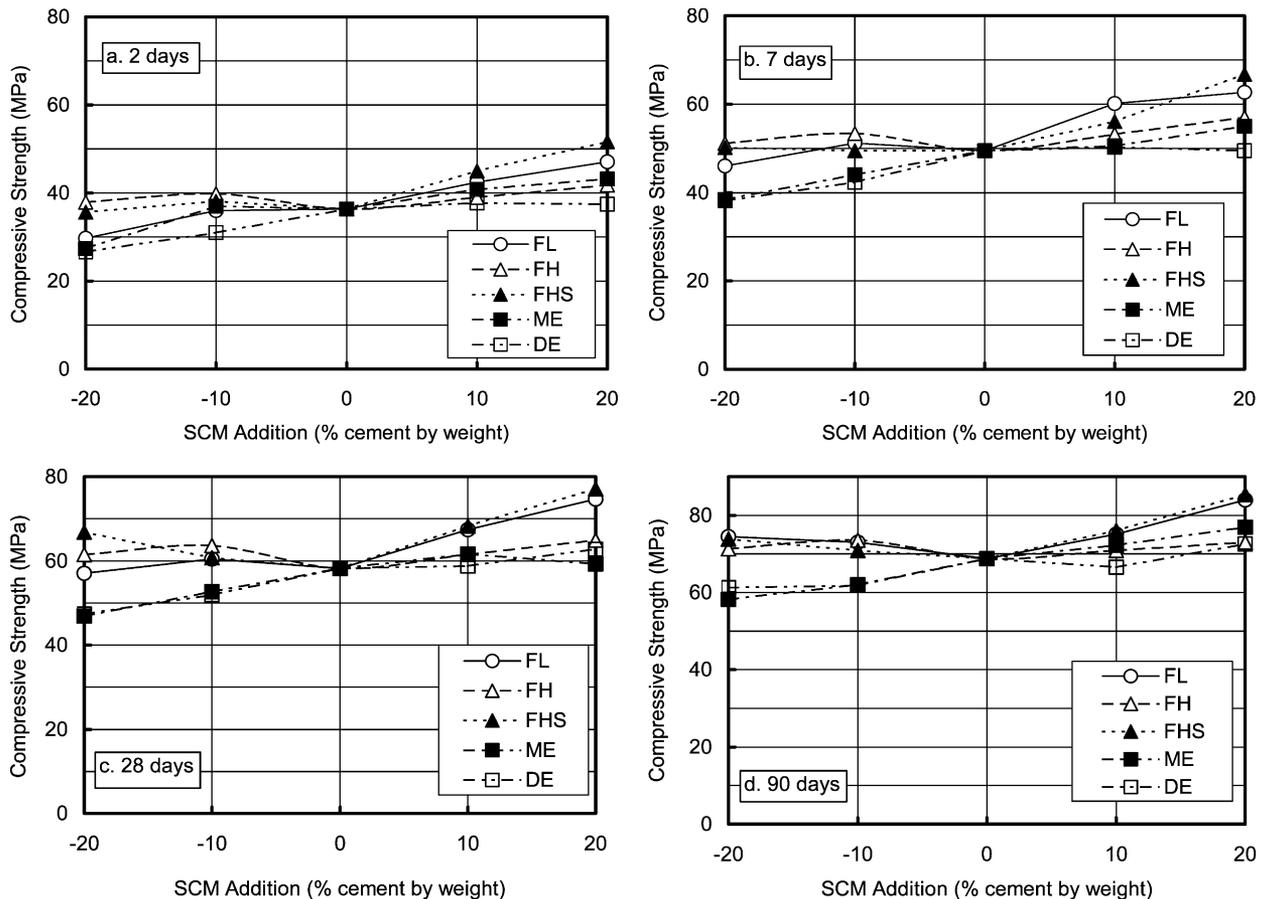
Fig. 1. Experimental results of compressive strength of SCM concrete specimens at various ages: (a) 2 days, (b) 7 days, (c) 28 days and (d) 90 days. The right-hand side refers to the case of aggregate replacement by SCM and the left-hand side refers to the case of cement replacement by SCM.
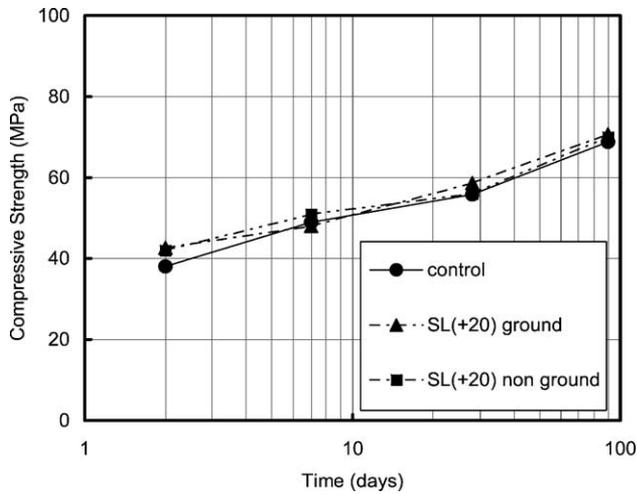
Fig. 2. Compressive strength development for concrete incorporating SL.

strength in hardened cement) in the SCM specimens, due to the reaction of the calcium hydroxide produced from cement hydration with the active silica of the SCM. There is a reasonable distribution of the strength increase according to the SCM content. When SCM replaces cement, the strength is reduced at first, but as time proceeds this gap is gradually eliminated. After 90 days, for all fly ash specimens, the strength becomes higher than that of the control. This ultimate improvement is due to the higher active silica content of fly ashes in comparison with the cement. However, in the case of natural SCM, the strengths are lower than the controls due to their lower content in available active silica [5–7]. Similarly, in the case of the SL, the strength results were almost identical to the controls, regardless of the slag was ground or not, as observed in Fig. 2.

In order to estimate the k-values, the following procedure was followed. The compressive strength f_c (MPa) of a Portland cement concrete can be estimated by the following empirical equation [11]:

$$f_c = K\left(\frac{1}{W/C} - a\right) \quad (1)$$

where W is the water content in the initial concrete mix (kg/m^3), C is the cement content in the concrete (kg/m^3), K is

a parameter depending on the cement type (MPa) and a is a parameter depending mainly on time and curing (Eq. (1)). For the Portland cement used in this work, the K was calculated as 38.8 MPa. Using the mean measured values of the compressive strength of the control specimen, a is estimated as 1.06, 0.72, 0.5 and 0.23 for 2, 7, 28 and 90 days, respectively.

In the case of SCM concrete, the following expression for compressive strength can be used which involves the concept of k-value:

$$f_c = K\left(\frac{1}{W/(C + kP)} - a\right) \quad (2)$$

where P is the SCM content in the concrete (kg/m^3). Using this equation, the measured values of the compressive strength given in Fig. 1 and the W, C and P contents given in Table 2, the k-values for the SCM of the present work were calculated and are given in Table 3. A comparison between the measured and the calculated compressive strengths, using Eq. (2) and the k-values of Table 3, is given in Fig. 3 and an excellent agreement is observed.

For fly ashes, the k-values are around unity ($K \approx 1$) at early ages and they exceed it as time proceeds. This means that up to a certain level [5–7], these specific pulverized fly ashes can substitute, equivalently, for Portland cement. The k-values calculated herein are in good agreement with those calculated earlier [12]. In a previous work [12], a k-value around unity was also calculated for the same high-calcium fly ash based on mortars. It must be noted that for a fly ash without calcium (anthracite fly ash) a k-value of 0.5 was calculated for 28 days of strength [12]. These very low calcium fly ashes are very common in the vast majority of European Union, where similar k-values are proposed (0.3–0.5) [8]. However, as time proceeds, higher k-values are calculated for these fly ashes approaching those of high-calcium fly ashes (0.7 for 91 days and 1.1 for 1 year) [12].

The natural SCMs exhibit much lower efficiency factors (0.3–0.4 for ME and 0.2 for DE). This is correlated with their low level of active silica content. Similarly, in the case of the SL, very low k-values of 0–0.1 were calculated,

Table 3
Efficiency factors (k-values) for various SCMs

Concrete property	FL[a]	FH[a]	FHS[a]	ME[a]	DE[a]	FZ[b]	SF[b]
Strength, 2 days	0.8	0.8	1.0	0.4	0.2	–	–
Strength, 7 days	1.0	0.9	1.0	0.3	0.2	–	–
Strength, 28 days	1.1	0.9	1.4	0.3	0.2	0.5	3
Strength, 90 days	1.2	0.9	1.2	0.3	0.2	0.7	2.4
Chloride resistance, 90 days	2.5	2	2	1	1	3	6
Carbonation resistance[b]	–	0.7	–	–	–	0.5	0.3

[a] This work.
[b] Previous work [12]. FZ: fly ash of almost zero calcium content, SF: silica fume.
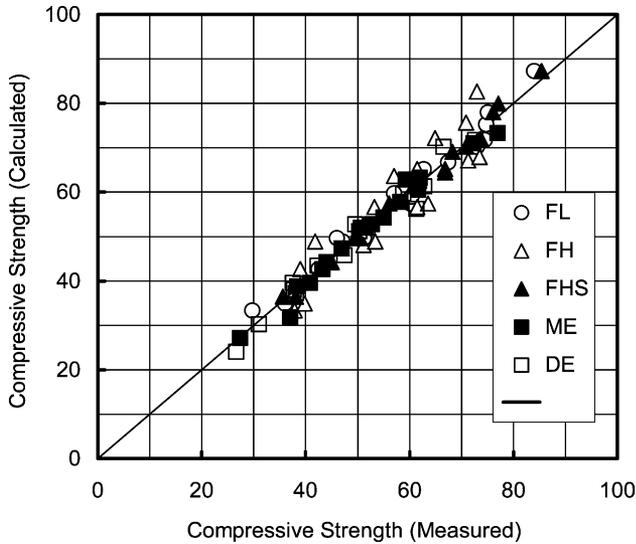
Fig. 3. Comparison between measured and calculated compressive strengths.

3.2. Chloride penetration

3.2.1. Chloride penetration and modeling

As observed in Fig. 4, the specimens incorporating a fly ash, whether it substitutes aggregate or cement, exhibit significantly lower chloride permeability as compared with the control specimen. Among all fly ashes tested, FL exhibited the lowest degree of chloride penetration followed by FH and then FHS the highest. As the fly ash content in the concrete volume increases, the chloride permeability decreases. There is a similarity in the results for natural pozzolans (ME and DE). However, in this case, the permeability is higher as compared with fly ash specimens, and when these materials replace cement in some cases, a chloride permeability higher than the controls is observed.

In many studies, chloride transport in concrete is modeled 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. Pereira and Hegedus [13] modeled chloride diffusion and reaction in fully saturated concrete as a Langmuirian equilibrium process coupled with Fickian diffusion. Papadakis et al. [14] and Papadakis [15] extended this approach to more general conditions, offering a simpler solution. The physicochemical processes of diffusion of Cl^- in the aqueous phase of the concrete pores, their adsorption and binding in the solid phase of concrete and their desorption therefrom are described by a nonlinear

partial differential equation for the concentration of Cl^- in the aqueous phase $[Cl^-(aq)]$ (in kg/m^3 pore solution), from which that of Cl^- bound in the solid phase $[Cl^-(s)]$ (kg/m^3 concrete) can be computed algebraically:

$$\frac{\partial[Cl^-(aq)]}{\partial t} = \frac{D_{e,Cl^-}(1 + K_{eq}[Cl^-(aq)])^2}{K_{eq}[Cl^-(s)]_{sat} + \varepsilon(1 + K_{eq}[Cl^-(aq)])^2}$$
$$\times \frac{\partial^2[Cl^-(aq)]}{\partial x^2} \quad (3)$$

$$[Cl^-(s)] = \frac{K_{eq}[Cl^-(aq)]}{1 + K_{eq}[Cl^-(aq)]}[Cl^-(s)]_{sat} \quad (4)$$

initial condition : $[Cl^-(aq)] = [Cl^-(aq)]_{in}$ at

$$t = 0 \text{ (initial concentration)} \quad (5)$$

boundary conditions : $[Cl^-(aq)] = [Cl^-(aq)]_0$ at

$$x = 0 \text{ (concrete surface)} \quad (6a)$$

$$\vartheta[Cl^-(aq)]/\vartheta x = 0 \text{ at } x = M \text{ (axis of symmetry)} \quad (6b)$$

In these equations, x is the distance from the concrete surface (m), t is the time (s), D_{e,Cl^-} denotes the intrinsic effective diffusivity of Cl^- in concrete (m^2/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
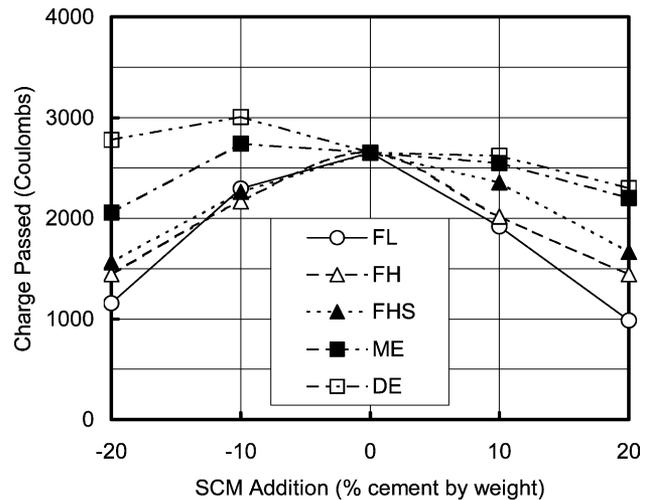
Fig. 4. Experimental results of rapid chloride penetration in SCM concrete specimens. The right-hand side refers to the case of aggregate replacement by SCM and the left-hand side refers to the case of cement replacement by SCM.

solid phase (kg/m^3 concrete) and ε the concrete porosity (m^3 pore volume/m^3 concrete). Eq. (3) can be solved only numerically, e.g., using a finite difference or element method. The solution of the above system allows estimation of the time (critical time for chloride-induced corrosion) required for the chloride concentration surrounding the reinforcement to increase over the threshold of depassivation of reinforcing bars.

3.2.2. Parameter estimation

In the case of "complete" hydration and pozzolanic action, the total porosity of concrete ε can be calculated using the mathematical expressions given elsewhere [5–7]. However, for the oxide analyses of the present materials, these expressions are simplified as follows:

$$\varepsilon = \varepsilon_{\text{air}} + (W - 0.227C - 0.19P)/1000 \tag{7}$$

where ε_{air} is the entrained or entrapped air content (Eq. (7)).

The intrinsic effective diffusivity of Cl$^-$ in concrete (m^2/s) can be estimated by the following semi-empirical equation [15] for NaCl (Eq. (8)):

$$D_{\text{e,Cl}^-} = \frac{2.4 \times 10^{-10}}{\left(\frac{C+kP}{\rho_C} + \frac{W}{\rho_W}\right)^2} (\varepsilon_{\text{eff}})^n \tag{8}$$

where n is a parameter equal with 3.5, k is the efficiency factor of the SCM for chloride penetration, ρ_C and ρ_W are the densities of cement and water, respectively (kg/m^3) and ε_{eff} an effective, for diffusion, porosity, calculated as follows (Eq. (9)):

$$\varepsilon_{\text{eff}} = W/\rho_W - 0.226 \times 10^{-3}(C + kP) \tag{9}$$

If sea attack concerns, the chloride concentration in the aqueous solution at the concrete surface $[\text{Cl}^-(\text{aq})]_0$ (kg/m^3 pore solution) depends on the sea location, e.g., Atlantic Ocean: 20 kg/m^3, North Sea: 16 kg/m^3 and Baltic Sea: 4 kg/m^3. The parameters $[\text{Cl}^-(\text{s})]_{\text{sat}}$ and K_{eq} can be determined from chloride binding isotherms. The following empirical expressions (Eqs. (10) and (11)) may be used [15]:

$$[\text{Cl}^-(\text{s})]_{\text{sat}} = 8.8 \times 10^{-3}(C + kP) \tag{10}$$

$$K_{\text{eq}} = 0.1 \text{ m}^3 \text{ pore volume/kg Cl}^- \tag{11}$$

3.2.3. Chloride threshold for reinforcement corrosion

It is very often reported that if the total Cl$^-$ content is more than 0.4% by weight of cement, the reinforcing steel is activated and corrosion may occur. Recently, it was demonstrated [16] that the threshold for uncracked sulfate-resistant Portland cement (SRPC) concrete is in the range of 1–1.3% total Cl$^-$ bw of binder, for SRPC concrete with 5% silica fume in binder is 0.8–1.0% and with 10–20%

low-calcium fly ash in the binder is about 0.7%. Thus, two critical total Cl$^-$ contents can be defined:

- a pessimistic: $(\varepsilon[\text{Cl}^-(\text{aq})]+[\text{Cl}^-(\text{s})])_{\text{cr,pes}} = 0.004C$ kg total Cl$^-$/m^3 concrete
- an optimistic: $(\varepsilon[\text{Cl}^-(\text{aq})]+[\text{Cl}^-(\text{s})])_{\text{cr,opt}} = 0.008(C+P)$ kg total Cl$^-$/m^3 concrete.

3.2.4. SCM efficiency factors for chloride penetration

The above model was applied and solved numerically using a finite difference method. In order for these predictions to fit the experimental data and taking into account the correlation of normal to rapid chloride penetration [15], the following optimum efficiency factors were estimated:

- $k=2.5$ for low-calcium fly ash (FL),
- $k=2$ for high-calcium fly ash (FH and FHS),
- $k=1$ for natural pozzolans (ME and DE).

These significantly higher k-values for SCM efficiency against chlorides as compared with the corresponding values for strength can be explained as due to important interactions of Cl$^-$ with the pore walls or by the electrical double layer at the pore walls–pore solution interface.

3.3. Concrete carbonation

Reinforcing bars are protected from corrosion by a thin oxide layer that forms on their surface due to high alkalinity of the surrounding concrete (steel passivation). Corrosion may start when this layer is destroyed:

- either by chloride penetration (and the chloride content exceeds a critical value)
- or by a reduction in the pH value of concrete to values below 9. Such a reduction in alkalinity is the result of carbonation of the Ca(OH)$_2$ in the concrete mass, i.e., of its reaction with the atmospheric CO$_2$ that diffuses through the concrete pores.

In marine or coastal environments and when deicing salts come in contact with the concrete surface, chloride penetration is the main mechanism that paves the way to initiation of reinforcement corrosion. In all other cases and especially in CO$_2$-rich urban areas, carbonation of concrete is the main mechanism leading to steel corrosion.

Papadakis et al. [17] developed and experimentally verified a fundamental and comprehensive model of the processes leading to concrete carbonation. For the usual range of parameters [especially, for relative humidity (RH) > 50%], certain simplifying assumptions can be made which lead to the formation of a carbonation front, separating completely carbonated regions from those in which carbonation has not yet started. The evolution of the carbonation depth x_c (m), with time t (s), is given by the following

analytical expression taking into account the concept of the efficiency factor [12]:

$$x_{c} = \sqrt{\frac{2D_{e,CO_2}(CO_2/100)t}{0.218(C+kP)}} \qquad (12)$$

where CO_2 is the CO_2 content in the ambient air at the concrete surface (%), k is the efficiency factor of SCM regarding carbonation resistance and D_{e,CO_2} is the effective diffusivity of CO_2 in carbonated concrete (m²/s). In an ambient RH (%), the diffusivity is given by the empirical equation [12,15]:

$$D_{e,CO_2} = 6.1 \times 10^{-6} \left(\frac{(W - 0.267(C+kP))/1000}{\frac{C+kP}{\rho_C} + \frac{W}{\rho_W}} \right)^3$$
$$\times (1 - RH/100)^{2.2} \qquad (13)$$

Eq. (12) predictions were fitted to experimental results [12] and after parameter optimization, k-values for resistivity against carbonation of 0.5 and 0.7 for low-calcium fly ash and high-calcium fly ash, respectively, were estimated (Table 3).

4. Mix design and lifetime prediction of concrete incorporating SCM

According to European Standard EN-206 [9], "additions of Type I (nearly inert additions) and Type II (pozzolanic or latent hydraulic additions) may be used in concrete in quantities as used in the initial tests." These additions may be taken into account in the concrete composition using the k-value concept. In all specifications for concrete production, among the main design parameters are the cement content (C) and the W/C. Thus, minimum values of cement content and maximum values of W/C ratio are specified according to the aggressiveness class of the surrounding environment.

Despite the exposure classes, whenever SCM is used in concrete, the total equivalent cement content should be taken into account:

$$C_{eq} = C + kP \qquad (14)$$

where C and P are the contents of Portland cement and SCM in concrete, respectively (kg/m³) and k the SCM efficiency factor (Eq. (14)). Usually, k-values of 2 and 0.5 for silica fume and low-calcium fly ash are proposed (for 28 days), respectively [9]. From the present work, new k-values (for strength) are proposed and summarized in Table 3. The k-values for strength of 2, 7 and 28 days or advanced hydration (90 days) may be used according to the specific project requirements. These values are valid for a certain amount of SCM in concrete. As given in previous publications [6,7], the maximum fly ash content in concrete shall be 25–50% of the

cement weight depending on calcium content of the fly ash. Further experiments are required for an accurate approach in the case of multicomponent SCM use in concrete.

After having specified the concrete composition (primarily C, W, P and A contents of Portland cement, water, SCM and aggregate, respectively, in kg/m³) that fulfils the strength expectations and standard requirements (e.g., minimum equivalent cement content, maximum W/C_{eq} ratio, etc.), the concrete durability should be examined. Let us suppose that the design service lifetime is L years. Thus, this specific concrete composition must be examined to determine whether it ensures a service lifetime greater than the design life in the deterioration environment in which the concrete will be exposed. In the present approach, only the carbonation and chloride-induced deterioration will be considered.

First, the case of concrete carbonation, if any, must be taken into account. The concrete cover c must be deeper than the expected carbonation depth within the lifetime L. An accurate prediction of this carbonation depth can be obtained using the Eqs. (12) and (13) with the appropriate k-value. If an unacceptable (for technical or economical reasons) cover is predicted, then either a different concrete composition (e.g., lower W/C_{eq} ratio, higher cement content, etc.) or a protective coating application should be proposed. Then, the calculation must be repeated until a satisfactory result is obtained.

Having specified the concrete composition and cover as above, the case of chloride penetration, if any, must then be considered. Eqs. (3)–(6b) have to be solved in order to predict the chloride profile in the concrete as a function of time. The k-values for resistance against chloride ingress must be used. Using the Cl^{-} profile in the time equal to L, the minimum concrete cover can be found at which and onwards the chloride concentration has lower values than the critical threshold for corrosion. If an unacceptable cover is predicted, then again either a denser concrete composition or a coating application should be considered and the calculation must be repeated until a satisfactory result is obtained.

The design parameters that ensure full protection, e.g., a deeper concrete cover or a denser concrete composition for resistance against carbonation and chloride penetration, must be finally proposed. If any other deterioration mechanism could arise, it has to be considered in a similar way. For instance, Greek high-calcium fly ash [18] contains high amounts of free lime, sulfates, unburned carbon, etc., which may cause durability problems in the construction (expansion, cracking, etc.). Thus, these specific durability risks have to be taken into account and confronted accordingly.

5. Conclusions

For comparing the relative performance of various SCMs (silica fume, fly ash, slag, natural pozzolans, etc.) as regards Portland cement, the concept of an efficiency factor may be applied. The efficiency factor (k-value) is defined as the part of the SCM in an SCM concrete, which can be considered as

equivalent to Portland cement. From the present work, efficiency factors for various SCMs are calculated and summarized in Table 3. These values are valid for a certain amount of SCM in concrete and they are different depending on the property that it concerns (compressive strength at various ages, chloride resistance and carbonation resistance).

When SCMs substitute aggregates, strengths higher than the controls are succeeded. When SCMs replace cement, the strength is reduced at first, but as time proceeds this gap is gradually eliminated and the strength becomes higher than that of the control for these SCMs with higher active silica content in comparison with the cement. By introducing the efficiency factor concept, the pulverized fly ashes of this work can substitute, equivalently, for Portland cement ($k = 1$). The natural SCMs exhibit much lower efficiency factors ($k = 0.2–0.3$). The concrete incorporating SCM, whether used as partial replacement for aggregate or cement, exhibited significantly lower total chloride content. Higher k-values for SCM efficiency against chlorides as compared with the corresponding values for strength were calculated ($k = 2–2.5$ for fly ashes and $k = 1$ for natural pozzolans). The use of SCM as an addition to Portland cement mixtures, replacing either aggregate or cement, should therefore significantly enhance the chloride-induced corrosion initiation stage. Finally, a mix design strategy, ensuring strength, specifications and service lifetime was presented by applying the concept of the SCM efficiency factor.

Acknowledgments

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