A STUDY ON THE APPLICABILITY OF THE EFFICIENCY FACTOR OF SUPPLEMENTARY CEMENTITIOUS MATERIALS TO DURABILITY PROPERTIES

Federica Lollini[1*], Elena Redaelli[2], Luca Bertolini[3]
Politecnico di Milano, Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", piazza Leonardo da Vinci 32, 20133 Milan, Italy
email: [1]federica.lollini@polimi.it, [2]elena.redaelli@polimi.it, [3]luca.bertolini@polimi.it

[*] Corresponding author
tel: +39 02 2399 3144
fax: +39 02 2399 3180

Abstract

Supplementary cementitious materials (SCMs), such as fly ash, pozzolan or blastfurnace slag, are widely used to produce blended portland cements, since they lead to a significant reduction in CO_2 emission in the production phase compared to portland cement. A practical and generally accepted approach to evaluate the contribution of SCMs to the strength of the hardened concrete is through the concept of the SCMs efficiency factor (i.e. *k*-value concept), which expresses the fraction of portland cement that can be replaced by a SCM at unchanged strength. In the literature some studies have also been focused on the use of the *k*-value approach also for the resistance against carbonation and chloride penetration of blended portland systems. However, limitations of applicability of SCMs efficiency factor to durability properties are not clear. In this paper the *k*-value of different SCMs, such as ground limestone, fly ash, natural pozzolan and ground granulated blastfurnace slag, was investigated to detect firstly if it can be applied to carbonation- and chloride-related properties and, secondly, if strength can be considered as a proxy-criterion for durability properties. Results showed *k*-values lower than 1 for all the SCMs with respect to compressive strength and that these values were valid also for resistance to penetration of carbonation. As far as the resistance to chloride penetration is concerned, *k*-values derived from strength tests were not applicable and specific *k*-values should be evaluated; values higher than 1 were calculated for fly ash and ground granulated blastfurnace slag, whilst values lower than 1 were obtained for ground limestone and natural pozzolan.

Highlight

Efficiency factor *k* is often used as a practical approach for determination of the role of SCMs on concrete strength.

The applicability of *k*-values to durability-related properties is questionable.

Strength –derived *k*-values showed to be appropriate as a proxy-criterion only for carbonation resistance.

Specific *k*-values are needed for chloride-resistance performance.

These *k*-values were around 1.5 for fly ash and slag and lower than 1 for ground limestone and pozzolan.

Keywords

Blended cement, Compressive strength, Carbonation, Chloride, *k*-value, durability

1. Introduction

A remarkable contribution towards a sustainable development of the cement and concrete industries can be achieved by the utilization of cementitious and pozzolanic by-products, such as fly ash (FA) and ground granulated blastfurnace slag (GGBS), produced by thermal power plants and metallurgical industries, or natural pozzolanic additions (PZ) as well as limestone [1-2]. The use of such supplementary cementitious materials (SCMs) leads to a significant reduction in CO_2

emissions per mass of concrete and, for some additions, it also allows to utilize by-products of industrial manufacturing processes.

Considering the percentages of replacement for the ordinary portland cement (OPC) indicated in the European Standard EN 197-1 (Cement - Part 1: Composition, specifications and conformity criteria for common cements – 2011), a practical and generally accepted approach to evaluate the contribution of SCMs to a specific property is the concept of the efficiency factor, i.e. *k*-value concept, firstly proposed by I.A. Smith [3]. The efficiency factor is defined as the fraction of SCM in a concrete, which can be considered equivalent to portland cement, without changing the property being studied (k = 1 for portland cement). The SCM efficiency has been traditionally determined with regard to the compressive strength of concrete; however the *k*-value concept has been also extended to other properties, e.g. the durability properties. For instance, the last version of the European Standard EN 206 (Concrete - Specification, performance, production and conformity - 2013) clearly indicates that this concept can also be applied to durability properties of concrete. However, as suggested by several Authors, it is not possible to determine a unique and universal *k*-value for any addition or property considered [4-8]. Indeed, EN 206 Standard implicitly recognizes this by stating that the *k*-value concept resulting from strength properties cannot be considered as a proxy-criterion for durability properties unless otherwise demonstrated. Therefore, there is a need for more investigations in this field.

It should be observed that, in general, the *k*-value approach is based on the assumption of the existence of a relationship between the tested property and a compositional parameter. The evaluation of the *k*-value, with regard to the compressive strength, is usually made from the relationship between strength and the water/cement ratio, i.e. the Abram’s law, for the reference portland-cement concrete, however also other approaches have been applied, e.g. the comparison of the strength of two mixes having the same workability [9]. In other cases, correlations between the *k*-value and the pozzolanic activity as well as the active silica content have been proposed [10].

The European Standard EN 206 broadly permits the *k*-value approach, without referring to a specific percentage of mineral admixture, curing time or *w/b* ratio and without clearly specifying the property to which it is referred. Nevertheless, it indicates a specific value of 0.4 for fly ash, whilst for ground granulated blastfurnace slag an “open value”, which should be set in the national regulations, is indicated, however suggesting the value of 0.6 as a starting point.

As far as the *k*-value proposed in the literature is concerned, Table 1 reports a summary of the *k*-values evaluated by several Authors, considering different SCMs and different percentages of replacement, usually in the ranges indicated, for each material, in the European Standard EN 197-1 [4,7,10-15]. Most Authors agree that the SCMs efficiency factor depends on the type of addition, curing time and also the strength class of portland cement.

As far as GGBS is concerned with regard to 28-day compressive strength, for low percentage of replacement (i.e. lower than 15%), a *k*-value around 1.28 was found [7,11], whilst it decreased to 0.6 when the percentage of replacement was about 80%. The *k*-value of fly ash, evaluated after 28 days of curing, was about 1 for low percentage of replacement and it dropped to values around 0.35 for high level of replacement; furthermore a different behavior as a function of the calcium level was observed, in particular higher performances were observed on fly ash of class C, with a high level of CaO, compared to fly ash of class F, with a low level of CaO [16,17]. 28-day cured natural pozzolans showed low efficiency factor also when the percentages of replacement were quite low.

As far as durability performances are concerned, only few data are reported in the literature and it can be observed in Table 1 that they are also controversial . As a matter of fact, by referring to the chloride resistance of fly ash concrete, *k*-values around 0.5 were obtained by some Authors [15] and conversely even around 2 for other Authors [12,13]. However it should be underlined that different curing times and percentages of SCMs were considered (it should also be observed that the relationships used as a basis for *k*-value estimation where not homogeneous).

In this paper, the efficiency of SCMs on the properties of concretes with different curing times was estimated. In particular, the *k*-values were evaluated considering compressive strength, carbonation rate and chloride diffusion coefficient with the aim of investigating whether strength can be considered as a proxy-criterion for durability properties. Furthermore some considerations on the clinker saving in order to achieve the same strength as well as to guarantee the same initiation time with a SCMs concrete compared to a OPC concrete will be addressed.

2. Materials and methods

A portland cement CEM I 52.5R (*OPC*), according to EN 197-1 standard, was used to produce blended portland cements. The cement clinker was partially replaced, in a cement factory, with 30% of ground limestone (*LI*), 30% of fly ash of class F (FA) (according to ASTM C618-15), 30% of natural pozzolan (PZ) and 70% of ground granulated blastfurnace slag (GGBS). The strength class of the portland cement was chosen to achieve for all the blended portland cements, at least, a class 42.5. The particle size analysis of *OPC* cement and SCMs are given in Figure 1, whilst chemical compositions are reported in Table 2.

These binders were used to make concrete mixes with three different water/binder ratios, equal to 0.42, 0.46 and 0.61, and two different binder dosages, equal to 300 and 350 kg/m^3. Crushed limestone aggregate with maximum size of 16 mm was used, and an acrylic superplasticizer was added to the mixtures in order to achieve a class of consistence *S4* according to EN 206 standard. Table 3 summarizes the concrete mixes.

After mixing, concretes were cast into moulds of various geometries (see later), covered with a plastic sheet and stored in laboratory at 20°C. After 24 hours the specimens were demoulded and curing continued at 20°C and 95% relative humidity.

Different tests were carried out after several curing times (part of the results has been published elsewhere [18,19]). Compressive tests were carried out, according to EN 12390-3 standard (Testing hardened concrete - Part 3: Compressive strength of test specimens – 2009), on two replicate 100 mm cubes after 1, 7 and 28 days of curing. In order to evaluate the resistance to the penetration of carbonation, 100 mm cube specimens, cured 1, 7 and 28 days, were masked with epoxy, so that carbonation was allowed to penetrate only from two opposite faces, and exposed, after 28 days (for specimens cured 1 and 7 days) and 30 days (for 28-day cured specimens) from casting, to an environment with 20°C, 65% R.H. and a constant flux of 2% CO_2 (accelerated carbonation). After different times of exposure, the minimum and the maximum carbonation depths were measured on 20 mm diameter cores taken perpendicularly to a mould surface, with the phenolphthalein test, and the average value between the two was determined. The accelerated carbonation coefficient K_{ACC} was evaluated interpolating, with the least squares methods, the average carbonation depths, d, measured at the different times, t, through the relationship:

$$d = K_{ACC} \cdot \sqrt{t} \qquad (1)$$

Resistance to penetration of chloride ions was tested, after 28 days of curing at T = 20°C and 95% R.H., on cylindrical specimens by means of the so-called Rapid Chloride Migration (RCM) test, according to NT-BUILT 492 standard (Concrete, mortar and cement-based repair materials: chloride migration coefficient from non-steady-state migration experiments – 1999). At the end of the test, the specimen was split axially, and on its fracture surface a colorimetric indicator (0.1 M $AgNO_3$) solution was sprayed. The average chloride penetration depth x_m (m) was measured and the chloride diffusion coefficient D_{RCM} was calculated as:

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

where R is the gas constant (J/K mol), T the average temperature in the anodic solution (K), z the absolute value of charge number, F Faraday's constant (96500 C/mol), t time (s); E =(U-2)/L (U is the applied voltage in V, L the thickness of the specimen in m) and α is defined as:

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

where c_d is the chloride concentration at which the colour change is observed (assumed equal to 0.07 N) and c_0 the chloride concentration of the test solution (2 N).

3. Results

3.1 *Compressive strength*

Figure 2 shows, for each curing time, the average values of compressive strength for the different binders as a function of the water/binder ratio and binder content. For all the concretes, the expected increase in compressive strength due to the decrease in water/binder ratio and to the increase in curing time can be observed. For instance, compressive strength of natural pozzolan concrete, cured 7 days and with a binder dosage of 300 kg/m^3, increased from about 35 to 55 MPa when water/binder ratio decreased from 0.61 to 0.46; increasing the curing time to 28 days, the strength of these mixes further increased, approaching values of about 45 and 70 MPa respectively. A slight and systematic positive effect was observed when decreasing the binder dosage.

Figure 2 also shows the influence of the partial replacement of portland cement with SCMs. At the same curing time and water/binder ratio, *LI*, *FA*, *PZ* and *GGBS* concretes showed lower compressive strengths compared to *OPC* concrete. For instance specimens with *w/b* of 0.46 and binder content of 300 kg/m^3, cured 28 days, had a strength that decreased from about 87 MPa when portland cement was used to 61, 76 and 70 MPa when 30% of cement was replaced respectively with limestone, fly ash and natural pozzolan and to 55 MPa when 70% of cement was replaced with ground granulated blastfurnace slag.

3.2 *Resistance to carbonation*

Figure 3 shows the carbonation coefficient, K_{ACC}, as a function of curing time, concrete composition, i.e. the SCMs, water/binder ratio and binder content. On concretes with *w/b* ratio of 0.42, carbonation tests were performed only on specimens cured 7 days.

At all curing times, a significant influence of the water/binder ratio, whose decrease led to a reduction in the accelerated carbonation coefficient, can be observed. For instance K_{ACC} of natural pozzolan concrete, cured 7 days and with a binder dosage of 300 kg/m^3, decreased from about 33 to 18 MPa when water/binder ratio decreased from 0.61 to 0.46. Comparing concretes with the same composition, a decrease in the carbonation coefficient can be observed when curing increased from 1 to 28 days. For instance in concrete with 30% of natural pozzolan, 300 kg/m^3 of binder and *w/b* ratio of 0.46, values of accelerated carbonation coefficient of 23, 18 and 11 mm/year$^{0.5}$ were evaluated respectively on specimens cured 1, 7 and 28 days. No systematic effect of the binder dosage on carbonation coefficient was observed.

For each curing time, OPC concretes performed better than SCMs concretes. For instance, for 1-day cured concretes with w/b = 0.46 and b = 300 kg/m^3, the accelerated carbonation coefficient was about 16, 30, 27, 23 and 32 mm/year$^{0.5}$ respectively for *OPC*, *LI*, *FA*, *PZ* and *GGBS* concretes.

3.3 Resistance to chloride penetration

The resistance to chloride penetration was investigated by means of the Rapid Chloride Migration test on specimens cured 28 days. Figure 4 shows the diffusion coefficient D_{RCM} as a function of concrete composition. The significant role of w/b ratio appears: for instance for *PZ* concrete the diffusion coefficient decreased from about $23 \cdot 10^{-12}$ to $13 \cdot 10^{-12}$ m^2/s, when the water/binder ratio decreased from 0.61 to 0.42. Occasionally D_{RCM} slightly increased after decreasing w/b ratio (for instance for concrete with 30%FA, w/b of 0.42 and 0.46 and binder dosage of 350 kg/m^3). No effect of the binder content was detected.

A remarkable influence of the type of binder was observed; with respect to OPC, the diffusion coefficient was roughly halved with FA (e.g. with w/b of 0.46 it decreased from about $8 \cdot 10^{-12}$ m^2/s to about $4 \cdot 10^{-12}$ m^2/s). With GGBS, D_{RCM} were significantly lower than with OPC (e.g. the D_{RCM} was lower than $2 \cdot 10^{-12}$ m^2/s for w/b = 0.46). Conversely for concrete mixes with natural pozzolan the diffusion coefficient was more than doubled compared to OPC. For instance D_{RCM} increased from $12 \cdot 10^{-12}$ to $22 \cdot 10^{-12}$ m^2/s for concrete with w/b = 0.61. D_{RCM} further increased for concrete mixes with limestone: for instance in concrete with w/b ratio of 0.61 values of D_{RCM} about $38 \cdot 10^{-12}$ m^2/s were obtained.

4. Discussion

Results presented in the previous section reflect the well-known effects of the water/binder ratio and the curing time on the properties of hardened OPC and SCM concretes. Both the decrease of w/b

ratio and the increase of curing time led to a refinement of the pore structure with beneficial effects on compressive strength and resistance to aggressive agents, i.e. carbon dioxide and chloride ions. On compressive strength, also a slight and positive effect of the binder content was observed when decreasing the binder dosage, in agreement with the decrease of the total concrete porosity, due to a lower amount of cement paste. Conversely on carbonation resistance this effect was not observed. As a matter of fact, the decrease in the amount of cement paste due to a decrease of the binder dosage leads to two opposing effects: on one hand the total porosity of concrete is lower; on the other hand the amount of portlandite is also lower, due to the lower amount of hydrated cement. The former hinders carbonation, the latter promotes it. Hence, these two effects could be compensated and none of them could be prevalent.

An effect of the type of SCM on the properties of hardened concretes was also assessed. A decrease of compressive strength was observed when the portland cement was partially replaced with 30% of ground limestone, fly ash and natural pozzolan, and with 70% of ground granulated blastfurnace slag. As far as the carbonation resistance is concerned, the OPC concretes showed a higher resistance than the SCM concrete; as a matter of fact, the hydration of pozzolanic materials or GGBS consumes lime and thus reduces its amount with respect to a cement paste obtained with portland cement and, hence, the $Ca(OH)_2$ available for the carbonation reaction is lower and it proceeds faster.

Both fly ash and ground granulated blastfurnace slag concretes showed an higher resistance to chloride penetration compared to portland concretes due to the well-known refinement of pores due to the formation of very fine products of hydration [20,21] and to the high fineness, and hence to the high reactivity, of these two SCMs which was comparable to that of OPC cement. Limestone concrete showed a poor resistance to chloride penetration: such a result is in agreement with the explanation that the reaction compounds of C_3A in portland limestone concrete have a lower binding capacity for chloride in comparison to the hydration products of aluminates in OPC concrete [22]. Also natural pozzolan concretes showed a lower resistance to chloride penetration than OPC and FA concretes. The different behaviour between the artificial (FA) and natural (PZ) pozzolan observed in this work can be ascribed to the different Al_2O_3 content and fineness of the two SCMs; as it can be observed in Table 2 PZ had a lower alumina content and fineness in comparison to FA. It is reasonable to assume that the lower amount of alumina in PZ cement led to a lower C_3A content in the PZ concretes and, hence, to a lower binding capacity for chloride in comparison to the FA concrete. Furthermore the higher fineness of the FA cement led to a higher reactivity in comparison to the PZ cement.

These results show that there is the need to evaluate the role of the type of SCM on each specific property.

4.1 Evaluation of the k-value

For the percentages of replacement and for the range of water/binder ratios and binder dosages considered in this work, *k*-values were evaluated for compressive strength and for the durability related properties.

4.1.1 Compressive strength

Firstly, the traditional application of the *k*-value approach to compressive strength was made. In order to estimate the *k*-values valid for strength, for each curing time, compressive strength $f_{c,cube}$ (MPa) data of the OPC concrete were interpolated (with the least squares method) through Abram's law:

$$f_{c,cube} = \frac{K_1}{K_2^{w/c}} \tag{4}$$

and K_1 and K_2 coefficients were determined.

For each curing time, the *k*-value for the SCM concretes of the present work was evaluated by interpolating (with the least squares method) Abram's law (equation (4)) with K_1 and K_2 evaluated for OPC concrete and replacing the cement content in equation (4), c, with the equivalent cement content, c_{eq}, according to:

$$c_{eq} = c + k \cdot A \tag{5}$$

where k is the k-value and A is the SCMs content in the binder.

Figure 5 shows the obtained k-values, whilst Figure 6 presents a comparison between the measured and the calculated compressive strength, using equation (4) and the k-values presented in Figure 5 and a good agreement can be observed.

For 30% limestone, k-values of 0.63, 0.35 and 0.13 were respectively determined for curing times of 1, 7 and 28 days. As discussed in a previous work [18], the relatively high values of the efficiency factors estimated at low curing times indicate that limestone has some beneficial consequences, which may be ascribed to the formation of nucleation sites of calcium hydroxide crystals, to an acceleration of the clinker hydration or to a beneficial filler effect of the fine limestone particles. The relatively low k-value after 28 days of curing indicates that the filler effect is not much effective with the extension of curing time and that limestone does not contribute to the compressive strength.

For 30% fly ash, k-values of 0.76, 0.42 and 0.6 were respectively determined for curing times of 1, 7 and 28 days. These results are in agreement with those calculated by other Authors [4,12,14].

For 30% natural pozzolan, the efficiency factor decreased in time, from a value of 0.69 after 1 day of curing to 0.4 after both 7 and 28 days of curing.

Finally, with 70% ground granulated blastfurnace slag, k-values of 0.53, 0.81 and 0.69 were obtained after 1, 7 and 28 days of curing, respectively. In spite of the high amount of replaced clinker, high values of k-value were determined in comparison with other Authors [7].

After 28 days of curing, comparable k-values were obtained for the 30% fly ash and the 70% ground granulated blastfurnace slag; conversely 30% natural pozzolan showed a k-value roughly halved in comparison with the previous SCMs, whilst the limestone's k-value was essentially nil. It should be reminded that, according the literature, probably higher k-values could have been obtained if the comparison between the SCMs and OPC concretes had been made with a cement with a lower strength class.

4.1.2 Resistance to carbonation

In order to apply the concept of *k*-value of the SCMs also in relation to the resistance to carbonation, a relationship between the carbonation coefficient and the water/cement ratio is required. Since in the literature there is not a general agreement on this relationship, an inverse approach was followed in this work and the *k*-values estimated for compressive strength were firstly applied to carbonation resistance. Figure 7 shows the relationship between the carbonation coefficient and the equivalent water/cement ratio at the different curing times and a good linear correlation can be observed between the carbonation coefficient and the equivalent water/cement ratio, regardless the type of binder (GGBS at 1 day of curing constitutes an exception) Hence, it may be assumed that, at least in the conditions tested in this work, strength was appropriate as a proxy-criterion for carbonation resistance and that *k*-values estimated for compressive strength could be considered valid also for the resistance to carbonation penetration. This confirms, as indicated also by other Authors [23,24], that these two properties are mainly depending on the same factors.

4.1.3 Resistance to chloride penetration

As far as the resistance to chloride penetration is concerned, first an inverse approach was followed, applying the *k*-values estimated for compressive strength to chloride resistance, which revealed to be inappropriate. Hence, following the approach used to determine the *k*-value for strength, a correlation between D_{RCM} and *w/c* ratio was assumed and used to interpolate data of the OPC concrete (with the least squares method). In particular the following linear relationship:

$$D_{RCM} = \mathrm{m}\cdot w/c + q \qquad (6)$$

suggested by Polder et al. [25] was applied.

The *k*-values for the SCM concretes of the present work were evaluated by interpolating (with the least squares method) equation (6) with *m* and *q* coefficients evaluated for OPC concrete and replacing the cement content in equation (6), *c*, with the equivalent cement content, c_{eq}, according to equation (5) and these values are reported in Figure 5. Figure 8 shows a comparison between the measured and the calculated diffusion coefficient, using equation (6) and the *k*-values presented in

Figure 5, and a good agreement can be observed. Regarding the chloride resistance, ground limestone showed a very low *k*-value, approximately 0.1, which means that this addition does not play any role in hindering chloride penetration. Both fly ash and ground granulated blastfurnace slag showed a *k*-value around 1.5, in agreement with the values reported by Tsimas et al. [12] and Papadakis et al. [13] for fly ash and by Gruyaert et al. [8] for ground granulated blastfurnace slag. The natural pozzolan showed a *k*-value around 0.6, which is significantly lower than the value obtained with the artificial pozzolan (fly ash), but also lower than those measured on natural pozzolan (vulcanic tuff and diatomaceous earth) by Papadakis et al. [13]. This may be attributed to the high variability in chemical composition and microstructure of this natural material.

4.2 Application

To detect the practical implications of the *k*-value and further underline the differences among the SCMs employed in this research with regard to the different properties, the evaluation of the water/binder ratio of a blended concrete in order to obtain the same performances of an OPC concrete and the estimation of the possible clinker saving were carried out. Considering that to achieve the same performance, the equivalent water/cement ratio of the SCM concrete should be equal to the water/cement ratio of the OPC concrete and the definition of equivalent cement content, c_{eq} (eq. 5), the water/binder ratio of the SCMs concrete can be evaluated according to:

$$w/b = w/(c'+\mathrm{SCM}) = w/c\,(1-\mathrm{P}+k\cdot\mathrm{P}) \qquad (7)$$

where *c*' is the clinker amount in the SCM concrete, *c* is the clinker amount in the OPC concrete, *P* is the percentage of replacement and *k* is the *k*-value.

Hence, the variation of the water/binder ratio can be evaluated as:

$$\Delta w/b = \frac{w/b - w/c}{w/c} = P\cdot(k-1) \qquad (8)$$

The clinker saving can be evaluated according to:

$$\text{clinker saving} = \frac{c-c'}{c} = \frac{k\cdot P}{1-P+k\cdot P} \qquad (9)$$

Figure 9 shows the variation of the water/binder ratio as a function of *k*-value for the two percentages of replacement considered in this work (e.g. 30% for LI, FA and PZ and 70% for GGBS). When *Δw/b* is negative, the water/binder ratio of the SCM concrete should be decreased in order to fulfil the same requirements of an OPC concrete, conversely when it is positive the water/binder ratio of the blended concrete could be increased. Figure 10 shows the clinker saving as a function of the *k*-value. The percentage of saved clinker increases with the *k*-value and, naturally, it is equal to the percentage of replacement when *k* is equal to 1.

Taking into account the *k*-values obtained in this work considering a range of water/binder ratios between 0.42 and 0.61 and of binder contents between 300 and 350 kg/m^3, to keep the same compressive strength of the OPC concrete at 28 days, the water/binder ratio should be decreased of 26, 11, 18 and 22% respectively for limestone, fly ash and natural pozzolan and ground granulated blastfurnace slag. For instance, it means that, considering a water/cement ratio of 0.5 for an OPC concrete, the *w/b* should be decreased to 0.37, 0.44, 0.41 and 0.39 respectively for limestone, fly ash, natural pozzolan and ground granulated blastfurnace slag. The clinker saving would be limited to 5%, 21%, 15% and 62% respectively for LI, FA, PZ and GGBS. The high value of clinker saving evaluated for GGBS, significantly higher than those obtained for the other SCMs, depended on the percentage of replacement, equal to 70%, considered in this work.

Since strength can be a proxy-criterion for carbonation resistance, to achieve the same initiation time for a structure subject to corrosion due to carbonation, t the water/binder ratio of a SCMs concrete should be decreased to the values previously indicated for compressive strength.

Conversely in a chloride contaminated environment, to guarantee the same initiation time, which means to keep the same resistance to chloride penetration, the use of 30% fly ash or 70% ground granulated blastfurnace slag would allow to increase the water/binder ratio of 14 and 35%, which is equivalent to a clinker saving of 39% and 77%. The use of natural pozzolan would lead to a decrease of the water/binder ratio of 11% and, hence, the clinker saving would be limited to 22%.

With limestone, the water/binder ratio should be considerably reduced and the clinker saving would be negligible.

5. Conclusions

The efficiency factor of different SCMs was studied by replacing portland cement with 30% of ground limestone, fly ash and natural pozzolan and with 70% of ground granulated blastfurnace slag. On the basis of results of experimental tests, carried out on concretes made with water/binder ratios between 0.42 and 0.61 and binder dosages between 300 and 350 kg/m^3, the following conclusions can be drawn:

1. After curing times up to 28 days, OPC concretes showed an higher compressive strength than SCMs concretes. After 28 days of curing, comparable *k*-values, of the order of 0.7, were obtained by the fly ash and the ground granulated blastfurnace slag; conversely natural pozzolan showed a *k*-value roughly halved in comparison to the previous SCMs, whilst limestone showed *k*-value almost nil.

2. The accelerated carbonation coefficient of concrete showed a good correlation with the equivalent water/cement ratio calculated considering the *k*-values evaluated for compressive strength at curing times of 1, 7 and 28 days. Hence, results presented in this work support the hypothesis that strength can be considered as a proxy-criterion for carbonation resistance.

3. The rapid chloride migration diffusion coefficient increased by replacing OPC with limestone and natural pozzolan, whilst it decreased using fly ash and ground granulated blastfurnace slag. It was observed that strength-based *k*-values were not applicable to the evaluation of chloride permeability. Assuming a linear correlation between the diffusion coefficient and the water/cement ratio, a chloride-permeability-related *k*-value was estimated of approximately 1.5 for both fly ash and ground granulated blastfurnace slag, around 0.6 for natural pozzolan and almost nil for ground limestone.

4. For each SCM, in order to achieve the same performance, i.e. the same compressive strength and the same initiation time for corrosion, relationships to evaluate the percentages of clinker saving and variation of the water/binder ratio were proposed as a function of the *k*-values.

Acknowledgments

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

References

[1] Aïtcin PC, Sustainability of Concrete, Modern Concrete Technology Series, Spon press, 2011.

[2] Thomas M, Supplementary cementing materials in concrete, 2013, CRC Press.

[3] Smith IA, The design of fly ash concrete. Proceeding of the Institution of civil engineers 1967;36(4):769-790. doi: 10.1680/iicep.1967.8472

[4] Babu KG, Rao GSN, Efficiency of fly ash in concrete. Cem Concr Comp 1993;15(4):223-229. doi:10.1016/0958-9465(93)90025-5

[5] Papadakis VG, Effect of supplementary cementing materials on concrete resistance against carbonation and chloride ingress. Cem Concr Res 2000;30(2):291-299. doi:10.1016/S0008-8846(99)00249-5

[6] Wong HS, Abdul Razak H, Efficiency of calcined kaolin and silica fume as cement replacement material for strength performance, Cem Concr Res 2005;35:696-702. doi:10.1016/j.cemconres.2004.05.051

[7] Sanjuán MA, Piñeiro A, Rodríguez O, Ground granulated blast furnace slag efficiency coefficient (k value) in concrete. Applications and limits. Materiales de Construcción 2011;61(302):303-313. doi:10.3989/mc.2011.60410

[8] Gruyaert E, Maes M, De Belie N, Performance of BFS concrete: k-value concept versus equivalent performance concept. Constr Build Mater 2013;47:441-455. doi:10.1016/j.conbuildmat.2013.05.006

[9] Hassaballah A, Wenzel TH, A strength definition for the water to cementitious materials ratio. In: Malhotra VM (Ed), Proceeding ACI Fifth International conference, fly ash, silica fume and natural pozzolans in concrete, Milwaukee, WI, USA, ACI, Detroit, 1995, pp. 417-437.

[10] Papadakis VG, Antiohos S, Tsimas S, Supplementary cementing materials in concrete. Part II: fundamental estimation of the efficiency factor. Cem Concr Res 2002;32(10):1533-1538. doi:10.1016/S0008-8846(02)00829-3

[11] Babu KG, Rao GSN, Efficiency of GGBS in concrete. Cem Concr Res 2000;30(7):1031-1036. doi:10.1016/S0008-8846(00)00271-4

[12] Tsimas S, Papadakis VG, Antiochos S, Study and upgrade of supplementary materials for cement and concrete, Second Internatinal Symposium, 6-10 September, 2000, Instambul, Turkey.

[13] Papadakis VG, Tsimas S, Supplementary cementing materials in concrete. Part I: efficiency and design. Cem Concr Res 2002;32(10):1525-1532. doi:10.1016/S0008-8846(02)00827-X

[14] Oner A, Akyuz S, Yildiz R, An experimental study on strength development of concrete containing fly ash and optimum usage of fly ash in concrete. Cem Concr Res 2005;35(6):1165-1171. doi:10.1016/j.cemconres.2004.09.031

[15] Aponte DF, Barra M, Vàzquez E, Durability and cementing efficiency of fly ash in concrete, Constr Build Mater 2012;30:537-546. doi: 10.1016/j.conbuildmat.2011.12.026

[16] Papadakis VG, Effect of fly ash on Portland cement system. Part I. Low-calcium fly ash. Cem Concr Res 1999;29(11):1727-1736. doi:10.1016/S0008-8846(99)00153-2

[17] Papadakis VG, Effect of fly ash on Portland cement system. Part II. High-calcium fly ash. Cem Concr Res 2000;30(10):1647-1654. doi:10.1016/S0008-8846(00)00388-4

[18] Lollini F, Redaelli E, Bertolini L, Effects of portland cement replacement with limestone on the properties of hardened concrete. Cem Concr Comp 2014;46:32-40. doi:10.1016/j.cemconcomp.2013.10.016

[19] Bertolini L, Lollini F, Redaelli E, Comparison of resistance to chloride penetration of different types of concrete through migration and ponding tests, RILEM Bookseries, Volume 5, 2011, pp. 125-135.

[20] Bertolini L, Carsana M, Frassoni M, Gelli M, Pozzolanic additions for durability of concrete structures. Proceedings of Institution of Civil Engineers: Construction Materials 2011;164(6): 283-291.

[21] Carsana M, Frassoni M, Bertolini L, Comparison of ground waste glass with other supplementary cementitious materials. Cem Concr Comp 2014;45:39-45. doi:10.1016/j.cemconcomp.2013.09.005

[22] Fagerlund G. Imaginable effects of limestone filler on chloride transport. Lund Institute of Technology Lund University. Report TVBM-7187; 2005.

[23] Neville AM. Properties of concrete. New York: John Wiley & Sons, 1973.

[24] Bertolini L, Elsener B, Pedeferri P, Redaelli E, Polder R. Corrosion of steel in concrete – Prevention, diagnosis, repair. second ed., Weinheim: Wiley VCH, 2013.

[25] Polder RB, van der Wegen G, Boutz M. In: Performances Based Evaluation and Indicators for Concrete Durability, Proceeding of International RILEM Workshop, Baroghel-Bouny, V. Andrade, C. Torrent R. and Scrivener K. (Eds.),2006, RILEM Publications S.A.R.L., Bagneux.

Table 1 Reported values of *k*-values for different properties, curing times and types of addition.

Property	Curing (days)	Addition Type	*w/b*	percentage	*k*-value	Ref.
Strength	28	fly ash	N.A. [a]	10-75	1.25-0.35[b]	[4]
	28	GGBS	0.25-0.75	10-80	1.29-0.7[b]	[11]
	28	low-Ca fly ash	0.38-0.71	5-15[c]	0.5	[12]
		high-Ca fly ash	0.38-0.71	5-15[c]	1	
	91	low-Ca fly ash	0.38-0.71	5-15[c]	0.7	
		high-Ca fly ash	0.38-0.71	5-15[c]	1	
	2	low-Ca fly ash	0.42-0.5	10-20[c]	0.8	[10,13]
		high-Ca fly ash	0.42-0.5	10-20[c]	0.8	
		natural pozzolan (vulcanic tuff)	0.42-0.5	10-20[c]	0.4	
		natural pozzolan (diatomaceous earth)	0.42-0.5	10-20[c]	0.2	
	7	low-Ca fly ash	0.42-0.5	10-20[c]	1.0	
		high-Ca fly ash	0.42-0.5	10-20[c]	0.9	
		natural pozzolan (vulcanic tuff)	0.42-0.5	10-20[c]	0.3	
		natural pozzolan (diatomaceous earth)	0.42-0.5	10-20[c]	0.2	
	28	low-Ca fly ash	0.42-0.5	10-20[c]	1.1	
		high-Ca fly ash	0.42-0.5	10-20[c]	0.9	
		natural pozzolan (vulcanic tuff)	0.42-0.5	10-20[c]	0.3	
		natural pozzolan (diatomaceous earth)	0.42-0.5	10-20[c]	0.2	
	90	low-Ca fly ash	0.42-0.5	10-20[c]	1.2	
		high-Ca fly ash	0.42-0.5	10-20[c]	0.9	
		natural pozzolan (vulcanic tuff)	0.42-0.5	10-20[c]	0.3	
		natural pozzolan (diatomaceous earth)	0.42-0.5	10-20[c]	0.2	
	28	fly ash	0.5-0.93	15-58	1.25-0.4	[14]
	180	fly ash	0.5-0.93	15-58	1.3-0.3	
	1	GGBS	0.4-0.7	15-85	0.5-0.7	[7]
	4	GGBS	0.4-0.7	15-85	0.8-0.5	
	7	GGBS	0.4-0.7	15-85	0.9-0.6	
	28	GGBS	0.4-0.7	15-85	1.28-0.6	
	91	GGBS	0.4-0.7	15-85	1.58-0.65	
	182	GGBS	0.4-0.7	15-85	1.62-0.62	
	266	GGBS	0.4-0.7	15-85	1.39-0.58	
carbonation resistance	365	low-Ca fly ash	0.38-0.71	5-15[b]	0.5	[12]
		high-Ca fly ash	0.38-0.71	5-15[b]	0.7	
chloride resistance	365	low-Ca fly ash	0.38-0.71	5-15[b]	3	
		high-Ca fly ash	0.38-0.71	5-15[b]	2	
	90	low-Ca fly ash	0.42-0.5	10-20[b]	2.5	[13]
		high-Ca fly ash	0.42-0.5	10-20[b]	2	
		natural pozzolan (vulcanic tuff)	0.42-0.5	10-20[b]	1	
		natural pozzolan (diatomaceous earth)	0.42-0.5	10-20[b]	1	
	28	GGBS	0.5	50-85	1.3-1.9	[8]
	28	FA	0.45 and 0.6	25-43	0.2-1.8	[15]
	90	FA	0.45 and 0.6	25-43	0.5-2	

[a] N.A. = not available;
[b] value of the overall efficiency factor, which is a combination of the two factors "general efficiency factor" and "percentage efficiency factor";
[c] the SCM was both replaced to the cement and aggregates.

Table 2 Main chemical components and specific surface area, σ, of portland cement and mineral additions.

	CaO (%)	SiO_2 (%)	Al_2O_3 (%)	SO_3 (%)	Fe_2O_3 (%)	MgO (%)	K_2O (%)	Na_2O (%)	Mn_2O_3 (%)	TiO_2 (%)	Cl^- (%)	σ (cm^2/g)
OPC	63.5	20.5	5.28	3.29	2.84	1.53	1.0	0.29	0.07	0.24	0.01	5340
LI	43.8	15.8	1.98	0.27	0.80	1.10	0.6	0.06	0.05	0.11	-	6102
FA	2.92	52.9	33.2	0.73	5.23	1.06	1.2	0.72	0.04	1.17	-	5437
PZ	4.49	54.6	21.1	0.14	4.4	1.19	7.0	3.52	0.15	0.55	0.01	4606
GGBS	41.7	33.9	13.0	2.10	0.37	6.62	0.3	0.45	0.24	0.54	0.257[a]	5624

Table 3 Mix proportion for concrete specimens.

Series	*OPC*[a] (%)	SCMs[a] (%)	*w/b*	water (kg/m^3)	binder (kg/m^3)	c (kg/m^3)	A[b] (kg/m^3)	Admixtures (kg/m^3)	Aggregates (kg/m^3)
OPC	100	-	0.61	183	300	300	-	2.5	1857
			0.46	138	300	300	-	6.8	1979
			0.46	161	350	350	-	3.5	1868
			0.42	147	350	350	-	9.2	1913
LI	70	30	0.61	183	300	210	90	2.5	1857
			0.46	138	300	210	90	7	1979
			0.46	161	350	245	105	5	1868
			0.42	147	350	245	105	5.4	1913
FA	70	30	0.61	183	300	300	90	2.5	1857
			0.46	138	300	300	90	6	1979
			0.46	161	350	350	105	3.5	1868
			0.42	147	350	350	105	5.4	1913
PZ	70	30	0.61	183	300	300	90	2.9	1857
			0.46	138	300	300	90	5	1979
			0.46	161	350	350	105	5.3	1868
			0.42	147	350	350	105	6.3	1913
GGBS	30	70	0.61	183	300	90	210	2.5	1857
			0.46	138	300	90	210	5	1979
			0.46	161	350	105	245	4	1868
			0.42	147	350	105	245	5.4	1913

[a] Percentage of the total mass of binder
[b] SCMs content in concrete

List of figures

Figure 7 Accelerated carbonation coefficient as a function of the equivalent water/cement ratio, calculated assuming strength *k*-values, for different curing times (white symbols: 1 day; grey symbols: 7 days; black symbols: 28 days).

Figure 8 Comparison between measured and calculated chloride diffusion coefficient, D_{RCM}.

Figure 9 Variation of the water/binder ratio as a function of the *k*-value and percentage of replacement to maintain the same properties of an OPC concrete.

Figure 10 Clinker saving as a function of the *k*-value and percentage of replacement to maintain the same properties of an OPC concrete.