

Study and Upgrade of Supplementary Materials for Cement and Concrete

Stamatis Tsimas

National Technical University of Athens, Department of Chemical Engineering
Athens, Greece

Vagelis G. Papadakis

TITAN Cement Company S.A., Department of Research & Technology
Elefsis, Greece

Stelios Antiochos

National Technical University of Athens, Department of Chemical Engineering
Athens, Greece

Abstract

Many solid industrial by-products such as siliceous and aluminous materials, which are extensively produced the recent years, may be characterized as supplementary cementing materials (SCM) as they exhibit cementitious (mainly pozzolanic but also hydraulic) properties. In Greece, among these materials are fly ashes from coal burning power plants, slags from various metallurgical furnaces, red mud from alumina production, etc. For comparing the relative performance of SCM as regards Portland cement, the concept of efficiency factor may be used. 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.

In this work, three typical SCM were studied: a silica fume, a low-calcium fly ash and a high-calcium fly ash. Compressive strength, accelerated carbonation and chloride penetration tests were performed. With regard to these characteristics, k-values for these materials were estimated, which may enable mix design to be accurately specified.

Introduction

The majority of concrete deterioration cases is connected to corrosion of reinforcement due to carbonation- or chloride-induced depassivation of steel bars [1,2]. On the other hand, it has been well established [3,4], that sustainable development of the cement and

concrete industries can be achieved by complete utilization of cementitious and pozzolanic by-products, such as fly ash, slag and silica fume, produced by thermal power plants and metallurgical industries. Besides the effect on usual structural properties, such as strength and volume stability, the durability of concrete incorporating these supplementary cementing materials (SCM) should be taken into account.

In previous publications [5,6], 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 an SCM-concrete. In the present work, a practical approach to the effect of SCM on Portland cement systems strength and resistance against carbonation and chloride penetration is presented, using the concept of the efficiency factor [7,8].

The efficiency factor (or k-factor) 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 ($k=1$ for Portland cement). The compressive strength is often used as the property for the evaluation of k-values. However, durability properties may also be used; such as carbonation depth, permeability, etc. In other words, the quantity of the SCM can be multiplied by the k-factor to estimate the equivalent cement content, which can be added to the cement content for the determination of the W/C, minimum required cement content, etc.

Experimental

Materials and Specimen Preparation

Three typical SCM, i.e., a silica fume (SF) from Norway, a low-calcium fly ash (FL) from Denmark, and a high-calcium fly ash (FH) from Greece were used, representing a wide range of chemical compositions, from highly pozzolanic to almost cementitious. A rapid setting Portland cement was used (410 m²/kg Blaine's fineness). The physical and chemical characteristics of all materials are presented in Table 1. Normal graded sand and a lignosulfonate plasticizer were used. Only mortars were prepared; therefore conclusions derived from mortars may or may not be applicable to concrete.

A constant volume unit (1 m³) of mortar 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. The mixture proportions of mortar specimens are summarized in Table 2. For the control specimen, the water-to-cement ratio (W/C) was 0.5 and the aggregate-to-cement ratio (A/C) was 3.

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. The specimens for strength measurements were prisms of 40 x 40 x 160 mm, cured under lime-saturated water at 20°C, and tested after 3, 14, 28, 49, 91, 182 and 364 days. The specimens for durability tests were cast in steel cylinders of 100 mm diameter and 200 mm height. The molds were stripped after 24 hr and the specimens placed under lime-saturated water at 20°C for 1 year. This long-term curing period under water ensures an advanced degree of both Portland cement hydration and pozzolanic activity.

Table 1 - Physical properties and chemical analyses of cement, silica fume (SF), low-calcium fly ash (FL) and high-calcium fly ash (FH)

	Cement	SF	FL	FH
<u>Physical Properties</u>				
Particle mean diam., μm	14.0	0.36	13.9	12.6
Density, kg/m^3	3160	2260	2250	2660
<u>Chemical Analysis, %</u>				
SiO ₂	20.10	90.90	53.50	39.21
Al ₂ O ₃	4.25	1.12	20.40	16.22
Fe ₂ O ₃	3.49	1.46	8.66	6.58
CaO (total)	63.20	0.69	3.38	22.78
free CaO	1.48	0.024	0.36	5.18
MgO	1.26	0.77	2.25	2.35
SO ₃	2.88	0.38	0.60	4.30
L.O.I.	1.75	3.00	2.20	2.10

Table 2 - Mixture proportions for mortars*

Specimen	C	W	P	A	W/C	P/C	A/C
Control	514.6	257.4	0.0	1543.8	0.50	0.00	3.00
SFA1	514.6	257.4	25.7	1513.4	0.50	0.05	2.94
SFA2	514.6	257.4	51.5	1483.0	0.50	0.10	2.88
SFA3	514.6	257.4	77.2	1452.6	0.50	0.15	2.82
FLA1	514.6	257.4	51.5	1482.7	0.50	0.10	2.88
FLA2	514.6	257.4	102.9	1421.7	0.50	0.20	2.76
FLA3	514.6	257.4	154.4	1360.6	0.50	0.30	2.64
FHA1	514.6	257.4	51.5	1492.1	0.50	0.10	2.90
FHA2	514.6	257.4	102.9	1440.5	0.50	0.20	2.80
FHA3	514.6	257.4	154.4	1388.8	0.50	0.30	2.70
SFC1	488.8	257.4	25.7	1535.3	0.527	0.053	3.14
SFC2	463.1	257.4	51.5	1526.9	0.556	0.111	3.30
SFC3	437.4	257.4	77.2	1518.4	0.588	0.176	3.47
FLC1	463.1	257.4	51.5	1526.6	0.556	0.111	3.30
FLC2	411.7	257.4	102.9	1509.4	0.625	0.250	3.67
FLC3	360.2	257.4	154.4	1492.3	0.715	0.429	4.14
FHC1	463.1	257.4	51.5	1536.0	0.556	0.111	3.32
FHC2	411.7	257.4	102.9	1528.3	0.625	0.250	3.71
FHC3	360.2	257.4	154.4	1520.5	0.715	0.429	4.22

* C, W, P, A: kg of cement, water, supplementary cementing material (SF, FL or FH) and aggregate (sand) respectively, per m³ of total mortar volume (for zero air-content); W/C, P/C, A/C: the water-cement, SCM-cement and aggregate-cement ratio (by weight) respectively.

Accelerated Carbonation

Slices 90 mm thick were cut from the middle of the specimens and covered with a gas-tight paint on the cylindrical surface, leaving free the two opposite ends to be exposed to carbonation. Two samples for each mixture were taken. The test specimens were kept for one month in a laboratory environment to stabilize internal humidity. They were then placed in a chamber with a controlled 3% concentration of CO₂, temperature 25°C and relative humidity 61%, for 100 days (Nordtest method NT Build 357, 1989). After carbonation, the specimens were cut normal to the exposed surfaces and the carbonation depth was determined by means of a phenolphthalein indicator. For each mixture, the average carbonation depth of the four measurements is reported.

Chloride Penetration

Slices 70 mm thick were cut from the initial specimens intended for long-term ponding experiments, according to Nordtest method NT Build 443 (1995). Prior to immersion, the samples were coated with epoxy resin and then a 10 mm thick slice was removed from one end. The samples were immersed in a chloride solution (165g NaCl/l) for 100 days. The temperature was kept constant at 20°C throughout the entire test period. At the end of the immersion period, the exposed surface was ground using a dry process to a diameter of 75 mm by removing thin successive layers from different depths. The total chloride content of the powders was determined by the Volhard titration method (NT Build 208, 1984).

Results and Discussion

Typical experimental results are summarized in Fig. 1 and 2. Relative values of compressive strength (1 year), porosity (1 year), carbonation depth, and total chloride content as regards the control mixture are given.

Compressive Strength

In order to estimate the k-factors, the following procedure was followed. The compressive strength, f_c , of a Portland cement concrete or mortar can be described by:

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

where K is a parameter depending on the cement type and curing and a a parameter depending mainly on time. It has been shown [9] that $a=0.5$ for 28 days and $a=0.4$ for 91 days or more. Using the mean measured values [5,6] of the compressive strength of the control specimen, 57.6 MPa, 67.1 MPa and 71.5 MPa for 28, 91 and 365 days, respectively, K is estimated as 38.4 MPa, 41.9 MPa, and 44.7 MPa respectively. In the case of pozzolanic concrete or mortar, the following expression for compressive strength is used which involves the concept of k-factor:

Fig. 1- Comparative experimental results of compressive strength, porosity, carbonation depth and total chloride content in the case of aggregate replacement by silica fume (SFA), low-calcium fly ash (FLA) and high-calcium fly ash (FHA)

Fig. 2- Comparative experimental results of compressive strength, porosity, carbonation depth and total chloride content in the case of Portland cement replacement by silica fume (SFA), low-calcium fly ash (FLA) and high-calcium fly ash (FHA)

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

Using this equation, the measured values of the compressive strength given in Ref. 5 and 6, and the W, C and P contents given in Table 2, the k-values for SF, FL and FH of the present work were calculated as follows:

- For equal 28-day strengths: k=3 for silica fume, k=0.5 for low-calcium fly ash, and k=1 for high-calcium fly ash
- For equal final strengths (1-year): k=2.2 for silica fume, k=1.1 for low-calcium fly ash, and k=1.1 for high-calcium fly ash.

The estimated values are very close to those used in practice in EU for SF and FL (2 and 0.5 respectively). The k-factor 1 for FH (reported for the first time) means that up to a certain level, pulverized FH can substitute, equivalently, for Portland cement.

Carbonation

For all SCM tested, the carbonation depth decreases as aggregate replacement by SCM increases, and it increases as cement replacement by SCM increases. Drawing a comparison between results for 10% SCM addition either replacing aggregate (Fig. 1) or cement (Fig. 2), the lowest carbonation depth is observed for high-Ca fly ash, then for low-Ca fly ash, and the highest one for silica fume.

Papadakis et al. [10,11] 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, with time, is given by an analytical expression. For a practical estimation of the SCM effect on concrete durability, the concept of the efficiency factor may be also used. Considering the equivalent amount of cement as C+kP (where P: SF, FL or FH), and substituting it in this expression, the predictions were fitted to experimental results and after parameter optimization, k-values for resistivity against carbonation of **0.3**, **0.5** and **0.7** for silica fume, low-calcium fly ash and high-calcium fly ash, respectively, were estimated.

Chloride Penetration

As observed, the specimens incorporating an SCM, whether it substitutes aggregate or cement, exhibit significantly lower total chloride content for all depths from the surface. Among all SCM tested, silica fume exhibited the lowest degree of chloride penetration, then low-calcium fly ash, and high-calcium fly ash the highest (Fig. 1 and 2). As the SCM content in the mortar volume increases, the chloride content decreases.

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, this 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 [12] modeled chloride diffusion and reaction in

fully saturated concrete as a Langmuirian equilibrium process coupled with Fickian diffusion. Papadakis et al. [13,14] 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, from which that of Cl^- bound in the solid phase can be computed algebraically. The solution of this 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.

The above model was applied and solved numerically using a finite difference method. In order for these predictions to fit the experimental data the following optimum efficiency factors were estimated:

- **k= 6** for silica fume,
- **k= 3** for low-calcium fly ash,
- **k= 2** for high-calcium fly ash.

These significantly higher k-values for SCM efficiency for chloride resistivity 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.

Concluding Remarks

From the present work, slightly different k-values (for strength) are proposed and summarized in Table 3. The k-values for strength 28 days, 91 days or advanced hydration (1 year) may be used, according to the specific project requirements. These values are valid for a certain amount of SCM in concrete. As proven elsewhere [5,6], the maximum silica fume content in concrete shall be 18% of the cement weight, for low-calcium fly ash 25%, and for high-calcium fly ash 50%, when they used separately. However, when two or more SCM are simultaneously used in the same concrete mixture, different maximum values may be valid. In the common case of the parallel use of silica fume and low-Ca fly ash, a reaction with silica fume will be dominant at the early ages of hydration. Thus, lower maximum values of SF and FL content in concrete should be expected, with a greater reduction in the FL maximum content. Further experiments are required for an accurate approach to multicomponent SCM use in concrete.

Table 3 - Efficiency factors (k-values) for various supplementary cementing materials for different concrete properties (this work)

	silica fume	low-Ca fly ash	high-Ca fly ash
Strength, 28 days	3	0.5	1
Strength, 91 days	2.4	0.7	1
Strength, 1 year	2.2	1.1	1.1
Carbonation Resist.	0.3	0.5	0.7

It is shown that for all SCM tested in this study, the carbonation depth decreased as aggregate replacement by SCM increased and it increased as cement replacement by SCM increased. Efficiency factors (k-values) are calculated of 0.3, 0.5 and 0.7 for resistivity against carbonation for silica fume, low-calcium fly ash and high-calcium fly ash, respectively.

The mortars incorporating SCM, whether used as partial replacement for aggregate or cement, exhibited significantly lower total chloride content. Efficiency factors of 6, 3 and 2 for resistivity against chloride penetration are calculated for silica fume, low-calcium fly ash and high-calcium fly ash, respectively.

The use of SCM as an addition to a Portland cement mixtures, replacing either aggregate or cement, should therefore significantly enhance the chloride-induced corrosion initiation stage. The use of SCM as an addition replacing aggregates would also prolong the carbonation-induced corrosion initiation stage. However, the results of this study show that when used as cement replacement, SCM may result in a shortened carbonation-induced initiation stage.

References

1. Basheer, P.A.M., Chidiac, S.E., and Long, A.E., 1996. Predictive Models for Deterioration of Concrete Structures, Constr. Build. Mater., Vol. 10, p. 27.
2. Thompson, N.G., and Lankard, D.R., 1997. Improved Concretes for Corrosion Resistance, Georgetown Pike, McLean VA, US Department of Transportation, Federal Highway Administration, Report No. FHWA-RD-96-207.
3. Mehta, P.K., 1998. Role of Pozzolanic and Cementitious Material in Sustainable Development of the Concrete Industry, Proceedings of the 6th International Conference on the Use of Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Bangkok, ACI SP-178, p. 1.
4. Berry, E.E., and Malhotra, V.M., 1987. Fly Ash in Concrete, in: Supplementary Cementing Materials for Concrete, Ed. V.M. Malhotra, CANMET SP-86-8E, p. 35, Ottawa.
5. Papadakis, V.G., 1999. Experimental Investigation and Theoretical Modeling of Silica Fume Activity in Concrete, Cement and Concrete Research, Vol. 29, p. 79.
6. Papadakis, V.G., 1999. Effect of Fly Ash on Portland Cement Systems. Part I: Low-calcium Fly Ash, Cement and Concrete Research, Vol. 29, p. 1727.

7. KEMA Environmental Technology, 1997. Determination of the k-value of Fly Ash, Report No. 00474-KET/R&B 97-4062, Arnhem.
8. European Standard preEN 206, 1997. Concrete – Performance, Production and Conformity, CEN, Brussels.
9. Herholdt, A.D., Justesen, C.F., Nepper-Christensen, P., and Nielsen, A., 1985. Beton-Bogen, 2nd ed., in danish, Aalborg Portland, Aalborg.
10. Papadakis, V.G., Vayenas, C.G. and Fardis, M.N., 1991. Fundamental Modeling and Experimental Investigation of Concrete Carbonation, ACI Materials Journal, Vol. 88, p. 363.
11. Papadakis, V.G., Fardis, M.N., and Vayenas, C.G., 1992. Effect of Composition, Environmental Factors and Cement-Lime Mortar Coating on Concrete Carbonation, Materials and Structures, Vol. 25, p. 293.
12. Pereira, C.J., and Hegedus, L.L., 1984. Diffusion and Reaction of Chloride Ions in Porous Concrete, Proceedings of the 8th International Symposium of Chemical Reaction Engineering, Edinburgh.
13. Papadakis, V.G., Fardis, M.N., and Vayenas, C.G., 1996. Physicochemical Processes and Mathematical Modeling of Concrete Chlorination, Chemical Engineering Science, Vol. 51, p. 505.
14. Papadakis, V.G., Fardis, M.N., and Vayenas, C.G., 1996. Mathematical Modeling of Chloride Effect on Concrete Durability and Protection Measures, in: Concrete Repair, Rehabilitation and Protection, Eds. R.K. Dhir and M.R. Jones, E. & F.N. SPON, p. 165, London.