Construction and Building Materials 126 (2016) 86–97

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Effect of fly ash chemical composition on the reinforcement corrosion, thermal diffusion and strength of blended cement concretes

N. Chousidis [a,*], I. Ioannou [b], E. Rakanta [a], C. Koutsodontis [c], G. Batis [a]

[a] School of Chemical Engineering, National Technical University of Athens, Athens, Greece
[b] Department of Civil and Environmental Engineering, University of Cyprus, Nicosia, Cyprus
[c] Titan Cement Company S.A., Group R&D and Quality Dept., Kamari Plant, Elefsina, Greece

HIGHLIGHTS

- The chemical composition of fly ash plays a decisive role in the durability of concrete.
- The existence of clay minerals in fly ash causes concrete to swell and crack.
- Fly ash from Northern Greece improves the quality and consistency of concrete.
- Greek fly ash addition leads to anticorrosion protection of reinforcement steel.
- Fly ash concretes exhibit low values of thermal diffusion compared with OPC concrete.

ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form 7 September 2016
Accepted 9 September 2016
Available online 12 September 2016

Keywords:
Fly ash
Reinforced concrete
Physicomechanical properties
Anticorrosion protection

ABSTRACT

This paper presents the results of an experimental study conducted to evaluate the influence of fly ash chemical composition on the physico-mechanical properties and the resistance of reinforced concrete against chloride penetration. The study examines cementitious composites prepared with two different types of fly ash, used at 5% w/w and 10% w/w as cement replacement, and compares them against reference specimens prepared without fly ash. Electrochemical (Half-cell potential, corrosion current) and mass loss of reinforcement steel measurements were performed, while the porosity, compressive/tensile strength and modulus of elasticity were measured to evaluate the quality of concrete; XRD patterns and SEM images coupled with EDX analysis were further recorded and used for mineral identification and microstructure observation respectively. The thermal properties of concrete samples were also estimated. Prior to testing, all specimens were partially immersed in 3.5% w/w NaCl solution. The experimental results indicate that the performance of hardened fly ash concrete depends not only on the CaO and SiO_2 content of the additive, but also on its fineness, free lime and sulfate ions content. In particular, the durability properties of concrete containing fly ash with high SO_3 and CaO_f contents are improved, while concrete containing fly ash with significant amounts of clay minerals exhibits low chloride penetration resistance and strength; additionally, the composite concretes demonstrate low values of thermal diffusion comparing with the OPC concrete.

1. Introduction

The durability of reinforced concrete structures is affected by many factors, including chloride ion penetration. Chlorides induce corrosion of embedded steel in concrete and therefore decrease the service life of reinforced concrete. There are several methods for preventing or delaying the penetration of chlorides and the corrosion of reinforcement steel in concrete, such as organic inhibitors and coatings [1–3]. Electrochemical methods leading to chloride extraction or cathodic protection have also been used to protect reinforced concrete structures [4,5]. The aforementioned methods have some drawbacks, such as the high application and maintenance cost of cathodic protection and electrochemical chloride extraction and the toxicity of some corrosion inhibitors.

A reduction in concrete porosity and permeability is strongly encouraged in coastal and submarine environments to avoid chloride attack. A relatively inexpensive method for reducing concrete porosity and permeability and hence for protecting reinforced concrete from chloride attack is the utilization of industrial

* Corresponding author.
E-mail address: nickhous@central.ntua.gr (N. Chousidis).

http://dx.doi.org/10.1016/j.conbuildmat.2016.09.024
0950-0618/

by-products or waste materials as cement replacement during concreting [6,7]. Incorporation of fly ash or silica fume (SF) in concrete leads to improved concrete performance due to the production of C–S–H. Although silica fume is a more efficient pozzolanic material than fly ash, it is possible to increase the cost of concrete. On the other hand, fly ash (FA) is an industrial by-product, usually generated by coal combustion in electricity power plants, which may be used to reduce concrete permeability [8]. It consists of magnetite, hematite, mullite, quartz, kaolinite, illite, amorphous phase and small amounts of heavy metals such as Cd, Cr, Pb and Cu [9,10]. In fact, Carette and Malhotra [11] demonstrated that the mineralogy of fly ash varies and depends on the composition of burning-coal. Fly ash comes in the form of spherical particles, which may form agglomerates [12]; usually high amounts of CaO in fly ash lead to reduced agglomeration [13]. The combustion process and furnace type affect the characteristics of fly ashes [14], while their fineness and chemical composition affect the properties of blended cements and thus concrete hydration [15]. In general, the reactivity of FA is a function of its chemical and mineralogical composition, fineness and amorphous (glass) content.

It is widely known [16,17], that the use of fly ash, as a replacement of cement, leads to a reduction in free chloride concentration, while FA concretes show much lower corrosion rates of reinforcement steel compared with OPC concretes. In addition, fly ash improves the long-term compressive strength of concrete [18], due to a reduction in its porosity, while the reaction of $Ca(OH)_2$ (C–H) with FA decreases the hydration heat release and drying shrinkage of the composite material. The final product of the aforementioned pozzolanic reaction is the formation of calcium silicate hydrate (C–S–H) (Eqs. (1) and (2)):

$$Ca(OH)_2 + H_4SiO_4 \rightarrow Ca^{2+} + H_2SiO_4^{2-} \tag{1}$$

$$Ca^{2+} + H_2SiO_4^{2-} + 2H_2O \rightarrow CaH_2SiO_4 \cdot 2H_2O \tag{2}$$

The chloride binding capacity in cementitious systems is dominated by the content of C_3A and C_4AF; chlorides are bound by C_3A and C_4AF to form Friedel's salt. The latter is either formed when aluminum is wholly or partly substituted by iron, or as the hydration product of the ferrite phase. Eq. (3) presents Friedel's salt formation. It should be mentioned, that fly ash addition raises the aluminum silicate phase (C_3A) of the cementitious material, consequently increasing the rate of Friedel's salt formation and reducing concrete's porosity.

$$\begin{aligned} &2Cl^- + 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 10H_2O \\ &\rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 10H_2O + SO_4^{2-} \end{aligned} \tag{3}$$

Despite the positive effects of FA in concrete, there are also some drawbacks. The carbonation depth in FA concrete is usually higher than the carbonation depth in OPC concrete, while pozollanic concrete exhibits low compressive strength at early ages (7 and 28 days). In general, the chemical composition and mineralogy of fly ash play a critical role in the properties of FA concrete. For instance, a high SO_3^{2-} content in FA results in the formation of ettringite and gypsum, leading to the cracking of concrete, while the existence of certain minerals, such as clays, cause swelling; thus, quality control of fly ash is required before using it in concrete mix design. The aforementioned disadvantages may be eliminated with FA grinding, which increases its pozzolanic activity, and/or with the addition of quicklime (CaO) or small amounts of $NaSiO_3$ [19,20].

The aim of this study is the comparison of the effect of two fly ashes, generated from different power thermal stations, on the chloride penetration resistance and the physico-mechanical properties of hardened concrete. The aforementioned cement replacement additives had different chemical/mineral composition, physical properties and particle sizes.

2. Experimental procedure

2.1. Raw materials and preparation of specimens

Five groups of test samples were produced: two groups with high SO_3^{2-} content FA (code: HCSFA); two groups with FA containing clay minerals (code: HCFA); and one group without FA addition for comparison reasons (code: reference). In total, fourteen (14) cubes measuring $100 \times 100 \times 100$ mm^3 were cast from each group mixture. Twelve of them were used for the compressive strength measurements, one cube was used for the evaluation of capillary porosity and one cube for ultrasonic-pulse velocity measurements. For the splitting strength test, three cylinders (H = 30 cm and d = 15 cm) for each group were prepared.

In addition to the aforementioned specimens, nine (9) cylindrical reinforced mortar specimens (H = 100 mm and d = 50 mm) for each mixture group were prepared (Fig. 1). Eight of them were used for the electrochemical measurements (Half-cell potential, corrosion current) and the other one for MIP measurements. The reinforcing steel used was the technical class *B500C* (weldable reinforcing steel) from Halyvourgiki Hellenic Steel Industry S.A. with H = 100 mm and d = 10 mm; the chemical composition of the steel bar was as follows: C = 0.240%, S = 0.055%, P = 0.055%, N = 0.014%, Cu = 0.850%, Ceq = 0.520%. A copper wire was enwrapped around each steel rebar for the electrochemical measurements. The steel rebars were embedded in the cement mortar specimens; the space between the bottom surface of each specimen and the steel bar was 15 mm. The top surface of the specimens was sealed with epoxy resin (ARALDITE AY-103-1) while a metallic rod was used for the compaction of the specimens; the mortars were demolded after 24 h and remained in water for 7 days. Subsequently, the reinforced mortar specimens were partially immersed in 3.5% w.w NaCl solution.

For the preparation of all specimens, CEM I 42.5 N, water from supply network and dry crushed coarse (4–20 mm) and fine (0–4 mm) limestone aggregates were used. The water:cement (w/c) ratio was 0.65 for all groups. The choice of high w/c ratio was intentional to produce relatively weak (C20/25) concretes, which would highlight the effect of FA additive. The above w/c ratio and C20/25 mix design, classifies the concrete in XC2 (carbonation – induced corrosion) according to the limiting values of EN-206 [21]. It is worth mentioning that such w/c ratios are not unusual in the building construction industry of Greece.

Two fly ashes were also used in the production of the concrete specimens; HCSFA from the Ptolemais area in Northern Greece and HCFA from the Rhenish area in the western part of Germany. Ptolemais and Rhenich regions produce 80% and 54% of Greek and German fly ash, respectively. The aforementioned fly ashes were used as a cement replacement at 5% w/w and 10% w/w proportions; both of them are classified as C-class (high calcium fly ash) in accordance with BS EN-450 [22]. This class of fly ashes has pozzolanic and some cementitious properties. Macroscopically, HCSFA was finer than HCFA. The chemical compositions of the two fly ashes and cement are presented in Table 1. Table 2 summarizes the mix design for each mixture group; fineness and specific gravity of the raw materials are also shown in Table 2.

For the casting, oiled molds were used, while compaction was performed using a vibrating table (ν = 3000 Hz) for 15 s. The cubic molds were made from polymeric material while the cylindrical molds were made from steel; prior to casting, the slump test was performed. The measured slump class was S3 (100–160 mm) for