Pergamon

Cement and Concrete Research 32 (2002) 1131–1132

CEMENT AND CONCRETE RESEARCH

An investigation on microstructure of cement paste containing fly ash and silica fume

H. Temiz*, A.Y. Karakeçi

Civil Engineering Department, Kahramanmaraş University, Kahramanmaraş, Turkey

Received 29 September 2000; accepted 28 January 2002

Abstract

In this study, high-calcium fly ash (HCFA) and silica fume (SF) were used as mineral admixtures. The effect of these admixtures on the microstructure of cement paste was investigated using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The reaction of HCFA and SF with portlandite, which occurs in Portland cement (PC), forms a new calcium-silicate-hydrate (C-S-H) gel.

Keywords: Fly ash; Silica fume; Calcium-silicate-hydrate (C-S-H); Microstructure; SEM; X-ray diffraction

1. Introduction

The reaction of cement with water causes a series of complex chemical reactions. Some hundred years ago, Le Chatelier was the first to observe that the products of hydration of cement were a combination of the products of the individual compounds under similar conditions [1]. Then, Le Chatelier's observation was supplemented by Stenior [2] and by Bogue and Lerch [3]. According to the supplementation, the products of reaction may themselves interact with the other compounds in cement. The main compounds in cement are two calcium silicates (i.e., dicalcium silicate and tricalcium silicate), and the physical behavior of these compounds is similar to that of cement during hydration.

Highly crystalline portlandite [$Ca(OH)_2$] and amorphous calcium-silicate-hydrate (C-S-H) are formed in the hydration of Portland cement (PC). The hydrated cement paste consists of approximately 70% C-S-H, 20% CH, 7% sulfoaluminate, and 3% secondary phases [4].

Calcium hydroxide, which is formed as a result of chemical reaction, is soluble in water and has low strength. These properties affect the quality of concrete negatively. Adding mineral admixtures to cement decreases the amount of $Ca(OH)_2$.

Some mineral admixtures are low-calcium fly ash (ASTM Class F) obtained by burning asphaltic coal, anthracite, and high-calcium fly ash (HCFA, ASTM Class C) that is produced by burning of lignite and bituminous coal [5]. Type C ashes have both pozzolanic and cementing properties. Because of these properties, HCFA is also used in cement and concrete.

According to Lessard et al. [6], cement paste containing silica fume (SF) produces amorphous C-S-H gel with high density and low Ca/Si ratio.

Table 1
Chemical analysis of cement, FA, and SF (%)

Chemical composition	PC (ASTM Type 1)	HCFA	SF
SiO_2	20.20	47.60	93.60
Al_2O_3	6.20	9.30	0.90
Fe_2O_3	2.90	9.00	0.70
Total	29.30	65.90	95.20
CaO	61.70	19.10	0.50
SO_3	3.30	1.50	–
MgO	2.70	–	0.90
Na_2O	–	–	–
Insoluble residue	1.8	1.60	1.03
Ignition loss	1.10	1.60	2.32
Blaine specific area (cm^2 g)	3302	5625	

* Corresponding author. Tel.: +90-344-251-2341; fax: +90-344-251-2342.

E-mail address: mkemal@ksu.edu.tr (H. Temiz).

PII: S0008-8846(02)00749-4

Table 2
Mixture proportions (mass%)

Specimens[a]	PC	HCFA	SF	W/B
1	100	0	0	40
2	70	30	0	40
3	70	24	6	40

[a] Specimen ages were 7, 28, and 90 days.

The aim of this study was to investigate the effects of HCFA and SF addition on the microstructure of hydrated cement paste.

2. Materials and methods

2.1. Materials

PC (similar to ASTM Type I Portland Cement) from Niğde Cement Factory, high-lime fly ash (FA) from Soma Thermic Electricity Station, and SF from Antalya Electrometallurgy Industry were used. Their chemical analyses are shown in Table 1. Three, 7-, 28-, and 90-day hydrated, cement samples were used in each for X-ray diffractions (XRD) and scanning electron microscopy (SEM) analysis.

2.2. Methods

For microstructural analysis, 100% PC, 70% PC + 30% HCFA, and 70% PC + 24% HCFA + 6% SF were mixed according to weight percentages [7]. The water-to-binder (w/b) ratio 0.40 was kept constant. Mixture proportions are shown in Table 2. Paste samples were placed in sealed tubes so that air transfer into tubes was prevented.

Pastes samples of 7, 28, and 90 days of hydration were ground and immersed into acetone for 24 h to prevent hydration. Then, they were dried in an oven at 45 ± 2 °C. Some of these samples were ground further for XRD.

3. Results and discussion

It was observed that large portlandite crystals appeared at the seventh day for samples containing no admixtures. Portlandite decreased in the samples with HCFA and HCFA + SF at 7 days. In the 28- and 90-day samples containing HCFA and HCFA + SF, portlandite decreased much more than in 7-day samples. $Ca(OH)_2$ is formed as a result of reaction of PC and water. Therefore, $Ca(OH)_2$ crystals decrease. Durning and Hicks [8] reported that in a mixture of 30% SF and 70% PC, $Ca(OH)_2$ disappears entirely. Kazuyiki and Mitsunori [9] found that $Ca(OH)_2$ also decreases when SF and FA are used together. Carette and Malhotra [10] and Mehta and Gjørv [11] demonstrates the positive effects on concrete strength and durability when FA and SF were used as admixtures.

4. Conclusion

It was found that there was significant amount of SiO_2 in the chemical composition of HCFA and SF. During the chemical reaction period of PC, this silicate reacted with free $Ca(OH)_2$ and formed amorphous C-S-H gel. Thus, the amount of $Ca(OH)_2$, which is harmful for concrete, decreased.

Acknowledgments

We would like to thank to Turkish Cement Manufacturers' Association staff for their help in this study.

References

[1] A.M. Neville, Properties of Concrete, Longman Scientific & Technical, Harlow, Essex, 1988.
[2] H.H. Steniour, The reactions and thermochemistry of cement hydration at ordinary temperature, Proceeding of the Third International Symposium on the Chemistry of Cement, London, Tankaya Press, Istanbul, 1952, pp. 89–261.
[3] R.H. Bogue, W. Lerch, Hydration of Portland cement compounds, Ind. Eng. Chem. 26 (8) (1934) 47–837.
[4] G.G. Bye, Portland Cement Composition Production and Properties, Pergamon, Oxford, UK, 1983 (published on behalf of the Institute of Ceramics).
[5] V.M. Malhotra, Role of supplementary cementing materials in concrete, Proceeding of the Eleventh European Ready Mixed Concrete Congress, İstanbul, Tankaya Press, Istanbul, 1995, pp. 84–90.
[6] M. Lessard, S.L. Sarkar, D.V. Ksinsik, P.C. Aïtcin, Long term behavior of silica fume concrete, Concr. Int. (1992) 25–30 (April).
[7] H. Temiz, The Properties of Mortar Which Fly Ash and Silica Fume are Mixed Together, PhD thesis, University Fırat, Elazığ, 1998.
[8] T.G. Durning, M.C. Hicks, Using microsilica to increase concrete's resistance to aggressive chemicals, Concr. Int. (1991) 42–48 (March).
[9] T. Kazuyiki, K. Mitsunori, Effect of fly ash and silica fume on the resistance of mortar to sulfuric acid and sulphate attack, Cem. Concr. Res. 24 (2) (1994) 361–370.
[10] G. Carette, V.M. Malhotra, Early-age strength development of concrete incorporating fly ash and condensed silica fume, ACI 79 (1983) 765–784.
[11] P.K. Mehta, O.E. Gjørv, Properties of Portland cement concrete containing fly ash and condensed silica fume, Cem. Concr. Res. 12 (1982) 587–595.