Pergamon

Cement and Concrete Research, Vol. 28, No. 11, pp. 1545–1553, 1998

0008-8846/98 $19.00 + .00

PII S0008-8846(98)00131-8

APPLICATION OF ENERGY-DISPERSIVE ANALYSIS TO PORTLAND AND PORTLAND FLY ASH CEMENT CORROSION

S. Miletić,[1]* M. Ilić,* and P. Jovanić†
*IMS Institute for Materials Testing, Bul. vojv. Mišića 43, 11000 Beograd, Yugoslavia
†ITNMS, Franše d'Eperea 86, 11000 Beograd, Yugoslavia

(Received September 30, 1997; in final form August 4,1998)

ABSTRACT

The behavior of Portland cement with and without 30% fly ash additive in aggressive solutions was studied. This paper considers the sulfate corrosion of hardened cement paste. Cement paste test samples were prepared, cured in water for 21 days, and then exposed to an aggressive environment (10% $(NH_4)_2SO_4$ solution). Several properties were measured and the results were analyzed. The surface composition and morphology of the cement paste test samples were imaged by scanning electron microscopy. The concentration gradient of sulfate ions in cement paste depth was obtained by energy-dispersive analysis. © *1998 Elsevier Science Ltd*

Introduction

Unless it is resolved successfully and as a part of integral environmental management, the problem of wastes could become a burden on future generations. Besides environmental pollution, some important economic factors are related to the growing price of raw materials and energy. That is why efforts—primarily on behalf of industrially developed countries—are directed more and more towards recycling and the various methods of using wastes.

Thermopower stations, which use coal as fuel, have mostly installed extremely efficient equipment to prevent the emission of solid particles (fly ash) into the atmosphere. In Yugoslavia, about 10 million tons of fly ash per year is emitted. Wetted material then is transferred to deposit areas, which presents a large ecological problem. By definition, fly ash is a fine powder consisting mainly of spherical, glassy particles that have pozzolanic properties and essentially SiO_2 and Al_2O_3. The aim of our first investigation was to establish a procedure for use of waste fly and bottom ash in building material production, which would reduce an enormous ecological problem while producing equal quality products (cement, mortar, concrete, bricks, etc.). Concrete has been the most important, widely used construction material in the world.

In actuality, concrete buildings suffer simultaneously from mechanical, chemical, and physical attacks. Therefore, the effect of mechanical stresses must be considered when the

[1]To whom correspondence should be addressed.

TABLE 1
Potential phase composition of Portland cement clinker.

Potential phase composition (% mass)	Portland cement clinker B
C_3S	57.5
C_2S	13.5
C_3A	13.3
C_4AF	8.7

durability and corrosion resistance of a concrete are estimated. Such study of stress corrosion of concrete is necessary and important for determining the durability of concrete (1–4).

Chemical corrosion of cement in concrete can be divided into two groups based on the cause of concrete failure: expansive corrosion and dissolving corrosion. The attack of sulfate ions on cement stone can cause expansion, generally due to the formation of ettringite $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$ in the shape of prismatic crystals (5–7). The consequences range from damage to the concrete to destruction at worst. Concrete corrosion by ammonium sulfate is the most aggressive corrosion on concrete; neither balancing nor creation of protective gel takes place. In this case, concrete is damaged not only by expansion, but also by dissolution of the cement stone (8,9).

In recent years, there has been an increasing need to develop new testing methods for monitoring sulfate attack on concrete structures. There are many test methods available to assess the quality and degradation of concrete structures. The basic idea of our work was to test the possibility of using energy-dispersive analysis. Our aim was to investigate sulfate attack on concrete structures, that is, to obtain concentration gradients of sulfate ions through samples of cement paste. This was done by monitoring the concentration of elementary sulfur through cross-sections of the sample, in line, because energy-dispersive analysis can deter-

TABLE 2
Fly ash chemical composition.

Chemical composition (% mass)	Fly ash
Loss on ignition	5.7
$SiO_2 + Al_2O_3 + Fe_2O_3$	84.2
CaO	6.5
MgO	2.7
SO_3	0.05
S	0.02
Na_2O	0.3
K_2O	0.7
Hydrated water	34.6
Insoluble residue	76.6

TABLE 3
Chemical composition of cements.

Chemical composition (% mass)	Cement PCB	Cement PCBP
SiO_2	19.7	14.0
Al_2O_3	7.0	6.2
Fe_2O_3	2.7	2.7
CaO	62.0	44.7
Insoluble residue	0.1	20.2
Loss on ignition	0.8	3.0
CO_2 in $CaCO_3$	0.4	0.4
CaO free	0.1	0.0
SO_3 in $CaSO_4$	2.0	2.0
MgO	2.2	2.4
Alkalies as Na_2O	0.4	0.4
K_2O	0.4	0.2
Cl^-	0.0	0.0

mine the elemental content in a very small surface area. The advantages of this method are that it is nondestructive and does not require additional sample preparation.

Experimental Methods

Portland cement and Portland fly ash cement manufactured in Yugoslavia were used as follows:

TABLE 4
Physicochemical properties of cements.

Physicochemical properties	Cement PCB	Cement PCBP
Sieve residue at 0.09-mm sieve (% mass)	1.8	5.2
Density (g/cm^3)	3.1	2.9
Specific surface (cm^2/g)	3320	3720
Setting		
Standard consistence (% mass)	25.8	28.0
Initial time (min)	165	240
Final time (min)	225	330
Soundness		
Le Chatelier test (mm)	1.0	1.0

TABLE 5
Standard strength of cements.

	Cement	
Strengths (MPa)	PCB	PCBP
Flexural		
2 days	4.4	2.5
3 days	5.3	3.6
7 days	7.2	6.2
28 days	8.0	8.3
Compressive		
2 days	15.7	8.8
3 days	19.8	14.9
7 days	30.2	24.2
28 days	40.3	39.5

1. Portland cement B (PCB), according to the European cement standard EN 197-1: CEM-I.
2. Portland fly ash cement B (cement clinker B) with 30% fly ash (PCBP), according to the European cement standard EN 197-1: CEM II/B-V.

All materials were analyzed chemically, and their physicochemical and mechanical properties were investigated. Resistance of the cement to the aggressive solution was tested on mortar prisms. The first results were published previously (10,11). The testing methods used in this part were determination of standard strength (EN 196-1), chemical analysis (EN 196-2), determination of setting time (EN 196-3), determination of the sieve residue (EN

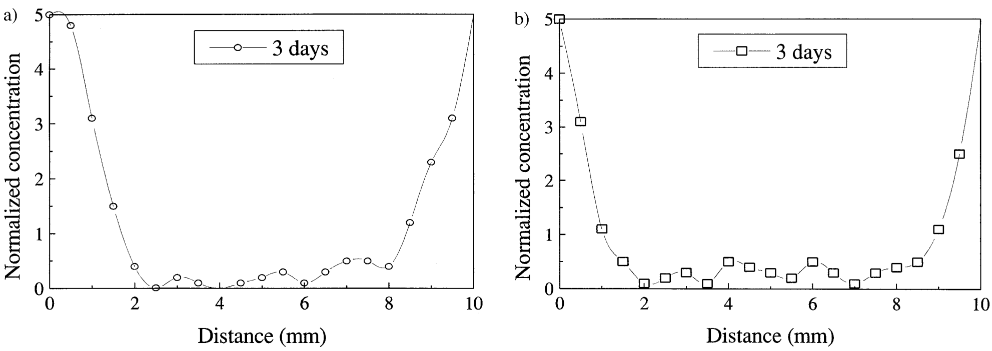

FIG. 1.
Concentration gradient of sulfur through the depth of the sample after 3 days in the aggressive environment, determined by the energy-dispersive analysis method, for (*a*) Portland cement and (*b*) Portland ash cement.

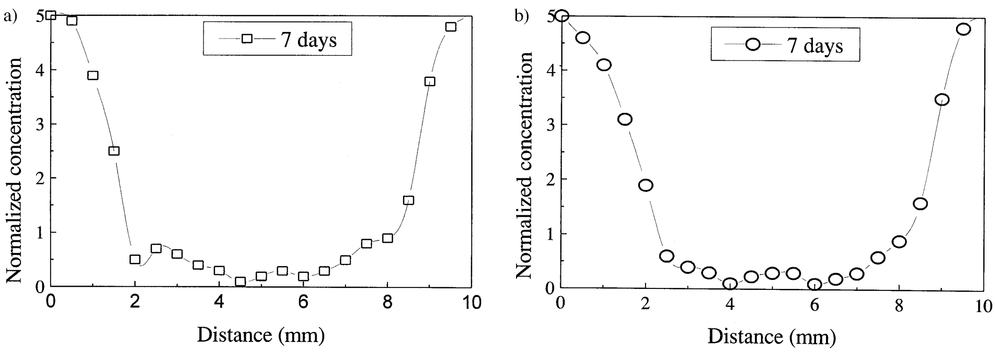

FIG. 2.
Concentration gradient of sulfur through the depth of the sample after 7 days in the aggressive environment, determined by the energy-dispersive analysis method, for (*a*) Portland cement and (*b*) Portland ash cement.

196-6), determination of specific surface (EN 196-6), and calculation of the potential phase analysis (ASTM C 150).

To analyze the degradation process caused by sulfate attack, samples were prepared as follows. The chemical resistance of the cements was tested with cement paste 1 × 1 × 6-cm test prisms prepared with a water-to-cement ratio needed for a standard consistency. Before exposure to the aggressive solution, the prisms were cured for 1 day in the mold and 20 days in water. A 10% $(NH_4)_2SO_4$ solution was used as the aggressive environment.

The concentration gradient of sulfate ions in prepared cement paste samples (dimensions 1 × 1× 6 cm and broken in halves to approximately 1 × 1 × 3 cm) was determined by an energy-dispersive method on an Edax 9900 apparatus at the cross-section of the broken sample. For this purpose, samples were mounted on stubs and pumped to a vacuum level of

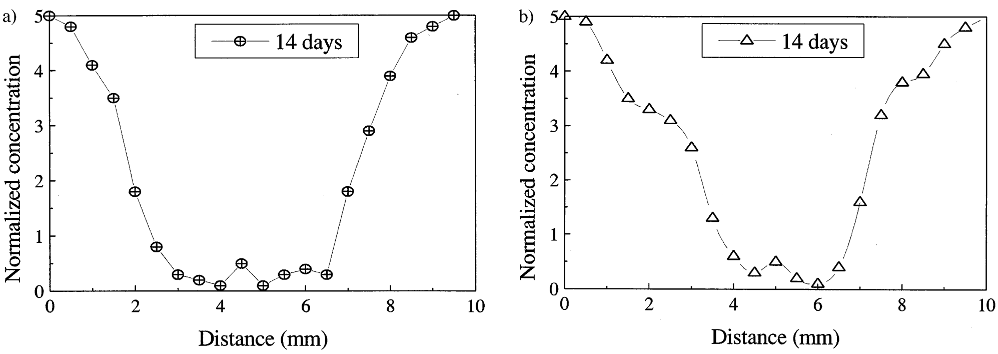

FIG. 3.
Concentration gradient of sulfur through the depth of the sample after 14 days in the aggressive environment, determined by the energy-dispersive analysis method, for (*a*) Portland cement and (*b*) Portland ash cement.

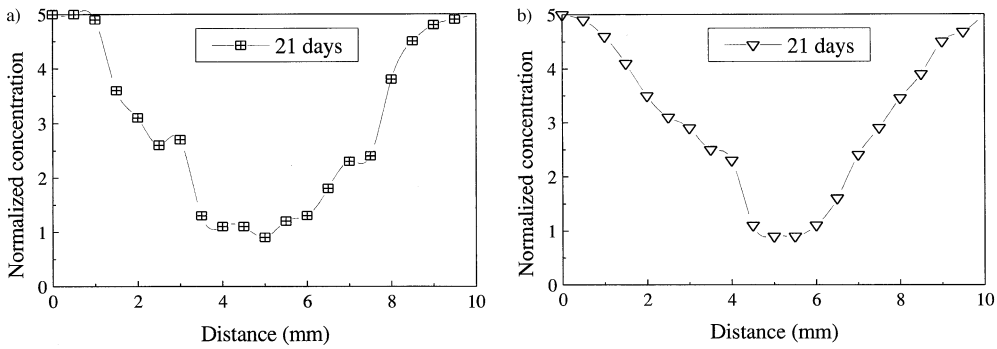

FIG. 4.
Concentration gradient of sulfur through the depth of sample after 21 days in the aggressive environment, determined by the energy-dispersive analysis method, for (*a*) Portland cement and (*b*) Portland ash cement.

1.33×10^{-6} Pa. Monitoring of elementary sulfur content was done at 20 points on 1-cm wide samples, so that monitoring on the center line of the cross-section was obtained. Morphological analysis by scanning electron microscopy was performed simultaneously, and the images were obtained by secondary electrons on a Philips 515.

Results and Discussion

The selected environment represents a very strong aggressiveness to ensure fast results for the real conditions that can be present in underground waters in Yugoslavia.

Potential phase analysis of the Portland cement clinker is given in Table 1. It can be seen that the cement has the usual C_3A content in clinker of 13.3%, influencing the sulfate

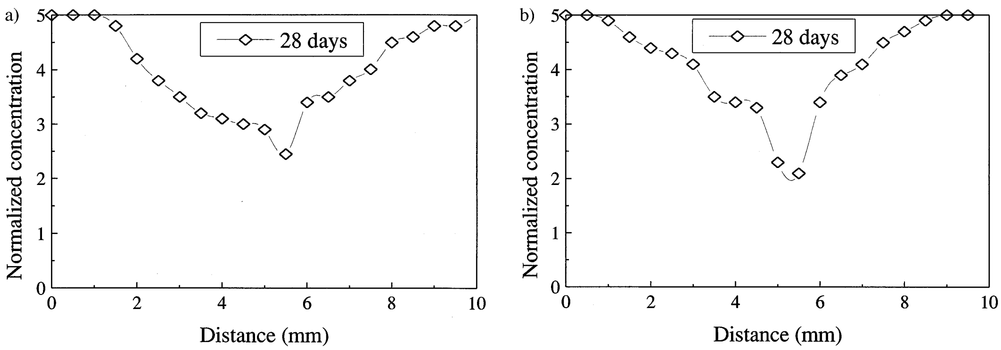

FIG. 5.
Concentration gradient of sulfur through the depth of sample after 28 days in the aggressive environment, determined by the energy-dispersive analysis method, for (*a*) Portland cement PCB and (*b*) Portland ash cement.

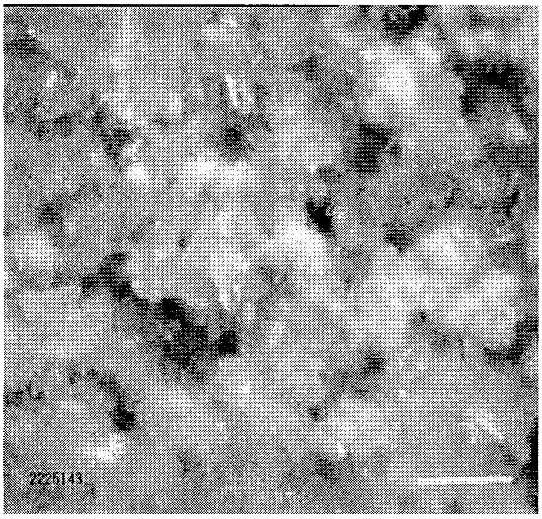

FIG. 6.
Micrograph of Portland cement after 14 days in the aggressive environment (magnification 150×).

resistance. Ordinary Portland cement, such as the one investigated, is not resistant to sulfate attack because it has a considerable amount of tricalcium aluminate C_3A, whose hydrates react with sulfate ions, giving expansive compounds. According to the literature, the difference in the C_3S content also can be significant with regard to sulfate resistance.

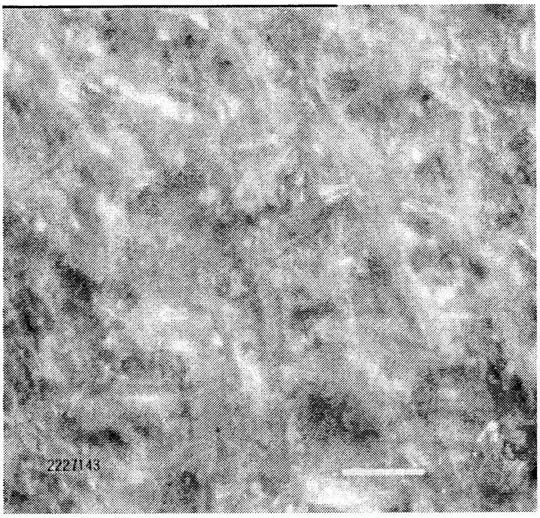

FIG. 7.
Micrograph of Portland ash cement after 14 days in the aggressive environment (magnification 50×).

Table 2 presents the chemical composition of fly ash. Because of the high content of SiO_2, Al_2O_3, and Fe_2O_3 and the low content of CaO, MgO, alkalis, and SO_3, fly ash is suitable for cement production, although loss on ignition and especially hydrated (bounded) water were relatively high.

The chemical composition of the cements is presented in Table 3. All cements meet Yugoslav standard JUS B.C1.011. Portland fly ash cement PCBP has a higher insoluble residue and loss on ignition than Portland cement PCB.

Table 4 presents values of fineness, density, standard consistency, setting time, and soundness of the test cements. Obviously, the addition of fly ash raises the water demand for standard consistency and sieve residue and extends setting time, but has no significant influence on other characteristics. All characteristics are in compliance with Yugoslav standard JUS B.C1.011.

Table 5 gives values for flexural and compressive strengths of cements after 2, 3, 7, and 28 days. The Portland fly ash cement PCBP had lower strengths, even after 28 days, than the corresponding Portland cement PCB.

The content of sulfur (i.e., sulfate) as determined by the energy-dispersive analysis method is given in Figures 1–5. The distance, given on the x axis, is from one side of the cross-section of the broken half to the other side (10 mm total) through the center line of the cross-section. It is important to emphasize that, in comparing the two tested cements, all curves obtained were very similar, which means the behavior of both cements in an aggressive environment is similar. But, with regard to the maximum normalized value of 5, it can be seen that Portland fly ash cement PCBP has less points at that level in all terms of the investigation, meaning that the sulfate content throughout the depth of the test sample was lower. Repeated testings gave the same results, so it can be concluded that this method has high accuracy. Such results also were obtained in previous investigations (10,11), showing that Portland fly ash cement PCBP is more suitable for use in an aggressive environment than ordinary Portland cement PCB.

Micrographs obtained by scanning electron microscopy helped to determine the morphological structure of the cement paste samples. Figures 6 and 7 show cross-sections of the broken samples after 28 days in the aggressive solution. Gypsum needles can be seen as the main corrosion product. (These are not very clear because of problems with the photomagnification device.) Both samples shown results very similar to those obtained by energy-dispersive analysis.

Conclusion

The results of testing the attack by aggressive sulfate solutions allow the following conclusions:

1. The selected environment represents a very strong aggressiveness to ensure fast results for the real conditions that can be present in underground waters in Yugoslavia.
2. Test results show that energy-dispersive analysis and scanning electron microscopy alone cannot represent the degradation process, but these in combination with other significant characteristics, such as mass change, x-ray diffraction, bonded SO_4^{2-} content, and flexural strengths (degradation and/or corrosion coefficients derived from them), represent valuable characteristics.

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