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SULFATE CORROSION OF PORTLAND CEMENT-PURE AND BLENDED WITH 30% OF FLY ASH

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ABSTRACT

This paper considers the sulfate corrosion of Portland cement-pure and blended with 30 wt% of fly ash. As raw materials, three kinds of Portland cements, with different content of C_3A (5.45-11.84 wt%), were applied. Fly ash was added so as to decrease the C_3A content (to 3.82-8.29 wt%). The test samples were exposed to the influence of aggressive environment (solutions with 1000 and 2000 mg/l of the SO_4^{-2} ions as well as 320 mg/l of the NH_4^{-2} ions). Experiments lasted six months, while the flexural strengths were measured after 1,2,4 and 6 months. The corrosion resistance factor was calculated. For the examined systems, a correlation was suggested. It expresses the resistance factor as a function of three independent variables (the C_3A content, duration of corrosion process and concentration of the SO_4^{-2} ions).

Introduction

Sulfate corrosion of cement and concrete is very serious problem caused by aggressive influence of sulfate solutions from many different sources. Natural groundwater might contain the SO_4^{-2} ions as a result of an oxidation of sulfide minerals [1]. Concentration of the SO_4^{-2} ions is particularly high in an industrial environment. Chemical wastes from industrial processes as well as application of fertilizers contribute to an appearance of the SO_4^{-2} ions. Very dangerous and aggressive is acid rain that contains the sulfuric acid, since it reacts with available compounds to give solutions of sulfate salts. Deterioration of concrete sewage systems is mostly caused by the presence of anaerobic bacteria that produces hydrogen sulfide. Once generated and dissolved in water, this gas can be used by some of aerobic bacteria so as to give aggressive sulfuric acid as well as the SO_4^{-2} ions [1,2].

Mechanisms of sulfate solutions attack on concrete are well known; the calcium hydroxide from concrete reacts with the aggressive SO_4^{-2} ions to form gypsum, that can be easily washed away [3]. On the other hand, anhydrite (anhydrous gypsum) reacts with the C_3A constituent of cement thus giving ettringite- mineral whose volume is few times greater than the volume of the initial compounds. Due to the increase of internal pressure, deterioration of system is probable as well as a decrease of its mechanical strength [4-6]. A level of

TABLE 1
Chemical Composition of Raw Materials

Oxide	Portland Cement			Fly Ash
	B	P	K	
SiO_2	19.95	19.94	21.15	44.12
Al_2O_3	5.86	5.2	4.43	14.55
Fe_2O_3	2.18	2.39	3.72	5.15
CaO	63.53	62.96	64.27	26.00
SO_3 in $CaSO_4$	2.80	2.20	1.57	0.27
CO_2 in $CaCO_3$	0.16	0.10	0.23	-
MgO	2.10	3.30	1.10	1.70
Na_2O	1.10	1.00	1.19	0.09
Insol. Residue	1.00	0.71	0.87	26.00

deterioration, by the SO_4^{-2} ions, depends even on the stage of cement hardening [7]. Undoubtedly, cement resistant to the severe sulfate corrosion has to have low both C_3A content and CaO content.

The C_3A quantity depends on the composition of available Portland cement clinker. However, its decreasing can be achieved by adding some raw materials unless they contain C_3A. At the same time, there is a need for using huge quantities of ash and similar, low quality remains. Many positive effects are associated with the presence of ash in cement mixture, such as: pozzolan activity, developing of microstructure of product, improvement of mechanical characteristics, etc. [8-10]. On the other hand, ash may contain free CaO, which is very sensitive to the SO_4^{-2} ion's attack, as proved by many investigations as well as by the thermodynamic analysis [11].

This paper considers a problem of using low quality fly ash in blending cements, satisfactory resistant to sulfate corrosion. For the examined systems, a correlation is suggested. It expresses the corrosion resistance factor as a function of the C_3A content, exposure time and concentration of the SO_4^{-2} ions. It could be useful in predicting the investigated systems behaviour as well as in determining optimal raw mixture recipe.

Characteristics of Raw Materials and Plan of Experiments

Three kinds of Ordinary Portland cement are the main raw materials. Their oxide as well as phase composition is presented in Tables 1-2. Also, low-quality fly ash (from the power

TABLE 2
Phase Composition of Raw Materials

Phase	Portland Cement		
	B	P	K
C_3S	50.93	45.42	56.92
C_2S	18.77	22.90	17.70
C_3A	**11.84**	**9.74**	**5.45**
C_4AF	6.63	7.27	11.31
CaO free	1.18	3.47	1.19
$CaSO_4$	4.76	3.74	2.81
MgO	2.10	3.30	1.00

plant Kolubara) was added by 30 wt% to all the cements and two times three systems were obtained. Oxide composition of ash is given in the last column of Table 1. The oxides are built in the following compounds: mullite, hematite, gehlenite, calcium silicate (C_2S) and calcium aluminate ($C_{12}S_7$). Also, a negligible quantity of C_3A was detected, as well as a significant quantity of quartz and free CaO.

The samples (10 × 10 × 30 mm prisms) were made from each of the six raw materials. To the materials, certain quantity of quartz- sand (0.4-0.5 mm granulation) was added, so that mass proportion of cement- component and sand- component was: 1/3.5, while the water/cement ratio was 0.4. The samples were moist-cured 14 days and tested for flexural strength. After the curing period passed, some of them were immersed into the water (from the Belgrade's network). These will be taken as the referential ones. The rest of the prisms were exposed to the influence of the SO_4^{2} ions and the NH_4^{-2} ions, for 1, 2, 4 and 6 months, that is, they were immersed into three solutions: solution I (1000 mg/l SO_4^{-2}), solution II (2000 mg/l SO_4^{-2}) and solution III (1000 mg/l SO_4^{-2} and 320 mg/l NH_4^{+}). Concentrations of the solutions were chosen after consulting the references [3, 7, 12]. According to the plan of experiments, each of the six systems was treated with each of the solutions, whose temperatures were kept at 20 ± 1 [°C]. The solutions stood still; losses due to vaporization were neutralized by adding the lost quantity; the solutions were renewed every month.

Corrosion Resistance Factor

Deterioration of samples was expressed by the Corrosion Resistance Factor:

$$\mathrm{CRF} = \frac{\text{Flexural Strength of Corroded Sample}}{\text{Flexural Strength of the SampleImmersed Into Water}} \qquad (1)$$

Introduction of such a quantifier enables not only mathematical modelling of system behaviour but also following changes in mechanical characteristics due to the corrosion.

Discussion of Results

Values of the Corrosion Resistance Factors are presented in contour graphics (Fig. 1). At early ages, the corroded samples can have higher strength than the uncorroded ones, probably because of the exponential generation of hydration products. They fill the pores of the structure thus increasing the density. Also, formation of monosulfate contributes to the compaction of the system. Independent variables are as follows: the C_3A content, the length of exposure and the concentration of the SO_4^{-2} ions (Figs. 1a and 1b) or the concentration of the NH_4^{+} ions (Fig. 1c).

The response of the systems to the aggression can be represented by a complex, multimodal function (surface). A correlation between the CRF and the C_3A content is particularly complex.. The global minimum (at the right, upper corner for all the systems) appears at the highest C_3A concentration and the longest exposure. High CRF values are typical of the lowest C_3A content (3.815 wt%), for the whole experimental period and both SO_4^{-2} concentrations. An increase of the C_3A quantity decreases the CRF values. However, this changes

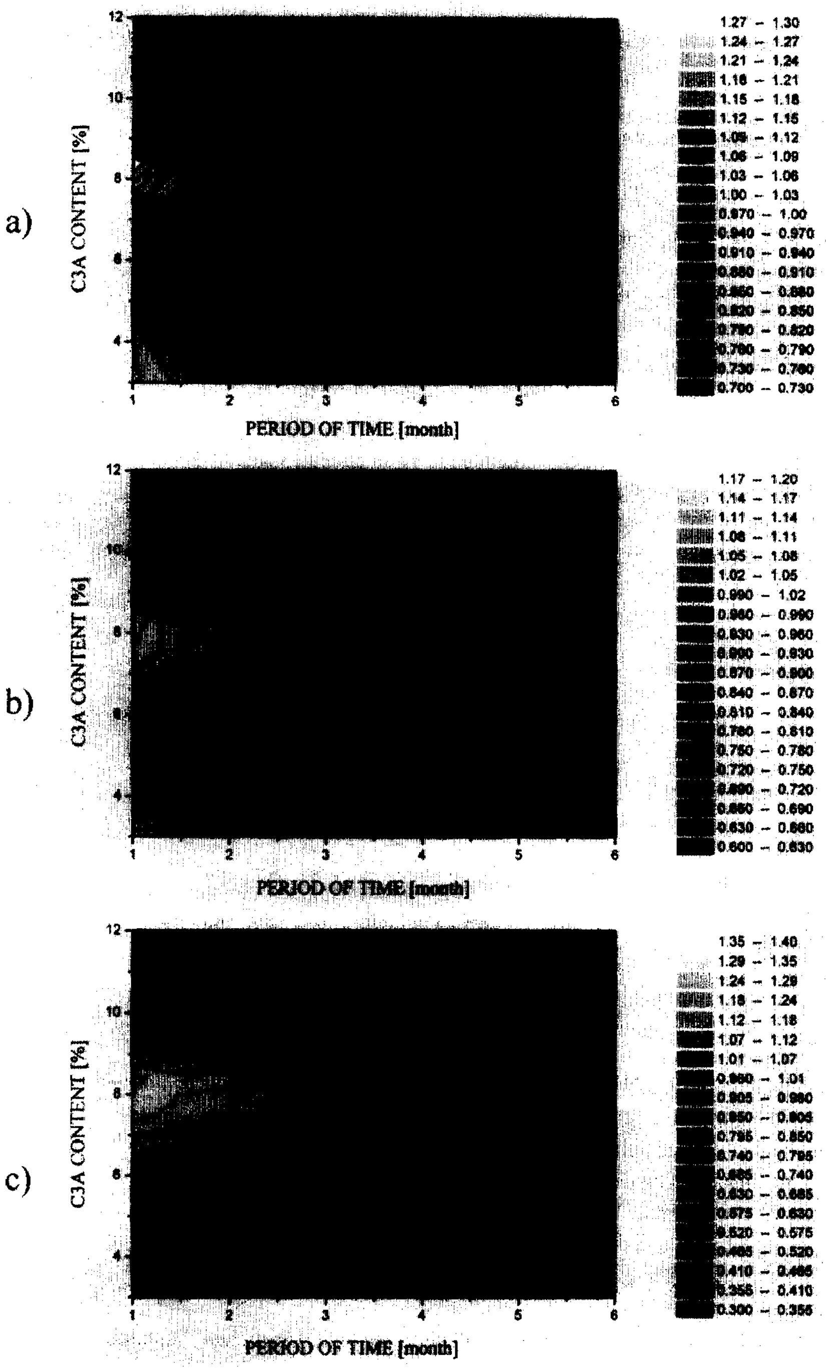

FIG. 1.

Influence of C_3A Content to the CR factor (a) 1000 mg/l SO_4^{-2}; (b) 2000 mg/l SO_4^{-2}; (c) 320 mg/l NH_4^+.

so that maximum of the CRF is achieved at ≈8.3 wt% C_3A (for entire period of exposure and both SO_4^{-2} concentrations). The optimal system contains cement B (with highest amount of the C_3A compound, i.e., 11.84 wt%) and 30 wt% of ash. It is an excellent example of how low quality raw material can improve quality of the mix. Such a result requires additional investigations. Obviously, some constituents of optimal samples act positively and all together gives a resistant system.

A correlation between the CRF and the concentration of the SO_4^{-2} ions is rather simple; that is, the higher the concentration the lower the resistance. Combined influence of both the NH_4^+ ions and the SO_4^{-2} ions (solution III) is slightly complicated. Generally, solution III is more aggressive than the solution I, although some exceptions could be noticed. Also, the lowest value of the CR Factor is found for the samples exposed to the influence of both ions at the same time. A correlation between the CRF and the length of time period is also simple. A short exposure is less dangerous than a long exposure.

Very important for this investigation is an analysis of fly ash influence to sulfate corrosion of the blended systems. Problems might appear due to an increase of free CaO. Simple thermodynamic considerations [11] show that CaO tends to convert into $CaSO_4$ and tends even more to convert into $CaSO_4 \times 2H_2O$. In the presence of C_3A, appearances of these sulfate salts might be dangerous; e.g., forming of undesired ettringite is (thermodynamically) very probable. Degradation of the system is, also, possible due to sulfates washing away. Fortunately, negative effects are covered by the positive ones. So, comparison among the CR Factors of no ash samples and ash samples shows positive influence of added ash, in the case of both types of ions (SO_4^{-2} and NH_4^+) as well as any applied concentration. One of the reasons must lie in the fact that ash contributes to the lowering of the C_3A content in the system. It, also, adds certain quantities of mullite and gehlenite. However, there must be other reasons too. As this kind of investigation can not answer the questions concerning mechanisms of ash influence, it is necessary to perform additional investigations.

Correlation for CRF

An attempt was made to define a correlation $CRF(x_1, x_2, x_3)$ for the examined systems. It might be used for predicting behaviour of the investigated systems as well as for determining an optimal raw mixture recipe. It is not suggested for all known systems because data base is too small for any kind of generalization.

The independent variables were as follows:

• x_1 [wt%]	percent of the C_3A compound in the mix,
• x_2 [month]	duration of the aggressive influence and
• x_3 [g/l]	concentration of the SO_4^{-2} ions in the solution.

Type of the correlation, which proved adequate, was:

$$CRF = \sum_{i=1}^{3} b_i x_i + \sum_{1 \le i < j \le 3}^{3} b_{ij} x_i x_j + \sum_{i=1}^{3} b_{ii} x_i^2 \qquad (2)$$

The b- coefficients were obtained by regression analysis (applied to the measured data) as given in Table 3. From the last column of this table it is obvious that the third- and the last-b are the most significant. They concern the third variable-concentration of the SO_4^{-2} ions.

TABLE 3
Coefficients in the Correlation (2)

Coefficients		
Symbol	Value	Significance
b_1	0.04525	0.0406
b_2	-0.05612	0.05211
b_3	**1.64554**	**0.27127**
b_{12}	-0.00404	0.00291
b_{13}	-0.00176	0.01116
b_{23}	0.01008	0.01548
b_{11}	-0.0036	0.00226
b_{22}	0.00458	0.00572
b_{33}	**-0.57452**	**0.11112**

Statistical analysis of the fit (2), performed by applying the One-Way ANOVA test and the Independent t-test, proved its adequateness for the examined systems.

Conclusion

The goal of this paper is to answer the question is the available, low-quality fly ash (which does not contain C_3A but containes free CaO) adequate for blending cement mixes which will be satisfactory resistant to sulfate corrosion. Positive answer is obtained. What is more, mixes with ash proved more resistant than the pure cement samples.

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