Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

FLY ASH - USEFUL MATERIAL FOR PREVENTING CONCRETE CORROSION

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Abstract

Large quantities of fly ash is produced in our country every year. Most of fly ash is got from lignite that means that this material is not so useful for concrete production. This paper presents results of investigations of sulphate corrosion of concrete made from portland cements and portland cements with the fly ash addition. The addition of fly ash appears to be very useful for preventing sulphate corrosion of concrete even in the case of very strong ammonium-sulphate corrosion according to our results.

The effect of ammonium sulphate solution on the durability of Portland cements (various C_3A content) with partial replacement of 30% mass percent fly ash was investigated. Results show that fly ash addition to Portland cement can improve resistance to ammonium sulphate attack.

Key words- Portland cement, fly ash, corrosion, ammonium-sulphate

1. Introduction

Concrete has been widely used as the most important constructional building materials in the world. More and more attention has been paid to the mechanical properties and durability of cement concrete. Generaly, the durability and the degradation coefficient of the concrete has been considered as a dominant factor in addition to the fact that the mechanical properties could satisfy the demand of the construction design.

In practise, concrete buildings suffer simultaneously mechanical, chemical and physical attacks. Therefore, the effect of mechanical stresses must be taken into consideration when durability and corrosion resistance of a concrete are estimated, i.e., the study of stress corrosion of concrete is necessary and very important for durability. [1-4]

Chemical degradation of concrete is the consequence of reactions between the constituents of cement stone, i.e. calcium silicates, calcium aluminates and above all calcium hydroxide etc., with certain substances from water, solutions of soil, gases, vapours, etc.[5-8] The most important aggressive ions are: SO_4^{2-}, Mg^{2+}, NH_4^+, Cl^-, H^+, HCO_3^-.

Primarily, the types of chemical corrosion of concrete can be devided into two groups, i.e., expansive corrosion and dissolving corrosion, with respect to the cause of failure of concrete. The attack of sulphate ions on cement stone can cause expansion, in general due to the formation of ettringite $C_3A{\cdot}3CaSO_4{\cdot}32H_2O$, in the shape of prismatic crystals.[9,10] The consequences are damages to the concrete and destruction at worst. The concrete corrosion by ammonium sulphate, for example, covers 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 dissolving the cement stone.

In this investigation the method of Koch and Steinegger[8] is used to test the sulphate resistance of the cements. According to the authors criterion of the sulphate resistance was the quotient:

$$RC = \frac{\text{Flexural Strength of the Sample Stored in the Sulphate Solution}}{\text{Flexural Strength of the Sample Stored in Water}} \qquad /1/$$

The results show that there is a considerable influence of the mineral composition of Portland cement clinker and cement on the behaviour of concrete in the presence of aggressive sulphate and ammonium ions. For the manufacture of concrete resistant to the attack of aggressive ions special attention should be paid to the selection of cement.[10]

2. Experimental

To investigate the resistance of cement to sulphate attack Portland cement and Portland fly ash cement manufactured in Yugoslavia were used:

- Portland cement B (PCB)- according to the European cement standard EN 197-1: CEM-I
- 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
- Portland cement K (PCK)- according to the European cement standard EN 197-1: CEM-I
- Portland fly ash cement K (cement clinker K) with 30% fly ash (PCKP)- according to the European cement standard EN 197-1: CEM II/B-V

The potential phase analysis, chemical contents, physico-chemical and mechanical properties were determined for all starting materials used.

Cement pastes were prepared by Koch-Steinegger method.[8] Specimens of 1x1x6 cm were molded and compacted by vibration. After one day at 100% relative humidity the specimens were demolded and kept immersed in water for 21 days. After that, samples were immersed in the aggressive solutions of different concentrations for different periods of time. Control samples were prepared and stored in distilled water under the same conditions as reference. As aggressive solution, ammonium-sulphate concentrations 2.5%, 5%, 7.5% and 10% was used, but, results only for 10% ammonium-sulphate solution are presented.

The mass change of samples, SO_4^{2-} content change in solution and flexural strength were measured after 7, 14, 28, 56, 90, 180 and 270 days of storage in the aggressive solution.

Other testing methods used in this work are:

1. Determination of standard strength (EN 196-1)
2. Chemical analysis (EN 196-2)
3. Determination of setting time (EN 196-3)
4. Determination of the sieve residue (EN 196-6)
5. Determination of specific surface (EN 196-6)
6. Calculating the potential phase analysis (ASTM C 150)

3. Results and discussion

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

TABLE 1
Potential phase composition of Portland cement clinker

Potential phase composition, %mass	Portland cement clinker	
	KB	KK
C_3S	57.5	67.0
C_2S	13.5	12.7
C_3A	13.3	6.6
C_4AF	8.7	9.1

The potential phase analysis of the Portland cement clinkers is given in Table 1. It can be seen that the cements have low and high C_3A content in clinkers of 6.6% and 13.3% influencing the sulphate resistance. The ordinary Portland cement is not resistant to the attack of sulphates because it has a considerable content of tricalcium aluminate - C_3A, whose hydrates react with sulphate ions, giving expansive compounds. Portland cement with increased resistance to sulphates must have a low content of C_3A. According to the literature the difference in the C_3S content could be significant regarding sulphate resistance too.

TABLE 2
Fly ash chemical composition

Chemical composition, %mass	Fly ash
LOI	5.7
SiO_2	50.9
Al_2O_3	21.7
Fe_2O_3	11.6
CaO	6.5
MgO	2.7
SO_3	0.05
Na_2O	0.3
K_2O	0.7
Hydrated water	34.6
Insoluble residue	76.6

Table 2. presents the chemical composition of fly ash. According to the high content of SiO_2, Al_2O_3 and Fe_2O_3 and the low content of CaO the fly ash is suitable for cement production though loss on ignition was relatively high.

TABLE 3
Chemical composition of cements

Chemical composition, %mass	Cement			
	PCB	PCK	PCBP	PCKP
SiO_2	19.7	21.0	14.0	15.6
Al_2O_3	7.0	5.3	6.2	4.9
Fe_2O_3	2.7	2.9	2.7	2.9
CaO	62.0	63.8	44.7	47.5
Insoluble residue	0.1	0.1	20.2	18.7
LOI	0.8	0.7	3.0	2.9
CaO free	0.1	0.4	0.0	0.0
SO_3 in $CaSO_4$	2.0	1.7	2.0	1.5
MgO	2.2	1.4	2.4	1.2
Alkalies as Na_2O	0.4	0.3	0.4	0.4
K_2O	0.4	0.3	0.2	0.3
MnO	0.07	0.07	0.04	0.05

The chemical composition of the cements is presented in Table 3. All cements meet Yugoslav standard JUS B.C1.011. Portland fly ash cements have a higher loss on ignition and contain less free CaO than Portland cements.

TABLE 4
Physico-chemical properties of cements

Physico-chemical properties	Cement			
	PCB	PCK	PCBP	PCKP
Sieve residue at 0.09 mm sieve, %mass	1.8	2.6	5.2	6.0
Density, g/cm^3	3.1	3.2	2.9	2.9
Specific surface, cm^2/g	3320	3100	3720	3710
Setting				
-standard consistence, %mass	25.8	23.8	28.0	27.5
-initial time, min	165	165	240	255
-final time, min	225	225	330	360
Volume stability				
-Le Chatelier test, mm	1.0	1.5	1.0	1.0

Table 4. presents figures characterizing fineness, density, standard consistency, setting time and volume stability 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
Standard strength of cements

Strengths, MPa	Cement			
	PCB	PCK	PCBP	PCKP
Flexural:				
-2 days	4.4	3.7	2.5	2.1
-3 days	5.3	4.4	3.6	2.9
-7 days	7.2	7.4	6.2	4.7
-28 days	8.0	8.9	8.3	8.4
Compressive:				
-2 days	15.7	13.2	8.8	7.4
-3 days	19.8	16.0	14.9	10.4
-7 days	30.2	32.8	24.2	19.4
-28 days	40.3	50.9	39.5	44.9

Table 5. gives values for flexural and compressive strengths of cements after 2, 3, 7 and 28 days. Due to the clinker phase composition, Portland cement PCK had lower initial strength but higher later strengths after 7 days. The Portland fly ash cements had lower compressive strength even after 28 days than the corresponding Portland cements.

In this way, complete characterization was implemented regarding all the cements used in this investigation.

Figs. 1. and 2. presented mass change of the samples immersed in mentioned aggressive solution. Generally, it is obvious that Portland ash cements had much lower mass change than Portland cements. Test samples from cement PCB lasted only 56 days due to expansion components formation. Capability of mass change for cements PCK and PCKP compared to cements PCB and PCBP was much higher. Those cements also lasted longer. The reason for this must be in clinker composition diferencies.

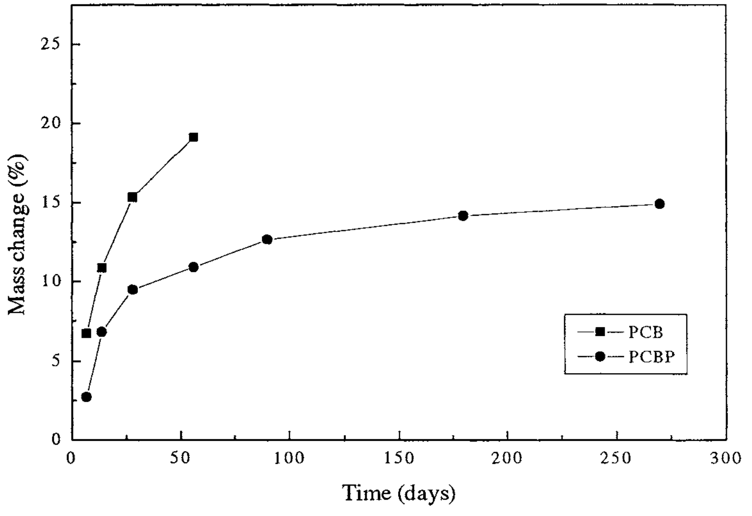

Fig 1. Mass change for Portland cement PCB and Portland fly ash cement PCBP

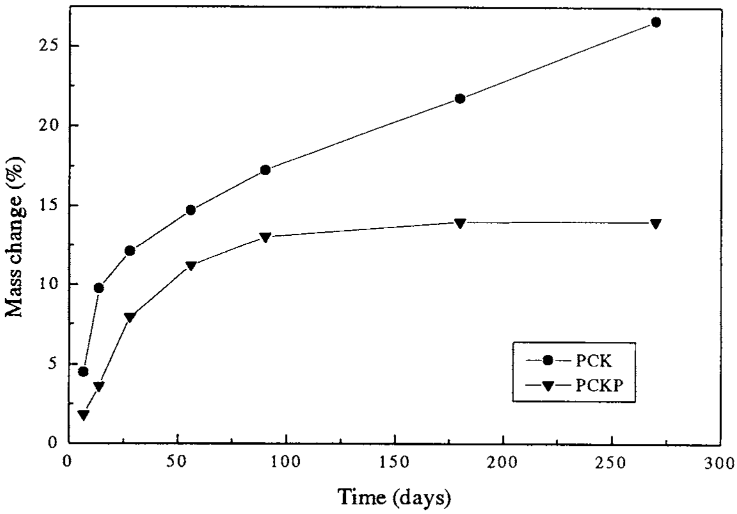

Fig. 2. Mass change for Portland cement PCK and Portland fly ash cement PCKP

Figs. 3. and 4. presented SO_4^{2-} content change of the aggressive solution where test samples were immersed. Generally, it is obvious that for Portland ash cements had much higher SO_4^{2-} content change than for Portland cements. Test samples from cement PCB lasted only 90 days due to expansion components formation. It is asumed that all SO_4^{2-} content changes in solution was directly connected with SO_4^{2-} bonding in test samples with aluminate components. Capability of SO_4^{2-} content change for cements PCK and PCKP compared to cements PCB and PCBP was much higher. Those cements also lasted longer. The reason for this must be also in clinker composition diferencies.

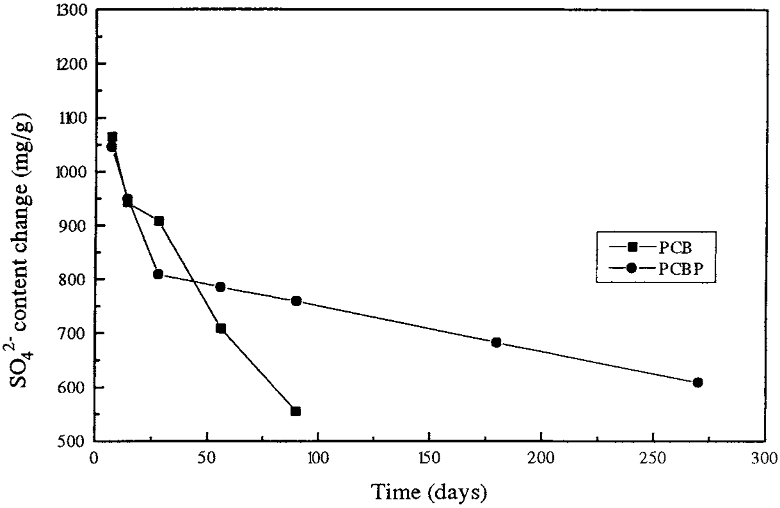

Fig.3. SO_4^{2-} content change for Portland cement PCB and Portland fly ash cement PCBP

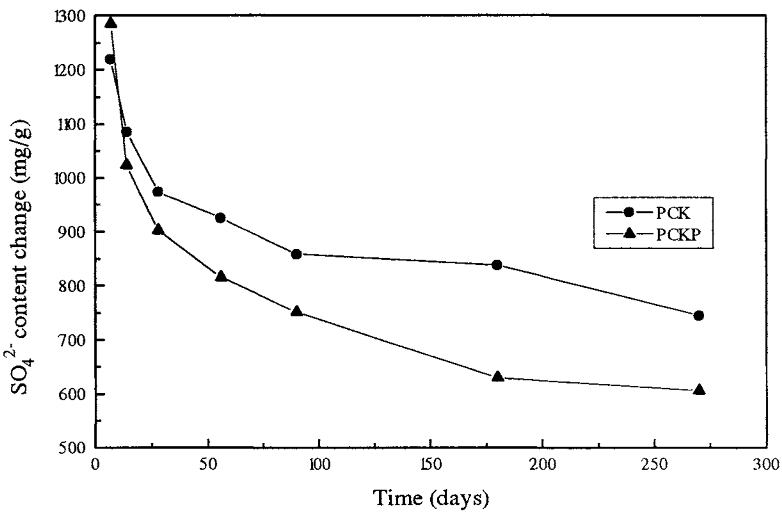

Fig.4. SO_4^{2-} content change for Portland cement PCK and Portland fly ash cement PCKP

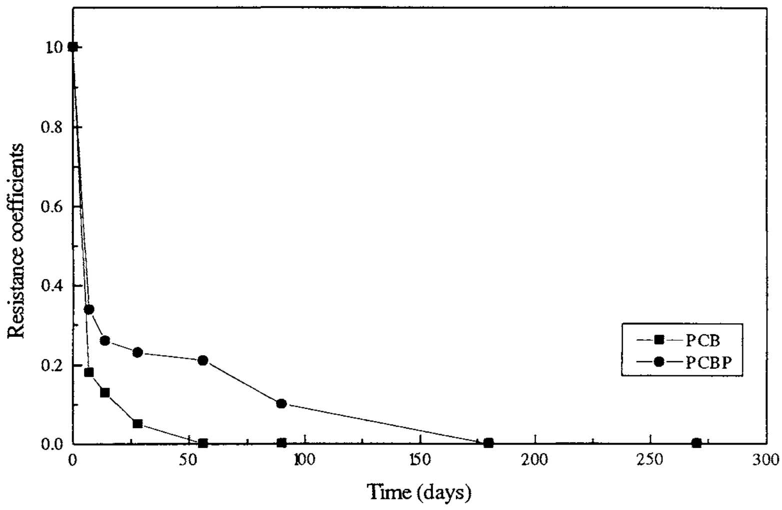

Fig. 5. Sulphate resistance coefficients for Portland cement PCB and Portland fly ash cement PCBP, according to Koch-Steinegger

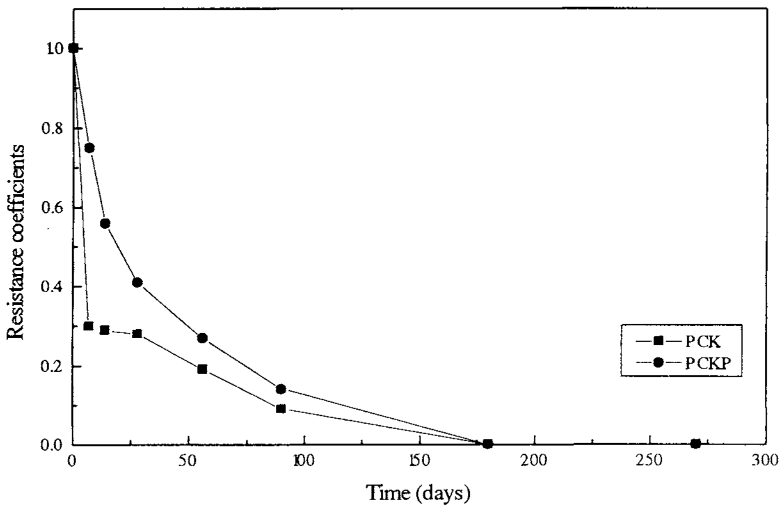

Fig. 6. Sulphate resistance coefficients for Portland cement PCK and Portland fly ash cement PCKP, according to Koch-Steinegger

Koch-Steinegger figures with sulphate resistance coefficients are presented in Figs. 5 and 6. It can be seen from Koch-Steinegger method that the Portland cement with fly ash has better resistance to sulphate aggression for the both kind of Portland cements. Hence, no one of the tested cements shows satisfactory resistance, what is understandable because 10% $(NH_4)_2SO_4$ solution was used instead of 4.4% Na_2SO_4 solution as aggressive medium. Used Portland cements with low content of C_3A with and without 30% fly ash (PCK and PCKP) had better sulphate resistance than Portland cements with high content of C_3A (PCB and PCBP).

The results of sulphate susceptibility tests according to Koch-Steinegger characterized by degradation coefficients are presented in Figs. 5 and 6. From the diagrams, it can be clearly seen that cements with the addition of 30% of fly ash showed distinct higher resistance against the ammonium sulphate solution. The increase of corrosion in the very begining for all cements is a normal phenomenon, because the creation of expansive compounds closes the pores and makes cement paste impervious to aggressive ions. However, further increase in the volume within the paste very quickly results in cracking. For the Portland cement PCB with the high content of C_3A this occured after 28 days only. Samples from Portland cement PCK and cements with fly ash addition have endured 90 days.

This can be explained by the fact that fly ash in cements has formed a protective layer thus retarding corrosion process and increasing durability. Portland cements, on the other hand, showed, depending on C_3A content, either linear or exponential type of degradation after initial period of forming the protective layer. This layer obviously became negligible due to the action of NH_4^+ ions thus opening new pores and accelerating corrosion process again.

The investigations are evidently encouraging, because the addition of fly ash has pointed to realistic prospects for its positive effect. Therefore, cement PCBP, with the addition of fly ash, shows good resistance to the aggressive attack by sulphate solution, although this cement is, due to its phase composition, very unsuitable in that sense.

It is evident that resistance of Portland cement to sulphate attack is directly related to its content of C_3A. This was confirmed even in the case of complete elimination of physico-chemical influence of fly ash on the properties of cement (bonding $Ca(OH)_2$, filling pores, etc.).

4. Conclusion

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

1. The resistance of cements to sulphate attack is higher with a lower content of tricalcium aluminate in clinker PCK and especially with addition of fly ash to the cement.

2. The addition of 30 % of fly ash to Portland cement as a replacement of clinker improves the durability of Portland cement to a considerable degree.

3. Koch-Steinegger method shows that both Portland cements did not resist the extremely strong attack of 10 % $(NH_4)_2SO_4$ solution.

Reference

1. Biczok,I.: Concrete Corrosion, Concrete Protection. 8th Edition. Budapest, 1972.
2. Mehta,P.K.: Mechanism of sulfate attack on Portland cement concrete - Another Look. Cem.Concr.Res. 13 (1983) pp. 39-51.
3. Mitrović,N. and Dučić,V.: Sulphate corrosion of concrete. Proc. of Yugoslav. Symposium, Split, 1985, pp. 59-75.
4. Moskvin,V.M., Ivanov,F.M., Alekseev,S.V. and Guzeev,E.A.: Korozija betona i železobetona. Moskva, 1980.

5. Regourd,M.: Structure and behaviour of slag Portland cement hydrates. 7th Intern. Congr.Chem.Cem., Paris, 1980, Vol. I, pp 278-291
6. Taylor,H.F.W.: Crystal structure of some double hydroxide minerals. Mineral.Mag. 39 (1973) pp. 247-256.
7. Miletić,S. and Ilić,M.: Sulphate corrosion of portland cement with various mineral compositions. Proc. 15. Symposi. Corrosion and Protection of Materials, Beograd, 1995, pp. 255-262.
8. Koch,A., Steinneger,H.: An rapid method for testing the resistance of cements to sulphate attack. Zement-Kalk-Gyps 13 (1960), No.7, pp. 317-324.
9. Matsufuji,Y., Koyama,T. and Harada,S.: Service life predictive method of building materials. Proc. Durability of Building Materials and Components 7, Vol. 1, Published by E&FN Spon, London, 1996, pp. 45-53.
10. Miletić,S. and Ilić,M.: Cement stone corrosion in sulphate environment. NTP VJ, 46, No. 3 (1996) pp. 23-31.
11. Miletić,S., Ilić,M., Ranogajec,J. and Djurić,M.: Sulphate corrosion of Portland cement and Portland cement mixed with fly ash and slag as a function of its composition. Proc. XVI Symposi. on Nordic Concrete Research, Helsinki, 1996, pp. 339-340.
12. Ranogajec,J., Ilić,M., Miletić,S., Lazar,S. and Milinković,Lj.: Effect of sulphate and ammonium ions on the cement stone corrosion. Proc. XX Congr. JUDIMK, Cetinje, 1996, pp. 97-102.