SULFATE RESISTANCE OF CEMENT WITH DIFFERENT VOLUMES OF FLY ASH

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SUMMARY: Sulfate attack is a complex severe set of chemical and physical processes that have great influence on concrete durability by changing the microstructure of the cement paste and concrete. Sulfate resistance of concrete should be obtained including requirements for low-permeability concrete, use of sulfate resistance cement and proper production of concrete. In this paper an extensive experimental research is presented on the possibility of using fly ash as a partial replacement of OPC clinker and its influence on the sulfate resistance of cement. For that purpose, four samples of fly ash from the TPP Bitola were taken in the time period of two weeks. All cement components including fly ash were completely tested from the aspect of chemical composition and physical properties. Two samples of fly ash which showed the biggest difference in their fineness were chosen for further investigations and preparation of cements. Laboratory cements were prepared by varying the quantity of fly ash as replacement of OPC clinker, from 0% to 50%. For all laboratory produced cements complete chemical analysis and determination of the physical and mechanical properties have been carried out. The method of Koch & Steinegger and the recommendations of the Technical Committee of Cement given in CEN/TR 15697 were used for determination of sulfate resistance of the laboratory cements. According to this method, small specimens (prisms with dimensions 10/10/60mm) were prepared and then cured in deionized water and aggressive solution – 4.4% Na_2SO_4. The corrosion coefficient calculated on the basis of flexural strength of the specimens tested after 56 days in aggressive solution was used as indicator of sulfate resistance of the cements. On the basis of the test results, it is determined that the fly ash and all laboratory cements fulfil the quality criteria defined in the standards. It is also concluded that the cements with 30% fly ash show the best results from the aspect of sulfate resistance.

KEY WORDS: fly ash, sulfate resistance, aggressive sodium sulfate solution, Koch & Steinegger method

1 INTRODUCTION

Sulfate attack is the term used to describe a series of chemical reactions between sulfate ions and the components of hardened concrete, principally the cement paste, caused by exposure of concrete to sulfates and moisture. As is the case with other aggressive chemicals, sulfates are potentially most deleterious to concrete when present in gaseous or liquid form, the latter situation being the most common; attack by solid sulfate-containing chemicals is rare [1].

Some accepted facts about sulfate attack are: sulfate attack is not a single or a simple chemical reaction; it is a complex sequence of physical and chemical processes resulting in chemical and physical (micro-structural) modifications of the cement paste matrix; restructuring of the matrix is eventually evidenced by several possible modes of deterioration and leads to loss of mechanical and physical properties expected of any particular concrete structure; sulfate attack is not fully characterized by any one of the many possible reactions between the sulfate and cement paste components (e.g., presence of ettringite, formation of gypsum, dissolution of calcium hydroxide or decalcification of calcium silicate hydrate); relationships between the degree of chemical, physical or microstructural change caused by sulfate attack reactions and the degree of mechanical damage are complex and non-linear [2].

The resistance that a cement matrix provides to sulfate attack depends on a number of factors included: nature of the reaction products formed with the sulfate solution and in particular, whether their formation results in disruptive expansion; impermeability of the matrix (including the important paste-aggregate interfacial zone) which provides a barrier against penetration of sulfate ions; concentration of sulfate ions (g/l SO_4); mobility of the sulfate containing groundwater; nature of accompanying cation e.g. Na^+, Mg^{2+}, Ca^{2+} etc.; pH of the sulfate bearing ground water/solution; presence of other dissolved salts such as chlorides; temperature of the exposure; degree of pre-curing before exposure, although in the field this is only likely to affect the performance of the concrete surface; presence of finely divided limestone (calcium carbonate) in the aggregate, or carbonate ions dissolved in the groundwater, which may promote the formation of thaumasite under low temperature conditions [3].

In the standard EN 206 sulfate corrosion is defined under the chemical attack according to the exposure classes XA2 and XA3 for which use of sulfate resistance Portland cement conforming to EN 197-1:2011 [4] is mandatory (Annex F Recommendation for limiting values of concrete composition from EN 206:2013+A1:2016 [5]).

Current sulfate resisting cements standardised in CEN members' countries can be divided into two categories: Portland cements (CEM I) with a maximum permitted C_3A content and Portland composite cements containing appropriate levels of glassy blast furnace slag, fly ash or natural pozzolana. Portland composite cements (i.e. CEM II, III, IV and V types) provide resistance to sulfate attack which is predominantly micro-structural in nature [3].

Use of mineral additives such as fly ash in the cements is most promising to control sulfate attack to concrete, but so far there is no sulfate resistance Portland fly ash cement approved by the EN 197-1:2011 [4]. The problem of defining sulfate resistance of Portland cement is because there are many different mortar test procedures: standardised ASTM C1012, GOST 4798, round robin as a draft EN standard under activities of WG12/TG1 and methods used in Germany such as Wittekindt, SVA and Koch Steinegger. The test procedures share the following characteristics: specimens have a high surface to volume ratio; with the exception of the GOST test procedure the use of highly concentrated Na_2SO_4 solutions (16 g/l SO_4^{2-} to 34 g/l SO_4^{2-}); replacement of the Na_2SO_4 solution at monthly intervals (apart from the ASTM C1012 timings which vary according to age); use of nationally (or European) standardised test sand; assessment of sulfate resistance at an early age e.g. 56 days in the Wittekindt test and rather poor reproducibility [3].

To determine the influence of mineral addition of fly ash to the sulfate resistance of Portland cement, a laboratory cements were produced with different percentage of fly ash ranging from 11% to 50% from the weight of OPC clinker. Following types of cement were used: C1-Portland cement CEM I, C1-11 Portland fly ash cement with addition of 11% of siliceous fly ash which simulate the properties of commercially available cement CEM II/A-V 42.5R from USJE factory TITAN Group, C1-20 Portland fly ash cement with addition of 20% of siliceous fly ash, C1-30 Portland fly ash cement with addition of 30% of siliceous fly ash, C1-40 Portland fly ash cement with addition of 40% of siliceous fly ash and C1-50 Portland fly ash cement with addition of 50% of siliceous fly ash.

Sulfate resistance of the cements was tested using the Koch &Steinegger method given in CEN/TR 15697:2008 [3] Cement – Performance testing for sulfate resistance – State of the art report. A 4.4% sodium sulfate solution Na_2SO_4 with solution concentration of 29.8 g/l SO_4^{2-}, was used for immersion of specimens for a certain time of period 21+56 days. Small size specimen prisms 10/10/60mm were used with surface/volume ratio of $0.43 mm^2/mm^3$. For 21 days the specimens first were cured in ionized water. Then certain number of specimens were immersed in sodium sulfate solution. The specimens were tested at age of 21+28, 21+56 and 21+90 days to determine the flexural strength and the compressive strength. Results from testing flexural strength were used to determine the sulfate resistance coefficient S_r at age of 21+56 days.

2 EXPERIMENTAL PROGRAM

2.1 Testing of components for preparation of laboratory cements

2.1.1 OPC clinker

OPC clinker is the main component used for preparation of laboratory cements. The same is taken from the regular production of Cement Factory TITAN Skopje. After crushing in laboratory crusher, the sieve analysis of the OPC clinker has been carried out. Complete phase composition was done using the XRD method (X-ray diffraction analysis) and it is concluded that the main component of the OPC clinker is calcium oxide (CaO) with content of more than 60% [6]. The content of C_3A is 13% which indicates that this OPC clinker is not resistant to sulfate attack.

The phase composition of the OPC clinker is carried out using the method of X-ray diffraction. The results are presented in Table 1. It is obvious that dominate mineral phase in the OPC clinker is C_3S phase with 60.7% followed by C_2S phase with 11.5%, C_3A phase with 13% and C_4AF phase with 7.7%.

Table 1: Phase composition of OPC clinker

Phase name	Mass.%
C_3S	60.7
C_2S	11.5
C_3A	13.0
C_4AF	7.7
Portlandite	1.7
Periclase	1.9
Arcanite	0.7
Lime	0.1
Quartz	0.9
Anorthite	1.6
Σ	100.0

2.1.2 Gypsum

Gypsum which was used for preparation of the cements is a product of Factory Knauf Radika from Debar. After drying, the gypsum was tested from the aspect of its grain size composition. The data for humidity, chemical and mineralogical composition of gypsum are taken from the regular periodic tests done in Cement Factory TITAN.

2.1.3 Fly ash

The siliceous fly ash from Thermal Power Plant Bitola was used as a mineral additive for the purpose of this experimental research. The samples for testing of fly ash were previously prepared using standard procedures. Complete chemical analysis according to EN 196-2:2013 [7] was carried out and the results are presented in Table 2 [6,8].

Table 2: Chemical composition of the fly ash

Chemical component	Mass.%
SiO_2	55.51
Al_2O_3	22.06
Fe_2O_3	8.25
CaO	5.20
SO_3	0.91
MgO	2.19
Na_2O	0.59
K_2O	2.80
Loss of ignition	1.41
Σ	98.92

From the aspect of chemical composition, the main component of the fly ash is SiO_2 with 55.51%. The content of CaO is 5.20%. According to the criteria for classification of fly ash given in EN 450-1:2012 [9], the fly ash used in this research is siliceous fly ash (V).

One factor that have positive influence on the sulfate resistance is the content of 0.91% SO_3 in the chemical composition of fly ash. Higher level of SO_3 in a range between 1% to 4% provide greater resistance to sulfate attack.

The improved resistance can be attributed to the increased level of sulfated phases, such as ettringite, formed during initial hydration, which are stable in the presence of an elevated sulfate level [3].

Morphology of the particles of fly ash is determined using SEM analysis. SE images of fly ash are presented below in Figure 1. It is evident that the fly ash contains agglomerates with different sizes mainly containing primary particles less than 10µm.

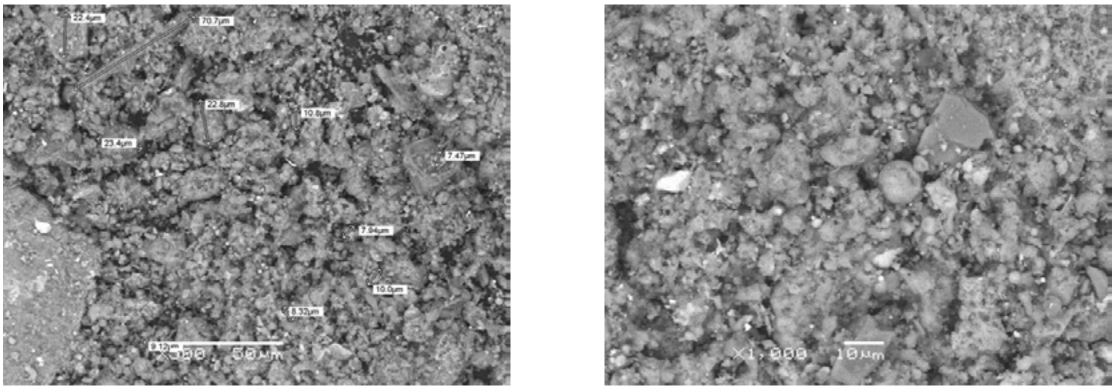

Figure 1: SE images of fly ash

The following tests are additionally carried out: determination of physical properties, mineralogical analysis and trace elements analysis as well.

2.2 Preparation and classification of laboratory cements

Laboratory cements were prepared by milling the constituents (OPC clinker, gypsum and fly ash). The capacity of the milling machine is 5kg with milling time of 35min. In order to achieve more efficient milling, special additive in amount of 2ml has been added.

For the purpose of this research, six laboratory cements were prepared by varying the quantity of fly ash as partial replacement of the OPC clinker from 0% to 50%. In Table 3 below, marking of all laboratory produced cements, as well as content of the constituents is presented [6,8].

Table 3: Laboratory produced cements

Cement type	Content of constituents (%)		
	OPC clinker	Gypsum	Fly ash
C	95	5	0
C-11	84	5	11
C-20	75	5	20
C-30	65	5	30
C-40	55	5	40
C-50	45	5	50

In accordance with the criteria for cement composition and marking given in EN 197-1:2011 [4], the laboratory cements can be classified as follows:

- Cement “C” – CEM I (Portland cement)
- Cement “C-11” and “C-20” – CEM II A/V (Portland cement with siliceous fly ash content between 6% and 20%)
- Cement “C-30” – CEM II B/V (Portland cement with siliceous fly ash content between 21% and 30%)
- Cement “C-40” and “C-50” – CEM IV/B (Pozzolanic cement with siliceous fly ash content between 36% and 55%)

All laboratory cements were tested from the aspect of their chemical composition and physical-mechanical properties. Additionally, the influence of content of fly ash in the cements on different parameters was analysed and certain conclusions were made. It is important to mention that the standard consistency increases with addition of fly ash in the cement in the range of 27.6% for Portland cement CEM I to 47% for cement C1-50. Standard consistency for the cements

C1-11, C1-20, C1-30, C1-40 and C1-50 are 31.6%, 32.0%, 38.4% and 46.0% respectively according to EN 196-3:2016 [10].

Determination of the cement compressive strength was performed using the EN Standard EN 196-1:2016 [11]. Results from the testing of compressive strength of cements is shown in Figure 2.

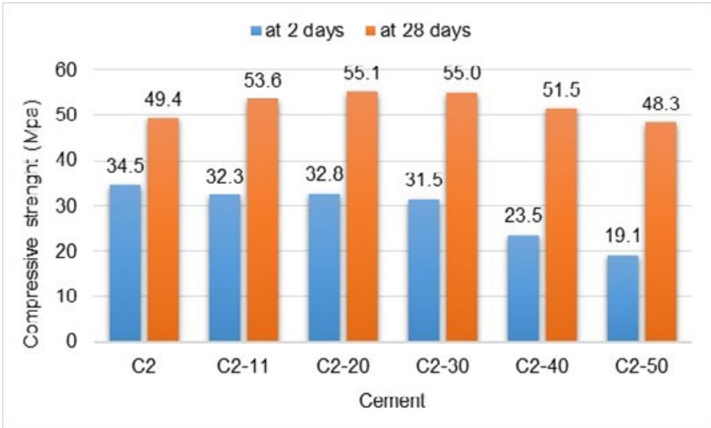

Figure 2: Compressive strength of cements at 2 and 28 days

According to the criteria given in EN 197-1:2011 [4], it can be concluded that all cements belong to the class of standard strength 42.5. The compressive strength of the cements at age of 28 days is within the limits of 42.5MPa and 62.5MPa. The pure cement and cements with 11%, 20%, 30% and 40% content of fly ash belong to the class of cement with high early strength 42.5R (compressive strength at age of 2 days higher than 20MPa). Only the cement with content of 50% fly ash belongs to the class of cement with normal early strength 42.5N (compressive strength R_C at age of 2 days<20MPa).

2.3 Testing of influence of fly ash on the sulfate resistance of laboratory cements

The sulfate resistance of cements was tested and determined using the Koch & Steinegger method and the recommendations of the Technical Committee for Cement given in CEN/TR 15697:2008 [3]. According to this method, small specimens-prisms with dimensions 10/10/60mm were prepared. Specimens were made of mortar with cement/sand ratio 1:3 and water-cement factor w/c=0.6.

The specimens were cured in the mould for 24h in laboratory conditions (temperature 20±2^oC and humidity higher than 80%). Then, the prisms were kept immersed in deionized water for 21 days. After that, half of the specimens were immersed in aggressive solution (4.4% Na_2SO_4) and the other half stayed immersed in deionized water for the whole testing period. The flexural and compressive strength of the prisms were tested at the age of 28, 56 and 90 days after immersing in aggressive solution and deionized water. The indicator of sulfate corrosion is the coefficient of sulfate resistance Sr, calculated as a ratio between flexural strength of the prisms cured in aggressive solution and the ones cured in deionized water at the age of 21+56 days. According to the Koch & Steinegger method, the cements are sulfate resistant if the value of this coefficient is higher than 0.7 [3]. Sulfate resistance coefficient is given by the following equation [3]:

$$S_r = \frac{\text{flexural strength of specimens cured in aggressive solution}}{\text{flexural strength of specimens cured in deionized water}} \geq 0.7$$

Figure 3. shows the way of curing the specimens in plastic containers.

Figure 3: Curing of specimens

Testing of the mechanical properties of the small specimens was carried out using hydraulic testing machine type "Controls 50kN". Due to the small dimensions of the specimens, additional elements for supporting and load application were made. The speed of load application was 0.5mm/min for testing of flexural strength and 10mm/min for testing of compressive strength. Figure 4. shows the way of testing the mechanical properties of the specimens.

Figure 4: Testing of flexural and compressive strength

It should be noted that during the testing period, some of the specimens cured in aggressive solution suffered deformation and degradation. The specimens made of pure cement were deformed 18 days after immersion in 4.4% Na_2SO_4 solution. Development of such deformation and degradation, as well as change in specimens shape were regularly followed and registered up to the end of testing period. The deformed specimens made of pure cement are presented in Figure 5 [6].

Figure 5: Deformed prisms made of pure cement 18 and 90 days after immersion in 4.4% Na_2SO_4

Deformation and degradation of the specimens made of cement with 11% and 20% fly ash were also noticed later during the testing period. For example, the prisms with 20% fly ash suffered initial deformation and change in the shape 50 days after immersion in aggressive solution, which is shown in Figure 6 below.

Figure 6: Deformed prisms made of cement with 20% fly ash

The corrosion coefficient was calculated only for the cements with 30%, 40% and 50% fly ash as partial replacement of OPC clinker, i.e., the cements with higher content of fly ash. The reason for this is the fact that during the experimental research some of the specimens treated in aggressive solution were destroyed before reaching the expected age (21+56 days). The corrosion coefficient for these cements is presented in Table 4 [6,8].

Table 4: Values of the corrosion coefficient

Cement type	S_r coefficient
C-30	1.63
C-40	1.17
C-50	1.18

From the results presented above, it is obvious that the corrosion coefficient for the cements with higher content of fly ash is higher than the minimum value (S_r=0.7). In other words, according to the criteria given in Koch & Steinegger method, cements C-30, C-40 and C-50 are sulfate resistant cements.

The cement C-30 has the highest value for the corrosion coefficient which is for about 38.7% higher than values of the coefficient for cements with 40% and 50% fly ash. On the other hand, S_r for C-30 is for about 2.3 times, for C-40 and C-50 1.7 times higher than the minimal value of the corrosion coefficient (S_r=0.7) respectively.

3 CONCLUSIONS

On the basis of the performed tests of sulfate resistance of laboratory produced Portland-fly ash cement, the following conclusions have been reached:

- Laboratory produced Portland cements CEM I, Portland-siliceous fly ash cements noted as CEM II/A-V and CEM II/B-V fulfil the quality criteria defined in EN 197-1:2011 [4].

- Fly ash fulfil the quality requirements in terms of chemical composition and physical properties given in EN 450-1:2012 [9].

- Phase composition of the tested OPC clinker, used for laboratory produced cements, shows that the content of calcium aluminate is approximately 13%. This value is greater than the permitted 5% for sulfate-resisting Portland cement CEM I/SR 5 defined in EN 197-1:2011 [4].

- In terms of sulfate resistance, best behaviour in 4.4% sodium sulfate solution(Na_2SO_4) shows cement with 30% fly ash replacement of OPC clinker with sulfate resistance coefficient S_r=1.63>0.7. Cements which have a higher addition of fly ash (40% and 50%) are also sulfate resistant but with lower values of sulfate resistance coefficient S_r=1.17 and S_r=1.18 respectively. Use of mineral additives such as siliceous fly ash generally improves permeability of the Portland fly ash cement but higher content of siliceous fly ash also put more alumina (Al_2O_3) in the system which decreases sulfate resistance of the Portland-fly ash cement.

- The Koch & Steinegger method is just a one of many different methods for sulfate resistance test of cement defined in MKTI CEN/TR 15697:2008 [3] to be able to conclude that Portland-fly ash cement is sulfate-resistant. It is necessary to perform tests by other methods and applications of various sulfate solutions.

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