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THE EFFECT OF SILICA FUME ADDITIONS ON THE DURABILITY OF PORTLAND CEMENT MORTARS EXPOSED TO MAGNESIUM SULFATE ATTACK

VPLIV DODATKA SILICA FUME NA TRAJNOST CEMENTNIH MALT PORTLAND, IZPOSTAVLJENIH DELOVANJU MAGNEZIJEVEGA SULFATA

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The deterioration of concrete structures due to the presence of sulfate in soils, groundwater and marine environments is a well-known phenomenon. The use of blended cements incorporating materials such as natural pozzolans, fly ash or silica fume have an important role in the long-term durability of concrete exposed to sulfate attack. In this work, the partial replacement (mass fractions 2–15 %) of commercially blended Portland cement (Type CEM IIA-S 42.5N) with silica fume (SF) was investigated in terms of the resistance of SF mortars to a magnesium sulfate ($MgSO_4$) solution ($\omega(SO_4)^{2-} = 2.5$ %; exposure time up to 6 months at 20 °C). The changes in the length of the mortars due to expansion, as well as the changes in the elasticity modulus and mechanical strength loss as a function of silica fume replacement were determined. Structural changes in the mortars due to magnesium sulfate attack were also evaluated by differential thermal analysis (DTA) and by X-ray diffraction (XRD) analysis. The results show that the replacement of SF in most cases has a positive effect on the magnesium sulfate resistance. Mortars containing more than 8 % of mass fraction of SF replacement are characterized by a good sulfate resistance and show lower expansion than the control mortar on the basis of the sulfate-resisting Portland cement, due to the absence of the gypsum and ettringite, detected by the XRD analysis. It is also shown that the elastic modulus is proportional to the compressive strength, but higher compressive strength does not necessary correlate with a better resistance to sulfate attack.

Key words: blended cement, silica fume, sulfate attack, durability, elastic modulus

Propadanje strukture betona v okolju sulfata (tla, podzemne vode in morska voda) je znan pojav. Uporaba mešanih cementov z dodatki, kot so naravni pucolani, leteči pepel ali "silica fume" (SF), ima pomembno vlogo pri dolgotrajni trdnosti betona, izpostavljenega sulfatni koroziji. V tem delu je preučevan vpliv SF (masni delež 2–15 %) kot nadomestni dodatek industrijskemu portlandskemu cementu (CEM IIA-S 42.5N) na odpornost cementne malte proti delovanju raztopin magnezijevega sulfata ($w(SO_4)^{2-} = 2.5$ %; čas izpostavljanja do 6 mesecev pri 20 °C). Merili smo naslednje parametre v odvisnosti od deleža SF: sprememba dolžine malt zaradi ekspanzije, spremembe modulov elastičnosti in izguba mehanične čvrstosti. Strukturne spremembe v maltah, izpostavljenih vplivu sulfatne korozije, smo spremljali z diferencialno termično analizo (DTA) in rentgensko difrakcijsko analizo (XRD). Rezultati kažejo, da nadomestni dodatek SF v večini primerov povečuje odpornost malt proti vplivu magnezijevega sulfata. Malte z masnim deležem dodatka SF, večjim od 8 %, so okarakterizirane kot dobro sulfatno odporne in kažejo manjšo ekspanzijo kot kontrolna malta na osnovi sulfatno odpornega portlandskega cementa, ker nimajo gipsa in etringita, kar je potrjeno z analizo XRD. Opaženo je tudi, da je modul elastičnosti proporcionalen kompresijski čvrstosti, toda večje kompresijske čvrstosti niso nujno povezane z večjo odpornostjo malt proti korozijskemu delovanju sulfata.

Ključne besede: mešani cement, «silica fume», sulfatna korozija, trajnost, modul elastičnosti

1 INTRODUCTION

Sulfate attack on cement concrete is a complex process and many factors such as cement type, sulfate cation type, sulfate concentration and exposure period can affect the sulfate resistance[1,2]. The sulfate ions react with the C_3A and $Ca(OH)_2$ in the concrete to produce expansive and/or softening types of deterioration associated with both the ettringite and gypsum formation. When the attacking solution contains Mg^{2+} ions, such as in magnesium sulfate ($MgSO_4$), the formation of magnesium hydroxide (brucite) and the conversion of the main cement hydrated product, calcium silicate hydrate (CSH gel), into magnesium silicate hydrate (MSH) are also observed[3-5]. Several ideas have been suggested to increase the resistance of concrete against sulfate attack either by decreasing the porosity (high cement content, low water-to-cement ratio) or by using more resistant types of binders (sulfate-resisting Portland cement, addition of pozzolanas and blast furnace slag). Studies[3,6-11] have shown that the addition of pozzolans such as silica fume enhances the strength and durability of mortars exposed to sulfate attack. This improvement in sulfate resistance for the Portland cement–silica fume blended concrete/mortars or pastes is attributed to the pore refining and pore refinement effect occurring due to a pozzolanic reaction between the calcium hydroxide liberated during the cement hydration process and the silica fume when a new CSH gel was formed. This CSH gel is more susceptible to the magnesium than to sodium sulfate attack. In the advanced stages of attack, therefore, the Ca ions in the CSH can be completely replaced by Mg ions, leading to the decalcification of the CSH, and the loss of the cementitious structure[12].

The aim of the this work is to give a comparative evolution of the sulfate resistance and durability of SF-blended cement mortars immersed in 2.5 % magnesium sulfate solution, as well as to evaluate the optimum dosage level of silica fume replacement to minimize the deleterious effects of the Mg-sulfate attack.

2 EXPERIMENTAL

Commercial blended Portland cement, CEM IIA-S 42.5N (the Dalmacijacement, Croatia), that was produced by grinding cement clinker and mixing with up to 5 % of gypsum and about 25 % of blast furnace slag was used in this investigation. Its Blaine specific surface area was 3,530 cm^2/g. The Bogue composition of the cement clinker was (in mass fractions): C_3S = 64.7 %; C_2S = 9.6 %; C_3A = 7.5 %; C_4AF = 10.1 %. The silica fume was collected from the production of ferrosilicon (ex the Dalmacija Ferroalloys Works, Dugi Rat, Croatia), containing mass fraction of SiO_2 about 90 %, having a surface area of 18 m^2/g, as measured by the BET nitrogen adsorption method, with extremely fine spherical and amorphous particles[9,10]. The sulfate-resisting cement (the Dalmacijacement, Croatia), Type V according to the ASTM C-150, was used as the control cement. Salts $MgSO_4$ x $7H_2O$, p. a. were used in the preparation of the magnesium sulfate solution, $\omega(SO_4)^{2-}$ = 2.5 % (25,000 mg/L). The mortars were prepared from a mixture of blended cement, standard quartz sand and mass fractions of silica fume (0, 2, 5, 8, 11 and 15) %, according to the Croatian Standard HRN EN 196-1 : 2005. The mortar samples were designated as P-0, P-2, P-5, P-8, P-11 and P-15, respectively. The water-to-binder (cement+SF) ratio varied from 0.50 to 0.67; the samples were prepared to have the same flow-table consistency. No super-plasticizer was added. Two kinds of mortar samples were prepared: (i) for mechanical strength tests, prismatic specimens of dimensions (40 × 40 × 160) mm, according to the Croatian Standard HRN EN 196-1:2005; (ii) for the potential sulfate-resistance tests, and for the modulus of elasticity tests, prismatic specimens of dimensions (25.4 × 25.4 × 285.75) mm with two stainless-steel inserts cast into the ends to facilitate accurate monitoring of the changes in length, according to the ASTM C.452-68. After a 24-hour setting period in a humid environment (20 °C, 90 % RH), the specimens were taken out of the moulds and immersed into tap water for 27 d. The first tests were carried out 28 d after the sample preparation, and then the samples were exposed to a magnesium sulfate solution. The changes in the samples due to magnesium sulfate attack were measured after 28 d and every 28 d thereafter for a 180-day period. The structural changes in the samples during sulfate attack were identified by X-ray diffraction analysis (XRD; a Philips PW 1010, Netherlands) with CuKα radiation in the ranges of Bragg's angles of 3–60° (2 theta). The quantity of calcium hydroxide and magnesium hydroxide (brucite) in the mortar samples during sulfate attack was determined by differential thermal analysis (DTA-DTG-TG; a Derivatograph MOM, Hungary).

3 RESULTS AND DISCUSSION

Figure 1 shows the compressive strength of the mortars exposed in the Mg-sulfate solution at room temperature. There was a continuous increase in compressive strengths with exposure time up to 90 d for all the SF-mortars, except the P-5 sample. After this period, the strengths decreased for all the samples exposed to sulfate attack. The increase observed in the compressive strengths for up to 90 d can be attributed to two types of reaction: (i) the continuous hydration of the unhydrated cement components to form more hydration products in addition to the reaction of SF (or slag from the blended cement used) with the liberated lime to form more CSH leading to increasing compressive strength, and (ii) the reaction of sulfate ions with the hydrated cement components to form gypsum and ettringite. Both reactions lead to a denser structure as a result of the precipitation of the reaction products within voids and micropores. After longer periods the magnesium sulfate attack becomes more dominant, leading to the formation of microcracks, which decreases the strength[11]. The results obtained also show that the sulfate resistance of these SF mortars seems to be slightly higher than the P-0 mortar, but lower than the control mortar based on the sulfate-resisting cement (designated SPC).

Figure 2 presents the results for the expansion of mortars exposed to the sulfate attack. It can be seen that the smallest expansion, even smaller than the control

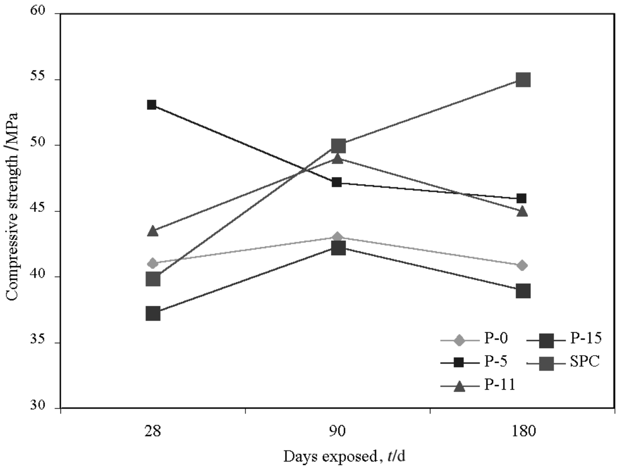

Figure 1: Mortars' compressive strengths *vs.* exposure time to $MgSO_4$ solution

Slika 1: Kompresijska čvrstost malt *vs.* čas izpostavljanja raztopini $MgSO_4$

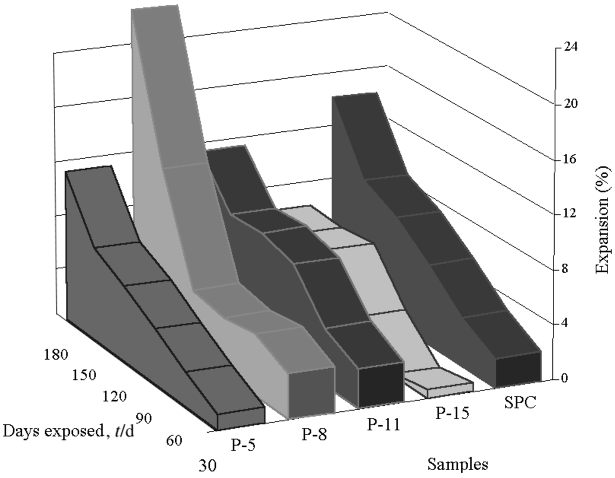

Figure 2: Expansions of mortars *vs*. exposure time to $MgSO_4$ solution
Slika 2: Ekspanzija malt *vs*. čas izpostavljanja raztopini $MgSO_4$

mortar on the basis of sulfate-resisting Portland cement (the SPC sample), comes from the samples containing mass fractions 11 % and 15 % of silica fume. The highest expansion of 107.82 % and 59.91 % and the intensive trend of the breakdown were observed in the sample without (P-0) and with 2 mass percent (P-2) of silica fume, respectively: the P-0 sample disintegrated after only 90 d, while the P-2 one lasted for 150 d of immersion in the $MgSO_4$ solution before breakdown due to corrosion[13]. The results obtained show that the greatest expansion was observed in the P-0 mortar, which did not exhibit the lowest compressive strength. The lack of correlation between the results of the compressive-strength measurements and the damage due to sulfate corrosion (microcracks) was also pointed out by other authors[14].

Figure 3 presents the XRD patterns of the P-0 and P-8 samples exposed to Mg-sulfate attack for 120 d. While the formation both of gypsum (G) and ettringite (E) as the result of sulfate corrosion is detected for the P-0 sample, in the P-8 sample these corrosion products were not found.

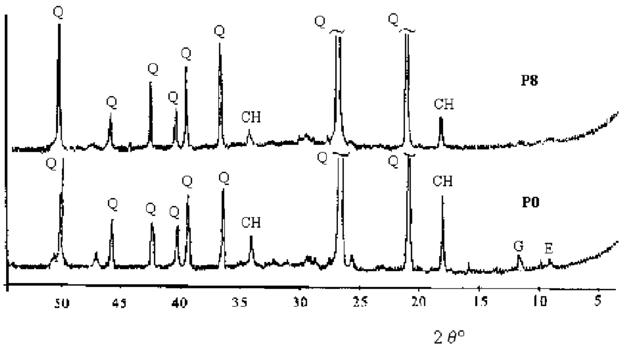

Figure 3: XRD diffractograms of the P-0 and P-8 mortar samples exposed to $MgSO_4$ solution for 120 d, where Q-quartz, CH-lime, G-gypsum, E-ettringite
Slika 3: XRD-difraktogrami za vzorce malt P-0 in P-8 po 120 d izpostavljanja raztopini $MgSO_4$, kjer so: Q-kremen, CH-kalcijev hidroksid, G-gips, E-etringit

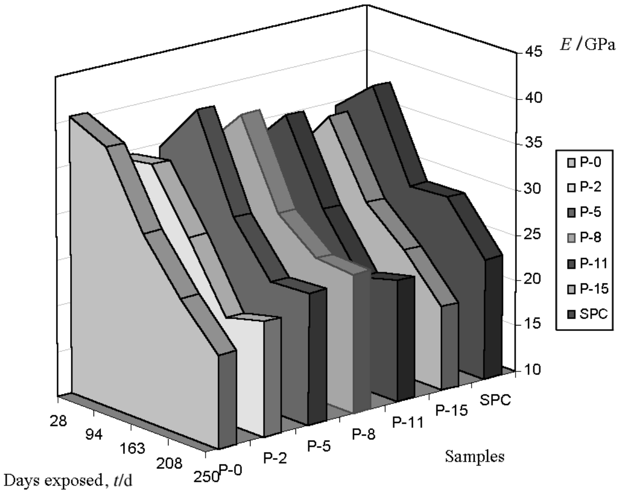

Figure 4: Variation of the dynamic modulus of elasticity with exposure time of mortars to $MgSO_4$ solution
Slika 4: Sprememba dinamičnega modula elastičnosti glede na časovno obdobje izpostavljanja malt v raztopini $MgSO_4$

Figure 4 presents the results of the changes in the elasticity modulus (E-modulus) of the mortars immersed in the Mg-sulfate solution, which were determined by measuring the dynamic resonance frequency. An electrosonometer[15] was used for this purpose. Details for the determination of the dynamic resonance frequency and for calculating the modulus of elasticity were described elsewhere[13,15]. It can be seen that all samples tend to show a continuous decrease in the E-modulus with the time of exposure. Mortars containing silica fume showed a similar or slightly higher E-modulus with respect to the mortar containing no silica fume (the P-0), but these samples showed a significant reduction in modulus with respect to the reference SPC mortars.

Figure 5 presents the E-modulus data mortars versus the square root of compressive strength for all the

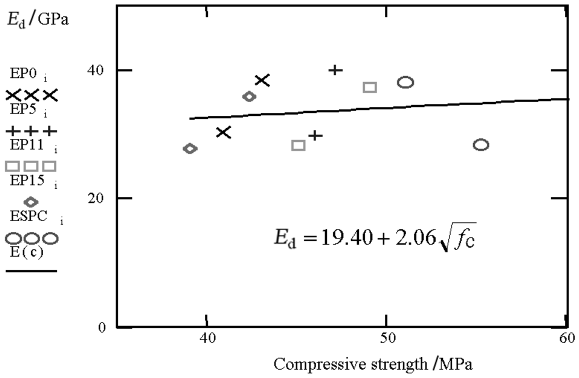

Figure 5: The dynamic modulus of elasticity *vs*. compressive strength for mortars exposed to $MgSO_4$ solution
Slika 5: Dinamični modul elastičnosti *vs*. kompresijska čvrstost za malte, izpostavljene delovanju raztopine $MgSO_4$

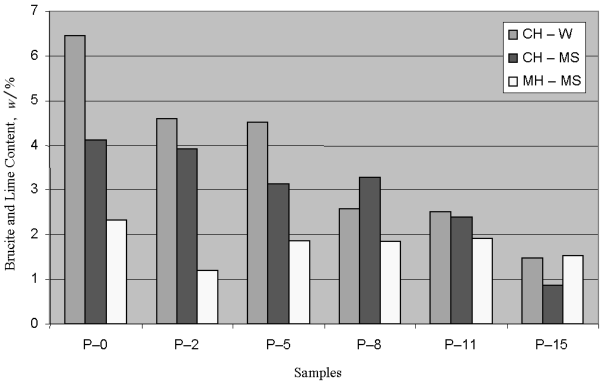

Figure 6: Lime and brucite content in the SF-mortar samples exposed to $MgSO_4$ solution for 120 d. Control SF-mortars are stored in tap water (designated CH-W)

Slika 6: Vsebnost kalcijevega hidroksida (CH) in brucita (MH) v vzorcih SF-malt po 120 d izpostavljanja raztopini $MgSO_4$. Kontrolni vzorci SF-malt so hranjeni v vodovodni vodi (označba CH-W)

mortars exposed to the $MgSO_4$ solution. Based on the experimental data following the correlation between the dynamic modulus of elasticity (E_d) and the compressive strength (f_c) was observed to be $E_d = 19.40 + 2.06 \sqrt{f_c}$, which is in good agreement with the relationship $E_d = 22 + 2.8 \sqrt{f_c}$, which is given in the British Standard B.S.CP 100:1972.

Figure 6 presents the results of the quantity of unleached lime and brucite formed in the specimens after 120 d of the magnesium sulfate immersion. The curve, designated W-CH, illustrated the relationship between the quantity of unleached lime and the SF replacement for samples cured in tap water[9,10]. More leaching in the $MgSO_4$ solution than in the water was demonstrated by the mortars with and without up to mass fraction 8 % of silica fume, suggesting that lime (calcium hydroxide) was converted to gypsum and brucite[4]. The presence of brucite, determined by DTA, in all the samples after 120 d of sulfate immersion was found, although the brucite formation was not observed by the XRD analysis. The relatively small concentration of brucite formed was related to the gypsum in the samples and explains why the observed XRD peaks due to brucite were always weak[16]. The presence of brucite obtained in the SF-mortar samples suggests a rapid attack by $MgSO_4$. However, as the pozzolanic reaction proceeded, the reduction in the permeability and the refinement of the pore structure overcame the negative effect of the sulfate attack.

4 CONCLUSIONS

Silica fume replacement enhances the durability of mortar exposed to magnesium sulfate attack due to the lowering of the lime content, and therefore the increase of the initial compressive strength, on account of the pozzolanic reaction. Thereafter, by the decreasing of lime content in mortars during the Mg-sulfate immersion the formation of gypsum and ettringite, which are responsible for the decreasing of mortar durability, decreases. Mortars containing the mass fraction more than 8 % of silica fume replacement are characterized by a good sulfate resistance and show lower expansion than a control sulfate-resisting mortar due to the absence of gypsum and ettringite, detected by XRD analysis. Although the formation of brucite, determined by DTA analysis, suggests a rapid attack by $MgSO_4$ solution and an affect on the compressive strength of SF-mortars, the pozzolanic reaction (reduction in permeability and refinement of the pore structure) overcame this negative effect. The elastic modulus is proportional to the compressive strength, but a higher compressive strength does not necessarily correlate with a better durability to sulfate attack. For these experimental conditions, the optimum dosage level of 15 % silica fume replacement to minimize the deleterious effects of magnesium sulfate attack can be proposed.

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5 REFERENCES

[1] A. Neville, Cem. Concr. Res. 34 (**2004**), 1275–1296

[2] F. Bellmann, B. Möser, J. Stark, Cem. Concr. Res. 36 (**2006**), 358–363

[3] M. D. Cohen, A. Bentur, ACI Mater. J. 83 (**1988**), 147–157

[4] R. S. Gallop, H. F. W. Taylor, Cem. Concr. Res. 26 (**1996**), 1013–1028

[5] P. K. Mehta, Cem. Concr. Res. 13 (**1983**), 401–406

[6] K. Torii, M. Kawamara, Cem. Concr. Res. 24 (**1994**), 361–370

[7] P. S. Mangat, J. M. Khatib, ACI Mater. J. 92 (**1995**), 542–552

[8] F. Türker, F. Aköz, S. Koral, N. Yüzer, Cem. Concr. Res. 27 (**1997**), 205–214

[9] E. Tkalčec, J. Zelić, Zement-Kalk-Gips 11 (**1987**), 574–579

[10] J. Zelić, R. Krstulović, E. Tkalčec, P. Krolo, Cem. Concr. Res. 29 (**1999**), 819–826

[11] E. E. Hekal, E. Kishar, H. Mostafa, Cem. Concr. Res. 32 (**2002**), 1421–1427

[12] M. Santhanan, M. D. Cohen, J. Olek, Cem. Concr. Res. 33 (**2003**) 341–346.

[13] I. Radovanović, Diploma Thesis, Faculty of Chemical Technology, University of Split, 2004

[14] E. F. Irassar, A. Di Maio, O. R. Batic, Cem. Concr. Res. 26 (**1996**), 113–123

[15] D. Tončić, P. Gugić, I. Mandić, Croatian J. Cem. Ind. 1 (**1982/83**), 3–6

[16] S. A. Hortshorn, J. H. Sharp, R. N. Swamy, Cem. Concr. Res. 29 (**1999**), 1331–1340