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INVESTIGATION OF THE MORTAR AND CONCRETE RESISTANCE IN AGGRESSIVE SOLUTIONS

Ksenija Janković, Ljiljana Miličić, Srboljub J. Stanković, Nenad Šušić

Preliminary notes

Testing the influence of two aggressive solutions - sulphate and nitrate on mortar and concrete was presented in this paper. Experimental work included testing of mortar prisms with 5 % special admixture. Also, four types of concrete were exposed to aggressive solutions. The chemical resistance was tested according to the Koch-Steinegger method. As a condition for resistance in aggressive solution means that flexural strength of mortar prisms is no less than 70 % of referent prisms cured in water it can be concluded that mortar and concrete made with combination of cement and admixture presented in this investigation are not resistant to ammonium nitrate solution, but are resistant to sulphate corrosion.

Keywords: *chemical aggression, concrete, Koch-Steinegger method, mortar*

Istraživanje otpornosti žbuke i betona u agresivnim rastvorima

Prethodno priopćenje

U radu je prikazan utjecaj dva agresivna rastvora – sulfata i nitrata na žbuku i beton. U eksperimentalnom radu ispitivane su prizme od žbuke s 5 % specijalnog dodatka. Četiri vrste betona su također izložene agresivnim rastvorima. Kemijska otpornost ispitivana je prema metodi Koch-Steinegger. Kako je uvjet za otpornost kod agresivnih rastvora da zatezna čvrstoća žbuke nije niža od 70 % u odnosu na referentne prizme njegovane u vodi, može se zaključiti da žbuka i beton izrađeni s kombinacijom cementa i dodataka, prikazani u ovom istraživanju, nisu otporni na rastvor amonijak nitrata ali jesu na sulfatnu koroziju.

Ključne riječi: *beton, kemijska agresija, Koch-Steinegger metoda, žbuka*

1 Introduction

The increasing attention is paid to the durability of concrete structures. They are important studies of different types of cement to determine the service life of concrete structures [1], and the combination of different types of cement and various aggressive solutions [2]. According to De Belie et al. [3], three factors seem to play an important role in the acid resistance of concrete: the permeability, determining the extent to which acids can penetrate into concrete, the alkalinity and the chemical composition of the cement paste. Previous studies have shown the positive influence of mineral additions, such as fly ash [4, 5], silica fume and blast-furnace slag [6, 7] because of the lower CH content, reduced Ca-to-Si ratio in calcium silicate hydrates and the refined pore structure they produce in concrete [3, 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, as well as other constituents, with certain substances from water, solutions of soil, gases, vapours, etc. The most important aggressive agents are: SO_4^{2-}, Mg^{2+}, NH_4^+, Cl^-, H^+, and HCO_3^-. Sulphate degradation primarily consists of the impact by sulphate ions on cement stone. The sulphate ion is the cause of one of the most dangerous corrosions, the corrosion of expansion and swelling, because it causes the occurrence of expansive compounds, the most important of which is ettringite, $C_3A \cdot 3CaSO_4 \cdot 32H_2O$, in the shape of prismatic crystals [8]. The consequences are damages to the concrete and destruction at worst. The concrete deterioration by ammonium sulphate, for example, covers the most aggressive corrosion on concrete and neither balancing nor creating of protective gel takes place. In this case concrete is damaged not only by expansion, but also by softening of the cement matrix. Addition of fly ash to Portland cement makes this cement become more resistant to the sulphate aggressive environment [9].

The chemical reactions between sulphates and hydrated cement components yield the following reaction products [10]: secondary gypsum ($CaSO_4 \cdot 2H_2O$), secondary ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), thaumasite ($CaSiO_3 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$), brucite ($Mg(OH)_2$), M–S–H ($3MgO \cdot 2SiO_2 \cdot 2H_2O$) and silica gel ($SiO_2 \cdot xH_2O$). Secondary ettringite formation causes expansion and cracking. Whether gypsum formation results in expansion is disputed in the literature [11]. Several researchers [12, 13] mention that ettringite as well as gypsum have an expansive and destructive character, while others [14] claim that the contribution of gypsum is limited and the expansion of ettringite dominates. Thaumasite formation leads to strength loss due to the decomposition of the strength-forming hydration products (C–S–H) [15].

As is well known [16, 17], ammonium nitrate solutions are very corrosive to cementations materials, which lead to dissolution of cement-based materials according to the following reaction:

$$2NH_4NO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + 2NH_3 + 2H_2O. \quad (1)$$

The reaction products are calcium nitrate and ammonia, both of which are easily dissolved in water. Furthermore, the dissolution of calcium hydroxide in the ammonium nitrate solution is higher than that in pure water. It is clear from the above-mentioned chemical reaction that the ammonium nitrate decalcifies the hardened cement paste due to removal of calcium hydroxide (Eq. (1)). This results in decalcification and dissolution of other products of the hardened cement paste and leads to a reduction of the pH-value. Consequently, steel reinforcement corrosion may occur at an accelerated rate. The deterioration and damage of the cement-based material must be intensified and accelerated, when the material suffers under a corrosive attack superimposed with a mechanical load.

As a part of a large program to study the behaviour of cement matrices in acid media and its influence on metal immobilization in the stabilization/solidification process of toxic wastes the authors have tried to evaluate the durability using the Köch-Steinegger test [18, 19]. This test is based on the evaluation of the degradation of the material in a certain medium by its loss of mechanical properties, especially the flexural strength, which is more sensible to the degree of degradation than is the compressive strength. To accelerate the processes and obtain results in a short period of time, the test uses small specimens that are immersed in aggressive solution. The concentration of the aggressive solution must be higher than that of the natural environment. The evaluation of the results is based on comparison of the behaviour of similar specimens immersed in the aggressive medium and in distilled water.

In this paper we represent results of the durability using the Köch-Steinegger test and other methods of investigation. If the strength is greater than 70 %, the material is considered durable in the tested medium.

2 Experimental work

Testing the influence of two aggressive solutions - sulphate and nitrate acid on concrete is presented. Experimental work included testing of mortar prisms with 5 % special admixture "Cementol Antikorodin" produced by TKK, Slovenia. Also, four types of concrete were exposed to aggressive solutions. The chemical resistance was tested according to the Koch-Steinegger method.

The specimens were made by using Portland-composite cement, CEM II A-M (S-V) 42.5 N (minimum 80 % Portland cement clinker and up to 20 % additions of slag and silicate fly ash). The chemical composition of cement is shown in Tab. 1.

Table 1 Chemical composition of cement (wt. %)

SiO_2	22,08
Al_2O_3	5,47
Fe_2O_3	2,25
CaO	60,75
MgO	2,03
SO_3	3,20
S^{2-}	0,07
Na_2O	0,32
K_2O	0,88
MnO	0,165
Loss on ignition	2,78
Cl-	0,005

Mortar prisms 10 × 10 × 60 mm were prepared from 450 g cement, 5 % admixture "Cementol Antikorodin", 1350 g standard sand and 200 g water. Referent prisms were stored in distilled water. Before the prisms were exposed to aggressive solutions, they were cured 1 day in the mould and 20 days in water. The influence of the 10 % Na_2SO_4 solution and 2 % NH_4NO_3 solution were tested. Compressive and flexural strength was determined after 7, 14, 28 and 56 days of storage in the aggressive solution.

The results, as an average value of three specimens are given in Figs. 1 and 2.

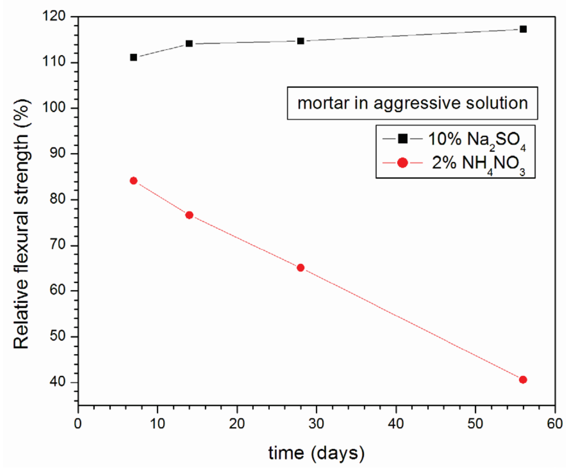

Figure 1 Relative flexural strength of mortar vs. time in aggressive solution

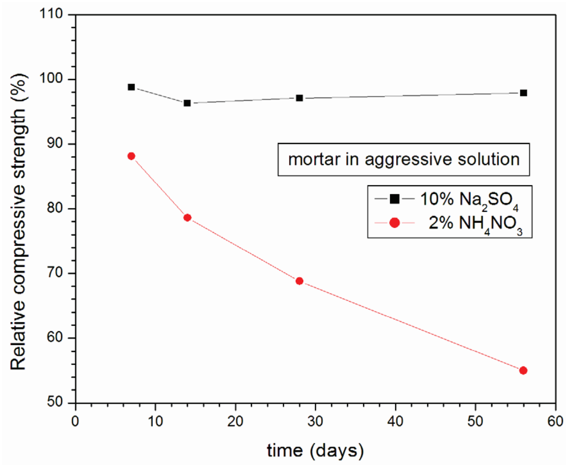

Figure 2 Relative compressive strength of mortar vs. time in aggressive solution

In the second phase, four types of concrete with admixture produced by SIKA and TKK were tested. The specimens were made with natural aggregate from river Drina, Serbia.

Information about composition of concrete is shown in Tab. 2. All types of concrete were made with the same cement content – 350 kg/m^3. Amounts of other component materials were adopted to obtain concrete with the same consistency.

Concrete types C1 and C2 were made with "Cementol Antikorodin". During the hydration process, "Cementol Antikorodin" reacts with calcium hydroxide, making it less available for reaction, thus reducing corrosion caused by salts which usually react with this hydroxide. "Cementol Antikorodin" also significantly reduces the permeability of concrete, and consequently its penetration by chemicals or aggressive substances.

Concrete C3 was made with combination of superplastisizer "Sika ViscoCrete 1020X" and "Sika Crete–AR", pozzolanic reactive addition with fluidificating action, for making cementations mortars and concretes with very high mechanical performances and very high values of resistance to chemical and weather aggression.

Concrete C4 was made with combination of superplastisizer "Sika ViscoCrete 1020X" and "Sika Fume-HR", fine (0,1 μm), latent reactive SiO_2. In the hardened concrete silica fume reacted with $CaOH_2$.

Before the cubes 7 × 7 × 7 cm were exposed to aggressive solutions, they were cured 1 day in the mould and 27 days in water. Compressive strength of specimens was tested after 28, and 84 days (56 days of storage in the aggressive solutions and referent concrete in water). Also, pH-values on the surface and middle of cubes after 84 days were tested. The results, as an average value of three specimens are given in Figs. 3 ÷ 5.

Table 2 Quantities of component materials of concrete

Type of concrete	C1	C2	C3	C4
Cement (kg/m^3)	350	350	350	350
Aggregate (kg/m^3)	1930	1900	1910	1845
Water (kg/m^3)	165	158	168	184
Additive (kg/m^3)	TKK Cementol Antikorodin 18	TKK Cementol Antikorodin 18	-Sika ViscoCrete 1020X, 3.85 -Sika Crete - AR, 20	-Sika ViscoCrete 1020X, 3.85 -Sika Fume - HR, 18

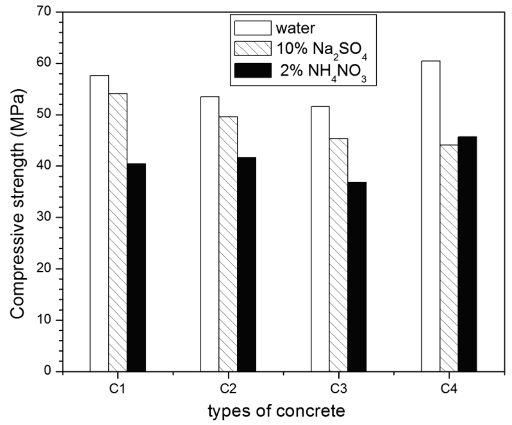

Figure 3 Compressive strength of concrete

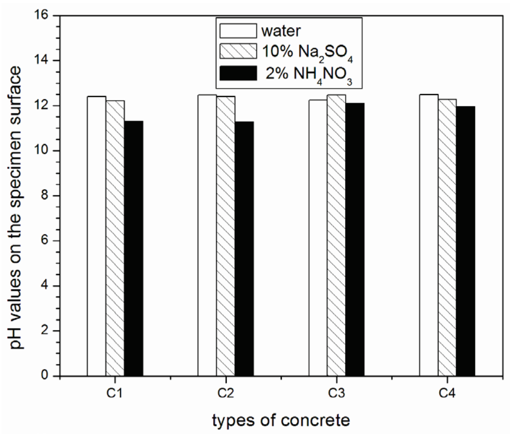

Figure 4 pH values on the surface of specimens

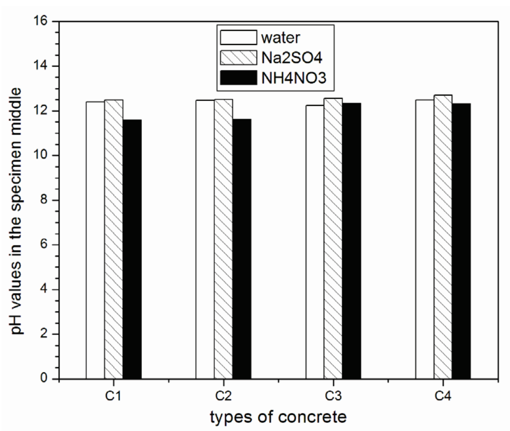

Figure 5 pH values in the middle of specimens

3 Discussion

Comparing flexural strength of mortar prisms exposed to aggressive solutions and referent specimens stored in water it can be concluded that combination of blended cement and special admixture (based on silica fume) is resistant to the influence of the 10 % Na_2SO_4 solution. After the 56 days in that solution flexural strength of mortar prisms was 17,3 % greater than that of control specimens. Also, results of compressive strength showed that specimens exposed to 10% Na_2SO_4 had 97,9 % value of referent specimens cured in water. The second aggressive solution – 2 % NH_4NO_3 is very corrosive to cementation materials. Flexural strength of the specimens cured 14 days in ammonium nitrate solution was reduced 23,4 % and after 56 days reduction was about 60 %. The results of the compressive strength are similar after 14 days, while after 56 days immersion the compressive strength was 55 % of referent specimens.

Analysing the results of compressive strength of concrete made with the same admixture as mortar (concrete types C1 and C2) it can be seen that specimens after 56 days immersion in 10 % Na_2SO_4 had 93 % value of referent specimens cured in water. Compressive strength of concrete C3 exposed to the same solution reached 88 % of referent concrete, while concrete C4 had 73 % of strength of specimens cured in water.

Compressive strength of concrete immersion for 56 days in 2 % NH_4NO_3 decreased by 22 ÷ 30 % related to control concrete cured in water.

There is no significant difference in pH-values on the surface and in the middle of concrete specimens.

4 Conclusions

Analysing testing results of mortar and concrete exposed to 10 % Na_2SO_4 it can be concluded that it is possible to get concrete resistant to sulphate corrosion using CEM II A-M (S-V) 42.5 N (minimum 80 % Portland cement clinker and up to 20 % addition of slag and silicate fly ash).

As a condition for resistance in aggressive solution means that flexural strength of mortar prisms is no less than 70 % of referent prisms cured in water it can be concluded that combination of cement and additive presented in this investigation is not resistant to ammonium nitrate solution.

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Authors' addresses

Ksenija Janković , Ph.D.,BSCE, senior research associate
IMS Institute
Bul. vojvode Misica 43, 11 000 Belgrade, Serbia
E-mail: ksenija.jankovic@institutims.rs

Ljiljana Miličić , B.Sc.Chem.
IMS Institute
Bul. vojvode Misica 43, 11 000 Belgrade, Serbia
E-mail: ljiljana.milicic@institutims.rs

Srboljub J. Stanković, M.Sc.E.E., research assistant
Institute of Nuclear Sciences Vinca, University of Belgrade
P. O. Box 502, 11001 Belgrade, Serbia
E-mail: srbas@vunca.rs

Nenad Šušić, Ph.D., BSCE, principal research fellow
IMS Institute
Bul. vojvode Misica 43, 11 000 Belgrade, Serbia
E-mail: nenad.susic@institutims.rs