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LONG-TERM DURABILITY PROPERTIES OF POZZOLANIC CEMENT MORTARS

DOLGOROČNA OBSTOJNOST PUCOLANSKE CEMENTNE MALTE

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Within the scope of this study, the durability properties of mortar prepared with pozzolanic cement were examined. The physical-mechanical properties of the mortars were determined after their exposure to various aggressive media (a sodium sulphate water solution, a magnesium sulphate water solution, seawater, and a water solution of NO_3^{2-}, SO_4^{2-}, and NH_4^-) and freeze/thaw cycling. Additionally, the depth of carbonation of the mortars was determined. The results showed that the mortar containing pozzolanic cement was sulphate resistant, but when it was exposed to a solution of NO_3^{2-}, SO_4^{2-}, and NH_4^- its strength was significantly reduced. On the other hand, the mortar was found to be sensitive to freezing/thawing, as its compressive strength decreased by 50 %, and its flexural strength by as much as 90 %. Due, especially, to its lack of resistance to freezing/thawing, the use of the investigated pozzolanic cement mortar is limited to indoor applications.

Keywords: pozzolanic cement, durability, sulphate attack, frost resistance, carbonation

V prispevku obravnavamo trajnostne lastnosti malte, pripravljene iz pucolanskega cementa. Določili smo fizikalno-mehanske lastnosti malte po izpostavitvi različnim agresivnim medijem (vodni raztopini natrijevega sulfata, vodni raztopini magnezijevega sulfata, morski vodi, vodni raztopina ionov NO_3^{2-}, SO_4^{2-}, NH_4^-) in cikličnemu zmrzovanju in odtaljevanju. Poleg tega smo določili tudi globino karbonatizacije. Na podlagi rezultatov ugotavljamo, da je malta s pucolanskim cementom odporna proti sulfatom, medtem ko se njena trdnost po izpostavitvi raztopini ionov NO_3^{2-}, SO_4^{2-} in NH_4^- močno zmanjša. Prav tako preiskana malta nima zmrzlinske obstojnosti, saj se njena tlačna trdnost zmanjša za 50 %, upogibna pa za 90 %. Na osnovi rezultatov ugotavljamo, da je malta zaradi slabe zmrzlinske obstojnosti uporabna le za notranje površine.

Ključne besede: pucolanski cement, obstojnost, sulfatna korozija, obstojnost proti zmrzali, karbonatizacija

1 INTRODUCTION

Over the past decade there has been a clearly perceptible trend towards the replacement of Portland cement, by up to 80 %, with various mineral additives, such as ground granulated blast furnace slag, natural (volcanic ash) and synthetic pozzolans (fly ashes, microsilica, rice husk ash), and ground limestone.[1–4] An important reason for the use of blended or pozzolanic cements lies in their good resistance to attack by chemical agents, especially seawater, and by sulphate-rich water.[5–7] In addition, the replacement of Portland cements with pozzolans has environmental benefits, since in this way waste materials can be used, thus contributing to the reduced use of naturally occurring raw materials, and less energy is consumed in their production compared with the production of cement clinker, reducing greenhouse-gas emissions and the overall CO_2 footprint.

The most widely used cement-replacement material is coal combustion fly ash. In the EU, the replacement of up to 33 % of the Portland cement with fly ash is permitted for a range of cement types, whereas in the case of pozzolanic cement a limit of 55 % has been specified (EN 197-1:2011).[8] The performance of concrete with added fly ash is frequently better than that of concrete mixed with Portland cement only. Although the pozzolanic reaction is slow, and can cause a significant decrease in early-age strengths, the use of fly ash in cement results in a generally improved workability, a higher late-age strength and increased durability, as well as improved sulphate resistance, and reductions in the heat of hydration and in the risk of the occurrence of an alkali silica reaction and efflorescence.[4,7,9] There are some situations, however, where the performance of concrete with added fly ash may not be so good, e.g., when such concrete is subjected to freeze-thaw actions. In this case concerns have been raised regarding the concrete's durability, especially when the fly ash is used at higher content levels.[10] Two main classes of fly ash can be defined: siliceous fly ash (low calcium fly ash; < 10 % CaO), which has been widely used as a replacement for cement, and calcareous fly ash (high calcium fly ash; > 10 % CaO). Calcareous fly ashes show a more rapid strength gain during early ages than in the case of concretes made with siliceous fly ashes.[11] This is because calcareous fly ashes usually exhibit a higher rate of reaction during early ages than siliceous fly ashes. Since a negative cement performance has been frequently connected with the presence of lime and sulphates, the limits of the existing standards are very strict, so that most calcareous fly ashes are rejected as unsuitable.[11] However, the large amounts of calcareous fly ashes that are produced have resulted in a pressing need for their utilization, especially if sustainability issues are to be adequately resolved in the construction industry.

In the present investigation the durability properties of mortars prepared with pozzolanic cement have been investigated. The pozzolanic cement used in the study was a mix of calcareous fly ash and Portland cement clinker designated as CEM IV/B-W 32.5 N according to EN 197-1:2011[8]. The physical-mechanical properties of mortars made using this type of cement were determined after the latter had been exposed to different aggressive media, as well as to freeze/thaw cycling.

2 EXPERIMENTAL

2.1 Materials and methods

A pozzolanic cement CEM IV/B-W 32.5 N (Lafarge Cement, d. o. o., Trbovlje, Slovenia) and CEN standard sand were used for the preparation of mortars. A cement: aggregate:water ratio of 1 : 3 : 0.6 was used, except for the investigation of the resistance to freezing/thawing and carbonation. The properties of the samples of fresh mortar (consistence EN 1015-3:2001[12], bulk density EN 1015-6:1999[13], air content EN 1015-7:1999[14]) for the investigation of the resistance to freezing/ thawing and carbonation are given in **Table 1**.

In order to evaluate the sulphate resistance of the pozzolanic cement mortar, samples having dimensions of 10 mm × 10 mm × 60 mm were cured for 21 d in deionized water. After this, some of the samples were exposed to a 4.4 % Na_2SO_4 water solution or a 3.73 % $MgSO_4$ water solution, whereas the remaining samples were left in the deionized solution. In order to compare the influence of the different curing media, another set of samples was cured in saturated lime water for 21 d, after which they were exposed to a 4.4 % Na_2SO_4 water solution, whereas the remaining samples were left in the saturated lime water. Compressive and flexural strengths according to EN 196-1:2005[15] were determined after (14, 28 and 56) d. The resistance of the investigated mortars to sulphate attack was investigated and evaluated using the Koch-Steinegger test.[16]

In order to assess the influence of various aggressive media on the long-term durability of pozzolanic cement mortar, samples having dimensions of 40 mm × 40 mm × 160 mm were cured for 28 d in saturated lime water. After this, some of the samples were exposed to a 4.4 % Na_2SO_4 water solution, as well as to seawater, and to a (NO_3^{2-}, SO_4^{2-}, NH_4^-) water solution, whereas the remaining samples were left in the saturated lime water. The compressive and flexural strengths of the mortar samples were determined according to EN 196-1:2005[15], after 1 and 2 years.

In order to investigate the resistance to freezing/ thawing of the pozzolanic cement mortar (in the absence and presence of de-icing salt) an air-entraining admixture was added to the mortar (Cementol Eta S, and Cementol Eta EM, produced by TKK Srpenica). The amount of air-entraining admixture used in the preparation of the mortar samples was determined by the consistence of the fresh mortar (EN 1015-3:2001)[12], by keeping a flow value (175 ± 5) mm (**Table 1**). For the investigation of the resistance to freezing/thawing in the absence of de-icing salt, mortar samples having dimensions of 40 mm × 40 mm × 160 mm were cured for 28 d in water at (20 ± 1) °C. After this, some of the samples were exposed to freeze/thaw cycling, whereas the remaining samples were left in the water at (20 ± 1) °C. Freeze/thaw cycling was performed according to the standard SIST 1026: 2008.[17] All the samples were exposed to 50 cycles of freezing/thawing, where one cycle consisted of 4 h at (–20 ± 2) °C and 4 h at (20 ± 2) °C.

The flexural and compressive strengths of the prepared mortar samples were determined according to EN 196-1:2005[15] after 50 cycles. In the case of freeze/thaw cycling in the presence of the de-icing salt solution (3 % NaCl), samples having dimensions of 200 mm × 200 mm × 50 mm were cured for 7 d at (20 ± 2) °C at a RH of (65 ± 5) %, and their resistance to freezing/thawing was assessed according to SIST 1026:2008.[17]

The carbonation of the mortar samples was assessed on mortar prisms having dimensions of 40 mm × 40 mm × 160 mm, according to EN 13295:2004.[18] The samples were cured for 24 h in a mould, wrapped in film. After de-moulding, the samples were cured for 48 h, wrapped in film, and then for 25 d at (21 ± 2) °C and at a RH of (60 ± 10) %. After this, they were placed in a chamber containing CO_2 1 %, at a RH of (60 ± 10) %. The depths of the carbonation were determined by spraying a phenolphthalein indicator solution onto the freshly broken surface. Another set of samples was exposed to the natural environment, i.e., to outdoor conditions in a sheltered area. The depth of carbonation was determined after (28, 56, 90, 180 and 270) d, using the phenolphthalein indicator solution.

3 RESULTS AND DISCUSSION

3.1 Resistance to the investigated aggressive media

The compressive and flexural strengths of the mortar specimens that had been immersed in the sodium sulphate solution and the magnesium sulphate solution were

Table 1: Properties of the samples of fresh mortar for resistance to freezing/thawing and carbonation
Tabela 1: Odpornost vzorcev sveže malte proti zmrzovanju/odtaljevanju in karbonatizaciji

Additive – cement (%)	Water/cement ratio	Consistence (mm), EN 1015-3:2001[12]	Bulk density (kg/m^3), EN 1015-6:1999[13]	Air content (%), EN 1015-7:1999[14]
–	0.5	174	2180	3.6
0.15 (Cementol Eta S)	0.5	175	2100	4
0.6 (Cementol Eta EM)	0.47	171	2105	7.4

determined and compared with those of the samples that had been immersed in deionised or saturated lime water. A difference in the initial strengths was observed, which depended upon which solution, i.e., deionised water or saturated lime water, had been used to cure the specimens prior to the test. The lower initial strengths obtained in the case of the deionised water suggest that the latter behaves as an aggressive solution, if compared to the saturated lime water.

According to the Koch-Steinegger test,[16] the criterion that can be used to classify a material as resistant or durable in a specific aggressive medium is that the corrosion index (i.e., the relative strength of the aggressive-solution-stored samples to the water-stored samples) must be higher than 0.7. As can be seen from **Figures 1** and **2**, the corrosion index for the mortar samples that were exposed to the investigated aggressive media was always above 0.7, in the case of both flexural and compressive strength. The corrosion index is slightly higher in the case of the magnesium sulphate solution. These results suggest that the pozzolanic cement mortar could be classified as durable or resistant to a sodium sulphate solution, as well as to a magnesium sulphate solution. This can be mainly attributed to the pozzolanic reaction, where the reactive siliceous and aluminous phases in the fly ash react with portlandite to form new C-S-H- or C-AS-H-type phases, provoking a refinement in the pore structure, and thus impeding the penetration and movement of potentially aggressive ions.[6,19]

The flexural and compressive strengths of the mortar samples, measured after long-term exposure to the investigated aggressive media, are shown in **Figures 3** and **4**. The results indicate that the mortar containing pozzolanic cement continued to be sulphate resistant after 2 years of exposure, but when it was exposed to seawater or a solution of NO_3^{2-}, SO_4^{2-}, and NH_4^{-} its strength was significantly reduced. This could be due to

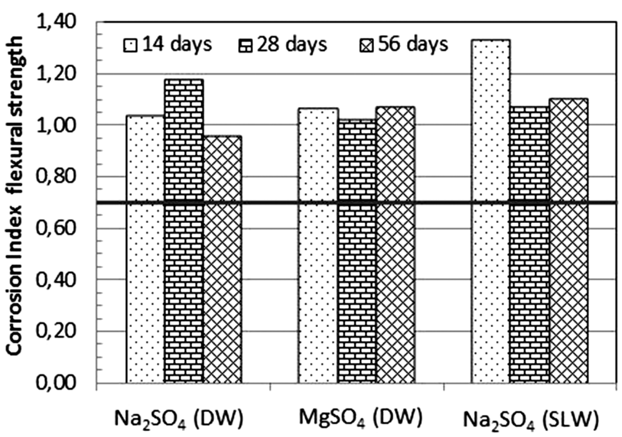

Figure 1: Corrosion index (flexural strength) for the mortar samples exposed to various solutions (DW – deionised water, SLW – saturated lime water)

Slika 1: Korozijski indeks (upogibna trdnost) za vzorce malte, izpostavljene različnim raztopinam (DW – deionizirana voda, SLW – nasičena apnena voda)

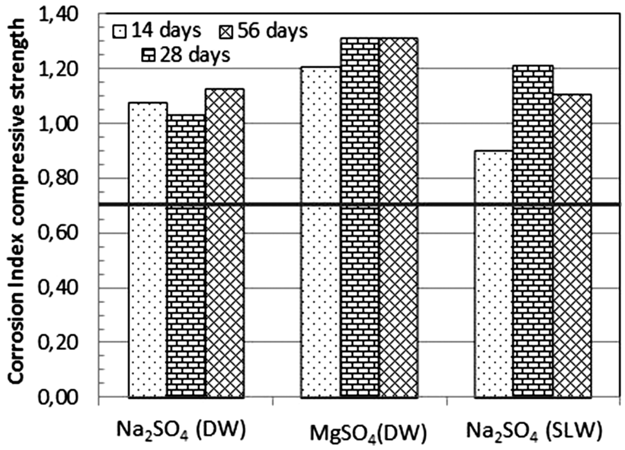

Figure 2: Corrosion index (compressive strength) for the mortar samples exposed to various solutions (DW – deionised water, SLW – saturated lime water)

Slika 2: Korozijski indeks (tlačna trdnost) za vzorce malte, izpostavljene različnim raztopinam (DW – deionizirana voda, SLW – nasičena apnena voda)

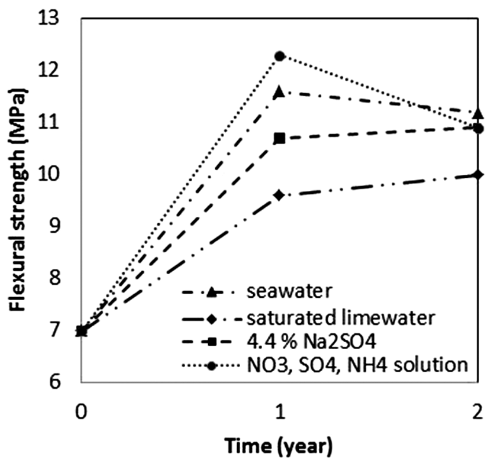

Figure 3: Flexural strength of the investigated mortar samples after long-term exposure to the investigated aggressive media

Slika 3: Upogibna trdnost preiskovanih malt po dolgotrajni izpostavitvi preiskovanim agresivnim medijem

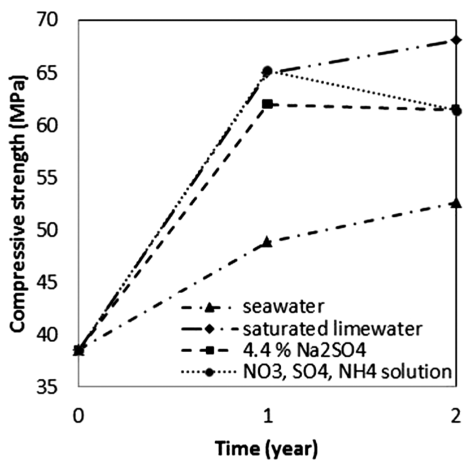

Figure 4: Compressive strength of the investigated mortar samples after long-term exposure to the investigated aggressive media

Slika 4: Tlačna trdnost preiskovanih malt po dolgotrajni izpostavitvi preiskovanim agresivnim medijem the removal of calcium hydroxide, the hardened cement paste will be decalcified, causing the pH value to decrease.[20]

3.2 Resistance to freezing/thawing

The results showed (**Table 2**) that, after the freeze/thaw cycling, the compressive strength of the investigated mortar samples decreased by more than 50 %, and their flexural strength by as much as 90 %. The observed decrease in strengths was higher in the case of the mortar with a higher air content.

In the presence of de-icing salt the loss of material exceeded the requirement according to the standard SIST 1026:2008[17] (0.35 mg/mm^2) already after 10 cycles of freezing/thawing. It was, however, higher in the case of the mortar with a higher air content, as the loss of material was 2.32 mg/mm^2 and, in the case of the mortar with a lower air content, 1.58 mg/mm^2. Thus, the investigated mortar is non-resistant to frost action, despite the addition of an air-entraining admixture. In general, the freeze-thaw durability of fly ash concrete, when a fly ash content of more that 20 % is used, is similar to or worse than that of Portland cement concretes, which could be attributed to compatibility problems between the fly ash and the air entraining agents.[10]

Table 2: Strengths of the investigated mortar samples after freeze/thaw cycling
Tabela 2: Trdnost preiskovanih malt po cikličnem zamrzovanju/odtaljevanju

Additive – sample (%)	Flexural strength (N/mm^2)		Compressive strength (N/mm^2)	
	cured in water	freeze/ thaw cycling	cured in water	freeze /thaw cycling
0.15 (Cementol Eta S)	7.7	1.3	52.1	31.2
0.6 (Cementol Eta EM)	9.3	0.5	57.3	23.1

3.3 Carbonation

The depth of carbonation of the mortar samples exposed to the accelerated carbonation was 10.2 mm after 56 d, and 15.4 mm after 90 d. On the other hand, the mortar samples that were exposed to the natural environment showed a reduced depth of carbonation, which amounted to 3.1 mm after 56 d, 3.9 mm after 90 d, and 6.1 mm after 270 d.

It has been reported that the carbonation of concrete increases significantly with increased fly ash content, i.e., when the fly ash content is higher than 30 %, as a large amount of fly ash delays the hydration and the increase of porosity.[21] However, when the binder used in the mortar samples contained just 10 % of fly ash, the carbonation level was equal to that of the samples containing Portland cement only, or was slightly higher. On the other hand, when the concrete incorporated calcareous fly ash, carbonation was reduced in comparison with the siliceous fly ash.[21]

4 CONCLUSIONS

The investigated pozzolanic cement CEM IV/B-W 32.5 N is resistant to the selected sulphate solution, whereas both of the selected (NO_3^{2-}, SO_4^{2-}, NH_4^-) solution and seawater had a negative effect, since the strengths of the tested mortar samples reduced over a period 1–2 years. However, there was a difference in the initial strengths, depending upon which solution, i.e., deionised water or saturated lime water, was used to cure the samples prior to testing. Deionised water behaves as an aggressive solution when compared to saturated lime water. On the other hand, the mortar was found to be sensitive to freezing/thawing in both the presence and the absence of de-icing salt, as its compressive strength decreased by 50 %, and its flexural strength by as much as 90 %. When exposed to a selected natural environment the mortar samples showed a reduced depth of carbonation with respect to the accelerated carbonation test.

Due, especially, to its lack of resistance to freezing/thawing, the use of the investigated pozzolanic cement mortar is limited to indoor applications.

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