The performance of concrete with pozzolanic cement a limit of 55 % has been specified in existing standards are very strict, so that most calcareous fly ashes are rejected as unsuitable. However, the large amounts of calcareous fly ashes that are produced have 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 CO₂ 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). 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. 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. 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. 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. 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 196-1:2005. 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, bulk density EN 1015-6:1999, air content EN 1015-7:1999) 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 % Na₂SO₄ water solution or a 3.73 % MgSO₄ 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 % Na₂SO₄ water solution, whereas the remaining samples were left in the saturated lime water. Compressive and flexural strengths according to EN 196-1:2005 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.

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 % Na₂SO₄ water solution, as well as to seawater, and to a (NO₃⁻, SO₄²⁻, NH₄⁺) 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, 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 consistency of the fresh mortar (EN 1015-3:2001), 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. 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 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.

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. 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 CO₂ 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 fresh mortar for resistance to freezing/thawing and carbonation

<table>
<thead>
<tr>
<th>Additive – cement (%)</th>
<th>Water/cement ratio</th>
<th>Consistence (mm), EN 1015-3:2001</th>
<th>Bulk density (kg/m³), EN 1015-6:1999</th>
<th>Air content (%), EN 1015-7:1999</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 (Cementol Eta S)</td>
<td>0.5</td>
<td>175</td>
<td>2100</td>
<td>3.6</td>
</tr>
<tr>
<td>0.6 (Cementol Eta EM)</td>
<td>0.47</td>
<td>171</td>
<td>2105</td>
<td>7.4</td>
</tr>
</tbody>
</table>
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, 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.

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 NO₃⁻, SO₄²⁻, and NH₄⁺ its strength was significantly reduced. This could be due to...
the removal of calcium hydroxide, the hardened cement paste will be decalcified, causing the pH value to decrease.\textsuperscript{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\textsuperscript{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.\textsuperscript{10}

<table>
<thead>
<tr>
<th>Additive – sample (%)</th>
<th>Flexural strength (N/mm(^2))</th>
<th>Compressive strength (N/mm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cured in water</td>
<td>freeze/thaw cycling</td>
</tr>
<tr>
<td>0.15 (Cementol Eta S)</td>
<td>7.7</td>
<td>1.3</td>
</tr>
<tr>
<td>0.6 (Cementol Eta EM)</td>
<td>9.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

### 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.\textsuperscript{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.\textsuperscript{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\(_3\)^–, 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.

### Acknowledgements

This study was financially supported by the Metrology Institute of the Republic of Slovenia.

### 5 REFERENCES

1. K. Sobolev, Mechano-chemical modification of cement with high volumes of blast furnace slag, Cement and Concrete Composites, 27 (2005) 7–8, 848–853
3. V. Ramasamy, Compressive strength and durability properties of rice husk ash concrete, KSCE Journal of Civil Engineering, 16 (2012) 1, 93–102
13 EN 1015-6:1999, Methods of test for mortar for masonry - Part 6: Determination of bulk density of fresh mortar, 1999
14 EN 1015-7:1999, Methods of test for mortar for masonry - Part 7: Determination of air content of fresh mortar, 1999
15 EN 196-1:2005, Methods of testing cement — Part 1: Determination of strength, 2005
16 A. Koch, H. Steinegger, A rapid test for cements for their behaviour under sulphated attack, Zement-Kalk-Gips, 7 (1960), 317–324
18 EN 13295:2004, Products and systems for the protection and repair of concrete structures - Test methods - Determination of resistance to carbonation, 2004
19 G. R. de Sensale, Effect of rice-husk ash on durability of cementitious materials, Cement and Concrete Composites, 32 (2010), 9, 18–25
20 U. Schneider, S. W. Chen, Behaviour of high performance concrete (HPC) under ammonium nitrate solution and sustained load, ACI Materials Journal, 96 (1999), 1, 47–51