

SULPHATE RESISTANCE AND PASSIVATION ABILITY OF THE MORTAR MADE FROM POZZOLAN CEMENT WITH ZEOLITE

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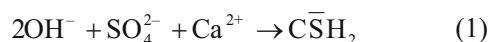
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Sulphate resistance and passivation ability of the mortars made from pozzolan cement of CEM IV/A (P) type according to European Standard EN 197-1 (zeolite blended cement with 60.82 mass% of PC clinker, 35.09 mass% of zeolite and 4.09 mass% of gypsum abbreviated as ZBC) and ordinary Portland cement (abbreviated as PC) are introduced. Resistance tests were performed in water and 5% sodium sulphate solution (both 20°C) for 720 days. The increased sulphate resistance of pozzolan cement relative to that of PC was found. The key quantitative insight into the hydrate phase behaviour is given by thermal analysis. This is due to pozzolanic reaction of zeolite with PC resulting in reduction of the formed Ca(OH)₂ opposite to the reference PC. Ability of pozzolan cements with 15 to 50 mass% of zeolite to protect steel against corrosion was verified in 20°C/85% RH – wet air within 180-day cure. Steel was not corroded in the mortars made with pozzolan cement containing up to 35 mass% of zeolite. Pozzolan cement of CEM IV/A (P) type containing 35 mass% of zeolite is a suitable cementitious material for concrete structures exposed to sulphate attack. Steel is protected against corrosion by this pozzolan cement in the same measure as the reference PC.

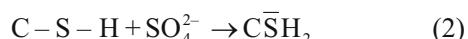
Keywords: cement, steel corrosion, sulphate resistance, thermal analysis, zeolite

Introduction

Two types of sulphate action on cement-based materials are distinguished: the formation of calcium sulphate dihydrate CaSO₄·H₂O (abbreviated as C \bar{S} H₂ marked as gypsum) and 3CaO·Al₂O₃·3CaSO₄·32H₂O (abbreviated as C₆A \bar{S} ₃H₃₂ marked as ettringite) [1]. Gypsum formation from calcium hydroxide Ca(OH)₂(CH) and C–S–H gel occurred in hydrated cement paste run according to formulae (1) or (2), respectively [2]:



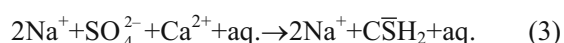
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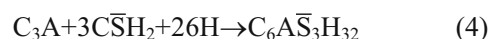
Besides ettringite and gypsum, non-binding mushy thaumasite (C₃S \bar{C} S \bar{S} H₁₅) can occur in cement-based composites under certain conditions also contributing to structural disintegration of the hydrate phase [3, 4].

The hydration rate of reaction (2) is much slower than that of reaction (1) giving less voluminous gypsum particles due to gellous character of origin C–S–H gel.

The reaction (1) is modified in the presence of sodium sulphate thus:



Ettringite is formed by the reaction of 3CaO·Al₂O₃ (C₃A) with gypsum (C \bar{S} H₂):



The increase in volume between the formed gypsum and origin Ca(OH)₂ is approximately 2.2 times – and between hydration products of C₃A and ettringite even 2.6 times higher in hydrated cement systems when exposed to the sulphate solution. The formation of such reaction products is then a source of internal expansive stresses, which in the final effect are responsible for the damaging expansion connected with the loss of integrity of cement-based materials as compared to water curing. Phenomena accomplishing cement hydration in sulphate solutions are: the increase in SO₃ content bound in the cement paste, formation and cumulating of reaction products (gypsum and ettringite) in developed pore structure. Air void supply disposable for reaction products deposition is exhausted after a certain period, dependent mainly on a sulphate solution concentration. Next gypsum and ettringite development leads to total destruction of cement-based materials due to crack propagation. The occurrence of such expansive growth does not take place in Portland cement systems kept in water. The first clear signs of sulphate action (crack propagation, breach of edges and spalling) in mortars with water to cement (w/c) ratio between 0.4 and 0.6 appear when the content of SO₃ bound in the cement paste increases by 5–6% from a starting value in non-attacked element. An increase by 10–12% is, as a rule, connected with a total de-

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struction of mortar or concrete [5–7]. Important factors influencing the resistance of concrete against sulphate attack are the type of mineral admixture used as a partial replacement of ordinary Portland cement [8], the fineness of cement and pozzolan [9], the amount of pozzolanic material [10], and the concentration of reactant in the pore solution [11].

Usually it is advantageous to modify Portland cement by natural or artificial materials reducing significantly the volume share of the cement in the blend. Many authors have investigated numerous blended cement systems with different origins and also studied their mechanical, microstructural and many other properties [12–14]. One of such addition is natural zeolite containing large quantities of reactive SiO_2 and Al_2O_3 . An average stoichiometric formula of the main mineral—clinoptilolite in zeolite mined in Slovakia (Nižný Hrabovec) is $(\text{Ca}, \text{K}_2, \text{Na}_2, \text{Mg})_4\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot 24\text{H}_2\text{O}$ [15]. The reaction kinetics in zeolite– CaO – H_2O system shows that Al-rich tobermorite is formed as a major phase of hydration process. Unreacted quartz, $\text{Ca}(\text{OH})_2$, and partially tobermorite were found in quartz– CaO – H_2O mixture [16]. Experimental results with cements made from Portland clinker and 10, 20 and 40 mass% of zeolite indicate that partial replacement of clinker with natural zeolite allows for the preparation of blended cements with technical performance better than those manufactured with industrial by-products. This is explained by higher reactivity of natural zeolite material with lime in comparison with industrial pozzolanic products containing also vitreous counterparts [17]. Materials made by hydrating of natural zeolite (clinoptilolite) with calcium hydroxide $\text{Ca}(\text{OH})_2$ indicate that compressive strength is dependent on the $\text{Ca}(\text{OH})_2$ content, clinoptilolite particle size and curing conditions. The $\text{Ca}(\text{OH})_2$ is consumed during curing and it is not present in high strength, fully cured materials. The results indicate the formation of hydration products with Ca/Si ratio in the range 0.8–1.2 and that a significant amount of unreacted clinoptilolite remains in optimized materials [18]. Zeolite demands more water to produce a paste of the same consistency compared to Portland cement paste. This means that when zeolitic cement is used for concrete production, it is likely that superplasticizer needs to be added in the mixture [19]. Zeolite is widely used in a cement industry in China as cement blending material, and obviously displaces about 10 mass% of normal Portland cement in concrete. When mixed with a suitable amount of superplasticizer, then a high-strength concrete at water to cement (w/c) ratios between 0.31 and 0.35 with compressive strength of about 80 MPa and slump of about 180 mm can be obtained. The strength of this concrete is about 10 to 15% higher

than that of the corresponding concrete mixed with normal Portland cement. Zeolite increases the amount of micropores ($d < 625 \text{ \AA}$) and decreases the amount of harmful large pores ($d > 938 \text{ \AA}$) in the cement paste. Hence, the strength of concrete is increased and its other properties are also improved. Furthermore, zeolite raises the SiO_2/CaO mass ratio in the transition zone to increase its C–S–H phase and decreases its calcium hydroxide content. Thus, the structure of the transition zone is improved, and as a consequence of this, the strength and resistance to permeability of concrete is increased [20–23]. The cement additive based on zeolite inhibits the alkali-aggregate reaction and corrosion of reinforcing steel, thereby protecting concrete constructions from deterioration [24]. The deleterious influence of various type of surrounding aggressiveness on cement-based materials is actually well-known [25–27]. Thus, in Portland cement–zeolite systems the formation of gypsum ($\text{C}\bar{\text{S}}\text{H}_2$) is reduced, mainly through pozzolanic reaction of zeolite with $\text{Ca}(\text{OH})_2$. A gradual chemical bonding of $\text{Ca}(\text{OH})_2$ by zeolite containing large quantities of reactive SiO_2 and Al_2O_3 causes formation of dense gel-like hydration products of C–S–H and C–S–A–H type rather than gypsum. Reduction in gypsum content yields less ettringite (reaction (4)). The available air void space is then large enough to avoid crack propagation due to extreme cumulating of voluminous reaction products in developed pore structure. There is still sufficiently large unfilled pore space in time. This explains that hydration process in Portland cement paste and Portland cement–zeolite paste is taking place by a different way. Partial substitution of Portland cement by zeolite contributes to the marked decrease in the volume of the arising solids and evident elimination of damaging expansion relative to that of alone Portland cement when exposed to the sulphate solution [28, 29].

This paper deals with hydration of the mortars made from ordinary Portland cement as reference and pozzolan cement of CEM IV/A (P) type with 35 mass% of zeolite and their resistance to sulphate attack and the ability of pozzolan cements containing of 15 to 50 mass% of zeolite to protect steel against corrosion.

Experimental

Materials

An ordinary Portland cement of CEM I 42.5 and natural zeolite from Nižný Hrabovec (Slovakia) were used for the tests. Mortars with cement to sand mass ratio of 1:3 and w/c=0.6 using Portland cement (abbreviated as PC) and pozzolan cement with the composition of 60.82 mass% of Portland cement clinker,

35.09 mass% of zeolite and 4.09 mass% of gypsum (zeolite blended cement abbreviated as ZBC) were prepared. Physical and chemical properties of the cements and natural zeolite are summarized in Tables 1–3. Standard siliceous sand with three size fractions: 0–0.5, 0.5–1.0 and 1.0–2.0 mm in mass ratio of 1:1:1 was used for a mortar manufacture.

Testing procedures

The specimens for resistance tests were made in steel moulds on a vibration table (50 Hz, 0.35 mm) with maximum vibration of 30 s, and stored 24 h at 20°C in wet air (100% relative humidity) and after remoulding kept in water for 27 days at the ambient temperature. After this basic curing half of the specimens was still maintained in water for 720 days and the second half was immersed in 5% sodium sulphate solution (an average 33800 mg SO₄²⁻ L⁻¹) also for 720 days using various specimens sizes until required testing. The solution was regularly checked on concentration and restored. The main character of mortar specimens on which all important tests were performed was a 40×40×160 mm prism. An expansion was measured on 20×20×120 mm prisms, mass increase on both prismatic specimens, and for the comparison also on cubes of 100³ and 150³ mm size as well. The tests on steel corrosion were performed on the mortars (40×40×160 mm) in an 85% R.H. – wet air within 28, 90 and 180-day cure. For comparison of the cements, zeolite contents were adjusted on 15, 25, 35 and 50 mass% substitution levels by PC and the obtained results were confronted with those of the reference Portland cement mortar (100 mass% of PC).

The mortar specimens were tested on flexural and compressive strength, mass increase, dynamic modulus of elasticity (DME), Young's modulus of elasticity and length changes. Ultrasonic pulse velocities were measured on an ultrasonic apparatus (UNIPAN 543). The density of mortars was estimated for specimens of known volume by weighing. DME was calculated using equation:

$$E_{bu} = \rho v_L^2 \frac{1}{k^2} \cdot 10^{-6} \quad (5)$$

where E_{bu} is DME (MPa), ρ is the volume density of prisms (kg m⁻³), v_L is the impulse speed of longitudinal ultrasonic waves (m s⁻¹) and k is the dimensional coefficient for 40×40×160 mm prisms ($k=1.0541$ at a Poisson ratio $\nu_{bu}=0.20$).

Young's modulus of elasticity E_b was calculated from equation:

$$E_b = \frac{\Delta\sigma}{\Delta\varepsilon} = \frac{\sigma_a - \sigma_b}{\varepsilon_a - \varepsilon_b} \quad (6)$$

where σ_a is the stress on the stress level $\gamma_\sigma=1/3$ MPa, ($\sigma_a=f_c/3$), f_c is compressive strength of concrete (MPa), σ_b is the starting stress (0.5 MPa), ε_a is average relative strain at the stress level $\gamma_\sigma=1/3\%$ and ε_b is average relative strain at the starting stress (%).

Deformations of prisms were measured by portable Graf–Kaufman comparator apparatus. The gauge length was 120 mm. The content of SO₃ bound in the hardened cement paste was estimated by standard analytical methods. The pore structure was studied by mercury intrusion porosimetry (MIP) using the high-pressure porosimeter mod. 2000 and macroporosimeter mod. 120 (Carlo Erba Science, Milan). Powder X-ray diffraction patterns were recorded on Philips diffractometer coupled with an automatic data recording system and CuK_α radiation and Ni-filter. The thermal analysis was conducted using the T.A.I SDT 2960 equipment at a heating rate 10°C min⁻¹ in static air atmosphere using 20 mg of sample material.

Steel corrosion was tested by the potentiodynamic method. This method enables the gradual linear increasing of the steel potential. Simultaneously, the current flowing through three-electrode measuring system is recorded and electrochemical corrosion state is evaluated. Potentiodynamic curves of steel in mortar extract were obtained using Potentiostat OH-405 (Radelkis, Hungary) at a polarisation rate of 30 mV min⁻¹. The pH values of mortar extracts were determined by the pH meter OP 113 (Radelkis, Hungary).

Results and discussion

The cements – PC and those with 15 to 50 mass% of zeolite – differ mainly in CaO, SiO₂ and Al₂O₃ quantities, insoluble residue and ignition loss values. The CaO content in pozzolan cements is markedly reduced relative to that of PC (Table 1). Zeolite with specific surface area over 1000 m² kg⁻¹ (Table 2) contributes to increasing the specific surface area of pozzolan cements opposite to PC (Table 3). Strengths of pozzolan cement decrease with the increasing substitution level of PC by zeolite (Table 4).

Resistance tests [Fig. 1 (specimens of size 20×20×120 mm), Fig. 2 (40×40×160 mm), Fig. 3 (100³ mm) and Fig. 4 (150³ mm)] show mass increases of mortar specimens with ZBC and PC kept in water and 5% Na₂SO₄ solution. Steady mass increases of PC mortar specimens exposed to sulphate solution, as the consequence of cumulating SO₃-rich reaction products in the attacked cement matrix, were found. Similar character of mass increases in ZBC mortar specimens is missing.

Strengths and elasticity module of the mortars are reported in Table 5. The strengths (flexural and compressive) and elasticity module (dynamic and

Table 1 Chemical composition of the cements

| Type of cement | Ignition to 100°C/ | Ignition loss/ | Insoluble residue/ | SiO ₂ / | CaO/ | MgO/ | Al ₂ O ₃ / | Fe ₂ O ₃ / | SO ₃ / |
|----------------|--------------------|----------------|--------------------|--------------------|-------|------|----------------------------------|----------------------------------|-------------------|
| | mass% | | | | | | | | |
| 100% PC | 0.08 | 2.08 | 2.20 | 19.16 | 60.51 | 2.78 | 6.50 | 3.46 | 3.23 |
| 85% PC+15% Z | 0.48 | 2.24 | 11.38 | 22.03 | 49.23 | 2.13 | 6.65 | 3.55 | 2.31 |
| 75% PC+25% Z | 0.92 | 2.93 | 13.03 | 23.99 | 45.13 | 1.95 | 6.85 | 3.10 | 2.10 |
| 65% PC+35% Z | 1.95 | 3.36 | 16.35 | 25.95 | 38.18 | 2.09 | 7.50 | 2.93 | 1.69 |
| 50% PC+50% Z | 2.11 | 4.69 | 19.64 | 28.56 | 31.37 | 1.38 | 7.96 | 2.82 | 1.47 |

Table 2 Composition and properties of natural zeolite from Nižný Hrabovec

| Chemical composition/mass% | Mineralogical composition/% | |
|---------------------------------|-----------------------------|---|
| Ignition loss | 10.99 | Clinoptilolite 68.0 |
| SiO ₂ | 66.72 | Crystobalite+quartz 13.7 |
| CaO | 5.25 | Clay/mica 13.2 |
| Al ₂ O ₃ | 14.97 | Plagioclase 4.8 |
| Fe ₂ O ₃ | 1.69 | Rutile 0.1 |
| SO ₃ | 0.19 | Apatite 0.2 |
| Moisture content at 105°C/mass% | | Specific gravity/kg m ⁻³ 2284 |
| 4.8 | | Specific surface area/m ² kg ⁻¹ 1.151 |
| Compressive strength/MPa | | Porosity/% 25 |
| 33 | | Effective diameter of pores/nm 0.4 |

Table 3 Basic physical properties of the cements

| Type of cement | Initial set/h/min | Final set/h/min | Normal consistency/% | Specific gravity/kg m ⁻³ | Specific surface area (Blaine)/m ² kg ⁻¹ |
|----------------|-------------------|-----------------|----------------------|-------------------------------------|--|
| 100% PC | 3/05 | 4/00 | 30 | 3136 | 363 |
| 85% PC+15% Z | 3/10 | 3/00 | 33 | 3031 | 478 |
| 75% PC+25% Z | 3/15 | 4/30 | 36 | 2917 | 578 |
| 65% PC+35% Z | 2/35 | 4/00 | 36 | 2779 | 660 |
| 50% PC+50% Z | 1/00 | 3/20 | 40 | 2593 | 824 |

Table 4 Strength characteristics of mortar specimens at various curing times

| Type of cement (w/c=0.6) | Flexural strength/MPa | | | | Compressive strength/MPa | | | |
|--------------------------|-----------------------|-----|-----|-----|--------------------------|------|------|------|
| | Curing/day | | | | | | | |
| | 28 | 90 | 180 | 365 | 28 | 90 | 180 | 365 |
| 100% PC | 6.1 | 7.8 | 8.3 | 9.4 | 35.8 | 36.6 | 38.4 | 39.8 |
| 85% PC+15% Z | 5.4 | 6.2 | 7.1 | 8.0 | 30.0 | 32.4 | 35.6 | 45.5 |
| 75% PC+25% Z | 4.8 | 5.0 | 5.5 | 6.2 | 26.6 | 27.3 | 29.9 | 33.1 |
| 65% PC+35% Z | 3.3 | 4.7 | 5.3 | 5.4 | 23.8 | 28.1 | 30.6 | 32.3 |
| 50% PC+50% Z | 3.2 | 3.8 | 4.5 | 4.5 | 16.9 | 17.3 | 19.8 | 24.1 |

Young's) of ZBC mortar cured for 720 days in water are very similar to those of PC mortar. It was found that the 35 mass% substitution level of PC by zeolite has only negligible influence on the decline of main utility properties of pozzolan cement in comparison with the reference PC. The resistance of ZBC mortar

against sulphate attack is contrary considerably higher than that of PC mortar. Typical symptoms of sulphate attack – the growth of measured strengths and elasticity module up to the point of reverse, and then their lasting decrease was found only in the PC mortar specimens. When all air void supply is ex-

hausted by newly formed voluminous reaction products (mainly CSH_2 according to reaction (3)), the pressure on the surrounding pore walls initiates mass growth and crack propagation. The ZBC mortar al-

lows deposition of reaction products opposite to the PC mortar. This is possible only due to marked reduction in gypsum content (reaction (1)) by a preferential pozzolanic reaction of zeolite with free $Ca(OH)_2$. As a

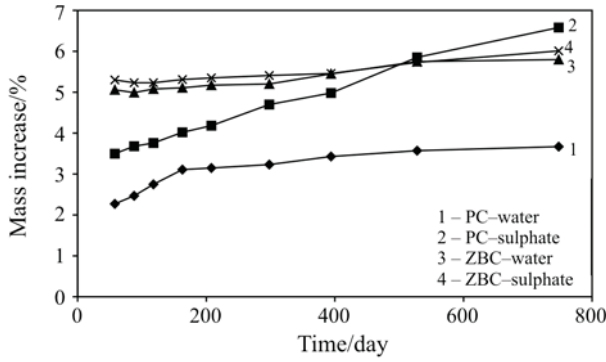


Fig. 1 Mass increase of 20x20x120 mm specimens

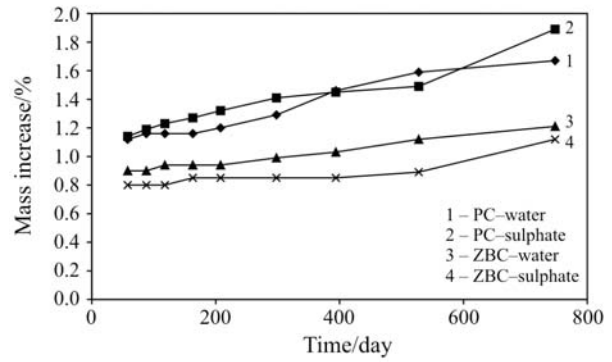


Fig. 3 Mass increase of 100x100x100 mm specimens

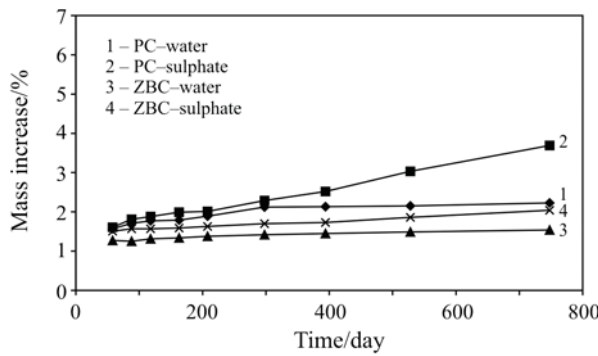


Fig. 2 Mass increase of 40x40x160 mm specimens

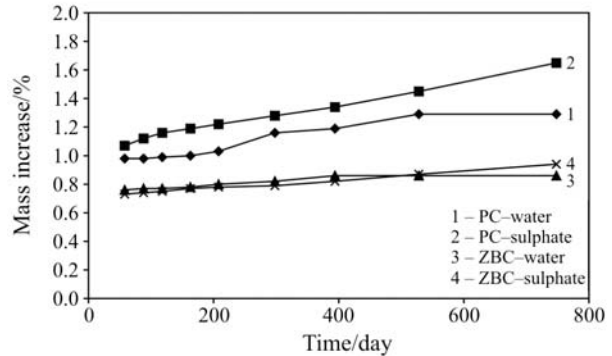


Fig. 4 Mass increase of 150x150x150 mm specimens

Table 5 Strength and modulus of elasticity of the mortars made with reference PC and ZBC

| Property tested | Curing medium | Time/day | Cement type | |
|--------------------------------------|------------------------------------|----------|-------------|------|
| | | | PC | ZBC |
| Flexural strength/MPa (40x40x160 mm) | water (20°C) | 90 | 6.4 | 5.5 |
| | | 365 | 6.5 | 7.0 |
| | | 720 | 6.7 | 7.1 |
| | 5% Na ₂ SO ₄ | 90 | 5.7 | 8.0 |
| | | 365 | 7.2 | 8.2 |
| | | 720 | 5.0 | 8.1 |
| Compressive strength/MPa | water (20°C) | 90 | 36.6 | 28.1 |
| | | 365 | 39.8 | 32.3 |
| | | 720 | 40.3 | 36.1 |
| | 5% Na ₂ SO ₄ | 90 | 33.7 | 32.3 |
| | | 365 | 39.8 | 35.2 |
| | | 720 | 32.6 | 35.3 |
| Dynamic modulus of elasticity/GPa | water (20°C) | 90 | 41.1 | 36.1 |
| | | 365 | 41.5 | 37.0 |
| | | 720 | 41.8 | 37.5 |
| | 5% Na ₂ SO ₄ | 90 | 40.1 | 35.3 |
| | | 365 | 41.6 | 36.4 |
| | | 720 | 39.1 | 37.3 |
| Young's modulus of elasticity/GPa | water (20°C) | 90 | 28.7 | 26.7 |
| | | 365 | 31.9 | 29.8 |
| | | 720 | 31.9 | 30.0 |

Table 6 Ignition loss, CaO and SO₃ content values and pore structure development of mortar specimens (40×40×160 mm)

| Mortar and curing | Time/day | Ignition loss/% | Content of | | Pore median radius/nm | Total porosity/% |
|--|----------|-----------------|------------|--------------------|-----------------------|------------------|
| | | | CaO/% | SO ₃ /% | | |
| PC water (20°C) | 28 | 5.35 | 55.12 | 2.12 | 54.4 | 12.3 |
| | 90 | 5.56 | 55.45 | 2.29 | 43.5 | 10.5 |
| | 365 | 5.69 | 54.52 | 3.23 | 35.6 | 8.8 |
| | 720 | 5.74 | 53.92 | 3.29 | 31.0 | 8.4 |
| PC 5% Na ₂ SO ₄ | 28 | 5.35 | 55.12 | 2.12 | 54.4 | 12.3 |
| | 90 | 5.58 | 54.81 | 3.77 | 37.7 | 10.6 |
| | 365 | 5.76 | 52.96 | 9.07 | 34.9 | 10.1 |
| | 720 | 6.10 | 48.43 | 9.38 | 41.9 | 11.6 |
| ZBC water (20°C) | 28 | 5.51 | 51.55 | 2.13 | 32.6 | 14.4 |
| | 90 | 4.92 | 52.01 | 2.57 | 25.5 | 13.1 |
| | 365 | 4.87 | 48.28 | 2.78 | 23.6 | 11.7 |
| | 720 | 4.20 | 46.20 | 3.29 | 24.4 | 11.7 |
| ZBC 5% Na ₂ SO ₄ | 28 | 5.10 | 51.55 | 2.13 | 32.6 | 14.4 |
| | 90 | 4.92 | 48.45 | 2.90 | 25.3 | 12.1 |
| | 365 | 4.94 | 46.32 | 4.08 | 24.7 | 11.3 |
| | 720 | 4.13 | 45.08 | 4.12 | 22.7 | 11.4 |

Table 7 The 720-day expansion of mortar specimens (20×20×120 mm)

| | PC mortar | | ZBC mortar | |
|-------------|--------------|------------------------------------|--------------|------------------------------------|
| | water (20°C) | 5% Na ₂ SO ₄ | water (20°C) | 5% Na ₂ SO ₄ |
| Expansion/% | +0.8362 | +9.3296 | +0.3274 | +0.6580 |

result, no evident mass growths (Figs 1–4) and crack propagation were observed in ZBC mortar. The effect of the duration of Na₂SO₄ attack on the increase in the SO₃ content, pore structure, and on the expansion of mortars is reported in Tables 6 and 7, respectively. As expected, the higher SO₃ content bound in the cement paste, the higher expansion of the mortar. Expansion was measured on the 20×20×120 mm specimens; therefore the results do not fully correspond with the measured values in Table 5. The expansion of PC mortar is related to the overgrowth of the formed reaction products, mainly CSH₂ and is clearly expressed by the content of SO₃ bound in cement paste in water and sulphate solution after 720 days. The content of bound SO₃ estimated in water and sulphate solution differs by 6.09% in PC mortar and by 0.83% in ZBC mortar only. The difference between bound SO₃ content in PC and ZBC mortar kept for 720 days in 5% Na₂SO₄ solution is 5.26%. It is clear that PC mortar is not sulphate resistant. The resistance of ZBC mortar against sulphate attack is extremely high, and comparable with that of sulphate-resistant Portland cement. Pore median radius and total porosity of both mortars kept in water, and those of ZBC mortar exposed to the sulphate are decreasing. The 720-day pore median radius and total porosity of PC mortar kept in sulphate solution, in accordance with ignition loss and SO₃ content growths, are getting increased.

Typical manifestation of a sulphate attack on the pore structure – its coarsening during the mortar expansion followed by crack propagation and consequent declines in elasticity module and strengths – is confirmed in the PC mortar. Structural disintegration of the PC mortar, mainly on the edges of the specimens has appeared. The ZBC mortar shows quite inverse behaviour. The specimens are compact, no crack propagation was visually observed, no pore structure coarsening was found, and finally no declines in strength and elasticity module values were measured. High sulphate resistance of the mortar made with pozzolan cement containing 35 mass% substitution of PC by natural zeolite (ZBC) was proved.

The X-ray and thermal analysis studies show different phase composition development in PC and ZBC mortar. As seen in Fig. 5, the PC mortar kept in water is characterized by a high content of Ca(OH)₂. When exposed to sulphate solution, Ca(OH)₂ is partially consumed forming voluminous CSH₂ evoking damaging expansion of the specimen, as proved previously. No Ca(OH)₂ is found in ZBC mortar kept either in water, either in sulphate. This means that no free Ca(OH)₂ is disposable for the reaction with sulphate ions – reaction (1), and no dangerous solid phase volume increase due to CSH₂ formation leading to crack propagation occurs in ZBC mortar, as proved previously. The results of thermal analysis of PC mor-

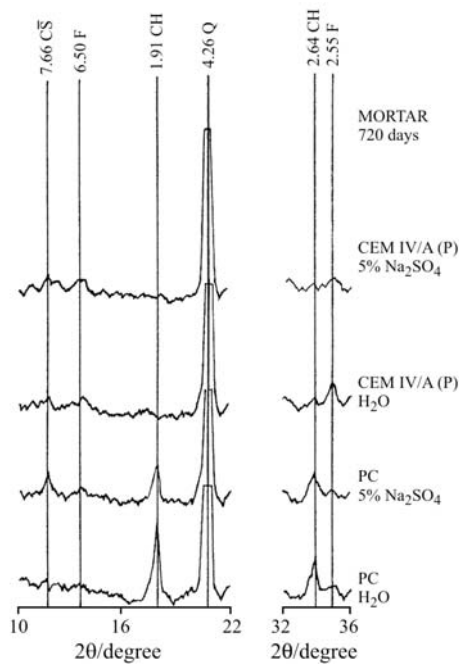


Fig. 5 X-ray patterns of the mortars kept in water and Na₂SO₄ solution; C \bar{S} – gypsum, F – feldspar, CH – portlandite and Q – quartz

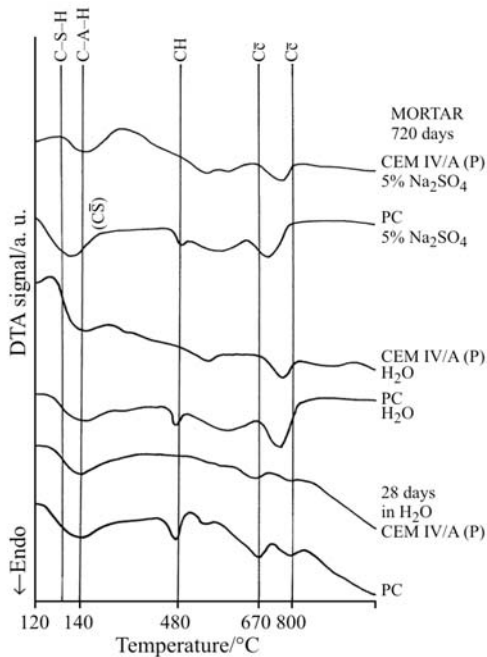


Fig. 6 DTA plots of PC and ZBC mortar kept in water and Na₂SO₄ solution; C \bar{S} – gypsum, CH – portlandite and Cc – calcite

tar and ZBC mortar are illustrated in Fig. 6. This method is very important to supplement the results of other methods [30]. No evidence of Ca(OH)₂ in ZBC mortar is found. Ca(OH)₂ occurs in PC mortar kept in water, whereas it is consumed when exposed to the sulphate solution. Instead of Ca(OH)₂–gypsum

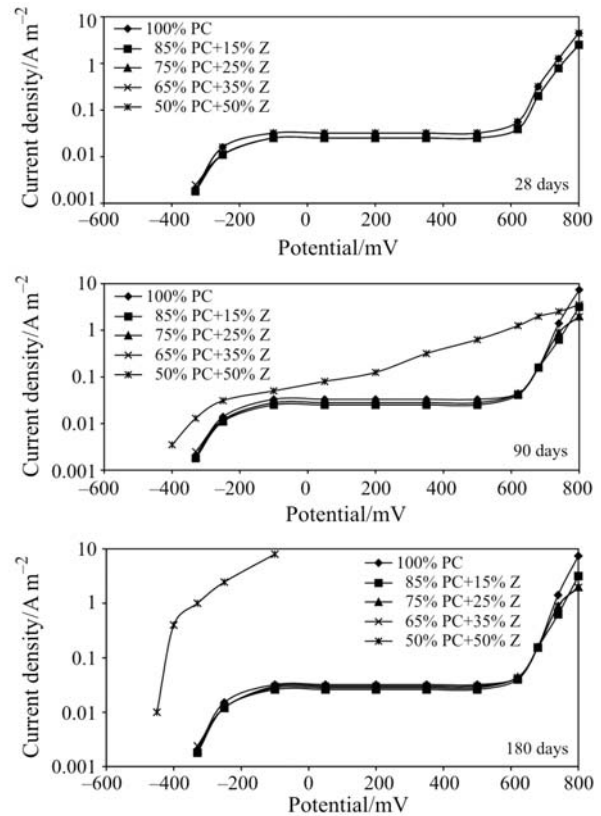


Fig. 7 Potentiodynamic curves of steel in extracts prepared from mortar specimens

(C \bar{S} H₂) is present. These results confirm those presented in Fig. 5 showing no evident formation of voluminous gypsum as a reaction product in the ZBC mortar, whereas large amount of damaging C \bar{S} H₂ occurs in PC mortar. The absence of gypsum – evoking strength decline and extreme expansion – is the reason of high sulphate resistance of ZBC mortar relative to that of PC mortar. In the PC mortar, free Ca(OH)₂ is preferably transformed to C \bar{S} H₂ in the excess of SO₄²⁻ ions, as described by the reactions (1) and (3).

The results indicate that pozzolan cement with 35 mass% of zeolite (ZBC) has markedly improved sulphate resistance opposite to PC. Sulphate resistance of ZBC can be claimed as very similar to that of a sulphate-resistant Portland cement [28].

Potentiodynamic curves of steel obtained in water extracts prepared from mortar specimens with 15–50% of zeolite are illustrated in Fig. 7. The results show sufficient conditions for passivation of steel up to 35 mass% substitution of Portland cement by zeolite at 180 days of wet curing. This electrochemical state of steel is characterized on the curve by the passive zone with constant value of current density over a wide range of potentials (the part of curve parallel to the x-axis). In this case steel is protected against corrosion in the same measure as in mortar with 100% of Portland cement. On the other hand – the large in-

crease in electrical current without the occurrence of passive zone (50 mass% substitution of Portland cement by zeolite) indicates that steel is corroded in such blended cement system.

Conclusions

- Pozzolan cement of CEM IV/A (P) type according to EN 197-1 containing 60.82 mass% of PC clinker, 35.09 mass% of zeolite and 4.09 mass% of gypsum has, in principle, the same important engineering properties as the fresh and hardened ordinary Portland cement.
- Sulphate resistance of the pozzolan cement is markedly higher than that of the Portland cement due to pozzolanic reaction of zeolite with CaO resulting in reductions of the formed Ca(OH)₂ opposite to hydrated Portland cement. Thermoanalytical data contribute to the identification of hydrate phase changes and give the answer if the reaction products are present and what is their percentage representation.
- Pozzolan cement is intended for a full replacement of sulphate-resistant Portland cement in the field.
- Steel is not corroded in the mortars made from the pozzolan cement to 35 mass% of zeolite. Steel reinforcement is protected against corrosion by the pozzolan cement equally as the reference Portland cement.
- Pozzolan cement of CEM IV/A (P) type gives promising perspective for application uses in the building industry.

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