PROPERTIES AND UTILIZATION OF ZEOLITE-BLENDED PORTLAND CEMENTS

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Abstract—The resistance to acidic and sulfate attack of Portland-pozzolan cement containing 35 wt.% of zeolite was compared with that of unamended Portland cement. Mortar specimens kept in 0.5% and 1.0% HCl solution, 5% Na_2SO_4 solution, and in reference water for 365 and 720 days were tested using a set of physical-mechanical and chemical techniques. The ability of mortars containing zeolitic cements with 15 to 50 wt.% of zeolite to protect steel against corrosion was verified by a potentiodynamic method. Mortar with zeolitic cement performs better when exposed to 1% HCl solution due to the presence of a finer pore matrix, a hydrate phase poorer in CaO-containing hydration products with lower leachability, and the high resistance of zeolite material itself to acidic attack, compared with Portland cement and siliceous sand. The improved sulfate resistance of the mortar with zeolitic cement is caused by the decreased C_3A in the cement blend in comparison with that in Portland cement, a reduction in SO_3 binding into the cement paste and decreased amount of CaO-containing hydration products capable of reacting with a sulfate solution forming voluminous reaction products, and consequent crack propagation, large expansion and structural disintegration. Passivation of steel in mortars with blends of Portland cement to zeolite percentage ratios of 85/15, 75/25 and 65/35 by weight is comparable to that of Portland cement mortar. This is particularly important because the mortar with zeolitic cement exhibits late strengths similar to that of Portland cement mortar. This confirms that zeolitic cement can replace Portland cement in many applications with the advantage of higher resistance to acidic and sulfate attack.

Key Words—Portland Cement, Zeolite Application, Zeolite-blended Cement.

INTRODUCTION

Natural zeolites contain large quantities of reactive SiO_2 and Al_2O_3 and have been used since Roman times as additives to cement. Zeolites are pozzolanic materials characterized by lime absorption values between 134 and 224 mg CaO g^{-1}. The highly porous structure of the typical natural zeolite raw material provides a large reaction surface for interaction of the zeolite with $Ca(OH)_2$ formed during the hydration of clinker minerals. Zeolite-amended cements have the characteristics of typical pozzolanic cements, with high late strengths and low heats of hydration but the disadvantage of low early strength (Tong *et al.*, 1983). Compared with Portland cement paste, a zeolite-amended cement requires more water to produce a paste of the same consistency. Thus, when zeolite-blended cement is used for concrete production, it is likely that a superplasticizer is required (Fragoulis *et al.*, 1997).

Zeolite is widely used in the cement industry in China as a cement blending material, where it displaces ~10 wt.% of Portland cement in concrete. A high-strength concrete with water to cement (W/C) ratios between 0.31 and 0.35, with compressive strength of ~80 MPa, and slump of ~180 mm can be obtained by mixing with a suitable amount of superplasticizer. The late strength of this concrete is ~10 to 15% greater than that of the corresponding concrete mixed with Portland

cement. Zeolite increases the number of micropores (d <625 Å) and decreases the amount of harmful large pores (d >938 Å) 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 weight ratio in the transition zone to increase its C-S-H phase content and decrease 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 is increased (Feng *et al.*, 1990; Poon *et al.*, 1999). The use of zeolite in concrete also inhibits the alkali-aggregate reaction and corrosion of reinforcing steel, thereby protecting concrete structures from deterioration (Tatematsu *et al.*, 1996). Zeolite has various applications in the cement and building industry, including shotcrete (Naidenov, 1991), lightweight concrete-blocks, wall panels, roof slabs (Fu *et al.*, 1996), and pre-formed building elements (Cioffi *et al.*, 1997). In addition, zeolite can act as a substitute for fine aggregate (sand) in cement mortars replacing up to 10 wt.% of fine aggregate without decreasing the mortar strength (Su *et al.*, 2001).

Natural zeolite was used widely with cement in Czechoslovakia, and since 1993 it has been used in the Czech Republic as the industrially made cement suspension with bentonite and zeolite, ZEOFIX® (Janotka *et al.*, 2002a). The geosynthetic mat, TATRABENT, made with a bentonite-zeolite mineral filler having a filtration coefficient <5 × 10^{-11} m s^{-1} has been manufactured in Slovakia since 1997 (Janotka *et al.*, 2002b). The production of two types of zeolite-

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Table 1. Composition and properties of the Portland cement studied.

Content of component (wt.%)		Content of major clinker phases according to Bogue (%)	
Insoluble residue	1.63	C_3S	49.45
SiO_2	20.64	C_2S	21.88
Al_2O_3	5.88	C_3A	10.28
Fe_2O_3	3.13	C_4AF	9.53
CaO	61.49	Specific gravity	3140 (kg m^{-3})
MgO	1.34	Specific surface area	336.2 (m^2 kg^{-1})
SO_3	2.30	Initial set	195 min
K_2O	1.82	Final set	260 min
Na_2O	0.53	3-day cement strength:	flexural/compressive 4.4/23.5 (MPa)
Loss on ignition	1.04	28-day cement strength:	flexural/compressive 7.9/41.7 (MPa)

blended cements [Portland pozzolan cement (CEM II/ B-P 32.5 R) and pozzolan cement (CEM IV/B 32.5)] according to European Standard 197–1 began in Slovakia in 2001 (Janotka *et al.*, 2002a).

Reaction in the zeolite-CaO-H$_2$O system produces an Al-rich tobermorite by heterogeneous nucleation on the solid CSH phase-liquid solution interface. A layer of CSH gel products is created directly on the surface of zeolite particles (Drzaj *et al.*, 1973). The reaction of clinoptilolite with CaO under saturated steam pressure gives 1.1 nm Al-rich tobermorite as the major phase of the hydration process. Unreacted quartz, Ca(OH)$_2$, and minor tobermorite are found in quartz-lime mixtures (Perraki *et al.*, 2003).

Experimental results with cements, made from Portland clinker and 10, 20 and 40 wt.% of zeolite, indicate that partial replacement of clinker with natural zeolite allows preparation of blended cements with better technical performance than those manufactured with industrial by-products. The increase in compressive strength may be explained by higher reactivity of the natural zeolite material with lime in comparison with industrial pozzolanic products containing vitreous components (Sersale and Frigione, 1987). Experiments on the hydration of clinoptilolite with calcium hydroxide Ca(OH)$_2$ indicate that compressive strength is dependent on the Ca(OH)$_2$ content, clinoptilolite particle size, and curing conditions. X-ray powder diffraction confirms that Ca(OH)$_2$ is consumed during curing and is absent in fully cured high-strength materials. Scanning electron microscopy (SEM) combined with energy dispersive X-ray (EDX) analysis indicates the formation of hydration products with Ca/Si ratios in the range 0.8–1.2, and a significant amount of unreacted clinoptilolite still remains in blended cements even after long hydration times (Ortega *et al.*, 2000).

Table 2. Composition and properties of natural zeolite from Nižný Hrabovec.

Chemical composition (wt.%)		Mineralogical composition (%)	
Loss on ignition	10.99	Clinoptilolite	68.0
SiO_2	66.72	Cristobalite + quartz	13.7
CaO	5.25	Clay/mica	13.2
Al_2O_3	14.97	Plagioclase	4.8
Fe_2O_3	1.69	Rutile	0.1
SO_3	0.19	Apatite	0.2

Moisture content at 105° (wt.%)	Specific gravity (kg m^{-3})	Specific surface area (m^2 kg^{-1})
4.8	2283.7	1150.5

Compressive strength (MPa)	Porosity (%)	Effective diameter of pores (nm)
33	25	0.4

Table 3. Composition and properties of zeolitic cement.

Component content (wt.%)		Basic properties
Insoluble residue	18.00	Specific gravity (kg m^{-3}) 2231
SiO$_2$	15.69	
Al$_2$O$_3$	8.09	Specific surface area (m^2 kg^{-1}) 950.2
Fe$_2$O$_3$	3.24	
CaO	41.80	Initial set 125 min
MgO	2.29	
SO$_3$	2.09	Final set 185 min
Loss on ignition	8.80	

The purpose of this paper is to show that the use of natural zeolite as a fine filler produces a cement blend with increased resistance to environmental attack and improved durability.

EXPERIMENTAL

Materials

Portland cement (PC) of CEM I 42.5 class and standard siliceous sand (SS), as well as zeolitic cement (ZC) with 65 wt.% of PC and 35 wt.% of zeolite mined in Nižny Hrabovec, Slovakia were used. Zeolite was first dried at 105°C and subsequently crushed and ground to a powder of grain-size <52.65 µm. It was then added to Portland cement and the blend was homogenized for 30 min in a mechanical agitator. The prepared ZC was mixed either with SS or zeolitic sand (ZS) in size-fractions of 0–0.3 mm, 0.3–1 mm and 1–2.5 mm. Mortars of the following mixture composition were prepared for the tests: PC:SS = 1:3 by weight with W/C = 0.6; ZC:SS = 1:3 by weight, W/C = 0.6 and ZC:ZS = 1:3 by weight, W/C = 2.1 having the same plasticity. The latter cement mortar has no technological advantages due to the extreme water demand caused by the zeolite sand with high suction capacity. Additionally, a set of zeolite-blended cements with 15–50 wt.% of zeolite contents were prepared in the ZEOCEM cement plant. The composition and properties of Portland cement, natural zeolite, and zeolitic cement are listed in Tables 1, 2 and 3, and those from the cement plant in Tables 4 and 5. The industrially formulated zeolite-based products (ZEOFIX, TATRABENT, CEM II/B-P 32.5 R and CEM IV/B 32.5) have their own national certificates, and complete verification tests on civil engineering properties were performed in National Testing Institutes in Slovakia and abroad.

Methods

Mortars with a weight ratio of cement to sand of 1:3 were prepared either with constant plasticity 170 (±10) mm for acid and sulfate resistance tests or with a constant water to cement ratio of 0.5 for steel corrosion tests (blended cements with 15–50 wt.% of zeolite). Mortar specimens 40 × 40 × 160 mm in size were cured for 24 h at 20°C and 95% relative humidity (RH). After remolding, the resistance test specimens were kept in water for 27 days (basic exposure), and then either in water (reference) or in 0.5% and 1.0% HCl solution for 365 days, and in 5% sodium sulfate solution (33,800 mg SO$_4^{2-}$ L^{-1}) for 720 days, respectively. The volume ratio between test specimens and solutions was held at 1:10. Regular control of pH level and SO$_4^{2-}$ ion concentration was provided. The solutions were restored when measured variables were changed by >10%. The mortars with ZEOCEM cements (15–50 wt.% of zeolite) for steel corrosion tests were kept for 180 days at 20°C/95% RH. Mechanical properties were tested up to a 365 day cure. The weight, dynamic modulus of elasticity, strength, and total porosity of all specimens were measured. The chemical composition was determined by standard analytical methods using procedures given in European Technical Standard EN 196-2 (Methods of testing cement; Chemical analysis of cement) and the pore structure was studied by mercury intrusion porosimetry (high-pressure porosimeter mod. 2000 with macroporosimetry unit mod. 120, Carlo Erba Science, Milan). Steel corrosion characteristics were estimated in mortar extracts by a potentiodynamic method using Potentiostat OH-405 (Radelkis, Budapest).

Table 4. Chemical composition (wt.%) of the cements.

Type of cement	Ignition to 100°C	Loss on ignition	Insoluble residue	SiO$_2$	CaO	MgO	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$
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 5. Basic properties of the cements.

Type of cement	Initial set (min)	Final set (min)	Normal consistency (%)	Specific gravity (kg m^{-3})	Specific surface area (Blaine) (m^2 kg^{-1})
100% PC	185	240	30	3136	363
85% PC+15% Z	190	180	33	3031	478
75% PC+25% Z	195	270	36	2917	578
65% PC+35% Z	155	240	36	2779	660
50% PC+50% Z	60	200	40	2593	824

Justification of procedures and evaluation methods

Assessments of chemical resistance of cement-based materials and steel reinforcement corrosion, as well as criteria of environmental attack, are mainly based on national recommendations, guidelines and technical standards. The unification of individual technical standards has begun in EU member and candidate countries. At present, procedures and evaluation methods differ from country to country.

It is therefore important to choose suitable experimental procedures and evaluation methods for the current investigation based on a long-term study of chemical resistance and steel corrosion, maintaining specimens under well defined curing conditions. Any experimental program must provide reproducible measurements and evaluations of the test results in order to describe accurately the effects of chemical attack or steel corrosion and the influence of individual factors on the mechanism and rate of corrosion processes.

Our tests of chemical resistance are based on the Slovak Technical Standard (STN) 73 1340 (Concrete constructions, Tests of corrosion resistance of concrete and General requirements – in Slovak). This standard was accepted on the basis of the previous international research collaboration among seven middle and eastern European countries (Bulgaria, Czechoslovakia, German Democratic Republic, Hungary, Poland, Romania and the Soviet Union) formerly grouped on the Council of Mutual Economical Cooperation (CMEC). In 1986 these countries formulated the common standardized chemical resistance tests and evaluation methods that were described in the CMEC Standard ST SEV 5852–86 (Corrosion protection in civil engineering, Concretes and General requirements for testing – in Russian). Test principles and exposure conditions were described therein, *e.g.* the shape and size of specimens (40 × 40 × 160 mm), exposure times in reference water and aggressive media (1, 3, 6, 12 and 24 months), non-destructive tests (visual inspection, changes in weight, volume density, dynamic modulus of elasticity and length), and destructive tests (*e.g.* flexural and compressive strength) and related methods such as porosity and chemical tests. For sulfate resistance, STN 73 1340 prescribes the use of a 34,000 mg SO_4^{2-} L^{-1} (we used a solution with 33,800 mg SO_4^{2-} L^{-1}, a 0.6% deviation from the standardized value). This standard also

prescribes the use of solutions with acidity of pH = 3, 4 and 5. In contrast, STN 73 1215 Standard (Concrete constructions, Classification of aggressive environments) includes a strong acid environment with pH <4, and we used an HCl solution with a pH of ~1.3. For comparison, the European Technical Standard EN 206-1 (Concrete, Part 1: Specification, performance production and conformity), currently valid in Slovakia, prescribes the most aggressive sulfate solutions (XA3) having a SO_4^{2-} ion concentration between 3000 and 6000 mg L^{-1} and similarly prescribes acid solution pH values between 4 and 4.5. The environmental influence in EN 206-1 is markedly weaker than those in both STN standards and the CMEC standard. Tests of chemical resistance using the STN standards also enabled us to use weaker mortars (W/C ratio of 0.6 having lower strength and higher permeability due to the resultant coarser pore structure), facilitating significant attack by the aggressive solution on the cement matrix. One- to two-year exposures of a weaker mortar to a stronger solution make possible critical evaluation of chemical resistance of any tested cement-based material. The related American Standards, *e.g.* ASTM C 452–60 T and ASTM C 267–65, are not used in Slovakia.

Steel corrosion measurements were performed on the basis of the standards TGL 28105/01 (Physicochemical tests, Testing of the influence of passivity behavior of concrete steels (the standard of the German Democratic Republic, written in German)) and TGL 28101/07 (Cements, Influence upon passivity behavior of concrete steel, Characteristic values – in German). The first standard describes steel corrosion measurements by the potentiodynamic method using a potentiostat apparatus and describes the wiring scheme and measurement conditions. The second standard gives the assessment criteria of the steel corrosion state such as stationary potential, potential of passivation, potential of breakdown, current density of passivation, and pH values. Based mainly on TGL standards and also other national standards, the common CMEC Standard ST SEV 4421–83 (Corrosion protection in civil engineering, Protection properties of concrete related to steel reinforcement, Electrochemical method – in Russian) was formulated in 1983. The method of electrical resistance for steel corrosion measurements was developed in Slovakia. This method, together with procedures

Table 6. Cube strength of mortars tested in water and HCl solutions.

Mortar	Medium	Cube compressive strength (MPa)			
		28 days	90 days	180 days	365 days
PC + SS	water	37.2	54.0	54.8	56.4
	0.5% HCl	37.2*	31.0	29.7	28.0
	1.0% HCl	37.2*	22.6	22.2	19.2
ZC + ZS	water	4.8	13.5	14.0	16.0
	0.5% HCl	4.8*	8.1	9.6	7.6
	1.0% HCl	4.8*	6.3	5.8	5.6

* 28-day basic exposure in water

described in the ST SEV 4421–83 Standard, is described in STN 73 1341 Standard (Corrosion protection of reinforcements provided by the properties of concrete, Methods of test). Our steel corrosion measurements were performed using this standard.

Uniform European Technical Standards for the measurement and evaluation of chemical resistance of concrete and steel corrosion do not currently exist. However, two European Technical Standards are in preparation, the standard for chemical resistance of aggregates and for steel corrosion measurements. American Technical Standards exist (G3–89, G5–87, G57–78, G59–91, G102–90) but their application in steel corrosion evaluation is uncommon in Slovakia.

RESULTS AND DISCUSSION

The effect of mortar composition on the compressive strength of the specimens is reported in Table 6. Bearing in mind that strength decrease is a typical symptom of acidic attack, it is important to note the progressive development of compressive strength in ZC + ZS mortar kept in water and even in 0.5% and 1.0% HCl solution. The low compressive strength of the ZC + ZS mortar is a consequence of water uptake due to zeolite sand addition (W/C = 2.1) relative to that in PC + SS mortar (W/C = 0.6) at the same plasticity. Clear dependence of strength development on mortar mixture composition was found, showing a positive influence of zeolite material on the growth in compressive strength and the resistance of zeolite mortar to acidic attack. This is mainly proved in

ZC + ZS mortar exposed to 0.5% HCl solution indicating a 365-day compressive strength value higher than that after 28-day basic exposure in water. This suggests that replacement of a siliceous constituent by zeolitic material contributes to an improved acidic resistance of the mortar.

The pore structure of the mortars is reported in Tables 7 and 8. The ZC + ZS mortar exhibits a greater volume of micropores, resulting in greater total porosity and smaller median pore radius relative to PC + SS mortar. Thus, the pore structure developed in ZC + ZS mortar is less permeable than that in PC + SS mortar. The results of pore-structure study, consistent with the increase in compressive strength of ZC + ZS mortar in HCl solutions, confirm the greater acidic resistance of this mortar compared with PC + SS mortar with a coarser pore matrix. This indicates favorable influence of zeolitic cement and sand on the increase of resistance to acidic attack.

The weight loss of ZC + ZS mortar kept in HCl solutions is greater than that of PC + SS mortar (Table 8). This is caused by zeolite sand that neutralizes HCl and thus reduces the detrimental attack on the highly alkaline cement paste. The pH values of sand in water extracts (50 g either of siliceous sand or zeolite sand in 200 mL of H_2O) were 8.2 and 7.6, respectively. The pH level at 0.5% HCl solution was 1.35, whereas the pH value of 50 g of SS in 200 mL of 0.5% HCl after 2 h of mixing was 1.35 and the pH value of 50 g of ZS was 6.67. Thus, the zeolite sand itself played an active role in HCl solution neutralization and reduction of acidic

Table 7. Pore-structure study of the mortars, kept for 365 days in water and HCl solutions.

Mortar	Medium	Volume of micropores $(mm^3\,g^{-1})$	Portion of macropores (%)	Median radius pore (nm)	micropore (nm)	Total porosity (%)
PC + SS	water	39.35	15.2	75.2	55.1	10.8
	0.5% HCl	42.38	14.3	102.9	69.2	9.4
	1.0% HCl	33.96	14.9	97.8	66.4	9.4
ZC + ZS	water	170.05	8.4	40.1	35.5	25.5
	0.5% HCl	230.10	4.3	29.4	26.6	30.1
	1.0% HCl	194.02	7.9	37.5	31.6	27.0

Table 8. Comparison of acid resistance of tested mortars.

| Quality criterion of tested mortars | Values of estimated quantities of the mortar in | | | | | |
| | water | | 0.5% HCl | | 1.0% HCl | |
	PC+SS	ZC+ZS	PC+SS	ZC+ZS	PC+SS	ZC+ZS
RCS changes[†] (%)	+51	+233	−25	+58	−48	+16
Rel. E_{bu} changes[†] (%)	+11	+48	−1.7	+34	−7.2	−8.0
Weight changes[†] (%)	+4.4	+3.9	+1.4	−3.3	−2.1	−6.6
Soluble portion (%)	21.8	52.7	19.4	55.7	19.5	56.4
CaO in soluble portion (%)	60.9	18.5	51.9	16.4	53.4	13.0
Cl^- in soluble portion (%)	0	0	3.3	0.4	3.4	0.9
CaO bound in $Ca(OH)_2$ (%)	2.7	1.9	2.5	1.7	2.4	1.2
Pore median radius (nm)	75	40	103	29	98	38
Micropore volume ($mm^3 g^{-1}$)	39	170	42	230	34	194
Total porosity (%)	10.8	25.5	9.4	30.1	9.4	27.0

Explanation of abbreviations: RCS – relative compressive strength
Rel. E_{bu} – relative dynamic modulus of elasticity
[†] The data represent the percentage increase (+) or decrease (−) at 365 day exposure relative to 28 day basic curing in water at 20ºC
Data on chemical analysis and the pore-structure study represent the measured values after 365 days of exposure

attack compared with siliceous sand. In contrast, zeolite sand has the disadvantage of requiring more water. The CaO decrease in the soluble portion of PC + SS mortar was 7.6% and in ZC + ZS mortar was only 5.5%. Markedly higher Cl^- ion contents in the less soluble portion of the PC + SS mortar confirms the evident Cl^- ion attack compared with ZC + ZS mortar with greater soluble portion. The chloride content in the soluble portion of ZC + ZS mortar was eight times less in the 0.5% HCl solution and four times less in the 1.0% HCl solution than in the soluble portion of PC + SS mortar. The previous results (strength and pore-structure characteristics) are supported by the results of chemical analysis also showing the increased acidic resistance of ZC + ZS mortar due to lower leachability of CaO-rich phases out of hydration products and lower binding of detrimental Cl^- ions into the cement matrix. Our results demonstrate that ZC + ZS mortar is more resistant against HCl solution attack up to 1% HCl solution concentration than PC + SS mortar. The disadvantageous high water uptake of ZC + ZS mortar is easily mitigated by replacing ZS by SS, thereby preparing a ZC + SS mortar with W/C = 0.6 at constant plasticity of 170 (±10) mm and improved acidic resistance similar to that of ZC + ZS mortar (Janotka, 1999).

The ZC + SS mortar was tested for sulfate resistance. A comparison of flexural and compressive strength of PC + SS and ZC + SS mortars is listed in Table 9. Replacement of ZS by SS in zeolite mortar kept in water caused a reduction of W/C to 0.6 at the same plasticity of fresh mortars and an enormous increase in compressive strength (Tables 6 and 9). Flexural and compressive strength of PC + SS mortar and ZC + SS mortar with 35 wt.% of zeolite attained the same levels underwater. In contrast, the resistance of ZC + SS mortar against sulfate attack was considerably higher than that of PC + SS mortar. The typical symptom of sulfate attack,

namely the growth of measured strength up to the point of reverse, and then its lasting decrease, was found only in the PC + SS mortar. In general, the damage to the structural integrity of the specimens commenced when the point of reverse was achieved.

The effect of the Na_2SO_4 solution on the amount of SO_3 bound in mortars, pore structure, expansion of mortars, as well as weight changes are reported in Table 10 and Figure 1. The bound SO_3 content in PC + SS mortar was approximately double that in ZC + SS mortar when attacked for 720 days by a sulfate solution. This is particularly important because the SO_3 content bound in the cement paste of mortars is the most significant indicator of sulfate resistance. As expected, a higher SO_3 content leads to greater expansion of

Table 9. Flexural and compressive strength of tested mortars, kept in water and sulfate solution.

| Tested property | Curing medium | Time (days) | Mortar | |
			PC + SS	ZC + SS
Flexural strength (MPa)				
	water	90	6.4	5.5
		365	6.5	7.0
		720	6.7	7.1
	5%	90	5.7	8.0
	Na_2SO_4	365	7.2	8.2
		720	5.0	8.1
Compressive strength (MPa)				
	water	90	36.4	33.2
		365	36.6	33.2
		720	40.3	36.1
	5%	90	33.7	32.3
	Na_2SO_4	365	39.8	35.2
		720	32.6	35.3

Table 10. Loss on ignition, CaO, SO$_3$ content values, pore-structure development and expansion of mortar specimens.

Mortar and curing	Time (days)	Loss on ignition (%)	Content of CaO (%)	SO$_3$ (%)	Pore median radius (nm)	Total porosity (%)	Expansion (‰)
PC + SS water	28	5.53	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	0.84
PC + SS 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	9.33
ZC + SS water	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	24.4	11.7	
	720	4.20	46.20	3.29	23.6	11.7	0.33
ZC + SS 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	0.66

mortars. Figure 1 shows a steady weight increase of PC + SS mortar specimens in time as the consequence of accumulation of SO$_3$-rich reaction products in the cement paste. A similar weight increase in the ZC + SS mortar was not observed.

The 720-day median pore radius and total porosity of the PC + SS mortar, in accord with loss on ignition and increase in SO$_3$ content, tended to increase. This confirms the characteristic manifestation of sulfate attack on the pore structure, coarsening during mortar expansion followed by crack propagation with a decrease in flexural and compressive strength, and consequent disintegration of the PC + SS mortar. No crack propagation or loss in the specimen integrity were observed in the ZC + SS mortar. This illustrates the high sulfate resistance of the mortar when Portland cement is replaced by zeolitic cement containing 35 wt.% of natural zeolite. These results indicate that the resistance of the ZC + SS mortar is similar to that of sulfate-

resistant Portland cement as previously shown (Janotka and Krajci, 2000) using 15 wt.% of zeolite. Moreover, along with high sulfate resistance, the cement blend with 35 wt.% of zeolite has an increased acid resistance relative to the PC + SS mortar.

Strength development in ZEOCEM cement mortars with 15–50 wt.% of zeolite (Z) in PC is listed in Table 11. The one-year compressive strength of the mortar made with 85 wt.% PC + 15 wt.% Z blend is slightly higher than the strength of PC mortar, although a larger zeolite content in the cement blend yielded a lower late compressive strength. The cement blend with 15 wt.% of PC displaced by zeolite has strength characteristics comparable with Portland cement.

Potentiodynamic curves of steel obtained in water extracts of the mortars are illustrated in Figure 2. The results show favorable conditions for passivation of steel in the mortars with zeolite-blended cement having a minimum 65 wt.% of Portland cement content in the
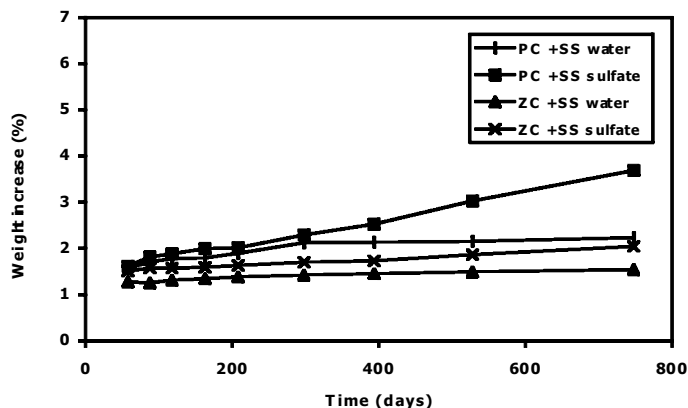

Figure 1. Weight increase of $40 \times 40 \times 160$ mm specimens.

Table 11. Strength characteristics of mortar specimens at various curing times.

Type of cement	Flexural strength (MPa)				Compressive strength (MPa)			
	Curing (days)							
	28	90	180	365	28	90	180	365
100% PC	6.1	7.8	8.3	9.4	35.8	39.3	41.7	44.8
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	17.8	18.1	24.6	28.3
50% PC+50% Z	3.2	3.8	4.5	4.5	16.9	17.3	19.8	24.1

blend, at 180 days of wet curing, as seen on related curves with a large passive zone. This region is represented by a constant value of current density over a wide range of potentials (the part of the curve parallel to the *x* axis). The large increase in electrical current without the occurrence of a passive zone (cement blend with 50 wt.% of zeolite) indicates unsuitable conditions for steel passivation and the steel is corroded. These results show that steel is protected against corrosion in

mortars made with cement blends containing up to 35 wt.% of zeolite in the same way as in Portland cement mortar.

Production of Portland-pozzolan cement (CEM II/B-P 32.5 R with a maximum of 35 wt.% of zeolite) and pozzolan cement (CEM IV/B 32.5 with 36–55 wt.% of zeolite) began in 2001 with the first 15,000 tons of industrially made cements in the ZEOCEM Ltd. cement plant, Bystre, Slovakia. The application fields for such
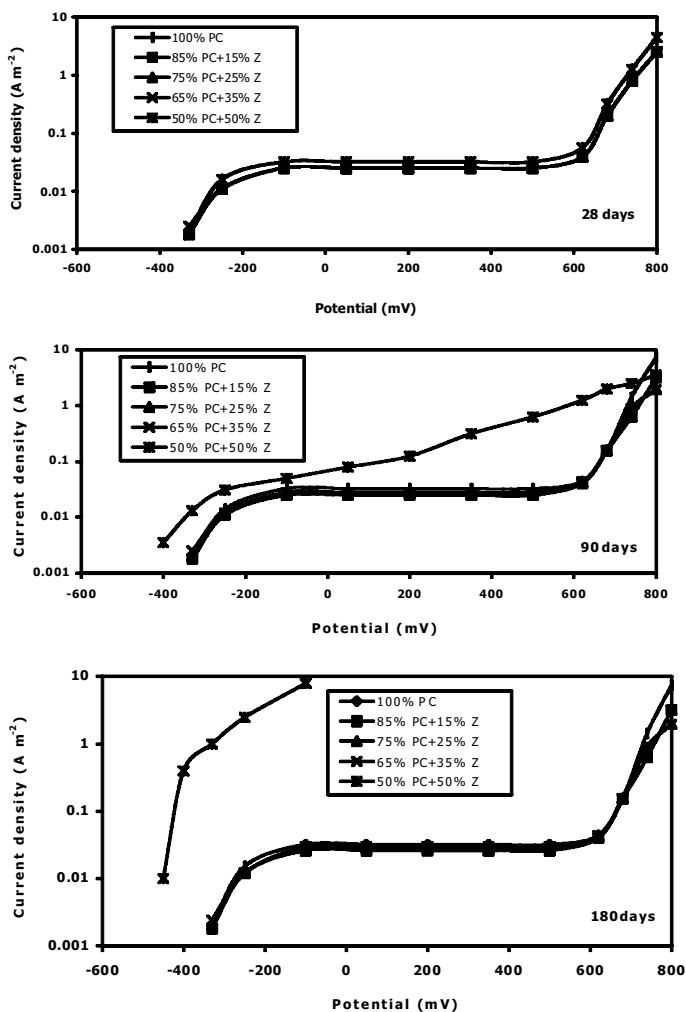

Figure 2. Potentiodynamic curves of steel in extracts prepared from mortar specimens.

cements are the same as for blast furnace-slag Portland cement (CEM II/B-S 32.5 R), but their chemical resistance is so high that they are suitable for concrete structures, grouting mixtures, and cut-off walls exposed to sulfate, CO_2-saturated and acidic waters. The above-mentioned cements were also used in solidification processes of secondary liquid waste from the Jaslovske Bohunice nuclear power plant in Slovakia in 2001.

CONCLUSIONS

Blending of Portland cement with natural zeolite is an efficient way to improve Portland cement resistance against acidic and sulfate attack. Mortar made with 65 wt.% Portland cement + 35 wt.% of zeolite possesses a variety of favorable properties, including:

(1) a pore structure characterized by a large volume of micropores and low micropore and pore median radius, resulting in 365-day compressive strength values of the specimens kept in 0.5% and 1.0% HCl solution greater than those measured after 28-day basic exposure in water, compared with Portland cement mortar;

(2) a hydrate phase formed with a lower CaO content and lower leachability of CaO-containing hydration products with less binding of detrimental Cl^- ions into the cement matrix, compared with Portland cement mortar;

(3) effective neutralization ability of zeolite materials (namely zeolite sand) resulting in an increase in the pH of acid solutions. This buffering effect is in contrast to the properties of siliceous sand, which has little or no buffering capacity.

The sulfate resistance of mortar made with 65 wt.% of Portland cement + 35 wt.% of zeolite is greater than that of Portland cement, due to (1) a significant reduction of SO_3 ions binding into the cement matrix; (2) a decreased amount of CaO-containing hydration products capable of reacting with a sulfate solution, thereby forming voluminous reaction products; and (3) a decreased amount of C_3A, resulting in large expansion and crack propagation that lead to a loss of structural integrity. Our results show that the sulfate resistance of 65 wt.% of Portland cement + 35 wt.% of zeolite blend is similar to that of sulfate-resistant Portland cement. A mortar made with 65 wt.% of Portland cement + 35 wt.% of zeolite blend also exhibits late strengths similar to that of Portland cement mortar. Finally, passivation of steel in mortars with blends consisting of Portland cement to zeolite percentage ratios of 85/15, 75/25 and 65/35 by weight is comparable to that of Portland cement mortar.

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