

THE INFLUENCE OF ZEOLITIC CEMENT AND SAND ON RESISTANCE OF MORTAR SUBJECTED TO HYDROCHLORIC ACID SOLUTION ATTACK

IVAN JANOTKA

*Institute of Construction and Architecture,
Slovak Academy of Sciences,
Dúbravská cesta 9, Bratislava, Slovak Republic*

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The acidic resistance of mortars with cement to sand ratio of 1 : 3 by weight and w/c = 0.6 made from blended cement with 35 wt.% of zeolite and zeolite sand as well as that of Portland cement mortar attacked for 365 days by 0.5 %, 1.0 % and 1.5 % solution of hydrochloric acid is studied. The results show that the batch water volume required for the same plasticity level is 3.5 times higher in the mortar made from zeolite constituents compared to that made from Portland cement and siliceous sand. It is caused by higher specific surface area of the zeolite cement relative to Portland cement. This is consequently confirmed by higher water absorption capacity and total porosity of zeolite mortars. Typical symptoms of acidic attack is a decrease in weight, dynamic modulus of elasticity, strength, CaO content and ignition loss values and an increase in insoluble residue and chloride content in cement mortars. These are evidently the least in the zeolite mortar. Zeolite sand neutralizes HCl solutions contributing thus to the increased acidic resistance of zeolite mortar.

INTRODUCTION

Zeolite is natural aluminosilicate mineral. It consists mainly of SiO_2 and Al_2O_3 . Main constituent in zeolite is K-Ca type of clinoptilolite with average stoichiometric formula $(\text{Ca}_{1.82}\text{Mg}_{0.24})_{2.06}(\text{Na}_{0.12}\text{K}_{1.88})_{2.00}\text{Al}_6\text{Si}_{30}\text{O}_{72} \cdot 24\text{H}_2\text{O}$ [1]. Zeolite is a pozzolanic material characterized by lime absorb value between 134 - 224 mg CaO g^{-1} . The highly porous structure provides large reaction surface for interaction of zeolite with $\text{Ca}(\text{OH})_2$ released at the hydration of clinker minerals. The cements blended with zeolites have characteristics of pozzolanic cement, such as high late strength and low heat of hydration. Meanwhile, they have the disadvantage of great water requirement and low early strength [2]. The reaction kinetics in the zeolite - CaO - H_2O system shows that tobermorite is formed 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 material [3]. The reaction of zeolite (clinoptilolite) with CaO under saturated steam pressure gives 1.1 nm Al-rich tobermorite as the major phase of hydration process. Unreacted quartz, $\text{Ca}(\text{OH})_2$ and partially tobermorite were found in quartz - lime mixture [4]. Experimental results with cements made from Portland clinker and 10, 20 and 40 wt.% of zeolite indicate that the partial replacement of clinker with natural zeolite allows the preparation of blended cements with technical performance better than those of typical pozzolanic cements 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 counterparts [5].

The paper deals with the resistance of mortars subjected to the hydrochloric acid solution when Portland cement and siliceous sand were substituted by equivalent amounts of zeolitic material in the composition of tested specimens.

EXPERIMENTAL PART

Materials

Ordinary Portland cement (PC) of class 42.5 (Ladce cement plant) and siliceous sand (SS) specified in ČSN 72 1208 Standard [6] were used. At the same time zeolitic cement (ZC) with the composition 60.82 wt.% of Portland cement clinker, 35.09 wt.% of zeolite tuff and 4.09 wt.% of gypsum by weight and zeolite sand (ZS) in fractions of 0 - 0.3 mm, 0.3 - 1 mm and 1 - 2.5 mm were used in mortar specimens. Properties of Portland cement are given in table 1 and those of zeolite tuff and zeolitic cement are reported in table 2 and table 3 respectively.

Experimental method

The mortars of this mixture composition were prepared for the tests:

Portland cement + Siliceous sand = PC: SS = 1:3
by weight, w/c = 0.6

Portland cement + Zeolite sand = PC: ZS = 1:3
by weight, w/c = 2.1

Zeolitic cement + Zeolite sand = ZC: ZS = 1:3
by weight, w/c = 2.1

Zeolitic cement + Siliceous sand = ZC: SS = 1:3
by weight, w/c = 0.6.

Table 1. Composition and properties of Portland cement employed.

Component content (wt.%)	Content of major clinker phases according to Bogue (%)	
Insoluble residue	1.63 C ₃ S	49.45
SiO ₂	20.64 C ₂ S	21.88
Al ₂ O ₃	5.88 C ₃ A	10.28
Fe ₂ O ₃	3.13 C ₄ AF	9.53
CaO	61.49	Specific gravity 3 140 kg m ⁻³
MgO	1.34	Specific surface area 336.2 m ² kg ⁻¹
SO ₃	2.30	Beginning of setting 3 hours 15 minutes
K ₂ O	1.82	Setting time 4 hours 20 minutes
Na ₂ O	0.53	3 day cement strength: flexural / compressive 4.4 / 23.5 MPa
Ignition loss	1.04	28 day cement strength: flexural / compressive 7.9 / 41.7 MPa

Table 2. Composition and properties of zeolite tuff.

Chemical composition (wt.%)	
Ignition loss	10.99
SiO ₂	66.72
CaO	5.25
MgO	0
Al ₂ O ₃	14.97
Fe ₂ O ₃	1.69
SO ₃	0.19
Humidity of zeolite tuff 4.78 wt.%	
Specific gravity 2 284 kg m ⁻³	
Specific surface area 1 150 m ² kg ⁻¹	

Table 3. Composition and properties of zeolitic cement.

Component content (wt.%)	Physical properties	
Insoluble residue	18.00	Specific gravity
SiO ₂	15.69	2 231 kg.m ⁻³
Al ₂ O ₃	8.09	Specific surface area
Fe ₂ O ₃	3.24	950 m ² .kg ⁻¹
CaO	41.80	Beginning of setting
MgO	2.29	2 hours 5 minutes
SO ₃	2.09	Setting time
Ignition Loss	8.80	3 hours 5 minutes

Fresh mortars were manufactured with constant plasticity 170 ± 10 mm according to ČSN 72 2441 Standard [7] and then cured 24 hours in moulds at the relative humidity of 95 % and temperature 20 °C, after demoulding specimens were kept 27 days in water at 20 °C.

After this basic curing mortar specimens (20 mm edge cubes and prisms of the size $20 \times 20 \times 120$ mm) were exposed to the action of 0.5, 1.0, and 1.5 vol.% solution of hydrochloric acid (HCl). A part of specimens was kept in water as reference test specimens. The volume ratio between test specimens and HCl solutions was 1:10. Regular control of the *pH* level in aggressive solutions was provided. The solution was restored when the *pH* level was decreased by value of 10 %.

The mortar specimens were tested for compressive and flexural strength, dynamic modulus of elasticity, weight changes, absorption capacity and total porosity. Absorption capacity was estimated by weighting of mortar specimens permeated with water and then dried at 105 °C. The calculation is based on differences in weight of water saturated and dried mortar specimen. Pore structure of mortars was calculated from estimated specific gravity and volume density according to ČSN 72 2447 Standard [8]. Chemical composition of mortar specimens was estimated by analytical methods. The oxide content in the soluble portion of mortars in wt.% was calculated. Total porosity of zeolite fine gravel with the average diameter of particles 5 mm was estimated by mercury porosimetry. The mercury porosimeter ERBA SCIENCE mod. 2 000 and mercury macro-porosimeter unit 120 for pore radius range between 3.75 nm to 0.2 mm estimation was used. The *pH* values of the 0.5 % HCl solution and its extracts with siliceous and zeolite sand were determined by pH meter OP 113 (Radelkis, Hungary). The 50 grams of each sand in the 0 - 2.5 mm fraction was added to 200 ml of hydrochloric acid and left to shaking for 6 hours. In the filtrate *pH* levels were measured again. The same procedure was done with water instead of the 0.5 % HCl solution. Absorption capacity of both sands was estimated by the same way as in mortars. For the tests 20 g of loose sand in the 1 – 2.5 mm fraction kept in ceramics crucibles during weighting was used.

RESULTS AND DISCUSSION

Changes in weight of mortar specimens are illustrated in figures 1, 2, 3 and 4. A permanent decrease in weight was found in mortars subjected to HCl solutions attack. The mortar composition had no expressive effect. However, mortars with zeolitic constituents exhibited larger weight loss in HCl solutions and more intense weight increment in water than those made from siliceous material.

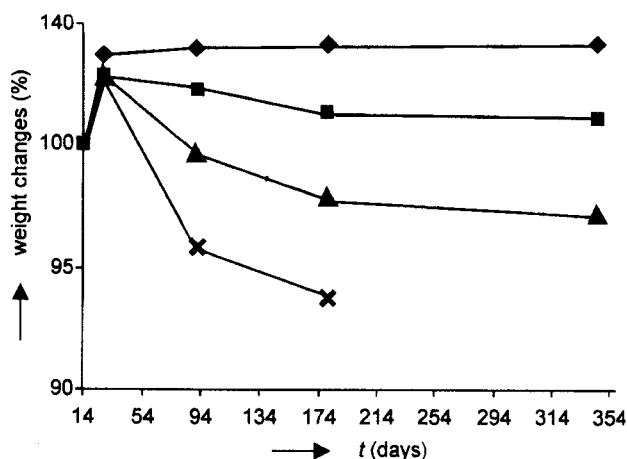


Figure 1. Changes in weight of the PC + SS mortar specimens cured in water and 0.5, 1.0, and 1.5 % solution of HCl.
 ◆ - Water, ■ - 0.5 % HCl, ▲ - 1.0 % HCl, × - 1.5 % HCl

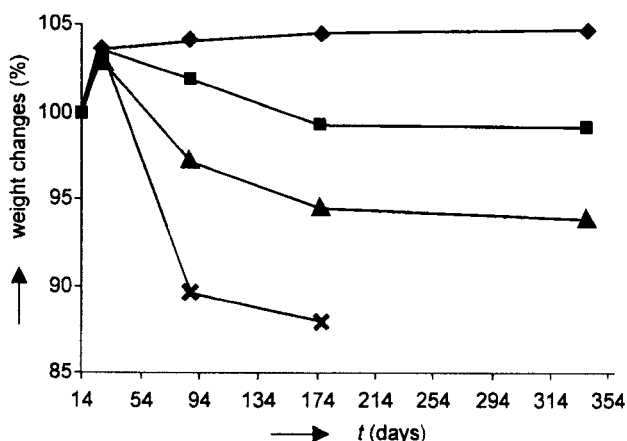


Figure 2. Changes in weight of the PC + ZS mortar specimens cured in water and 0.5, 1.0, and 1.5 % solution of HCl.
 ◆ - Water, ■ - 0.5 % HCl, ▲ - 1.0 % HCl, × - 1.5 % HCl

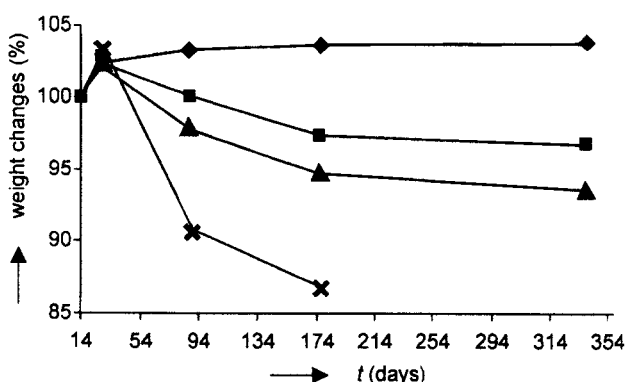


Figure 3. Changes in weight of the ZC + ZS mortar specimens cured in water and 0.5, 1.0, and 1.5 % solution of HCl.
 ◆ - Water, ■ - 0.5 % HCl, ▲ - 1.0 % HCl, × - 1.5 % HCl

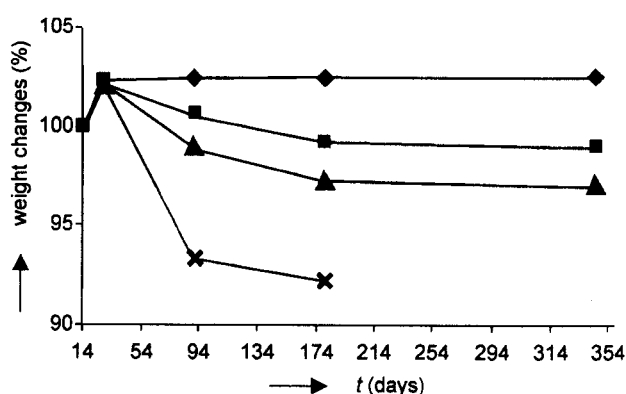


Figure 4. Changes in weight of the ZC + SS mortar specimens cured in water and 0.5, 1.0, and 1.5 % solution of HCl.
 ◆ - Water, ■ - 0.5 % HCl, ▲ - 1.0 % HCl, × - 1.5 % HCl

Table 4 and 5 show the effect of mortar composition on cube compressive strength (CCS) and dynamic modulus of elasticity (DME) of mortar specimens. The extent of zeolitic constituents (ZC + ZS and PC + ZS mortars) causes the decrease in CCS and DME. It is caused by higher water requirement for manufacture of ZC + ZS and PC + ZS mortars as compared to that in PC + SS and ZC + SS mortars.

Figures 5, 6 and 7 illustrate the time dependent relative compressive strength (RCS) development of mortar specimens. The RCS is calculated using formula: $[(CCS_T - CCS_{BC}) / CCS_{BC}] \cdot 100$ and is expressed in wt.%. Subscripts T and BC signify time of curing or basic curing. The RCS is increasing more progressively in

Table 4. Changes in cube compressive strength of mortars.

Mortar	Curing (days)	Medium			
		water	0.5 % HCl	1.0 % HCl	1.5 % HCl
PC + SS	28	37.2	37.2	37.2	37.2
	60	-	-	-	11.2
	90	54.0	31.0	22.6	10.6
	180	54.8	29.7	22.2	9.3
	365	56.4	28.0	19.2	-
PC + ZS	28	9.8	9.8	9.8	9.8
	60	-	-	-	3.4
	90	12.8	11.0	6.9	2.9
	180	13.7	11.4	6.8	1.2
	365	15.4	10.1	5.2	-
ZC + ZS	28	4.8	4.8	4.8	4.8
	60	-	-	-	1.9
	90	13.5	8.1	6.3	1.3
	180	14.0	9.6	5.8	1.2
	365	16.0	7.6	5.6	-
ZC + SS	28	24.1	24.1	24.1	24.1
	60	-	-	-	8.5
	90	33.3	24.7	20.6	7.7
	180	38.9	31.3	20.2	6.8
	365	39.0	24.2	19.2	-

Table 5. Changes in dynamic modulus of elasticity of mortar.

Mortar	Medium	Dynamic modulus elasticity (GPa)		
		28 days	180 days	365 days
PC + SS	water	40.7	45.2	45.3
	0.5 % HCl	40.7	40.3	40.1
	1.0 % HCl	40.7	38.1	37.8
	1.5 % HCl	40.7	31.0	-
PC + ZS	water	14.7	16.8	17.0
	0.5 % HCl	14.7	14.6	14.7
	1.0 % HCl	14.7	12.7	11.2
	1.5 % HCl	14.7	10.4	-
ZC + ZS	water	10.4	14.4	15.2
	0.5 % HCl	10.4	13.1	13.6
	1.0 % HCl	10.4	10.3	9.3
	1.5 % HCl	10.4	5.3	-
ZC + SS	water	32.4	34.9	35.6
	0.5 % HCl	32.4	33.6	34.6
	1.0 % HCl	32.4	31.0	30.9
	1.5 % HCl	32.4	27.1	-

mortars with zeolitic constituents cured in water, 0.5 % and 1.0 % HCl solution. The best effect on the RCS development was reached in the most zeolite-rich ZC - ZS mortar specimen. Under this aspect it is clear that replacement of siliceous constituents by zeolitic material in mortars contributes to the decrease of CCS as well as to the RCS values increase with time when cured either in water or 0.5 % and 1.0 % HCl solutions. A similar tendency was observed for dynamic modulus of elasticity. The probable cause of these phenomena lies in different phase composition and pore structure development in tested mortars. It is supposed that zeolite consumes CaO and develops gel - like hydration products instead of bulky $\text{Ca}(\text{OH})_2$ crystals formed prevalingly in mortars made from Portland cement and siliceous sand. In spite of this, ZC + ZS and PC + ZS mortars showed increased resistance against the 0.5 % and 1.0 % HCl solutions attack opposite to PC + SS and ZC + SS mortar specimens. Phase composition and pore structure development of mortars were studied as well to explain the behaviour of attacked mortars in a more detail. An extension of this work will be given by achieved results.

Changes in absorption capacity (AC) and total porosity (TP) of PC + SS and ZC + ZS mortar specimens cured 365 days in water and HCl solutions are seen in table 6. The AC and TP of ZC + ZS mortar specimens are higher than those of PC + SS ones. It is the cause of low CCS of zeolite - rich mortar specimens. The reason of this fact may also lie in higher absorption capacity and porosity of zeolite sand as compared with that of siliceous one. Absorption capacity of siliceous sand is 24.1 wt.% and that of zeolite even 59.8 wt.%. Total

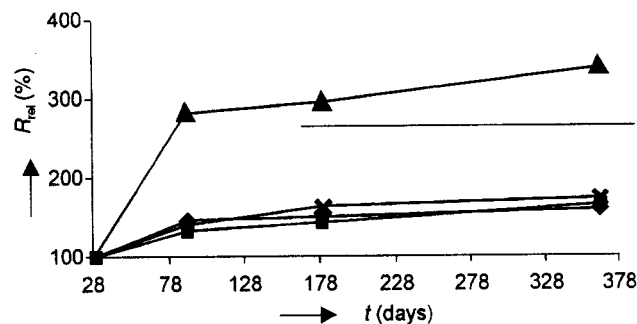


Figure 5. Increase in relative compressive strength of mortars cured in water.

◆ - PC + SS, ■ - PC + ZS, ▲ - ZC + ZS, × - ZC + SS

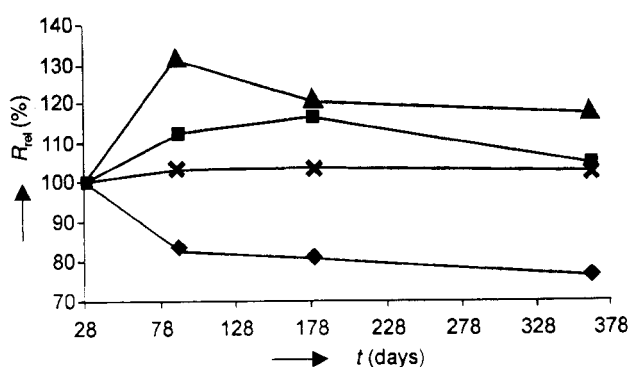


Figure 6. Changes in relative compressive strength of mortars exposed to 0.5 % solution of HCl.

◆ - PC + SS, ■ - PC + ZS, ▲ - ZC + ZS, × - ZC + SS

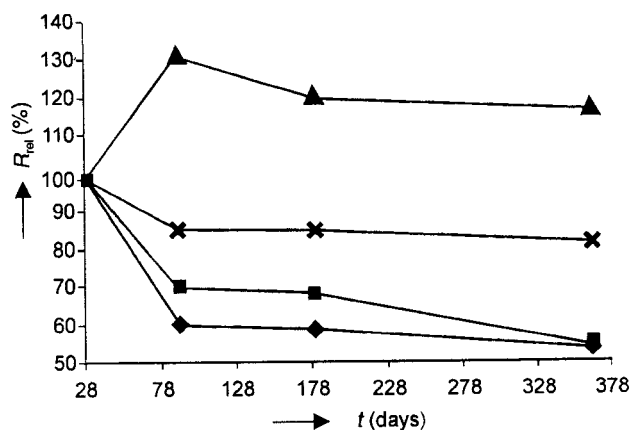


Figure 7. Changes in relative compressive strength of mortars exposed to 1.0 % solution of HCl.

◆ - PC + SS, ■ - PC + ZS, ▲ - ZC + ZS, × - ZC + SS

porosity between 3.75 nm and 0.2 mm of pore radius is 19.4 % in zeolite sand. The value 24.1 % was calculated on the basis of ČSN 72 2447 Standard [8]. This statement is confirmed by significantly higher water re-

quirement of ZC + ZS and PC + ZS mortars opposite to PC + SS and ZC + SS mortar specimens. It is therefore suggested that AC, TP and water requirement of tested mortars are influenced to a large extent by the type of sand in comparison with the origin of cement used for the manufacture of mortar specimens. The type of the sand plays an important role also in improving the resistance of mortar specimens against the acidic attack. It was found that the *pH* value of the 0.5 % HCl solution is 1.35. The *pH* level in the siliceous sand extract made with 0.5 % HCl is 1.36 whereas in the zeolite sand extract 6.67. The chloride ion content in the original siliceous and zeolite sand is equal to zero. The siliceous sand extracted in 0.5 % solution of HCl contains 0.03 % of chloride ions. By contrast, the chloride ion quantity bound in the zeolite sand extracted in the hydrochloric acid solution under the same conditions is 0.23 %. It is evident that zeolite sand is able to neutralize hydrochloric

acid solution. This result is of great importance when considering that *pH* values of water extracts with siliceous and zeolite sand made under the same conditions are 8.2 and 7.6, respectively.

Table 6. Absorption capacity and total porosity of mortar specimens cured 365 days in water and HCl solutions.

Mortar	Medium	Absorption capacity (wt.%)	Specific weight (kg m ⁻³)	Total porosity (%)
PC + SS	Water	9.5	2 574.0	11.83
	0.5 % HCl	10.0	2 578.0	13.16
	1.0 % HCl	10.5	2 579.7	14.99
ZC + ZS	Water	36.4	2 234.0	18.63
	0.5 % HCl	36.5	2 237.0	23.24
	1.0 % HCl	40.5	2 241.0	26.63

Table 7. Chemical composition of mortars after 365 - day curing in water and HCl solutions.

Mortar	Medium	Chemical composition of mortars (wt.%)								
PC + SS	Water	Ign. loss	11.70	Composition of soluble portion						
		Ins. port.	66.51	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	21.79	5.12	13.28	1.27	1.21	0.31	0.60	-
		Total content	100	Oxide content in soluble portion						
	0.5 % HCl	Ign. loss	11.88	Composition of soluble portion						
		Ins. port.	68.74	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	19.38	4.32	11.22	1.30	1.03	0.36	0.52	0.63
		Total content	100	Oxide content in soluble portion						
	1.0 % HCl	Ign. loss	11.08	Composition of soluble portion						
		Ins. port.	69.47	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	19.45	5.42	10.38	1.12	1.07	0.42	0.39	0.65
		Total content	100	Oxide content in soluble portion						
ZC + ZS	water	Ign. loss	18.43	Composition of soluble portion						
		Ins. port.	28.84	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	52.73	32.23	9.78	1.78	6.84	1.61	0.55	-
		Total content	100	Oxide content in soluble portion						
	0.5 % HCl	Ign. loss	16.82	Composition of soluble portion						
		Ins. port.	27.45	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	55.73	36.38	9.13	1.93	6.95	0.68	0.42	0.22
		Total content	100	Oxide content in soluble portion						
	1.0 % HCl	Ign. loss	16.10	Composition of soluble portion						
		Ins. port.	27.45	SiO _{2,s}	CaO	Fe ₂ O ₃	Al ₂ O ₃	MgO	SO ₃	Cl
		Sol. port.	56.45	39.24	7.34	1.54	6.89	0.77	0.19	0.48
		Total content	100	Oxide content in soluble portion						

Chemical composition of PC + SS and ZC + ZS mortar specimens cured 365 days in water and HCl solutions are given in table 7. The CaO decrease in the soluble portion of the PC + SS mortar specimen is 7.6 % whereas that of the ZC + ZS only 5.5 %. On the contrary the chloride content of the soluble portion of the ZC + ZS mortar specimen is cca 8 times less in 0.5 % solution of HCl and cca 4 times less in 1.0 % solution of HCl opposite to the PC + SS one. It is caused by the hydrolysis, dissolution and leaching of the cement matrix components and cumulation of chloride ions in residual bonding system of cement mortars which is typical for acidic corrosion process.

It is evident that the action of HCl solutions causes the decrease in weight, CCS, DME, CaO content and ignition loss and the increase in AC, TP, insoluble residue and chloride content in tested mortars. The results show permanent degradation of mechanical properties and clear signs of leaching of cement matrix components beginning on the edges of mortar specimens. This is a proof of acidic corrosion as the consequence of the destruction and loss of cement matrix in tested mortars. This process is stronger in mortars based on siliceous constituents (PC + SS, ZC + SS) as compared with those where prevails zeolite material (ZC + ZS, PC + ZS mortars). Zeolite - containing specimens are more resistant against the 0.5% and 1.0% HCl solutions attack than those made from PC and SS. The resistance of all mortars against the attack of 1.5 % solution of hydrochloric acid was found unsatisfactory.

CONCLUSIONS

1. Utility properties of tested mortars are decisively influenced by their material composition. Zeolite constituents as compared with siliceous ones contribute to decreasing in compressive strength, dynamic modulus of elasticity and increasing in absorption capacity and total porosity of tested specimens due to higher demands on batch water required for the same plasticity of fresh mortars.
2. Resistance of mortar specimens containing zeolite material against the attack of 0.5 % and 1.0 % solution of hydrochloric acid is higher than those with siliceous constituents. It is supposed that this fact is caused by chemical bonding of CaO by zeolite and reducing the $\text{Ca}(\text{OH})_2$ content in mortar specimens. Typical symptoms of acidic corrosion - hydrolysis, dissolution and leaching of the cement matrix components are significantly reduced in the zeolite - modified mortars opposite to those made from siliceous constituents. Zeolite sand neutralizes HCl solutions and thus weakens their detrimental effect on hardened cement paste.
3. Practical application of mortars with zeolite constituents is conditioned by the use of water - reducing admixtures to achieve similar utility properties as known for Portland cement or blastfurnace slag Portland cement based materials.

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Submitted in English by the author.

VPLYV ZEOLITOVÉHO CEMENTU A PIESKU NA ODOLNOST MÁLT VYSTAVENÝCH ÚČINKU ROZTOKOV KYSELINY CHLOROVODÍKOVEJ

IVAN JANOTKA

Ústav stavebníctva a architektúry, Slovenská akadémia vied,
Dúbravská cesta 9, 842 20 Bratislava

Prešetrovali sa malty zhotovené z Portlandského cementu (PC) a kremičitého piesku (KP) podľa ČSN 72 1208, Portlandského cementu a zeolitového piesku (ZP), zeolitového cementu (ZC) a zeolitového piesku. ZC obsahuje 60,82 % portlandského slinku, 35,09 % zeolitového tufu a 4,09 % sadrovca, ZP pozostáva z troch frakcií s veľkosťou zŕn 0 - 0,3 mm, 0,3 - 1 mm a 1 - 2,5 mm. Skúšky sa uskutočnili s maltami s hmotnostným pomerom použitého cementu a piesku 1 : 3 a konštantnou plasticitou 170 ± 10 mm podľa ČSN 72 2441. Po 28 dňovom základnom uložení vo vode pri 20 °C sa skúšobné vzorky exponovali 365 dní vo vode, 0,5%, 1,0% a 1,5% roztoku kyseliny chlorovodíkovej (HCl).

Zo štúdia mált vyplývajú nasledovné poznatky:

- ZC+ZP a PC+ZP skúšobné malty potrebujú 3,5 x väčšiu dávku zámesovej vody na dosiahnutie rovnakej plasticity ako ZC+KP a PC+KP vzorky. Príčinou je vyššia nasiakavosť a celková pórovitosť zeolitového materiálu v malte v porovnaní s kremičitými zložkami. To sa potvrdzuje aj nižšími kockovými pevnosťami mált modifikovaných zeolitovým materiálom oproti PC+KP skúšobnej vzorke.
- typické symptómy kyslej korózie preukázané hydrolýzou, rozpúšťaním a vylúhovaním zložiek cementovej matrice a permanentnou degradáciou mechanických vlastností mált sú významne znížené v skúšobných vzorkách so zeolitovým cementom a zeolitovým pieskom oproti malte zhotovenej z Portlandského cementu a kremičitého piesku. Najvyššia odolnosť oproti 0,5% a 1,0% roztoku HCl sa zistila v ZC+ZP malte. Zeolitový piesok neutralizuje kyslý roztok kyseliny chlorovodíkovej a tak prispieva k zvýšenej odolnosti zeolitom modifikovaných mált.