

# THE PROPERTIES OF MORTAR USING BLENDS WITH PORTLAND CEMENT CLINKER, ZEOLITE TUFF AND GYPSUM

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*This paper deals with the properties of mortars containing the mixtures of Portland cement clinker, zeolite tuff and gypsum. The mortars consisting of mixtures with 87.42 to 87.99 % of Portland cement clinker, 9.62 to 9.99 % zeolite tuff and 2.02 to 5.63 % of gypsum were prepared and compared to zeolite - free control mortar with 95.2 % of Portland cement clinker and 4.98 % of gypsum. The 1 095 day compressive strength of zeolite-modified mortars is comparable to that in the control one. Contemporarily a portion of micropores with radius less than 100 nm in the pore structure of zeolite-modified mortars is larger than in the control one. The presence of zeolite tuff in the mortars has not negative effect on steel corrosion.*

## INTRODUCTION

The activity of pozzolanic materials is characterized by their absolute susceptibility to combine with CaO and its reaction kinetics with Ca(OH)<sub>2</sub> in the presence of water under normal temperature [1]. In zeolite tuff+Ca(OH)<sub>2</sub> binder pastes 2:1 and 1:1 hydration products of C-S-H gel and tobermorite were distinguished whereas binder paste of zeolite tuff + C<sub>3</sub>A gives hydration products of C<sub>3</sub>AH<sub>6</sub> and hydrogarnet phase [2]. Due to the zeolite tuff the process of bonding of SO<sub>3</sub> in the Portland cement mortar is considerably slowed down and thereby the resistance of the mortar against action of 55 percent solution of Na<sub>2</sub>SO<sub>4</sub> during 510 day's cure is substantially increased [3]. By replacing parts of clay with finely ground zeolite tuff considerable improvement of corrosion resistance of cement suspension used in underground sealing wall in Vernéřov (Czech Republic) was achieved when contacted with an aggressive water containing in average 2 000 mg l<sup>-1</sup> of sulfates and having a pH value of 4.5 [4].

It was found that ordinary Portland cements without gypsum as regulator of setting are characterized by an accelerated setting time and high early strength when Portland clinker is ground to a specific surface area of 400 - 550 m<sup>2</sup> kg<sup>-1</sup> in the presence of efficient grinding aids [5]. Gypsum-free pastes of ground Portland cement clinker tend to harden very rapidly generating considerable heat of hydration. At present an attention is

devoted to ground Portland cement clinker with the replacement of the function of gypsum by other substances [6,7,8,9]. In most cases, the added modifiers retard the setting time of Portland cement pastes without gypsum addition to cement and decrease the compressive strength compared to unmodified control specimens.

Six blends with Portland cement clinker, zeolite tuff and gypsum are introduced and compared to the Portland cement properties in this paper. The main aim of this work is to compare physico-mechanical properties, phase composition and pore structure of modified mortars with that without zeolite tuff addition. The ability of mortars to protect steel reinforcement against corrosion was verified too.

## EXPERIMENTAL PART

### Materials

Ordinary Portland cement of class 400 and sand specified in ČSN 72 1208 Standard [10] were used in all mixes. An aliquot portion of the Portland cement clinker was replaced by zeolite tuff. The composition of the zeolite-modified cement clinker was adjusted to 100 % of dry constituents by the CaSO<sub>4</sub>·2H<sub>2</sub>O addition. The properties of the employed cement and composition of cement mixtures manufactured in ZEOCEM cement works, Bystré nad Topľou, Slovakia are given in Table I and Table II. Commercial zeolite tuff was used as cement modifier. Its properties are listed in Table III.

Table I. Composition and properties of the Portland cement employed

Component content (wt.%)		Content of major clinker phases according to Bogue (%)	
Insoluble residue	1.63	C <sub>3</sub> S	49.45
SiO <sub>2</sub>	20.64	C <sub>2</sub> S	21.88
Al <sub>2</sub> O <sub>3</sub>	5.88	C <sub>3</sub> A	10.28
Fe <sub>2</sub> O <sub>3</sub>	3.13	C <sub>4</sub> AF	9.53
CaO	61.49	Specific gravity	3 140 kg m <sup>-3</sup>
MgO	1.34	Specific surface area	336.2 m <sup>2</sup> kg <sup>-1</sup>
SO <sub>3</sub>	2.30	Beginning of setting	3 hours 15 minutes
K <sub>2</sub> O	1.82	Setting time	4 hours 20 minutes
Na <sub>2</sub> 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 II. Properties of cement mixtures based on zeolite tuff addition to Portland cement clinker

Cement property	Cement mixtures						
	1	2	3	4	5	6	
Beginning of setting (hr/min)	0/40	1/20	1/40	2/35	2/15	0/35	
Setting time (hr/min)	1/25	3/45	3/15	3/30	4/40	1/25	
Ignition loss (%)	9.20	5.59	5.63	8.88	6.27	7.06	
Content of SO <sub>3</sub> (%)	1.60	1.18	1.74	2.62	0.94	1.59	
Content of CaO (%)	51.03	54.67	54.39	50.75	54.67	53.55	
Standard strength (MPa)	flexural <sup>1)</sup>						
	3 days	2.9	2.7	4.2	3.4	3.3	3.6
Standard strength (MPa)	compressive <sup>2)</sup>						
	3 days	11.4	9.0	16.5	12.7	14.6	14.2
Residue on fine -mesh screen (wt.%)	28 days	26.7	31.4	33.5	28.9	23.1	31.3
	0.2 mm	0.2	0.2	1.3	0.4	0.1	0.1
	0.09 mm	3.5	1.8	6.5	7.6	0.9	1.4

<sup>1) 2)</sup> Standard strength was determined according to ČSN 72 2117 Standard

Table III. Composition and properties of zeolite tuff

Chemical composition (wt.%)	
Ignition loss	10.99
SiO <sub>2</sub>	66.72
CaO	5.25
MgO	0
Al <sub>2</sub> O <sub>3</sub>	14.97
Fe <sub>2</sub> O <sub>3</sub>	1.69
SO <sub>3</sub>	0.19
Humidity of zeolite tuff (wt.%)	
4.78	
Specific gravity (kg m <sup>-3</sup> )	
2 283.7	
Specific surface area (m <sup>2</sup> kg <sup>-1</sup> )	
1 150.5	

### Experimental method

Control mortar (C) and zeolite-modified mortars (M1 - M6) were prepared using mix proportions given in Table IV. Mortar specimens having size of 40 x 40 x 160 mm were moulded and cured 28 days at 20 °C/95 % R.H. - moist and then in water for 1 095 days also at 20 °C. By the contrast with it cement mixtures with 79 % of Portland cement clinker, 15 % of zeolite tuff, 6 % of gypsum and 83 % of Portland cement clinker, 15 % of zeolite tuff, 2 % of gypsum were verified too. Plasticity of the mortars was adjusted to 160 mm ± 5 mm according to ČSN 72 2441 [11]. The mortar specimens were tested for compressive and flexural strength, dynamic modulus of elasticity, absorption capacity and total porosity. Absorption capacity was estimated by weighing 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. Total porosity of mortars was calculated on basis of estimated specific gravity and volume density.

Pore structure of mortar specimens was studied by means of high-pressure mercury porosimeter mod. 2000 and macroporosimetry unit 120 (both Erba Science, Milan). This apparatus enables to estimate pore radius between 3.75 nm and 0.2 nm.

The phase composition of the mortars were estimated by X-ray diffractograph Philips using CuK<sub>α</sub> radiation and thermal analysis apparatus Derivatograph Q 1 500, MOM Budapest.

Table IV. Mix proportion of mortars with cement mixtures

Composition of mixtures					
Cement : sand (by weight)	clinker (wt.%)	zeolite (wt.%)	gypsum (wt.%)	WC	
C	95.02	-	4.99	0.33	
M1	86.70	9.86	3.44	0.38	
M2	87.64	9.82	2.54	0.38	
1:1.5	M3	86.64	9.62	3.74	0.38
	M4	84.42	9.95	5.63	0.38
	M5	87.99	9.99	2.02	0.38
	M6	86.97	9.62	3.41	0.38

Corrosion of steel was tested in mortar extracts by potentiodynamic method according to ČSN 73 1341 Standard [12]. For corrosion tests steel bar of class 10 425 with diameter 6 mm was used. Potentiodynamic curves of steel were obtained by Potentiostat OH 405 (Radelkis Budapest) under polarisation rate 30 mV min<sup>-1</sup>.

### RESULTS AND DISCUSSION

Due to similarity in composition of M1 - M6 cement mixtures the rate of setting is not affected significantly by the content of gypsum in amount of 2.02 - 5.64 %. When the zeolite tuff content is enhanced to 15 wt.% distinct changes in setting time of cement mixtures were observed. The setting time of the mixture with 2 % of gypsum is less than 45 minutes and the beginning of setting was prolonged up to 5 hours and 5 minutes in the cement mixture with 6 % of gypsum. The 15 % content of zeolite tuff in the cement mixtures worsens markedly compressive strength of the mortars. The 28-day compressive strengths varied between 11.8 and 14.6 MPa. This invention into the cement mixture composition compared to that with 10 % content of zeolite tuff evoked unwishful changes in setting characteristics of cement mixtures and distinct decrease in compressive strength of mortar specimens. Therefore further tests with cement mixtures containing 15 % content of zeolite tuff were not carried out. Figure 1 exhibits compressive strength of control mortar and zeolite-modified mortars versus curing period before and after water immersion. The effect of cement composition on compressive strength of mortars is hardly recognized. The compressive strength of modified mortars after water immersion rises with an increase in the fineness of cement mixtures and decrease in gypsum content of cement mixture. Figure 2 illustrates the flexural strength of mortars versus curing period before and after water immersion. In both cases, the strength loss of zeolite-modified mortars in comparison with control one

is caused by partial replacement of Portland cement clinker by aliquot portion of zeolite tuff and gypsum.

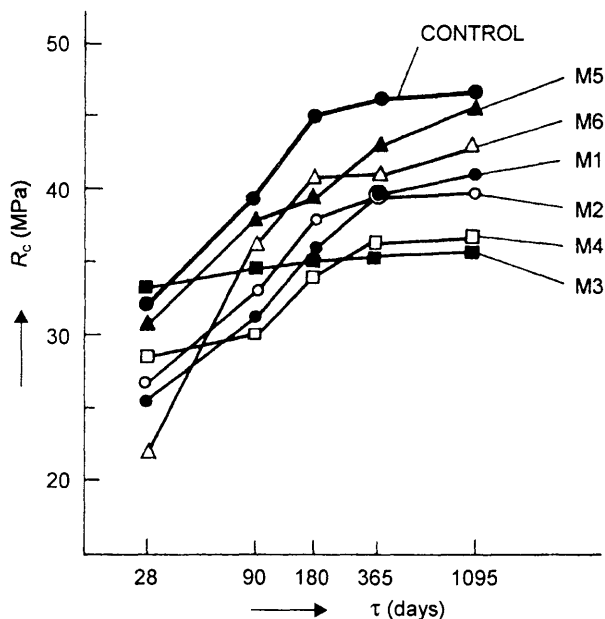


Figure 1. Compressive strength of mortars vs. curing period in water

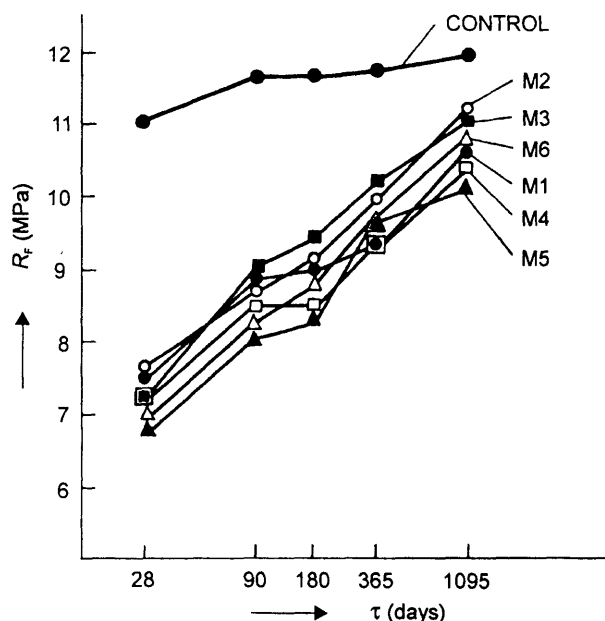


Figure 2. Flexural strength of mortars vs. curing period in water

Table V represents the relationship of dynamic modulus of elasticity, absorption capacity and total porosity of mortars versus curing period. Differences in dynamic modulus of elasticity in tested mortars are of negligible importance. Absorption capacity and total porosity of control mortar is about a one fifth to one third of those in zeolite-modified mortars. The effect of

zeolite tuff on absorption capacity and total porosity of mortars placed 1095 days underwater is much the same as those on the flexural strength of zeolite-modified mortars. These mortar properties are worsened.

Table V. Dynamic modulus of elasticity, absorption capacity and total porosity of mortar specimens cured 1 095 days in water at 20 °C

Type of mortar	Dynamic modulus of elasticity (GPa)	Absorption capacity (wt.%)	Total porosity according to ČSN 72 2447 (vol.%)
Control	30.8	7.0	13.3
M1	31.1	10.5	18.9
M2	30.9	10.4	16.5
M3	30.3	11.0	16.5
M4	31.2	10.5	15.2
M5	30.7	11.8	15.9
M6	31.2	11.4	15.7

Comparison of the results of porosimetric analysis specified in Table VI and Table VII shows that median pore radius and pore size distribution of mortar specimens depend decisively on the cement composition. Pore size distribution in the mortars containing zeolite tuff is markedly different compared to that in the control mortar. The portion of micropores with radius less than 100 nm is enhanced when cement clinker is partially replaced by zeolite tuff. This phenomenon is caused by higher fineness of zeolite tuff.

The relative content of  $\text{Ca(OH)}_2$  and main clinker minerals of mortars were determined by comparing the characteristic diffraction intensities (Figures 3 and 4). The presence of  $\text{Ca(OH)}_2$  is detected by diffraction intensities of 4.92 Å ; 3.11 Å, 2.63 Å, 1.92 Å and 1.79 Å. The relative amount of unreacted alite and belite is characterized by the doublet at 2.78 Å and 2.74 Å. Diffraction intensities 3.86 Å, 3.03 Å, 2.09 Å and 1.87 Å belong to  $\text{CaCO}_3$ . The remaining correspond to  $\text{SiO}_2$ .

Table VI. Results of pore structure study of mortar specimens cured 1095 days in water at 20 °C

Type of mortar	Volume of micropores (%)	Median of pore radius (nm)	Porosity according to Hg - porosimetry (%)
Control	90.10	46.99	10.40
M1	95.38	49.92	13.05
M2	94.10	52.38	13.52
M3	96.58	49.57	13.35
M4	92.00	39.00	14.42
M5	95.30	49.20	15.47
M6	94.67	43.46	15.08

Table VII. Pore size distribution in mortar specimens cured 1 095 days in water at 20 °C

Pore radius	Pore size distribution (%)						
	control	M1	M2	M3	M4	M5	M6
to 50 nm	44.59	50.82	46.89	49.87	60.05	52.16	57.85
50-100 nm	25.93	29.58	32.97	37.40	18.08	29.54	24.00
100-1000 nm	14.52	12.89	12.45	7.21	6.51	11.31	13.71
1000-3000 nm	4.14	0.76	2.19	1.91	2.17	1.25	2.40
3000-7500 nm	2.08	1.51	0.74	1.13	4.34	1.57	1.71
to 7500 nm (micropores)	91.26	95.56	95.24	97.52	91.15	95.83	95.67
over 7500 nm (macropores)	8.73	4.43	4.75	2.48	8.83	4.14	4.33

The content of  $\text{Ca(OH)}_2$  is slightly higher in the control mortar than in those containing zeolite tuff. The reason lies in lesser amount of CaO in the cement mixture modified by zeolite tuff and also in susceptibility of zeolite tuff to combine with CaO due to its pozzolanic origin. By the contrast with it modification of cement mixture by zeolite tuff results in a slight increase in  $\text{CaCO}_3$  content. Cement mixture modified by zeolite tuff has a similar effect on the hydration of the cement paste of mortar specimens as revealed by mildly decreased content of  $\text{Ca(OH)}_2$  and roughly equal diffraction intensities of unreacted alite and belite compared to that prepared from Portland cement.

These interesting facts follow from the results of thermal analysis (Table VIII). A relative high content of bound water in hardened cement paste is typical for all cured mortars. The amount of bound water in zeolite-modified mortars is affected by the zeolite tuff content in cement mixtures. However, the 10 % content of zeolite tuff does not influence markedly bound water content in the hydrate phase of mortar specimens between temperature 100 and 420 °C. With respect to the 10 % replacement of Portland cement clinker by zeolite tuff in cement mixtures total content of CaO bound in  $\text{Ca(OH)}_2$  and  $\text{CaCO}_3$  in zeolite-modified mortars is slightly lower than that in the control mortar. The reason lies in the lower CaO content in the composition of M1 - M6 cement mixtures than that of Portland cement.

The corrosion characteristics of steel in mortar extracts obtained by potentiodynamic method are given in Table IX. The course of potentiodynamic curves of steel is shown in Figure 5. Differences in values of current density of passivation, potential of break-down as well as in pH of mortar extracts between zeolite-modified mortars and control one are of negligible importance. The steel is always in the passive state. The achieved results confirm that zeolite tuff in cement mixture does not initiate the corrosion of steel in the mortars.

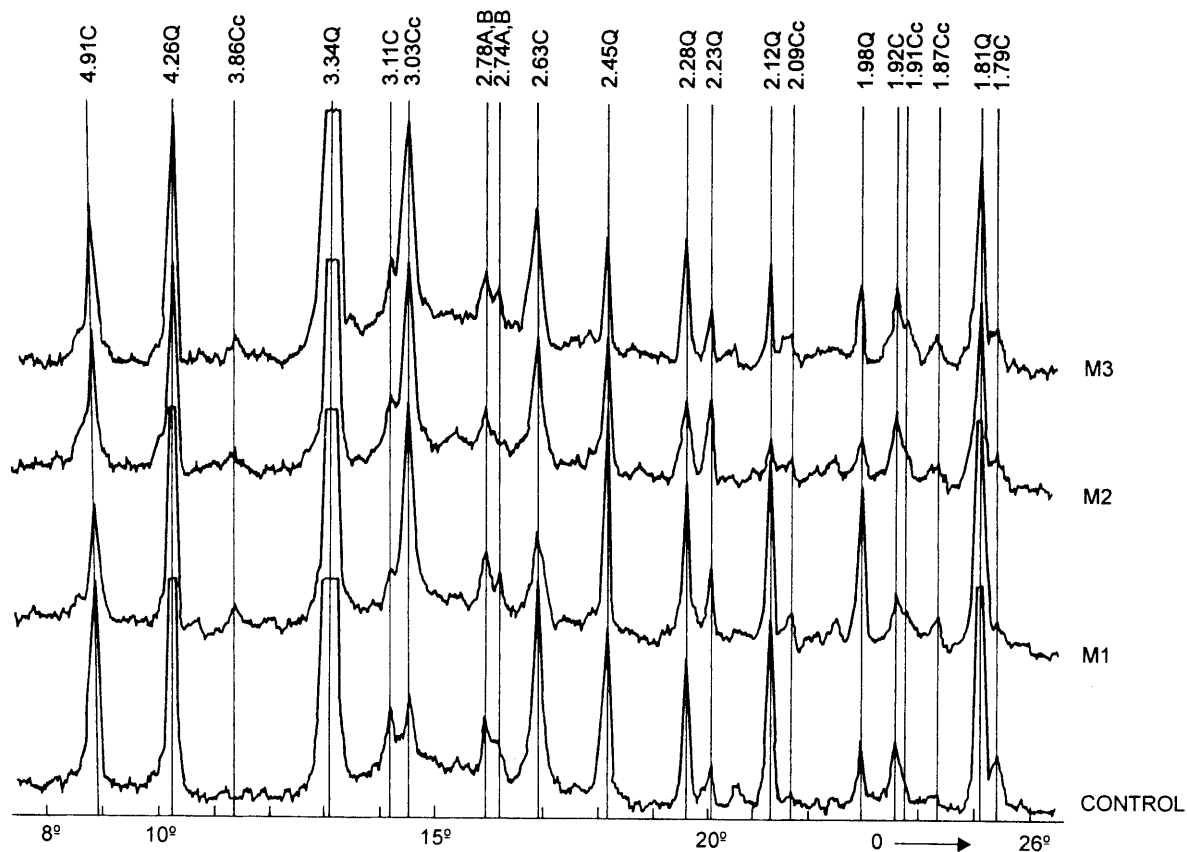


Figure 3. X-ray diffraction patterns of tested mortars cured 1 095 days in water at 20 °C

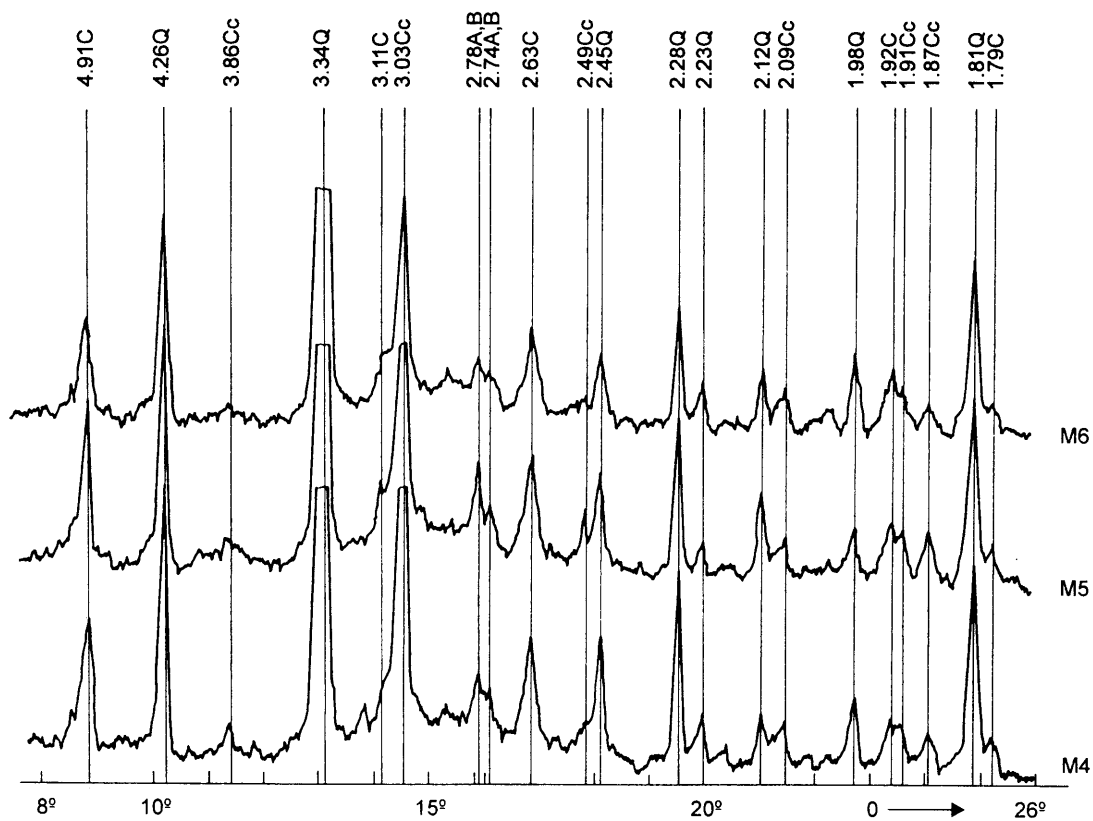


Figure 4. X-ray diffraction patterns of tested mortars cured 1 095 days in water at 20 °C

Table VIII. Results of thermal analysis of tested mortars cured 1 095 days in water at 20 °C

Type of mortar	Ignition loss to 420 °C (%)	Ignition loss to 1 000 °C (%)	CaO bound in		Total content of CaO in Ca(OH) <sub>2</sub> and CaCO <sub>3</sub> (%)
			Ca(OH) <sub>2</sub> (%)	CaCO <sub>3</sub> (%)	
Control	6.30	15.71	1.89	2.56	4.45
M1	5.26	14.22	1.32	2.63	3.95
M2	7.36	16.98	1.57	2.64	4.21
M3	6.04	14.58	0.94	2.29	3.23
M4	6.00	16.09	1.40	3.12	4.32
M5	8.48	18.20	1.44	2.83	4.27
M6	6.84	15.53	1.19	2.95	4.14

Table IX. Corrosion characteristics of steel of mortars cured 1 095 days in water at 20 °C

Type of mortar	Stationary potential (mV)	Current density of passivation (A m <sup>-2</sup> )	Potential of break - down (mV)	State of reinforcement	pH of extract
Control	-330	0.031	570	passive	12.47
M1	-330	0.029	570	passive	12.40
M2	-330	0.030	575	passive	12.47
M3	-330	0.033	575	passive	12.41
M4	-330	0.029	560	passive	12.43
M5	-330	0.026	565	passive	12.45
M6	-330	0.026	565	passive	12.42

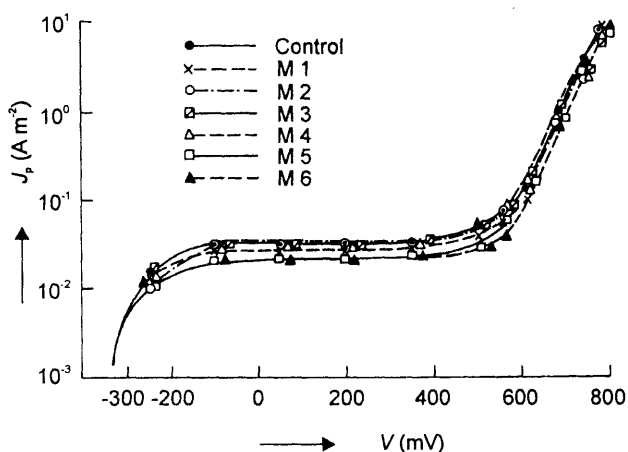


Figure 5. Potentiodynamic curves of steel in extract of cured mortars (current density vs. potential of steel)

## CONCLUSIONS

1. The beginning of setting and setting time of cement mixtures M1 - M6 consisting of Portland cement clinker, zeolite tuff and gypsum are accelerated markedly in comparison with that of Portland cement. When cement mixture contains 15 % of zeolite tuff setting characteristics depend significantly on gypsum content in the cement mixture.
2. The compressive strength of the control mortar after 1 095 days of water immersion is slightly higher than those prepared from cement mixtures containing up to 10 % of zeolite tuff. Compressive strength of zeolite-modified mortars is enhanced with increasing fineness of cement mixture and decreasing gypsum content in cement mixture M1-M6. A significant strength loss of the mortars containing 15 % of zeolite tuff was observed.
3. A large portion of micropores with radius less than 100 nm is a typical feature of the pore structure of zeolite-modified mortars. The higher relative representation of micropores in mortars containing zeolite tuff than that in the control one is caused by higher fineness of zeolite tuff.
4. Both, hydration of the control and zeolite-modified mortars advances sufficiently. Cement mixture modified by zeolite tuff does not affect significantly the degree of hydration. A lesser content of CaO bound in Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in mortar containing zeolite tuff is caused by the lower CaO content in cement mixtures with zeolite tuff than that containing Portland cement.

5. The replacement of the Portland cement clinker by zeolite tuff up to 10 % in cement mixture has no negative effect on the ability of mortars to protect steel against corrosion.

6. The mentioned cement mixtures have been experimentally manufactured in the cement factory already. From this viewpoint the verification of their properties and properties of mortars made from these blends seems to be of great importance. The investigation of zeolite-modified mortars exposed to different liquid aggressive media is just going on.

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*Submitted in English by the authors*

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#### VLASTNOSTI MÁLT ZA POUŽITIA ZMESÍ Z PORTLANDSKÉHO SLINKU, ZEOLITOVÉHO TUFU A SADROVCA

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Prešetrovali sa cementové zmesi s rozdielnou dávkou Portlandského slinku, zeolitového tufu a sadrovca. Ku skúškam sa použili malty s hmotnostným pomerom cementovej zmesi a piesku 1:1.5 s plasticitou  $160 \pm 5$  mm. Malty sa ošetrovali 1 095 dní vo vode s teplotou  $20 \pm 2$  °C. Účinok rôzneho zloženia cementových zmesí sa preveroval z hľadiska pevností, fázového zloženia, pórovej štruktúry a pasivačných vlastností mált.

Zo štúdia cementových zmesí a mált vyplývajú nasledovné poznatky:

- počiatok a doba tuhnutia cementových zmesí s prídavkom zeolitového tufu sa mení v závislosti od dávky sadrovca, vo väčšine prípadov sa však skraca v porovnaní s počiatkom a dobou tuhnutia Portlandského cementu,
- pevnosť v ťahu ohybom a pevnosť v tlaku mált zhotovených z cementových zmesí je nižšia ako malty s Portlandským cementom,
- vyššia jemnosť zeolitového tufu a nižší obsah sadrovca v cementovej zmesi spôsobujú nárast pevnosti v tlaku mált,
- hydratácia cementových zmesí a Portlandského cementu má podobný priebeh, v maltách so zeolitovým tufom je vyšší podiel mikropórov s polomerom menším ako 100 nm,
- náhrada Portlandského slinku zeolitovým tufom do 10 % hmot. v cementovej zmesi nemá negatívny účinok na schopnosť malty chrániť oceľovú výstuž pred koróziou.