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Hydration of Portland cement – natural zeolite mortar in water and sulphate solution

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Abstract: The objective of this paper is to characterise sulphate resistance of mortars made from ordinary Portland cement (PC) and Portland – pozzolan cement with 35 wt % of zeolite addition-zeolite based cement (ZBC). Mortars with two different cement types were tested in water and 5 % sodium sulphate solution for 720 days. The reason of increased sulphate resistance of the cement with zeolite addition relative to PC is discussed and explained.

Introduction

Two types of sulphate action on cement – based materials are distinguished: the formation of calcium sulphate dihydrate $CaSO_4$ x 2 H_2O (abbreviated as $C\overline{S}H_2$ and marked as gypsum) and 3 CaO . Al_2O_3 x 3 $CaSO_4$ x 32 H_2O (abbreviated as $C_6A\overline{S}_3H_{32}$ 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]:

$$2\,OH^- + SO_4^{2-} + Ca^{2+} \rightarrow C\overline{S}H_2 \quad (1) \qquad \text{or} \qquad C - S - H + SO_4^{2-} \rightarrow C\overline{S}H_2 \quad (2)$$

The hydration rate of reaction (2) is much more 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 (3) :

$$2\,Na^+ + SO_4^{2-} + Ca^{2+} + aq. \rightarrow 2\,Na^+ + C\overline{S}H_2 + aq. \quad (3)$$

Ettringite is formed by the reaction of 3 CaO . Al_2O_3 (C_3A) with gypsum ($C\overline{S}H_2$).

$$C_3A + 3\,C\overline{S}H_2 + 26\,H \rightarrow C_6A\overline{S}_3H_{32} \quad (4)$$

The increase in volume between the formed gypsum and origin $Ca(OH)_2$ is approximately 2.2 times and between hydration products of C_3A and ettringite even 2.6 times higher in hydrated cement systems when exposed to the sulphate solution. The formation of reaction products is a source of internal expansive stresses responsible for the damaging expansion and crack propagation. The first clear signs of sulphate action in mortars and concrete with water to cement ratio (W/C) between 0.4 and 0.6 appear when the content of SO_3 bound in the cement paste increases by 5 - 6 % from a starting value in non – attacked element. An increase by 10 - 12 % is connected with a total destruction of mortar or concrete [3-5]. 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 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 [6,7]. Zeolite increases the amount 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 [8].

This paper deals with hydration of normal Portland cement and Portland cement–natural zeolite mortars as well as their resistance against sulphate attack comparing differences in hydration processes of cement pastes with different mixture composition and important mechanical properties of attacked and non – attacked cement mortars.

Experimental

A normal Portland cement of CEM I 42.5 and natural zeolite from Nižný Hrabovec (Slovakia) were used for the tests. Mortars with cement to standard sand weight ratio of 1 : 3 and w/c = 0.6 using Portland cement (PC) and zeolite - blended cement with the composition of 60.82 wt. % of Portland cement clinker, 35.09 wt. % of zeolite and 4.09 wt. % of gypsum (ZBC) were prepared. Physical properties and chemical composition of normal Portland cement and zeolite – blended cement are given in Table 1 and 2.

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_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	3 140 kg m^{-3}
MgO	1.34	Specific surface area	336.2 m^2 kg^{-1}
SO_3	2.30	Initial set	3 hours 15 minutes
K_2O	1.82	Final set	4 hours 20 minutes
Na_2O	0.53	28 day cement strength:	flexural / compressive 7.9 / 41.7 MPa
Ignition loss	1.04		

The mortar specimens were made in steel moulds on a vibration table (50 Hz, 0.35 mm) with maximum vibration of 30 seconds. The specimens were stored at 20 °C in wet air (100 % relative humidity) and then in water for 27 days at the ambient temperature. After this curing half of the specimens was still maintained in water for 720 days and the second half was kept in 5 % sodium sulphate solution (an average 33 800 mg SO_4^{2-} per litre) also for 720 days using various specimens sizes until required testing. The Na_2SO_4 solution was regularly checked on the SO_4^{2-} ion concentration. The ratio between the volume of mortar specimens and sulphate solution was maintained on the constant level of 1 : 30.

Table 2. Composition and properties of zeolite blended cement

Component content (wt. %)		Physical properties
Insoluble residue	18.00	Specific gravity ($kg.m^{-3}$)
SiO_2	15.69	2 231
Al_2O_3	8.09	Specific surface area ($m^2.kg^{-1}$)
Fe_2O_3	3.24	950.2
CaO	41.80	Initial set
MgO	2.29	2 hours 5 minutes

Testing procedures

The mortar specimens were tested on dynamic modulus of elasticity, flexural and compressive strength. 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 in dynamic air atmosphere using 20 mg of sample material.

Results and discussion

The PC and zeolite-blended cement differ in the chemical composition, mainly in CaO, SiO_2 and Al_2O_3 quantities, insoluble residue and ignition loss values (Table 1 and 2). This is caused by the 35 wt. % replacement of PC by zeolite. Finely ground zeolite with surface area over 1000 $m^2.kg^{-1}$ contributes to the markedly higher specific surface area of zeolite–blended cement relative to that of PC. Comparison of basic mechanical properties of the mortars made from both cement types is reported in Table 3. The behaviour of ZBC mortar is comparable to that of reference PC mortar. It proves that zeolite addition to Portland cement has negligible influence on the decline of measured mechanical properties.

Table 3. Basic mechanical properties of PC and ZBC mortars

Property tested	Curing	Time (days)	Cement type	
			PC	ZBC
Flexural strength (MPa)	water	720	6.7	7.1
	Na_2SO_4	720	5.0	8.1
Compressive strength (MPa)	water	720	40.3	36.1
	Na_2SO_4	720	32.6	35.3
Dynamic modulus of elasticity (MPa)	water	720	39.1	37.5
	Na_2SO_4	720	31.9	37.3

The resistance of ZBC mortar against sulphate attack is considerably higher than that of PC mortar. Increase in weight of PC mortarkept in sulphate solution, as seen in Fig. 1, gives clear evidence of

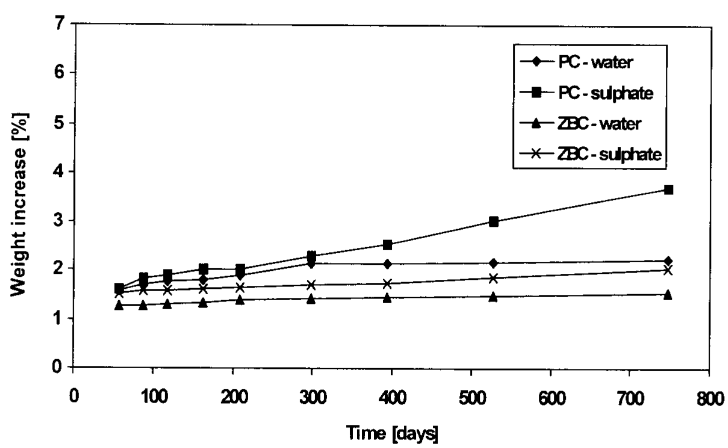

Fig. 1. Weight increase of mortar specimens kept 720 days in water and sulphate solution

voluminous reaction products formation. The consequence of this, crack propagation and decline in strength and dynamic modulus of elasticity during a sulphate attack is observed. Mortar made with the zeolite–blended Portland cement indicates minor weight increase showing negligible reaction products cumulation. The increase in weight is connected with damaging expansion. The 720 – day expansion of PC mortar kept in sulphate is 9.3 ‰ (water 0.8 ‰) and that of zeolite – blended Portland cement stored in Na_2SO_4 solution only 0.7 ‰ (water 0.3 ‰). The measured expansion values confirm the growth of solid phase volume in PC mortar exposed to sulphate attack, whereas in ZBC mortar not.

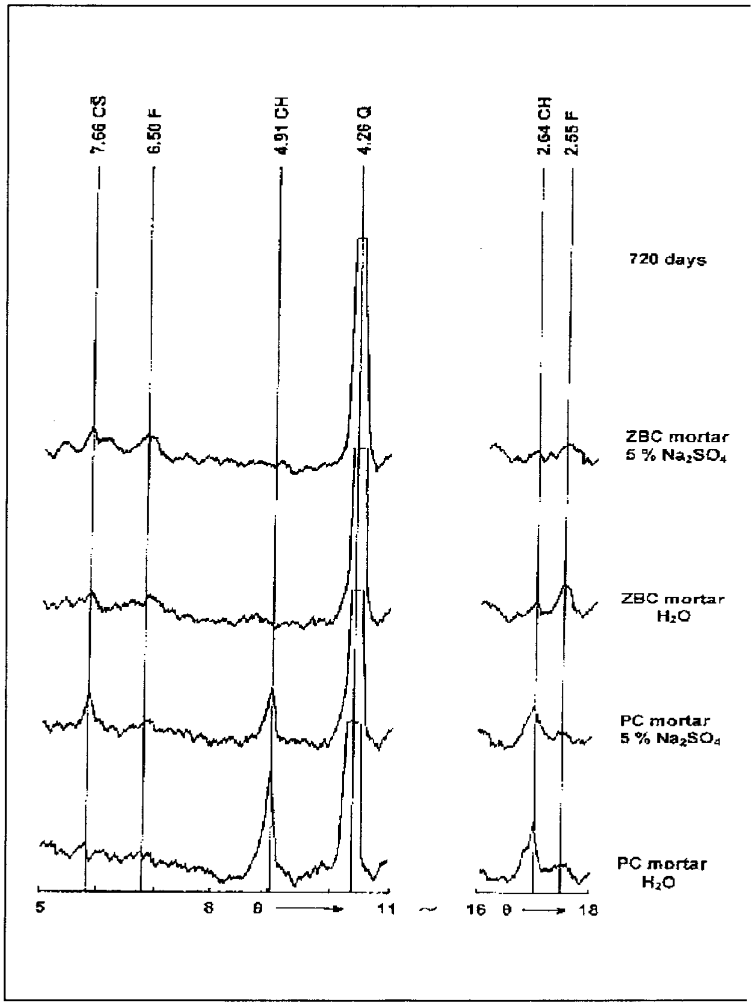

Fig. 2. X - ray diffraction patterns of mortars with Portland- and zeolite-blended cement

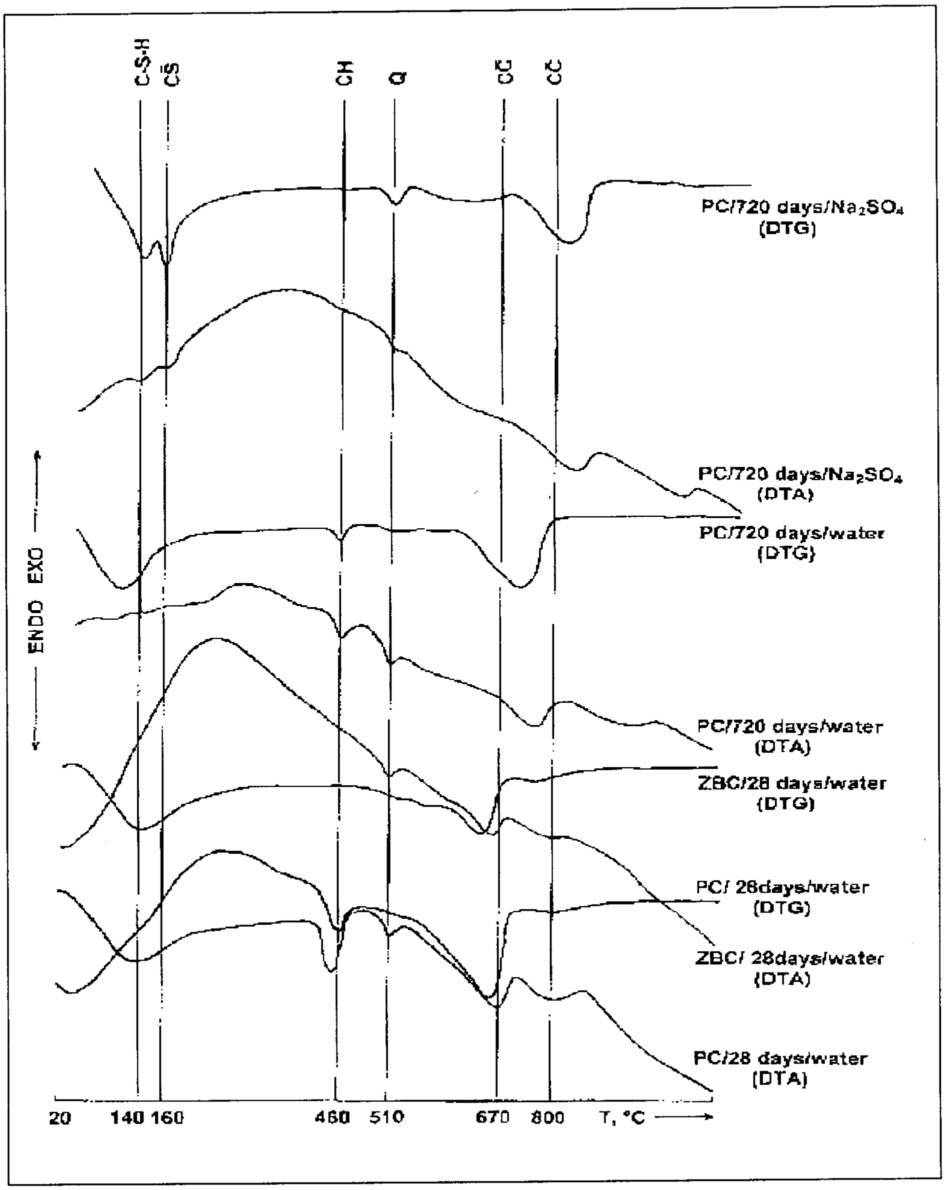

Fig. 3. DTA - DTG plots of Portland cement mortar kept in water and Na_2SO_4 solution

X–ray diffraction and thermal analysis studies show different phase composition development in PC and ZBC mortar. As seen in Figures 2, 3 and 4 the PC mortar kept in water is characterised by a high content of $Ca(OH)_2$. When exposed to sulphate, $Ca(OH)_2$ is partially consumed forming voluminous $C\bar{S}H_2$ causing damaging cracking of the specimen. No $Ca(OH)_2$ in ZBC mortar due to pozzolanic reaction of zeolite with portlandite is found kept in water and sulphate. This proves that no free $Ca(OH)_2$ is disposable for the reaction with sulphate ions and no dangerous cracking and decline in strength due to $C\overline{S}H_2$ formation is occurred in ZBC mortar specimen.

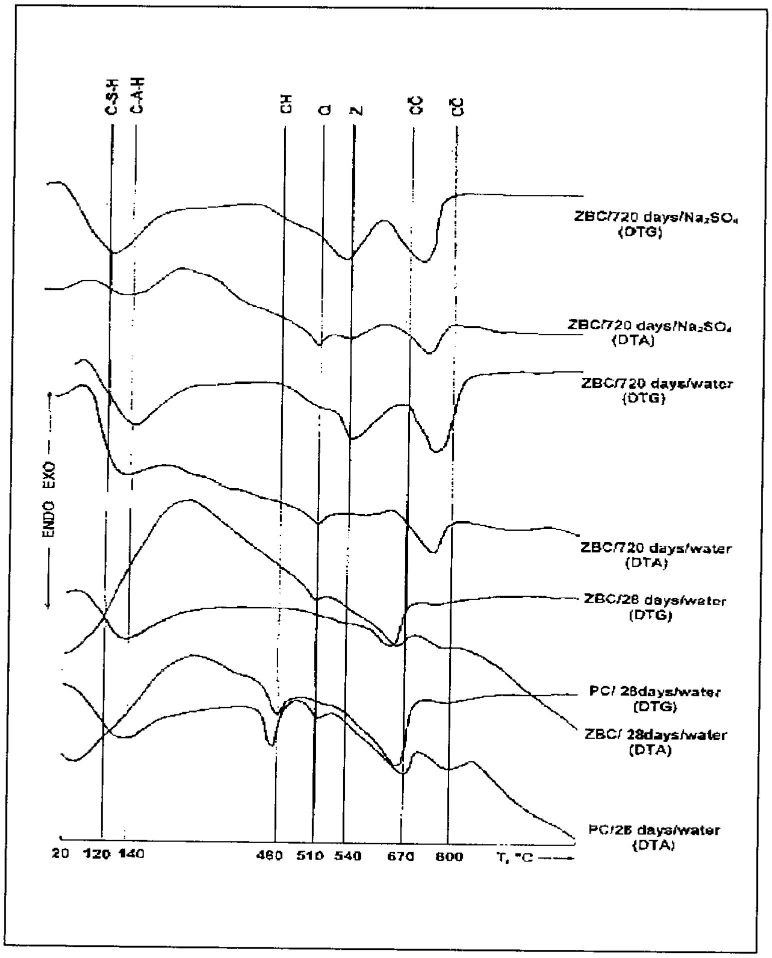

Fig. 4. DTA - DTG plots of mortars with zeolite-blended cement kept in water and sulphate

Conclusions

Zeolite-blended cement containing 60.82 wt. % of PC clinker, 35.09 wt. % of zeolite and 4.09 wt. % of gypsum has the same important engineering properties in the fresh and hardened state PC. The sulphate resistance of ZBC is markedly higher than that of PC. Similar civil engineering properties of ZBC and its improved sulphate resistance compare to PC give predict the perspective application of cement-zeolite materials in the future.

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