ZEOLITE BLENDED CEMENT FOR BETTER SULPHATE RESISTANCE

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ABSTRACT

Sulphate resistance of cement suspensions made from ordinary Portland cement (reference PC) and bentonite, and those where bentonite was completely replaced by zeolite and silica fume in the weight ratio of 1:3 and 3:1 is reported in this paper. The suspension mixture composition was modified by fine iron powder addition. The mortars were made from reference PC and Portland - pozzolan cement with 35 wt. % of zeolite addition (ZBC). Suspensions (to 20 wt. % of zeolite – 'ica fume addition, W/C = 1.0) and mortars (cement to sand weight ratio of 1:3 and W/C = 0.6) were prepared and tested in water and sodium sulphate solution for 180 days (suspension) and 720 days (mortar) using 20 x 20 x 120 mm and 40 x 40 x 160 mm specimens. The results show that zeolite addition markedly increased the sulphate resistance of cement suspension and mortar.

Keywords: cement suspension, Portland - pozzolan cement, zeolite, and sulphate attack

INTRODUCTION

Important factors influencing the resistance of cement based materials (CBM) against sulphates are the type of mineral admixture used as a partial replacement of ordinary Portland cement, such as fly ash, silica fume, blast-furnace slag and trass; the fineness of cement and pozzolan; the amount of pozzolanic materials and the concentration of reactant in the pore solution [1, 2, 3].One of the naturally occurring pozzolans is zeolite. Zeolites are hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals. The essential structural feature of a zeolite is a three-dimensional tetrahedral framework, which allows only certain size molecules to pass through. The conversion of calcium hydroxide into a voluminous calcium sulphate dihydrate and reaction of calcium aluminates with sulphate into sulphoaluminate hydrates (ettringite or monosulphate) represent the aggressive effect of sulphate solution on CBMs. Typical symptoms of sulphate attack on CBMs are transient increase in strength and elasticity modulus up to the point of reverse, which is then followed by lasting decrease. These processes are accomplished by crack propagation due to extreme expansion and steady weight increase until the loss of integrity as a consequence of sulphate ions binding into the cement matrix [4]. In Australia the results of investigation into the use of zeolites for encapsulation of solid wastes in concrete were reported in 1993 [5]. The effectiveness of zeolite was attributed largely to the general improvement of concrete durability [6]. The results of previous investigation show that clay - cement suspension with bentonite replaced by 10 - 15 wt. % of zeolite (industrially– made ZEOFIX®) and zeolite blended cement (78 wt. % of Portland cement clinker, 15 wt. % of natural zeolite and 7 wt. % of gypsum) can be classified either as a chemical resistant cement suspension or as a special Portland - pozzolan cement of 42.5 class (II/A - P) with sulphate resistance similar to that of a sulphate resistant Portland cement [7,8], and increased acidic and sulphate resistance of zeolite blended cement (60.82 wt. % of Portland cement clinker, 35.09 wt. % of zeolite and 4.09 wt. % of gypsum) compared to that of ordinary Portland cement [9,10]. This paper deals with the sulphate resistance of cement suspensions based on zeolite – silica fume addition and mortars made from zeolite blended cement with 35 wt. % of zeolite and compares important properties of attacked and non - attacked specimens.

EXPERIMENTAL

Portland cement of CEM I 42.5 (PC), natural zeolite (Nižný Hrabovec, Slovakia), silica fume (Iron Works, Mnisek pod Brdy, Czech Republic) and iron powder (Slovak Technical Standard STN 42 8084) were used for the tests. Cement suspensions with 19 – 20 wt. % of zeolite – silica fume addition in the ratio of 3 : 1 and 1 : 3, and those with 17 – 18 wt. % of zeolite – silica fume addition with 8 wt. % of fine ground iron powder, with W/C = 1.0 compared to clay – cement suspension with 10 wt. % of sodium bentonite were tested. Mortars with cement to sand weight ratio of 1:3 and W/C = 0.6 using Portland cement and zeolite blended cement (ZBC - 60.82 wt. % of Portland cement clinker, 35.09 wt. % of zeolite and 4.09 wt. % of gypsum) were prepared, and both were kept in water and 10 % (suspensions for 180 days) and 5 % (mortars for 720 days) Na_2SO_4 solution (an average 67 600 mg SO_4^{2-} and 33 800 mg SO_4^{2-} per litre). Cement suspensions and mortars were tested for strength, elasticity modulus and length changes.

RESULTS AND DISCUSSION

Two – day compressive strength of clay – cement suspension was determined as 0.9 MPa, and that of 180 – day 5.8 MPa. Cement suspension with zeolite – silica fume addition with or without iron powder has 2 – day compressive strength of 1.5 – 1.6 MPa, and 180 – day compressive strength in water of 8.9 – 10.8 MPa. Iron powder markedly improves the resistance of CBMs to carbon dioxide and acidic water by its dissolution thus sealing the pore matrix by the formation of more voluminous salts compared to origin Fe – powder. Iron powder does not negatively influence compressive strength and dynamic modulus of elasticity (Table 1).

Table 1 Strength and elasticity modulus growth of cement suspensions kept in 10 % sodium sulphate solution

Cement suspension	Curing (days)	Compressive strength (MPa)	Elasticity modulus (GPa)
Bentonite (B)	2 180	1,0 4,4*	0,9 4,9*
Zeolite (Z) : silica fume (SF) = 3 : 1 by weight	2 180	1,2 15,2	1,5 9,5
Zeolite : silica fume = 3 : 1 + iron powder (IP)	2 180	1,2 15,0	1,5 9,3
Zeolite (Z): silica fume (SF) = 1 : 3 by weight	2 180	1,6 14,8	1,6 8,3
Zeolite : silica fume = 1 : 3 + iron powder (IP)	2 180	1,6 16,3	1,6 9,5

* Data after 30 - day exposure in the Na_2SO_4 solution, specimens were up to the 60th day disintegrated due to extreme expansion and consequent crack propagation
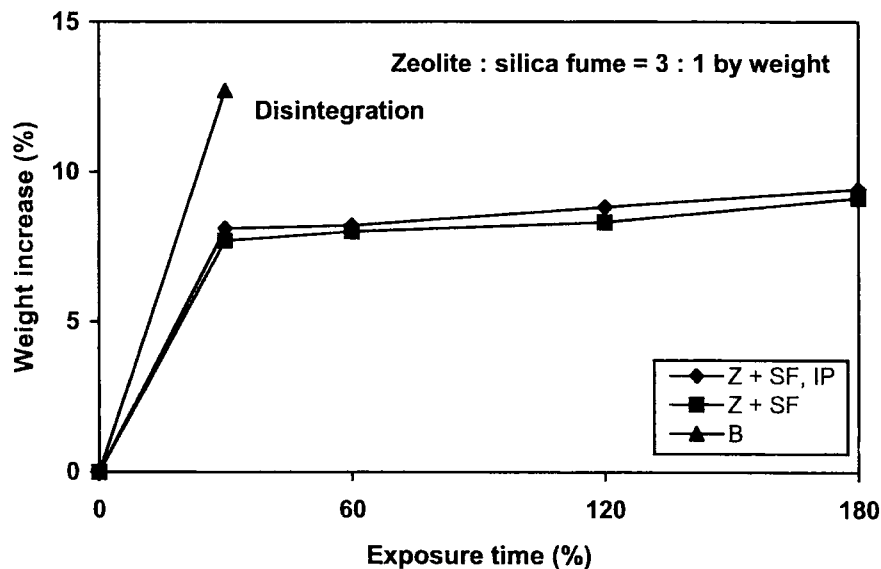
Fig 1 Influence of ground zeolite, silica fume (3:1 by weight) and iron powder on weight increase of cement suspensions kept in 10 % Na_2SO_4 solution

235
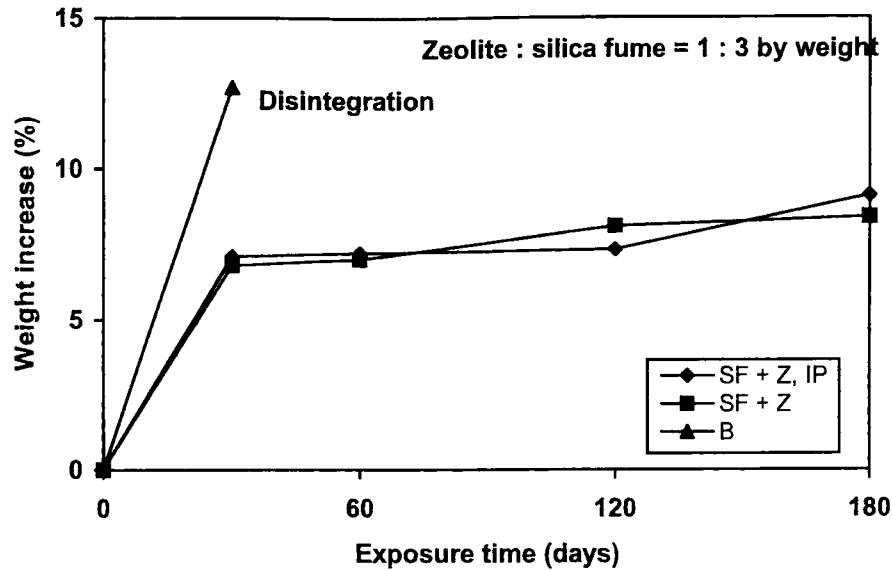
Fig 2 Influence of ground zeolite, silica fume (1:3 by weight) and iron powder on weight increase of cement suspensions kept in 10 % Na₂SO₄ solution

High sulphate resistance of cement suspensions consisting of zeolite – silica fume addition with or without iron powder is clearly confirmed by weight increases of the specimens relative to clay-cement suspension that was deteriorated between the 30th and 60th day of exposure in the Na_2SO_4 solution. No crack propagation even on edges of the observed 20 x 20 x 120 mm specimens with cement and zeolite – silica fume (+ iron powder) was observed. Properties of PC (used for suspension and mortar preparation) and ZBC are given in Tables 2 and 3. Zeolite contains 66.72 % of SiO_2 and 14.97 % of Al_2O_3 [6], silica fume 96.39 % of SiO_2, and iron powder 99.13 % of Fe. Comparison of basic mechanical properties of both cement types is reported in Table 4. An increase in weight of mortar specimens kept in water and 5 % Na_2SO_4 is illustrated in Figures 3 (20 x 20 x 120 mm), and 4 (40 x 40 x 160 mm).

Table 2 Composition and properties of Portland cement employed

| Component content (wt%)		Content of major clinker phases according to Bogue (%)	
Insolubleresidue	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	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 3 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$_2$O$_3$	8.09	Specific surface area ($m^2.kg^{-1}$)
Fe$_2$O$_3$	3.24	950.2
CaO	41.80	Initial set: 2 hours 5 minutes
MgO	2.29	
SO$_3$	2.09	Final set: 3 hours 5 minutes
Ignition loss	8.80	

Data in Tables 2 and 3 confirm chemical dissimilarities between PC and ZBC attributable to 35 wt. % replacement of CaO – rich Portland cement clinker by CaO – poor and Al$_2$O$_3$ - rich zeolite. ᵣᵢitial and final set of ZBC is accelerated by an hour compared to that of PC but without affecting ᵣₑ workability. The use of ZCB is comparable to that of reference PC. It is evident from module and strength values of both cements. Flexural and compressive strength, dynamic and Young's modulus of elasticity development in PC and ZBC mortars cured 720 days in water are very similar as seen in table 4. It proves that 35 wt. % portion of zeolite in the cement composition has a negligible importance on the drop of measured mechanical properties in comparison with reference PC. Contrary the resistance of ZBC mortar to sulphate attack is considerably higher than that of PC mortar. Typical symptoms of sulphate attack - the growth of measured strengths and elasticity modulus up to the point of reverse, and then their lasting decrease was found only in the PC mortar specimens. The ZBC mortar is sulphate resistant indicating an inverse behaviour to that of PC mortar. Figures 3 and 4 show steady weight increases of PC mortar specimens in time as the consequence of cumulating SO$_3$ - rich reaction products in the attacked cement. Similar character of weight increase in ZBC mortar specimens is missing.

Table 4 Comparison of basic mechanical properties using 40 x 40 x 160 mm specimens

Property tested	Curing medium	Time (days)	Cement type	
			PC	ZBC
Flexural strength (MPa)	water	90	6.4	5.5
		365	6.5	7.0
		720	6.7	7.1
	Na$_2$SO$_4$	90	5.7	8.0
		365	7.2	8.2
		720	5.0	8.1
Compressive strength (MPa)	water	90	36.6	33.2
		365	36.4	33.2
		720	40.3	36.1
	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	90	41.1	36.1
		365	41.5	37.0
		720	41.8	37.5
	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	90	28.7	26.7
		365	31.9	29.8
		720	31.9	30.0
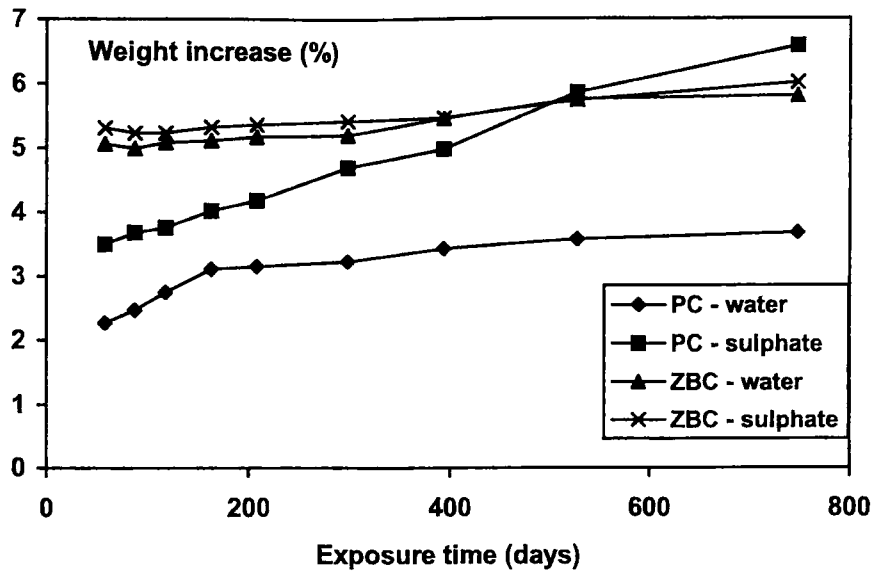
Figure 3 Weight increases of 20 x 20 x 120 mm mortar specimens
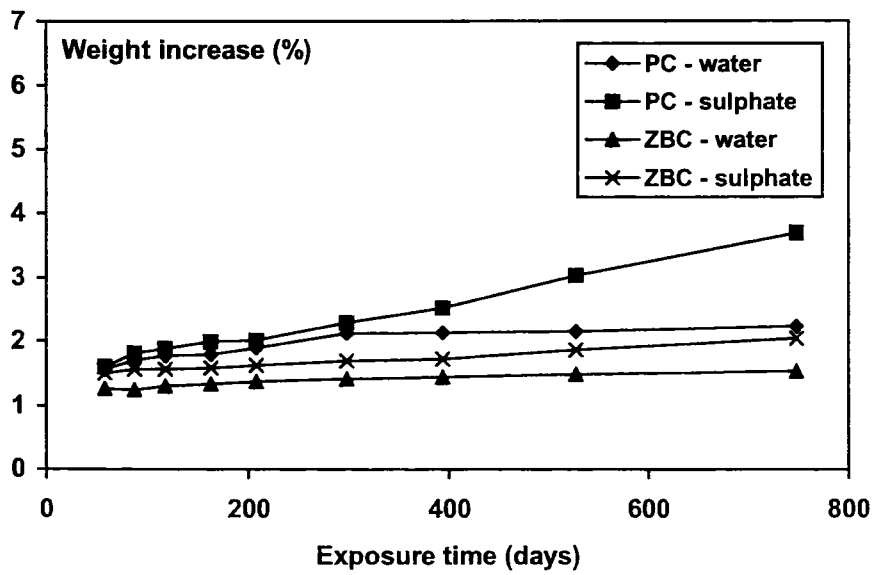
Figure 4 Weight increases of 40 x 40 x 160 mm mortar specimens

Table 5 Ignition loss, CaO and SO₃ content values and pore structure development of mortar specimens (40 x 40 x 160 mm)

Mortar and curing	Time (days)	Ignition loss (%)	Content of CaO (%)	Content of SO₃ (%)	Pore median radius (nm)	Total porosity (%)
PC water	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 % Na₂SO₄	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	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
ZBC 5 % Na₂SO₄	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

The effect of the duration of Na₂SO₄ on the increase in SO₃ content and pore structure, and on the expansion of mortars is reported in Tables 5 and 6, respectively. The content of bound SO₃ was found to be more than double in the PC mortar relative to that in ZBC mortar after 720 days. As expected, the higher the SO₃ content bound in the cement paste, the higher the expansion of the mortar. Expansion was measured on the 20 x 20 x 120 mm specimens. These results, therefore, do not fully correspond with the measured values in Table 4.

Table 6 Expansion of mortar specimens after 720 days

Expansion (‰) 20 x 20 x 120 mm	PC mortar water	PC mortar sulphate	ZBC mortar water	ZBC mortar sulphate
	+ 0.8362	+ 9.3296	+ 0.3274	+ 0.6580

The pore median radius and total porosity of both mortars kept in water, and those of ZBC mortar exposed to the sulphate were found to be 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, started to increase. This confirms characteristic manifestation of sulphate attack on the pore structure coarsening during the mortar expansion followed by crack propagation with the decrease in elasticity module and strength, and consequent disintegration of the PC mortar. The ZBC mortar shows an inverse behaviour and its high sulphate resistance is clearly demonstrated.
The results indicate that 1) zeolite – silica fume addition with or without iron powder markedly improves sulphate resistance of cement suspension compared to clay - cement suspension, and 2) zeolite blended cement with 35 wt. % portion of natural zeolite is a special Portland - pozzolan cement of CEM II/ B-P type with mechanical properties very similar to ordinary Portland cement with markedly increased sulphate resistance. The resistance of Portland – pozzolan cement of CEM II/B-P 32.5 according to European Technical Standard EN 197 – 1 (ZBC) is very similar to that of a sulphate resistant Portland cement.

APPLICATION OF ZEOLITE

The first application of zeolite in cement – bentonite suspension modified by zeolite addition was carried out at the construction of cut – off wall (Vernerov, Czech Republic) in 1989. The suspension was produced under these environmental conditions: content of sulphate ions in water 3 000 mg - 6 000 mg SO_4^{2-} litre and pH = 4.0 – 4.5 with the commercial name ZEOFIX® having National certificate of the Czech Republic. In 2001 production of two zeolite – blended cements was started in the cement plant Bystre (Slovakia). Portland – pozzolan cement CEM II/B – P 32.5 with max. 40 wt. % of zeolite replaced by ordinary Portland cement and pozzolan cement CEM IV/B 32.5 with max. 55 wt. % of zeolite found the application in concrete. These cements are suitable not only for concrete but also for slurry cut – off walls, grouting mortars and micro piles exposed to aggressive acidic, CO_2 – saturated and sulphate waters. Significant application of pozzolan cement was realized in 2001 in Jaslovske Bohunice nuclear power plant (Slovakia) at solidification processes of secondary radioactive waste. It is noteworthy that the production of geosynthetic clay liner TATRABENT with mineral filler ZEOBENT consisting of the sodium bentonite – natural zeolite filler started in 1997 in Tatrabent LCC Slovakia. The TATRABENT liner has National certificate of the Czech Republic, Hungary, Poland and Slovakia. The manufacture of the above products has continued. In Australia, there has been considerable research interest in recent years in the application of zeolite-cements in the retention of low level radioactive wastes [11,12].

CONCLUSIONS

The sulphate resistance of cement suspensions where bentonite is replaced by zeolite – silica fume addition having mutual weight ratio 1: 3 and 3: 1, and zeolite – silica fume addition combined with iron powder is considerably increased compared to clay – cement suspension usually applied for the construction of slurry cut – off walls. Zeolite – silica fume addition increases compressive strength and elasticity modulus of the suspensions kept in water and sulphate solution reducing weight increment to non – dangerous values thus avoiding extreme expansion and crack propagation, and in the final effect the loss of integrity of cement suspension with zeolite – silica fume addition. It is worth noting that zeolite – silica fume – iron powder acts as a "universal anticorrosive admixture" suitable for use in acidic, carbon dioxide and sulphate waters.

Zeolite blended cement consisting of 60.82 wt. % Portland cement clinker, 35.09 wt. % zeolite and 4.09 wt. % gypsum has, in principle, the same important engineering properties in the fresh and hardened state as ordinary Portland cement. The sulphate resistance of such a cement: Portland-pozzolan cement CEM II/B-P 32.5 according to European Technical Standard EN 197 - 1 is markedly higher than that of PC, and is the same as the resistance of sulphate resistant Portland cement having the C_3A content below 3.5 %. Moreover the potential energy savings and reduction of CO_2 - emissions to the atmosphere due to 35 wt. % Portland cement clinker replacement by zeolite, and the similarity of mechanical properties of Portland pozzolan cement with 35 wt.% content of zeolite and ordinary Portland cement clearly indicate a promising future for the manufacture and application of cements with natural zeolite addition. To this end, the use of zeolite blended Portland cements in many parts of Australia where acid sulphate soil is a recognised problem for concrete technologists would seem to have a great potential.

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