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Sulphate attack resistance of cement with zeolite additive

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Abstract

Concrete as one of the most common building material, exposed to groundwater, soil and seawater is often object to sulphate attack. Partial replacement of Portland cement by natural zeolite has been proven to be effective in reducing sulphate attack. The results of cement sulphate resistance after 52 weeks in Na_2SO_4 solution are presented. The sulphate resistance of mortars was examined by determination of linear changes of specimens immersed in Na_2SO_4 solution. The studies of microstructure of cement mortars were carried out by scanning electron microscope equipped with energy dispersive spectrometer (EDS). Investigation includes also pictures of samples after 32 weeks exposition in corrosion solution.

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Keywords: clinoptilolite; sulphate attack; corrosion resistance of Portland cement

Nomenclature

Notification for oxides compounds:

A	Al_2O_3
C	CaO
S	SiO_2
H	H_2O

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1. Introduction

Among the currently known engineering materials, concrete belongs to a group of the most common applications. Due to the different corrosive environments, which it is exposed to, including marine construction or hydraulic engineering, the precedent characteristic, that determines the use of concrete, has become its durability [1], [2], [3], [4]. One of the factors characterizing this feature of the concrete, is type of cement. For decades, a special role in shaping the physicochemical properties of concrete, play also mineral additives [6], [7], [8], [9], [10], [11]. It has been proven, that the use of the pozzolanic additives for cements increases their resistance to corrosion, due to the highly waterproof, decrease in the content of $Ca(OH)_2$ and reducing the presence of capillary pores in the matrix. In fact, it hinders the penetration of aggressive media [12]. Due to economic and technological benefits, new functional mineral additives in construction sector were required. In this group of materials, having unique properties, are zeolites [13], [14], [15], [16], [17], [18]. Natural zeolites are a group of hydrated tektoaluminosilicates, with a specific hierarchical structure. A characteristic feature of their framework is system of tetrahedra TO_4 †, linked together via shared oxygen atoms, and the presence of voids filled ions and water molecules, having great freedom of movement [19], [20], [21]. Clinoptilolite is the most abundant and economically important natural zeolites. Based on literature data [14], [22], [23], [24] it can be concluded, that this mineral in the presence of water, has pozzolanic properties, reacts with the calcium hydroxide to form a product having binding properties (C-S-H). Determinant of pozzolanic activity is the quantity and the rate of binding of $Ca(OH)_2$ by active ingradients of pozzolans (SiO_2+Al_2O_3). Clinoptilolite similarly as diatomite or volcanic tuffs, belongs to the group of pozzolans of moderate activity relative to the $Ca(OH)_2$, compared to the less active siliceous or calcareous fly ash, gaize and highly active metakaolinite or silica fume [14], [25].

So far, little publications on the influence of zeolite on the process of binding sulphate ions and corrosion resistance of cements with this addition have been noted [26], [27], [28], [29], [30], [31], [32], [33]. Therefore, it seems necessary addition to the data on the effect of zeolite on the mechanism of sulphate attack on cements, that are exposed to aggressive environment. In the paper results of investigation of sulphate resistance of cement mortars exposed 52 weeks in Na_2SO_4 solution were presented. The mortars made of Portland cement (CEM I) and cement with mineral addition of zeolite (CEM II/A-P, CEM IV/A, CEM II/B-P, CEM IV/B ‡) were tasted. Investigation of linear changes of mortars have been supplemented with visual assessment in the form of photographs of samples and SEM/EDS analysis.

2. Materials and experimental methods

2.1. Materials

In investigations Portland cement CEM I 42.5 R, natural clinoptilolite and anhydrous sodium sulfate (chemical pure) were used. Chemical and mineralogical composition of raw materials has been shown in Table 1 and 2. Authors have divided the research focus on the following steps:

- Stage I - study of measurement of linear changes of cement mortars with zeolite additive according to the Polish standard PN-B-19707:2003 and estimating the expansion of those mortars, immersed in Na_2SO_4 solution by 52 weeks,
- Stage II - assessment of the impact of zeolite on resistance of cement to sulphate attack, by visual and microscopic observation of specimens, the condition of their surface, exposed to aggressive Na_2SO_4 solution

† Where: T – Si^{4+} or Al^{3+} ions, and also Na^+, K^+, Mg^{2+}, Ca^2+, Sr^{2+}, Ba^{2+} cations

‡ Cements according to EN 197-1: CEM II – Pozzolan Portland Cement (where P – natural pozzolan and A - 6÷20% additive in cement, B - 21÷35% additive in cement), CEM IV – Pozzolanic Cement (where symbol means: A - 11÷35% or B - 36÷55% additive in cement)

Table 1. The chemical composition of Portland cement and natural zeolite, mass %.

Ingredient		SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	SO_3
Amount, %	cement	20.6	4.5	63.5	2.3	1.0	0.2	2.3	0.3	3.2
	zeolite	68.2	12.3	2.9	0.9	2.8	0.8	1.3	0.2	-

Table 2. Phase composition of raw materials.

	phase composition of cement clinker				mineral composition of zeolite				
phase	C_3S	C_2S	C_3A	C_4AF	clinoptilolite	cristobalite	Clay mica	plagioclase	quartz
Amount, %	65.3	15.8	8.2	3.6	84	8	4	3	traces

Mortars were prepared in accordance with PN-EN 196-1: 2006, p.6. The binder are composed with Portland cement (CEM I) with 25 and 40 wt. % natural zeolite additive. Water-binder ratio was 0.5.

Table 3. Binder compositions in mortars.

Recipe	The amount of additive in binder, %		Equivalent of cement
	cement	zeolite	
0	100	0	Portland Cement: CEM I
A	75	25	Pozzolan Portland Cement: CEM II/A-P or Pozzolanic Cement: CEM IV/A
B	60	40	Pozzolan Portland Cement: CEM II/B-P or Pozzolanic Cement: CEM IV/B

The amount of zeolite in cement samples was chosen to correspond with the blends CEM II/A-P or CEM IV/A (if zeolite content is 25 wt. %), or CEM II/B-P or CEM IV/B (if zeolite content is 40 wt. %).

2.2. Methods

Resistance tests of cement to sulphate attack, was carried out according to PN-B-19707:2013 „*Cement. Cement specjalny. Skład, wymagania i kryteria zgodności. Załącznik C: Oznaczanie odporności cementu na agresję siarczanową*" [34]. The basis of this method is to determine the expansion (linear changes) of samples of cement mortars, stored for 52 weeks in a solution of Na_2SO_4. Furthermore, the destructive changes of mortars, such as: cracks, lesions, leaks, discoloration, efflorescences, etc. in comparison to standard samples held in the water are recorded. Lack of volume stability and destruction process of mortars is associated with destructive effects of SO_4^{2-}reaction products on hardened cement pastes. Examples of such reactions are formation of ettringite and gypsum in Na_2SO_4 solution, which is accompanied by a significant increase in volume [11]. The speed of the corrosion process is determined by suitably high concentration of SO_4^{2-}(16 ± 0.5 g / l), by a low degree of compaction of the samples (single compaction - 10 shocks) and due to the high surface to volume ratio of the sample (sample size: 20 × 20 × 160 mm). Cement is considered to be resistant to sulphate, where the expansion of the year is less than 0.5%, and there were no cracks, discoloration, efflorescences etc. on the surface of the sample.

3. Result and discussion

3.1. Linear changes of mortars

The study of linear changes of mortars, presented in figure 1, showed that 25% addition of zeolite to the binder caused a 6-fold decrease in the mortar expansion of A relative to the mortar standardized 0 (without zeolite additive), after 52 weeks of regular observations, while 40% of zeolite additive decreased significantly mortar expansion value B relative to the reference cement, and even inhibited the growth after 20 weeks aggressive action

Na_2SO_4. Destruction of the reference mortars (without zeolite), storage in solution of sodium sulfate (VI), has occurred after 44 weeks.

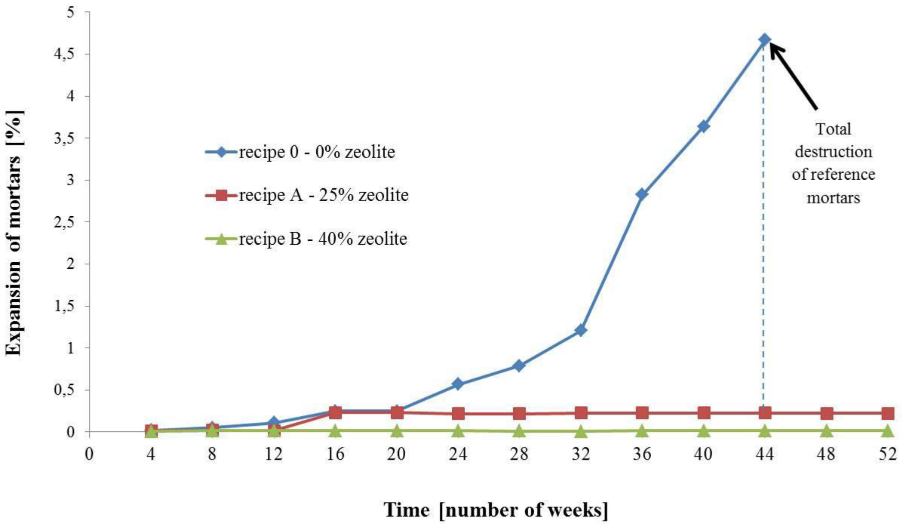

Fig. 1. Expansion of mortar specimens exposed to Na_2SO_4 solution.

3.2. Visual observation of destructive changes of investigated specimens

Visual observations of mortars, shown at figure 2, confirmed the beneficial effect of the zeolite additive to cement mortars, which hadn't visible damage of the surface, in aggressive sulphate solution, while in the reference mortar a pronounced micro-cracks of surface, exfoliation of corners and color changes (yellow and grey raids on the walls of samples), progressive over time were observed. The destruction of the surface by exfoliation of external batch of materials, is related to the crystallization of expansive ettringite and mirabillite salts, in the pore of mortars:

$$Na_2SO_4 + 10H_2O \rightarrow Na_2SO_4 \cdot 10H_2O \text{ [11]}$$

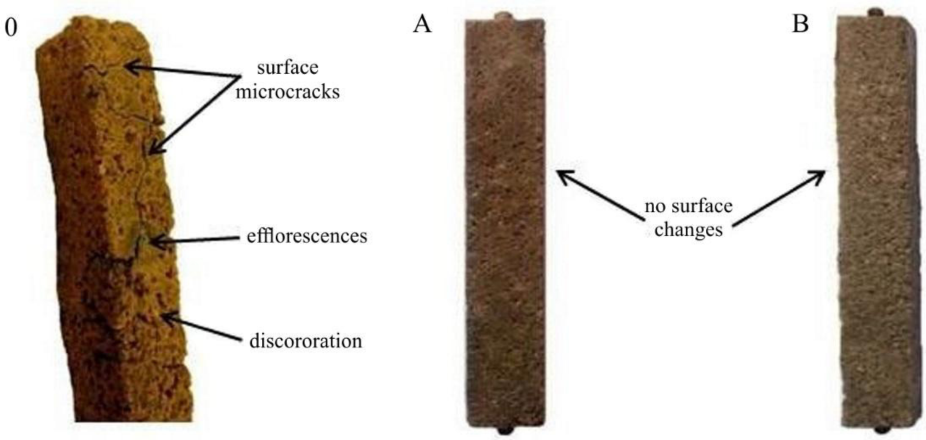

Fig. 2. Visual observation of mortars from recipe 0, A and B after 32 weeks of exposition in Na_2SO_4 solution.

3.3. Microscopic observations

Figure 3 shows images made in the scanning electron microscope (SEM / EDS) for the mortar 0, A, B, after 52 weeks their storage in a corrosive solution of Na_2SO_4.

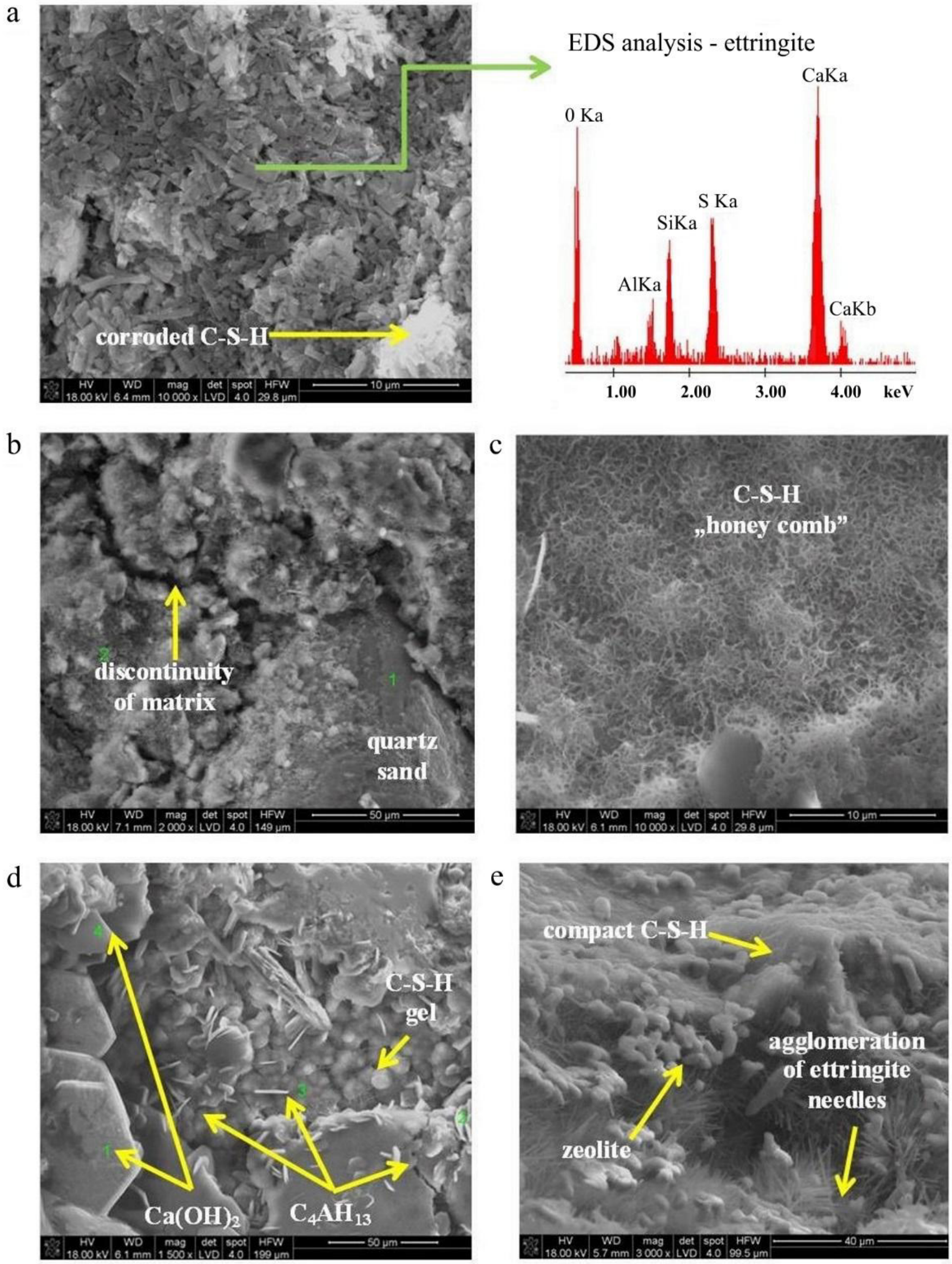

Fig. 3. The microstructure of mortars with different amount of zeolite, after 52 weeks of exposure in Na_2SO_4 solution: (a) and (b) 0% zeolite; (c) and (d) 25% of zeolite; (e) 40% zeolite additive in cement.

As can be seen on figure 3a and 3b, matrix of mortars with reference cement with no zeolite addition, is very damaged. There is a large amount of gypsum crystals (in the form reminded of gold bars), crystallizing both in microcracks and in all corroded cement matrix . Ettringite exists in the form of massive needle with a length of approx. 5 µm, forming numerous clusters. Further corroded C-S-H phase is noticeable. Matrix of mortars containing zeolite, is compact and there is no signs of sulphate destruction in the form of cracks. Honey comb (Fig.3c) and dense, compact gel (Fig. 3d,e) are the most common form of C-S-H in zeolite mortars. Sparse bushy formations of ettringite, are located in the pores (Fig. 3e). They are accompanied by the hexagonal aluminate - C_4AH_{13} and plate of portlandite – $Ca(OH)_2$. Gypsum is practically imperceptible. Very effective zeolite activity, can be justified by the relatively rapid binding of $Ca(OH)_2$ in the pozzolanic reaction, and because of the more preferable evolution of microstructure, by the formation of C-S-H phase, that makes matrix more sealed. It is also possible that the SO_4^{2-}anions have been physical adsorbed on the zeolite surface, that impeded the possibility of their reaction with the cement paste, and stopped the formation of expansive products of corrosion in mortars.

4. Conclusions

Cements containing natural zeolite exhibit improved resistance to sulphate attack. It can be seen both in the reduced value of expansion of mortars made with the zeolite additive, exposed in an corrosive environment of sulphates, and in positive visual assessment of these mortars, after long-term exposure in a Na_2SO_4 solution.

Due to specific features of natural clinoptilolite, it can be successfully used as a valuable mineral additive to Pozzolan Portland Cements CEM II/A-P or CEM II/B-P, and Pozzolanic Cements CEM IV/A or CEM IV /B.

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