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INFLUENCE OF THE PUZZOLANIC ADDITIVES TRASS AND ZEOLITE ON CEMENT PROPERTIES

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ABSTRACT

The active puzzolanic additives decrease the participation of clinker in the cement composition by decreasing the calcium hydrate products and improving the chemical, acidic and sulphate stability, and mechanical properties. In this paper the properties of cement containing natural puzzolanic additives trass and zeolite are studied. The experimental part comprises two stages. In the first stage, a complete mineralogical characterization of the puzzolanic additives trass and zeolite was performed. In the second stage, the mechanical and physical properties of blended cements incorporating 0 to 30 $\%_{mass}$ of fine puzzolanic additives (trass and zeolite) were determined. It is technologically and economically effective to use active puzzolanic additives in the cement production.

Keywords: puzzolanic additives, trass, zeolite, cement, physical-mechanical properties.

INTRODUCTION

It is technologically and economically effective to use active puzzolanic additives in the cement production [1 - 3]. The active additives decrease the participation of clinker in the cement composition by decreasing the calcium hydrate products and improving the chemical, acidic and sulphate stability. They can be milled before or milled together with the clinker. Natural active additives as diatomaceous rocks, containing mainly opal (SiO_2nH_2O); trepel, containing amorphous SiO_2 with particle size under 2 nm, and clay additives, quartz and feldspar; porous rocks, built up of amorphous fine grain SiO_2 or of volcanic origin (tuff-volcanic glassy or crystal rocks, containing from 40 - 75% SiO_2) find wide application [3 - 6]. Zeolite may be designed in accordance with the EN 197-1 [7] as natural puzzuolana. Like other puzzuolanas, being mixed with water, it does not harden, but if smoothly grinded, reacts in the presence of water at normal temperature with the soluble hydroxide of calcium, to silicates and aluminates of calcium, which are responsible for the increased hardness [8].

Natural zeolites are a large group of minerals, possessing an alumosilicate skeletal structure. Their formation is connected to the hydrothermal influence on alkaline rocks, followed by slow crystallization at particular temperature and pressure. Zeolites are frequently found in basalts, volcanic tuffs next to hot mineral springs, etc. [9]. In connection with the searching and prospecting of new deposits of acid volcanic tuffs for the ceramic industry, it was established that the geological structure in the foots of Chala elevation was formed as a result of polychromic and polyphase high-explosive acid to medium-acid volcanism. A considerable part of the volcanic activity in this region is represented by neck (tuffisite) facies and is part of an intense volcano-tectonic zone [10]. It is known that the zeolites increase the sulfate resistance of Portland cement [11]. The role of zeolite as an active additive is in binding the CaO and the formation of calcium hydro silicates, in this way restricting the formation of $Ca(OH)_2$ and the subsequent reaction with gypsum [12]. The partial substitution of Portland cement with zeolites decreases the volume of C_3A in the cement [13]. The sulphate resistance of cement is increased at higher content of zeolites; such cements can be used in aggressive media. It is also established that small quantities of zeolite in special cements for building up of coast walls of rivers significantly improve the stability of concrete. The suspension on the bases cement and zeolite are lamination more slowly. The stabilizing effect of zeolite in the cement mixture is basically connected to the absorption and transfer capability of zeolite [14]. The zeolite as a puzzolanic additive is recommended for the concrete [15 - 17]. It increases the compressive strength of the concrete, its corrosive and chemical resistance and decreases the concrete expansion [18].

The aim of the present work is the investigation of the influence of the combination of the active additives trass and zeolites on the properties of Portland cement type CEM I 52.5 R.

EXPERIMENTAL

For preparation of the cement mixtures the puzzolanic additives trass and zeolite were used. Trass is a natural product from "Trass Engineering" Kardjali with the chemical composition shown in Table 1. The mineral composition of trass is mainly volcanic glass, zeolitized to a different extent (clinoptilolite), and secondary components from crystaloclasts of magnetite, zircon, apatite, biotite, quartz, sanidine, plagioclase (Fig. 1). The used zeolite from the region of southeast Rodopi contains about 85 % clinoptilolite (Fig. 2). The chemical composition of zeolite is presented in Table 2. Cement compositions with the participation of clinker 65 $\%_{mass}$ (constant value), gypsum – 5 $\%_{mass}$ (constant value) and combinations of puzzolanic additives (trass and zeolites) in total quantity of 30 mass. %, were investigated (Table 3). A composition without additives corresponding to Portland cement type CEM I 52,5 R was also prepared and used for comparison. The clinker is from "Zlatna Panega Cement" Ltd. Gypsum is from Koshava mine, Vidin. The raw materials for each sample in quantity 3 kg each were milled in a laboratory mill for 45 min. The milled product was sieved with a sieve 1.6 mm. The quantities of raw materials in the investigated mixtures are presented in Table 3.

The following properties of the obtained cement products were determined:

• sieve analysis EN 196-6 [19]. The fineness of the cement was determined by sieving on standard sieves with 90 mm and 45 mm openings (automatic apparatus 200 LS-N Hosocawa Alpine).

Table1. Chemical analysis of trass.

Oxides	LI	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
%	3,19	71,80	12,57	0,27	0,40	1,68	0,38	5,25	1,88

Table 2. Chemical analysis of zeolite

Oxides	LI	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O
%	6,19	73,21	11,42	0,13	0,74	2,08	0,21	5,25	1,27

Table 3. Investigated compositions.

Composition	Clinker, $\%_{mass}$	Gypsum, $\%_{mass}$	Trass, $\%_{mass}$	Zeolite, $\%_{mass}$
1	95	5	0	0
2	65	5	30	0
3	65	5	24	6
4	65	5	18	12
5	65	5	12	18
6	65	5	6	24
7	65	5	0	30

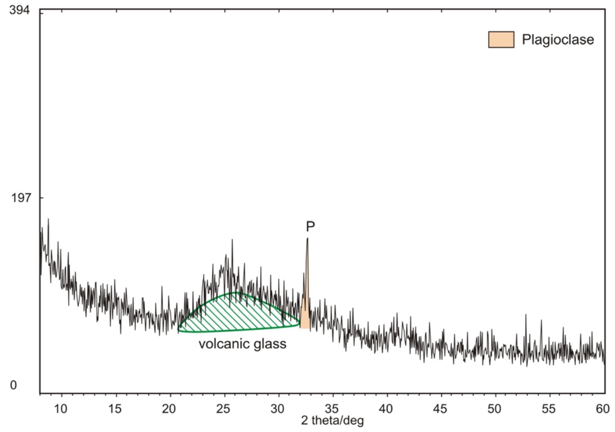

Fig. 1. XRD of the used trass from "Trass Engineering" Kardjali.

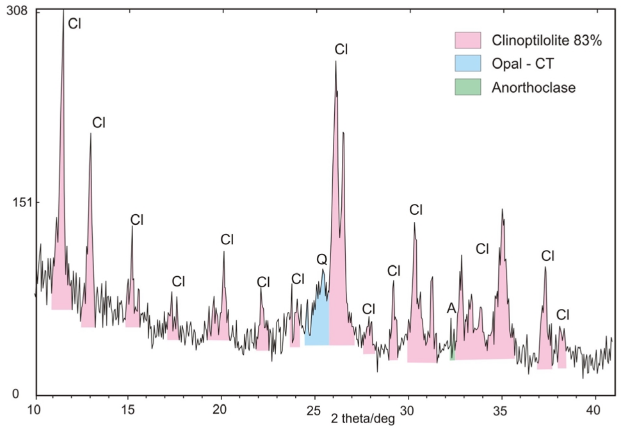

Fig. 2. XRD of the used zeolite from the region of southeast Rodopi.

- Determination of the specific surface according to Blane – EN 196-6 [19] (Blane apparatus was used).
- Determination of standard consistency – EN 196-3 [20] (Vicat apparatus was used).
- Determination of the setting time of the cement dough – EN 196-3 (Vicat apparatus was used with the rod replaced by a needle).
- Determination of the compressive strength – EN 196-1 [21]. Performed on test bodies with the shape of a prism with dimensions 40x40x160 mm, prepared from building solution containing one mass part cement to 3 mass part sand standardized according to CEN and B/C – 0.5. The test for compressive strength of the test bodies was run on the first, second, seventh and the twenty eight'h day.

RESULTS AND DISCUSSION

The obtained results for the specific surface of the cement, beginning and end of the setting time, consistency and compressive strength on the second, seventh and twenty eight'h day are presented in Tables 4 and 5, below. Sample one is a standard sample with 95 $\%_{mass}$ clinker and 5 $\%_{mass}$ gypsum as a regulator of the setting time. It is estimated as Portland cement CEM I, since it contains 95 % clinker without additives. The obtained strength is 52.5 R, which means strength on the 28th day higher than 52.5 MPa, and on the second day - compressive strength higher than 30 MPa. The whole cement brand is CEM I 52.5 R and the setting time corresponds to the requirements for more than 45 min. The type of the obtained cement product from samples 2 to 7 is determined as to the Portland puzzolanic cement CEM II/B-P, as it contains Portland cement clinker, gypsum as a setting time regulator and puzzolanic additives from 6 to 35 %. The strength is 42.5 N as on the 28th day, the compressive strength is more than 42.5 MPa and on the second day it is 10 - 20 MPa (Fig. 3). The sieve analysis shows the easier milling of the material at decreasing of the percentage of trass and increas-

Table 4. Properties of the investigated cements compositions.

Cement composition	Specific surface area, $cm^2 g^{-1}$	Initial Setting Time, min	Final Setting Time, min	Consistency, mm
1	2234	140	185	25,8
2	2105	240	300	27,4
3	5579	260	310	27,8
4	5897	130	190	28
5	4672	120	150	27,2
6	6698	120	170	28,8
7	6945	130	203	29,4

Table 5. Sieve analysis of the investigated cements.

Cement composition	45 µm	90µm
1	15	0,8
2	38,5	17,6
3	38,2	17,2
4	35,7	15,0
5	34,7	13,2
6	30,5	10,4
7	25,5	7,8

ing that of zeolite. This is best represented in sample 7, where the trass is totally replaced by zeolite. It is important to point out that the zeolite is preliminarily milled to sieve 0.8 mm. The specific surface according to Blane, the following correlation is observed – with the decrease in the trass quantity and with the increase of the quantity of zeolite the specific surface increases, which leads to bigher mobility of the cement. The standard consistency of sample 1, when compared to the rest of the samples shows increased water supply with the additives increase. This can be explained with the hydrolyticity of the puzzolanic additives. The setting time decreases with the increase of the amount of the zeolite and the decrease of the trass quantity. The results show that the earlier and final hardnesses increase with the increase of the zeolite and the decrease of the trass quantity. The results are of interest for future industrial tests due to the fact that higher strength parameters can be obtained at a constant clinker content. This can lead to a decrease in the CO_2 emissions released in the atmosphere during clinker production. It may be supposed that in milling with a vertical mill, the compressive strength parameters can be event higher than these in ball milling.

CONCLUSIONS

As a result of the experiments carried out on the puzzolanic cement preparation with the participation of a combination of natural puzzolanic additives, it was proved that the replacement of trass with zeolite is with high efficiency. The zeolite, containing over 80 % clinoptilolite, the same as the one used in the experiments, shows several advantages as a puzzolanic additive: easily milled, due to the big number of channels and cavities; decreases the specific cement mass and increases the specific surface of the cement; the increasing of the percentage of zeolite and the decreasing of the trass quantity favors the diffusion of water and dissolution of the clinker components due to its microporous structure and accelerated setting time.

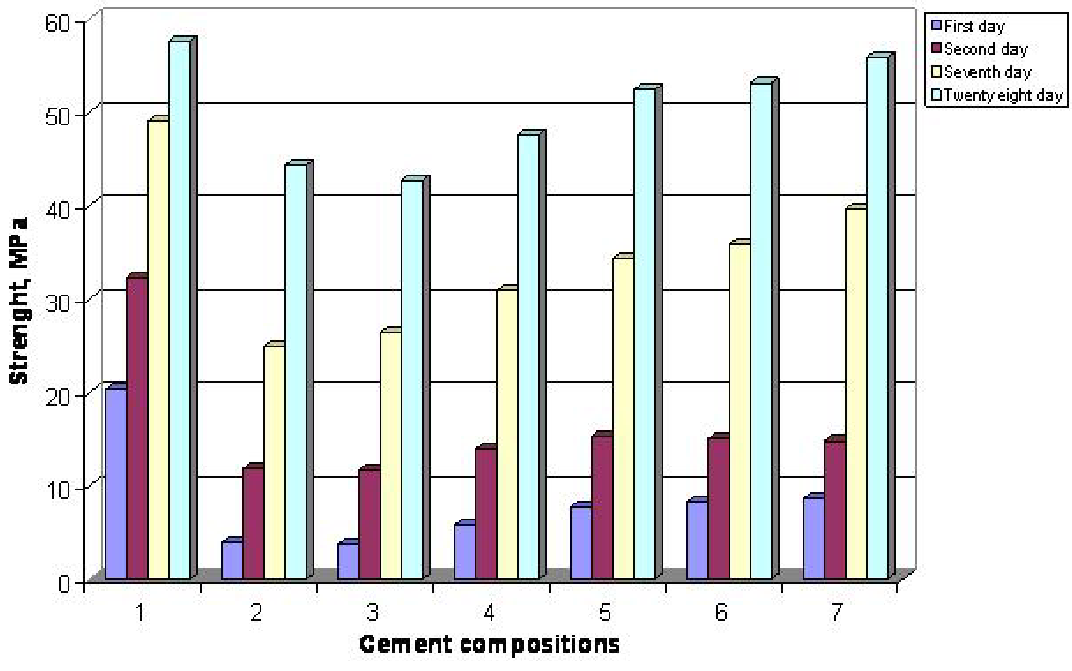

Fig. 3. Compressive strength of the studied cement compositions.

The obtained puzzolanic cement CEM II/B-P with the participation of zeolite is characterized by high physical-mechanical properties. It is established that the strength increases with the increase of the zeolite quantity and the decrease of the trass and on the 28th day, the compressive strength reaches that of the standard composition, without the participation of puzzolanic additives.

The replacement of cement clinker with zeolite in quantity 30 $\%_{mass}$ will decrease the price of the obtained puzzolanic cement and could lead to decrease in the CO_2 emissions, released in the atmosphere during clinker production.

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