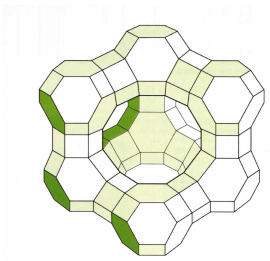
ZEOLITE – Anticorrosive and stability addition agent for cements

With the reference to a large scale research of zeolites, which was carried out in the localization Nižný Hrabovec, a restructuring of production program in the ZEOCEM, a.s. Bystré company takes place. It shall result in a complex treatment and processing of natural zeolite (klinoptilolite type) in order to use all of its unique features. One of these exploitations is also the building and construction industry.

The zeolite from the Nižný Hrabovec localization is a natural rock, which principal part is composed of crystalline hydrated aluminosilicate of alkaline metals and metals of alkaline soils (Ca, K, Na, Mg) so-called klinoptilolite. The structure of the klinoptilolite is based on the three dimensional skeleton consisting of $(SiO_4)^{4-}$ tetrahedrites interconnected via oxygen atoms, while a part of silicon atoms is replaced with $(AlO_4)^{5-}$ aluminium atoms. A certain oxygen atom is common for only two central atoms in the bridge: O/(Si + Al) = 2. So the characteristic space structure is formed with a significant occurrence of cavities, interlinked to channels, in which metal cations are placed (they are compensating deficit of charge caused b the replacement of Si^{4+} ions by Al^{3+} ions) or molecules of water. This structural configuration enable a wide range of zeolite utilization such as changer of ions, adsorbent and a preparation for a reversible hydrating and dehydrating.



Schema of klinoptilolite structure

The zeolite may be designed in accordance with the ENV 197-1 as natural puzzuolana. Similarly as other puzzuolanas, after being mixed with water, it does not harden, but if smoothly grinded, it reacts in the presence of water in normal temperature with soluble hydroxide of calcium, where compounds of silicates of calcium and aluminates of calcium are formed, which are responsible for an increasing hardness.

<u>Effect of zeolite on an increase of sulphate resistance of the Portland cement</u>

A sulfate corrosion is characterized by the formation of $CaSO_4 \cdot 2\ H_2O$ (CSH_2) gypsum and together with ($C_6AS_3H_{32}$) ettringite. The gypsum is formed by a reaction of sulfate ions with the $Ca(OH)_2$ (OH^-) hydroxide of calcium or calcium silicate hydrate jelly (C-S-H).

$$2\ OH^- + SO_4^{2-} + Ca^{2+} \rightarrow CSH_2 \quad \text{or} \qquad (1)$$

$$\text{C-S-H} + SO_4^{2-} \rightarrow CSH_2 \quad \text{when in the } Na_2SO_4 \text{ solution occurs a reaction} \qquad (2)$$

$$2\ Na^+ + SO_4^{2-} + Ca^{2+} + aq. \rightarrow 2\ Na^+ + CSH_2 + aq. \qquad (3)$$

The gypsum is bound with three calcium aluminate (C_3A) to a high volume reaction product – ettringite.

$$C_3A + 3\ CSH_2 + 26\ H \rightarrow C_6AS_3H_{32} \qquad (4)$$

The formation of the ettringite in a smaller range is supported by a reaction of the gypsum with the C_4ASH_{12} mono-sulfate.

$$C_4ASH_{12} + 2CSH_2 + 16\,H \rightarrow C_6AS_3H_{32} \qquad (5)$$

Typical symptoms of the sulfate corrosion regardless the more complicated variants with $MgSO_4$ and $(NH_4)_2SO_4$, where an exchange of Mg^{2+} and NH_4^+ ions for Ca^{2+} ions occur and as well as the combined sulfate corrosion with corrosion of ion exchanges, are as follows: formation of aluminum because of the formation of voluminous reaction products of the corrosion (CSH_2 a $C_6AS_3H_{32}$), an extreme expansion and finally a complete destruction of cement composites. The decisive indicator of the sulfate corrosion intensity is the amount of SO_3 bound in the cement matrix of the attacked composite.

The elimination of the sulfate corrosion may be ensured by an application of sulfate resistant Portland cement with a low C_3A content (up to 3.5 % hm.) or by an application of Portland puzzuolana cement. The zeolite binds CaO by a puzzuolana reaction. So the formation of $Ca(OH)_2$ is limited and consequently its reaction with gypsum is limited too. So So a low quantity of dangerous gypsum is formed according to the reaction mechanism described by means of the equations (1), (2) and (3). The ion exchange capacity of the zeolite to Ca^{2+} ions is 1.82 mmol Ca^{2+} . g^{-1}, so after the calculation it is 0.073 g Ca^{2+} . g^{-1} of zeolite. The partial substitution of the Portland cement for the zeolite decreases the volume of C_3A in the cement and in interoperation with the restriction of CSH_2 formation according to the (1), (2) and (3) the formation of the voluminous reaction product – ettringite in accordance with the equation (4) and partially in accordance wit the equation (5) is limited.

It was found out that in application of 15 % hm. Of zeolite in form of a partial substitution for a current Portland cement the same sulfate resistance of the mixture cement is achieved, the same as in case of a sulfate resistant Portland cement. Such cement may be classified as special Portland puzzuolana cement with the sulfate resistance on the level of currently accessible sulfate resistant Portland cements. Higher doses of zeolite in the mixture Portland – Zeolite cement contribute to its increased sulfate resistance. Therefore this type of cement is recommended for application in difficult sulfate aggressive environment, such as cement suspensions, grouts and concretes for special foundations.

Characteristic changes of physical and mechanical properties of a cement-stone by effect of sulfate water

By effect of sulfate water on cement-stone (concrete, cement mortar) changes of its physical and mechanical properties occur. These changes may significantly affect the resistance of concrete and concrete structures and so they functionality may be affected too.

The figure No. 1-4 shows the characteristic course of changes related to selected physical and mechanical properties of test samples prepared of current Portland cement - PC (C_3A 10,3 %), sulfate resistant

Portland cement – SPC (C_3A 2,0 %) and Portland puzzuolana cement - PPC (15 % of zeolite, C_3A 9,6 %) exposed to the effect of 5 % solution of Na_2SO_4.

Utilization of zeolite in clay-cement mixtures

Clay-cement mixtures used in the area of special foundations (for example: underground walls, grouting, etc.) are not characterized by a sufficient resistance against high concentration of aggressive substances, which are present in incursion water (sulfates, aggressive carbonic oxide) and at the same time they no justified ability to bound ions of heavy metals. These facts impede the use of clay-cement mixtures in extreme conditions (for example: when sealing toxic dumps) The above mentioned problems are solved by use of special clay-cement mixtures with an addition of zeolite (AO 274399, Authors Janotka, Jeřábek, Špaček), which are widely used by the Zadladáni staveb, a.s. Praha company under the Zeofix® registered mark.

Utilization of zeolite as stability addition agent

During the preparation of cement suspension for special purposes such as underground sealing walls, grouting and sealing of micro-hoods as well as grouting mixtures for cable cavitations it was found that even a small quantity addition of zeolite significantly improved the stability of mixtures. The cement-zeolite suspensions settle slowly and their division to solid phase and liquid is also slower. The stability effect of the zeolite in cement suspensions is certainly related also to absorption and exchange capacities of the zeolite and probably to a specific volume of cement and ground zeolite.

Other utilization of zeolite

Thanks to their unique physical and chemical features the zeolite products, which are manufactured by the ZEOCEM, a.s. Bystré company, are increasingly used in various applications in agriculture and ecology areas.

In the area of agriculture, these products are used mainly as additives for feeding mixtures, binding elements for myco-toxic substances, as insecticide and accaricide preparations, for the production of granular fertilizers, as auxiliary soil elements. In the area of agriculture they are used for purification and treatment of potable and sewage water when eliminating the NH^{4+} and heavy metals, for the production of industrial composts and geo-synthetic mats.

ZEOCEM is preparing the extension of its range of goods represented by products of the line called Natural Zeo Products (such as aquarium filters, absorbers of humidity and odors) assigned for retail trade.

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