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The effect of synthetic zeolite on hardened cement paste microstructure and freeze-thaw durability of concrete

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HIGHLIGHTS

- Zeolite from waste of AlF_3 production was obtained two hours by low-temperature synthesis.
- Concrete samples with zeolite (up to 10%) admixture were produced.
- Synthetic zeolite from waste of AlF_3 increases the closed porosity.
- Synthetic zeolite increases concrete durability.

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ABSTRACT

Tests were done with synthetic zeolite obtained by synthesizing alumina fluoride production residue, sodium hydroxide and alumina hydroxide. The synthesis lasted for two hours at 95 °C temperature. The obtained product was a mix of synthetic zeolite of modifications A and X. The binding material was cement CEM I 42.5R. The test results revealed that substitution of cement with 10% of synthetic zeolite reduces water absorption of hardened cement paste ~23.8%; the addition of air entraining admixture does not change the rate of water absorption. With the increase of zeolite content in concrete with and without air entraining admixture increases the volume of closed pores from 1.6% to 2.1% and from 4.1% to 7.6% respectively. The open porosity determined by water absorption of concrete with and without air entraining admixture changes insignificantly. The average distance between pores reduces from 360 μm to 190 μm when part of concrete is replaced by zeolite addition without air entraining admixture and from 190 μm to 130 μm in the case of using air entraining admixture. The addition of 10% of synthetic zeolite results in reduced content of portlandite and development of hydro aluminate compounds C_3AH_6 (cubic crystals) in hardened cement paste. Rose-shaped plates of calcium hydrosulphoaluminates (mono sulphate form) were also detected. These crystals together with hydroaluminates fill in the pores of hardened cement paste and thus reduce the open porosity of concrete. Substitution of 10 wt% of cement with synthetic zeolite addition increases the freeze-thaw resistance of concrete, i.e. reduces the loss of surface mass after 28 freeze-thaw cycles more than 1.6 times without the air entraining admixture and up to 3.5 times with air entraining admixture.

1. Introduction

Hardened cement paste, mortar or concrete are porous materials able to entrain gas and liquids. The pores can have an effect on the properties of the material in different ways. The compressive strength is primarily related to the total porosity, the size of pores and their distribution, the size and form of the biggest pores and the relation between the pores. Shrinking is the function of energy exchange on the surface of pore walls. Durability depends on freeze-thaw resistance and is controlled by the volume of air entrained in the pores and spaces between the pores [1,2].

Numerous tests have been done in the world with concrete modified by active mineral admixtures, such as silica dust, fly ash, zeolites, etc. Both natural zeolites (there are more than 50 types such as clinoptilolite, mordenite, filipsite, ernonite, chabazite, vermiculite, etc.) and specially designed synthetic zeolites (A, X, Y, L, ZSM-5 etc.) [3]. Synthetic zeolites are some of the most prominent additions of concrete in the development of new construction materials, such as super strong concrete, special concrete

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that can absorb heavy metals or radiation. Zeolites enable to reduce the weight of structural elements without undermining the strength. Zeolites are widely used in finishing grouts for evener surface and faster settling of the grout. Zeolite additions change and accelerate the hydration process of Portland cement, change its physical and mechanical properties [4]. Zeolites have a high content of SiO_2 and Al_2O_3. Silica dioxide and fly ash are similar to other pozzolanic materials and can improve the strength properties of concrete through $Ca(OH)_2$ reactions with pozzolans. On the one hand, zeolites, like other pozzolanic materials, give higher strength to concrete compared to cement. On the other hand, zeolites promote the formation of undesirable products, such as alkali and other complex compounds. Researchers have proven that zeolites of different modifications act as pozzolanic additions in concretes [5–7].

The production of wet process phosphoric acid generates the industrial residue hexafluorosilicic acid. The neutralization of this acid with alumina hydroxide produces alumina fluoride and industrial residue. Alumina fluoride is used as a component of electrolyte in aluminium production processes. Industrial residue AlF_3 is amorphous fine grained material called silica gel.

G. Skripkiūnas with co-authors in the patent LT 5756 B "Composite zeolite addition and the method of obtaining it" patented a synthetic zeolite obtained at 95–105 °C during 1–3 h [8]. The addition of synthetic zeolite, obtained from aluminium fluoride industrial residue, into cement paste enables to increase the compressive strength and density, and reduce the content of $Ca(OH)_2$ in the specimens. The result is lower probability of corrosion, higher density and reduced porosity of hardened cement paste and subsequently reduced water permeability. Besides, this zeolitic addition may be used in concrete or mortar mixes to improve their performance. This zeolitic addition is also relatively cheap as it is produced from aluminium fluoride industrial residue. Zeolites have a high content of active SiO_2 and Al_2O_3. According to D. Vaičiukynienė and co-authors the pozzolanic activity of hydrosodalite (zeolite) and the formation of hydroaluminate phases in hardened cement paste have a positive effect on the compressive strength, especially at the beginning of hydration process. The biggest compressive strength was recorded in specimens containing 15% of modified hydrosodalite. Higher strength of the specimens may be related with active SiO_2 and Al_2O_3 present in modified hydrosodalite [9].

Physical and mechanical properties of porous materials depend on the distribution of different size pores in the material. Materials with similar total porosity may have different properties because of a small number of big pores and big number of small pores. The characterization of a porous structure is difficult due to the difference in the pore form and size and the relationship between the pores [10].

The hydraulic pressure varies depending on the degree of pore filling with water and freezing speed. If less than 75% of pores are filled with water, the freezing water pressure is not harmful. Apparently, osmotic pressure is present in the freezing product. Water in the pores contains dissolved compounds and salts. When water turns into ice, the solution concentration increases and osmotic pressure is built up. Mechanically stronger and more resilient materials with less water in the pores are more resistant to freezing. Water absorption and freeze-thaw resistance of hardened cement paste depends on the size of pores and capillaries, their type and distribution and the closing of the pores. Closed and small pores are not filled with water completely. Pores that are not filled up with water are called reserve pores. In freezing conditions some water from fully filled pores may move to these reserve pores and thus create a space for ice expansion. The distance between filled and not filled pores must be small so that the freezing water would move from filled to unfilled pores. Evidently, the sufficient distance between pores in hardened cement paste is 0.25 mm [11].

The strength and durability properties of hardened cement paste depend on the amount of cement used and water-cement ratio (W/C). The higher is W/C ratio, the lower is the quality of concrete [10].

According to K. P. Mehta, the pores in hardened cement paste can be divided into three main groups according to their form and size: capillary pores, gel pores and air pores [12].

Capillary pores in hardened cement paste are formed through the evaporation of excessive water used in producing the cement paste. Usually, the cement paste is made using more water than it is necessary for chemical reactions that occur during the setting of concrete. According to A. K. Kallipi, capillary pores are open and easily fill with water. The destructive effect during freezing depends on the amount of water in hardened cement paste. Presumably the bigger amount and size of the pores reduce the freeze-thaw resistance of concrete [10]. According to I. Soroka and G. Skripkiūnas, the amount of capillary pores in hardened cement paste depends of W/C ratio [13,14]. According to T. C. Powers, the freeze-thaw resistance of hardened cement paste increases when W/C ratio is lowered to 0.4 and more [15]. R. Feldman found out that water in capillary pores freezes completely when the temperature falls below–13 °C, whereas ice formation in the pores occurs in the temperature range from 0 °C to –13 °C [16].

Gel pores have no influence on freeze-thaw resistance of hardened cement paste because they are very small, ranging from 1.5 to 2.0 nm in size [10,13,17,18]. H. Romberg found that gel pores do not have a significant effect on the strength and permeability of concrete due to their fineness and absence of free water in the pores [19].

S. Zhenhua with co-authors found that air-entraining admixtures reduce the expansion of concrete specimens and decrease the surface deterioration by salt solutions [20].

According to A. K. Kallipi, air pores create reserve volumes. In contrast top capillary pores, air pores increase the freeze-thaw resistance of hardened cement paste because they are closed and do not fill with water, their they have a spheric shape, their size varies from 50 to 300 μm, they are formed during the mixing of the paste [10].

The fineness of air pores is another feature that influences the freeze-thaw resistance of concrete. With the same amount of air in the hardened cement paste there are more fine air pores and distances between them are smaller. In this case water affected by the pressure of the ice has to permeate to the air pore. When the internal distance between air pores is smaller than 200 μm, the hardened cement paste is freeze-thaw resistant [10,13,21,22].

The material is destructed due to cyclic freezing and thawing for several reasons [13,23–25]:

- Hydrostatic pressure of water that builds of when water freezes and its volume increases;
- Formation of ice crystals and their growth in capillary pores;
- Osmotic pressure resulting from the differences of alkali and salt concentration in the liquid phase.

A film can be formed on micro capillaries, the radius of which is below 0.1 μm, as a result of vapour absorption from the environment. Macro capillaries with the radius above 0.1 μm may be filled with water only if there is a direct contact. Besides, macro capillaries do not absorb moisture from the environment but give away moisture to the environment instead [10].

The porosity of concrete is a very important parameter in the evaluation of concrete durability. Capillary porosity and air content can be controlled in concrete production process. The system of pores in cement concrete is made of four types of pores: gel pores;