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THE EFFECT OF SYNTHETIC ZEOLITE OBTAINED FROM ALUMINIUM FLUORIDE WASTE PRODUCTION ON HARDENED CEMENT PASTE

Zeolites can be found in nature; however, not all natural zeolites can be synthesized and not all analogues of synthetic zeolites can be detected in natural surroundings. Synthetic zeolites rather than the natural ones are used more frequently, as they are cleaner and the particles of synthetic zeolites are more uniform. It should be considered that synthetic zeolites are obtained from production waste, the utilization of which is a relevant issue these days. Zeolites are attributed to frame aluminosilicates with an open crystal lattice. The topology of the frame is the only criterion for identifying the structure of zeolites. Theoretically, a number of the structures of the frame can be counted; however, only 32 types of those can be explained. Synthetic zeolites form heating the suspensions of alkali aluminosilicate mixtures, i.e. those made of SiO_2, Al_2O_3, alkali and water. Zeolites can be synthesized from crystalline or amorphous materials, aluminosilicate gels or alkaline metals. The initial formation of the structure of zeolites can only take place in the presence of water.Synthetic zeolites appear as the most promising concrete components in developing new building materials such as very strong concretes and special concretes having the property to absorb heavy metals or inhibit from the emitted radiation. The use of zeolites can reduce the weight of the structural elements of buildings without a decrease in strength indicators. Zeolites are widely applied for decoration and producing smoother surfaces as well as mortar hardens faster. Zeolite additives change and allow speeding up the hydration process of Portland cement thus causing variations in its physical and mechanical properties.

For producing wet-process phosphoric acid, hexafluorosilicic acid, as waste, forms. For obtaining aluminium fluoride and waste, this acid is neutralized with the help of aluminium hydroxide. Aluminium fluoride in Lithuania is produced by the Joint-Stock Company *Lifosa* that is a fertilizer factory situated close to Kedainiai town. Aluminium fluoride is used as an electrolyte component for producing aluminium. The annual received waste of aluminium fluoride makes on average 5927 tons. AIF_3 production waste is amorphous, ultra-dispersive substance called silica gel. In their patent LT 5756 B *"AComposite Zeolite Additive and a Method for Obtaining It"*, G. Skripkiūnas, D. Vaičiukynienė, V. Sasnauskas and M. Daukšys patented the synthetic zeolite obtained within the synthesis process at a temperature of 95–105 °C for 1–3 hours.

For conducting research, Portland-cement CEM I 42,5 R.

For modifying cement-concrete, the zeolite additive consisting of aluminium fluoride production waste, sodium hydroxide and aluminium hydroxide was used. Synthesis was performed according to patent LT 5756 B *“AComposite Zeolite Additive and a Method for Obtaining It”.*

For analysing zeolite additives and the structure of the modified samples of hardened cement paste, scanning electron microscope SEM JOEL JSM-7600F was employed: the resolution of the device is 1.5 nm, magnification – from 25 to 1 000000 times, the conducted experiment used the voltage of 10.0 kV, the surface of the tested samples were coated with gold. Diffracto-meter DRON-7 was used for performing an X-ray examination. The size of the binder and the particles of zeolite additives as well as their distribution were determined employing the dry-wet method and laser granulometer CILAS 1090. The particles of the synthetic zeolite additive are spherical, the average size of the particles is approximately 11 μm, and they are made of a large number of small plate-shaped irregularly located crystals the size of which is approximately 100 nm.

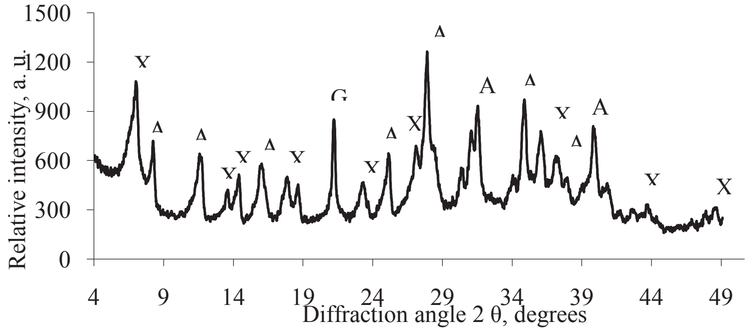
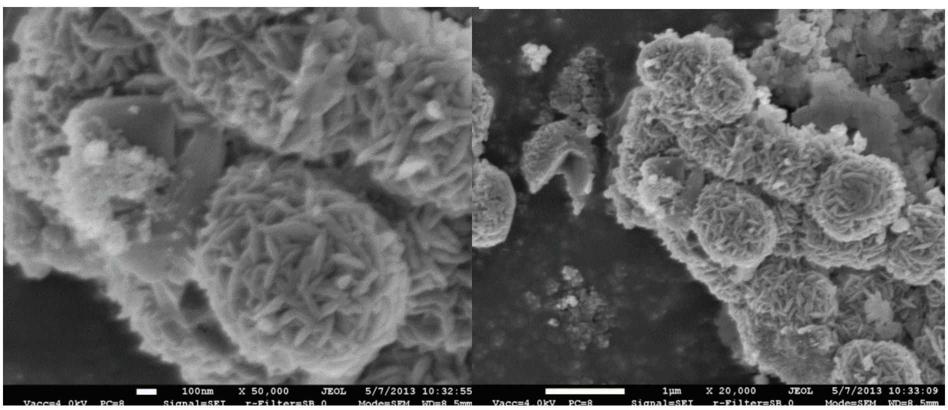


Fig. 1. Modified with $CaCl_2$ zeolite additive radiograph: X – X zeolite modification; A – A modification of the zeolite; G – gibbsite



a) b)

Fig. 2.The microstructure of the synthetic zeolite from AlF_3 waste a) 50 000 times magnification; b) 20 000 times magnification

X-ray diffraction examination has showed that the synthetic zeolite is made of the zeolite of X ($Na_{88}Al_{88}Si_{104}O_{384}H_2O_{220}$) and A ($Na_{12}Al_{12}Si_{120}O_{48}H_2O$) modifications.

To assess how different zeolite additives influence the pH values of the binder, research on grout having different zeolite additives was carried out. The plasticizing admixture is an acid solution having the pH of 5.05, and zeolite additives are alkaline having the pH □ 7, i.e. the value of zeolite additive is 9.93. The pH of the grout modified with the synthetic zeolite and having the content of the zeolite additive increased up to 10 % slightly varies. The electrical conductivity of the grout with the synthetic zeolite additive is by 32.4 % lower than that of the grout with no additive.

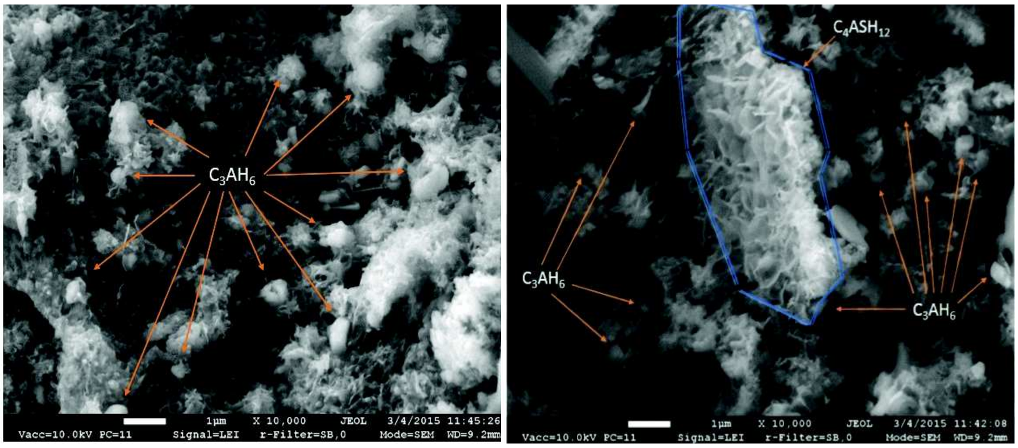


Fig. 3. SEM of hardened cement paste with a 10 % zeolite additive

X-ray structural research on the specimens shows that, after the insertion of up to a 10 % zeolite additive into hardened cement paste, a reduction in portlandite is recorded and hydroaluminate compounds C_3AH_6 are detected. SEM research has identified the form of hydroaluminates (cubic crystal structure). Also, the 'rose-shaped' plate-like crystals of hydrosulphur-aluminates of monosulphate calcium, which, along with hydroaluminates fill the pores of hardened cement paste thus decreasing the open porosity, i.e. water absorption, of the paste, have been detected.

The replacement of cement with the synthetic zeolite by 10 % shows that concrete density remains almost unchanged after 7 and 28 days, whereas the compressive strength of hardened cement paste, though keeps on staying almost in the same position after 7 days, following a longer hardening time, i. e. 28 days, increases by 13.4 % and 28.6 % using 5 % and 10 % of the synthetic zeolite respectively.

Within the period of stiffening, water absorption of hardened cement paste sharply decreases from 14.5 % after 7 days of stiffening to 5.9 % after 28 days. Replacing 10 % of cement in hardened cement paste with the synthetic zeolite provides that water absorption, following 28 days of stiffening, significantly drops to 1.5–2.9 %.

The synthetic zeolite additive received from aluminium fluoride production waste changes the processes of cement hydration thus binding portlandite formed within hydration and making new cement hydration products such as calcium hydro aluminium C_3AH_6 as well as increasing the content of calcium hydro-sulphate-aluminates $C_4A\acute{S}H_{12}$ in hydrated hardened cement paste.While supplementing hardened cement paste with the synthetic zeolite additive received from aluminium fluoride production waste, the compressive strength and density of the specimens can be increased and the content of $Ca(OH)_2$ can be reduced, which results in a decrease in the probability for corrosion, a growth in the density of hardened paste and a reduction in porosity, which causes reduced water permeability. Moreover, the latter zeolite additive can be included into the composition of concrete or mortar thus improving their performance. Also, this zeolite additive is characterized by low cost, as the main raw material to produce the supplement is aluminium fluoride production waste.

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СОВЕРШЕНСТВОВАНИЕ ТЕХНОЛОГИИ ПРОИЗВОДСТВА СТРОИТЕЛЬНОЙ ИЗВЕСТИ ИЗ ПЕРЕУВЛАЖНЕННОГО СЫРЬЯ

В связи с ростом производства автоклавных материалов на основе строительной извести повышаются требования к её качеству, в том числе к стабильности её основных свойств.

До недавнего времени строительная известь производилась на всех заводах Республики Беларусь по мокрому способу. Несмотря на многие достоинства этого способа, такие как высокая реакционная способность получаемой извести и однородность её вещественного состава, ему присущ большой недостаток, а именно его высокая энергоёмкость, достигающая 310–320 кг условного топлива на тонну извести[1].

В связи с ростом стоимости углеводородного топлива технологию производства извести необходимо было модернизировать. Это привело к необходимости перехода на сухой способ, при котором количество испаряемой влаги из сырья снизилось с 38–40% до 26%, что сократило расход с 320 кг до 240 кг условного топлива на тонну извести. Производство извести по такой технологии впервые в Беларуси было налажено в филиале ОАО «Белорусский цемент-