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ZEOLITES AS STRUCTURE FORMATION PRODUCTS OF ALKALINEOUS CEMENTS HYDRATION

The paper concerns analysis of theoretical and experimental studies, according to which, in conditions of artificial stone making for buildings purposes (cement, concrete), synthesis of alkaline aluminosilicates similar to natural minerals of zeolitic group occurs. Presence of such new formations in hydration products of standartized type alkaline cements provides their high running abilities and durability.

Key words: hydration, zeolite, alkaline cements, hydronefeline, analcime, pectolite

Наведено аналіз теоретичних і експериментальних досліджень, згідно з якими в умовах отримання штучного каменю будівельного призначення (цементи, бетони) здійснюється синтез лужних алюмосилікатів, аналогічних природним мінералам з групи цеолітів. Наявність таких новоутворень в продуктах гідратації лужних цементів стандартизованих типів забезпечує матеріалам високі експлуатаційні властивості і довговічність.

Ключові слова: гідратація, цеоліти, лужні цементи, гідронефелін, анальцим, пектоліт.

Alkaline cements are proposed as the alternative to Portland cement for several reasons: existence of some special properties which stiffen high durability to concretes on their basis, ecological advancement due to decreasing polluting emissions into environment [1]. Scientific concept originality of such materials consist sin providing the interaction conditions for the system “alumosilicate – alkaline” resulting in synthesis of new formations which are the analogous of the natural minerals of zeollitic groups [2]. Obviously, durability of natural formations such as zeolite and analcimic sandstones runs into millions of years. This makes it reasonable to suppose that artificial formations of such compositions would be characterized by similar durability.

Due to high basicity and non-stability of minerals (C_3S, C_2S, C_3A, C_4AF), hydration processes in calcium-based cements are realized in artificial conditions more actively, than in natural processes of alkaline rocks formation of stable structure. To accelerate such processes, which can be carried out inartificial conditions according to the principles of natural mineral formation, it is necessary to transform original substances from their stable (low-activity) state into non-stable (activity) state including vitreous one, and to introduce alkalis on the outside and in more concentrated state. Such substances include techno genic products of vitreous structure as granulated blast furnace slag, fly ash, waste products from basalt fiber production etc.

Therefore, opportunity of natural process reproduction when obtain in artificial to neswerelaidin the basis of alkali cement designing in the capacity of theoretical conception formulated in priority scientific studies of V.D. Glukhovsky [2, 3] and studies of scholar school of Kiev national university of building and architecture [4, 5, 6].

The Object of this review is analysis of the role of artificial zeolites in formation of cements tone characteristics as the matrix of compositional building materials of different purposes.

Mechanism of high-basic silicate sand aluminates clinker hydration process activation by alkaline metal compounds is well-known. In accordance with this mechanism, small quantities (1-2%) of alkali do not change substantially the composition of new formations, and compounds that are typical for hardening

Portland cement continue to be the structure formation hydrates in such systems [7]. The mechanism noticeably differ from the abovementioned when alkaline compound is added in quantity 12% by mass. and takes participation in formation of hydrated products, the nature of which differ from ones that are formed in Portland cement hardening processes. Just by this quality such cements are put into the group of alkaline cements [1,8,9].

Different type soft alkaline cements according to ДСТУ Б В.7.-181 are determined by alumosilicate component composition and alkaline consuming in terms of R_2O. Therefore it defined the priority of formation character of hydrated product sand opportunity to obtain the artificial stone with regulated properties. This thesis is explained by Fig.1, according to which in the case of priority of R_2O-Al_2O_3-SiO_2-H_2O (for example, $Na_2OAl_2O_32SiO_22H_2O$) system compounds in the hydration products at minimum presence of RO-SiO_2-H_2O (for example, $CaOSiO_2H_2O$) system formations, alkalinous cements take up outer position by composition and properties relating to the cement of type ЛЦЕМ I (vector on the right). When the quantity of alkaline hydrosilicates in hydration products is minimum and the quan tity of calcium hydrosilicates (vector on the left) is maximum, the system is approaching to the cement of type ЛЦЕМ II. The medium places in such vectors are occupied by the cements of type ЛЦЕМ III, ЛЦЕМ IV, ЛЦЕМ V.

R_2O-Al_2O_3-SiO_2-H_2O
ЛЦЕМ II 0% --→ 100% ЛЦЕМ I
ЛЦЕМ III , ЛЦЕМ IV, ЛЦЕМ V

RO-SiO_2-H_2O
ЛЦЕМ II 100% ←--------------------------------------- 0% ЛЦЕМ I
ЛЦЕМ III , ЛЦЕМ IV, ЛЦЕМ V

Fig.1. Principles cheme of alkaline cement type determination by the character of hydration products

Alkaline cement of type ЛЦЕМ I could be presented by the system R_2O-RO-Al_2O_3-SiO_2-Fe_2O_3-FeO, where the granulated blast furnace slag is used as silicate constituent. Such types of cements are the most investigated ones from the point of view concerning influence of the alkaline component nature, chemical composition of slag and hydration temperature on the genesis of new formations and cement properties [9, 10, 11].

By physical and chemical investigations, it is stated that on the initial stage of hydration in normal conditions the basic new formations are calcium hydro silicate soft obermorite group and geleous phase of variable composition.

Increasing of the temperature up to (70 – 80) ^{o}C results in formation on the basis of such amorphous phase, obtained by using the slag from M_o> 1,0, calcium hydroalumo silicates in the form of jasmondine $Ca_2Al_4O_{16}9H_2O$, faujasite $CaAl_2O_84H_2O$, and additionally thomsonite, that is related to zeolitic group, in the case of using acid and neutral slag.

The most important is the development of the crystallization process by time: after 180 days of hardening the zeolite-like phasesofhydronepheline $Na_2OAl_2O_32SiO_22H_2O$ (d = 0,638; 0,368; 0,285; 0,279; 0,213 nm) and natrolite $Na_2O\cdot Al_2O_3\cdot 3SiO_2\cdot 2H_2O$ (d = 0,443; 0,343; 0,247; 0,219; 0,201 nm), are quite noticeable on the x-ray diffraction pattern of hydration products. In the specimen of on the basis of acid slag analnime is presented - $Na_2OAl_2O_3$ $4SiO_2$ $2H_2O$ (d=0,560;0,390;0,343 nm). The character of new formations thermograms evidences availability of chemically bounded water dehydration of which is shown by deepen do effect in the range of (410 – 425) ^{o}C, that is typical for zeolites; exoeffect at 900 ^{o}C is related to recrystallization of the substance into the waterless alkaline alumosilicate of nepheline composition $Na_2O\cdot Al_2O_3\cdot 2SiO_2$, which is similar to the natural mineral.

Kinetics of the new formation synthes is in the cement stone influences its properties. As for example, when sodium silicates $Na_2OxSiO_2nH_2O$ (x = 1,0-3,2) are used as acid substance, the cement on the basis of acid slag is characterized by corresponding prolongation of setting terms from 20 min. to one and half hour, intensity changes concerning formation of initial strength of standard specimens (two days) in the range of 40 – 70 MPa and maximum on 28-th day in the range of 45-140 MPa. The end products of hardening in such systems are to bermorite $C_5S_6H_n$, ksonotlite C_6S_6H and analcime NAS_4H_2 phases. The data presented in Fig. 2 evidence principle difference in development of structure formation process sin the case of granulated blast furnace slag interaction with calcium and sodium compounds.

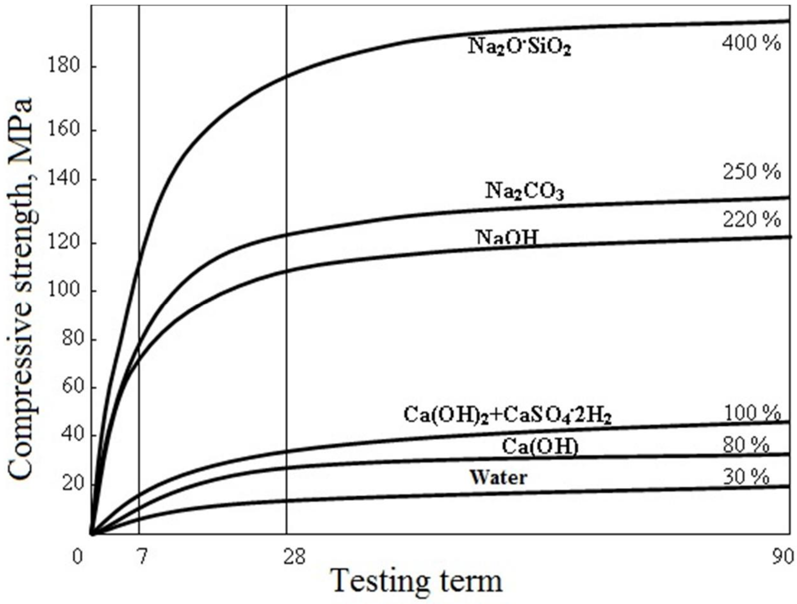

Fig.2. Strength of specimens of standard density paste on the basis of granulated blast furnace slag with different activators and water

The most important indicator of positive role of synthetic zeolite in property formation of such cement is corrosion stability. The particular investigations showed that ЛЦЕМ I is characterized by resistance coefficient in the range 0,9 – 1,1 when implementing standard investigations in the water solutions of sulphate and magnesian salts, nitrates, sea water and soft water, benzene, concentrated ammonia, 20 % sugar solution, lean solution of lactic acid etc.

Presence of well-developed gel porosity due to both zeolitic and hydrosilicate constituents of new formations in the cement matrix, that under goes some regulations, provides freeze resistance of concretes in the range of 1000 standard cycles of cyclic freezing and defrosting [4, 6].

ЛЦЕМ II is regarded as opposition to ЛЦЕМ I by calcium constituent in the form of clinker – it is maximum. Reasonability of alkaline compound introducing is stipulated by significant increasing of clinker hydration degree at lower basicity of the hydrosilicate phase. As for example sodium silicate implements structure formation function with formation variable composition hydrates in the system $[Na_2O–Al_2O_3–SiO_2–H_2O] – [CaO–Al_2O_3–SiO_2–H_2O]$.

Presence of decelerate additive, that was used in the investigations on the bases of research [12, 13] in the form of semiaquatic calcium sulphate, is obligatory technological element.

The most important result of such alkaline cement hydration is absence of portlandite and high basicity calcium hydrosilicates in hydration products. Alongside with CSH (I) phases, ksonotlite, riversidite and hydrolite, presence of zeolite-like phase that is analogous to hydronifeline $NaO·Al_2O_3·2SiO_2·2H_2O$ (d = 0,76; 0,46; 0,293; 0,284; 0,279; 0,260 nm) is noticed. Increasing of initial (2 days) compression strength up to 32 MPa against 22 MPa for the analogue without alkaline and improving of plasticizing properties is explained by participation of zeolite phase in the structure formation process.

ЛЦЕМ III-3, along side with slag, contains fly ash in minimum quantities of Portland cement (20%) as well as alkaline compound in quantity from 1,5 to 12 % [14]. According to x-ray analysis data[15], phase composition of the new formations of such cements after 28 days hardening in standard conditions is presented mostly by poorly crystallized low-basicity calciumhydrosilicatesof type CSH (B) (*d*= 0,301 0,304; 0,276; 0,210; 0,184; 0,181; 0,168 nm), j is maundine $Ca_2Al_4O_{16}9H_2O$ (*d*= 0,188; 0,273; 0,274; 0,418 nm), pectolite - $NaCa_2[Si_3O_8(OH)]$ (*d*= 0,290; 0,274; 0,192 nm). Pectolite synthesis is confirmed by double end effects at (750 – 800) °C. Cement activity fter 28 days is in the range of (34 – 41) MPa, depending on fly ash content and respective alkaline component. Corrosive resistance of the concrete on the basis of alkaline cement ЛЦЕМ III-З is explained by presence of zeolitic phase in the hardened cement matrix and absence of portlandite. Analysis of fig. 3 [15] data concerning Na_2O distribution evidences the fact that structure formation in the cement matrix provides even bounding of alkaline ions by the material volume.

Alkaline puzzolanic cement in stead of ash possibly could have basalt rock or wastes of basalt fiber production – ЛЦЕМ III-Б. It is stated [16], that hydration of such cements results in formation of almost the same compounds but due to increasing content of vitreous phase in entering system, the greater volume of such new formations as analcime and natrolite are fixed and calcium hydrate is presented as hydrogranates of variable composition and AF_m-phase. Cement M400 allows to obtain concretes characterized by high resistance in 5 % solutions of sodium and magnesium sulphates, at that the resistant coefficient after 12 month is equal to 1,1 and 0,9, correspondingly [16].

Alkaline Portland cement ЛЦЕМ IV contains (36 – 89) % slag, (11 – 64) % clinker and, depending on the content and composition, is characterized by makes M400 i M500. Addition of calcium sulphate hemi hydrate as setting decelerator allows to use such cements in ready-mixed concretes [12,13]. According to chemical and physical data, $CaSO_40{,}5H_2O$ and Na_2CO_3 which are presented in the composition facilitate to avoid tenardite (Na_2SO_4) formation in hydration products and to form zeolite-like phase of pectolite $NaCa_2Si_3O_8OH$ (d = 0,274; 0,193; nm) alongside with CSH (B) and C_2SH (II)

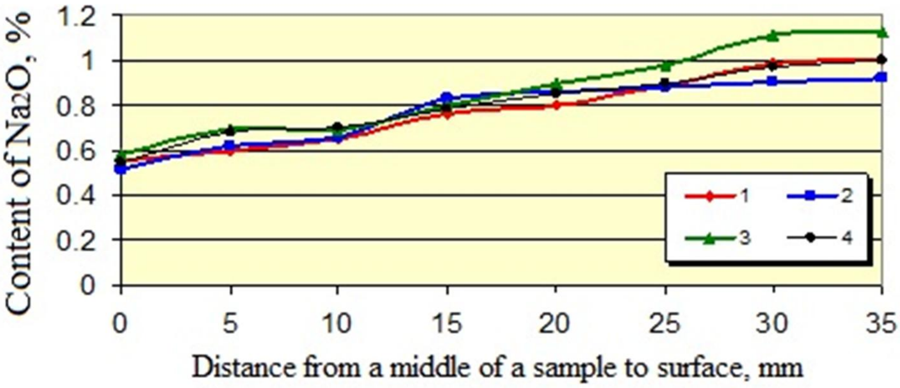

Fig. 3. Diagram of mass transferring of Na_2O in the concrete after 7 days hardening in systems: 1 – «ash – slag – Portland cement – alkaline component – additive ПАР», 2 – «ash – Portland cement – alkaline component – additive ПАР», 3 – «ash – slag – Portland cement – alkaline component – additive ПАР», 4 – «fly ash – slag – Portland cement – alkaline component – additive ПАР Neolith» [15]

Therefore, the presented analysis of long-term experimental investigations has shown that theoretically proposed principle of similarity between natural processes of mineral formation and structure formation of the artificial stones was realized at new cementitious systems creation. It is proved that building materials properties on the basis of alkalineous cement system “alkaline metal hydroxide – alumosilicate of non-stable (amorfous or vitrous) structure” are mainly determined by formation, in standard and hydrothermal hardening conditions, of alkaline and mixed alkali-earth hydroalumosilicates that are similar by their crystallographic characteristics to zeolitic group minerals.

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