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Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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THE STUDY OF THE PROPERTIES AND STRUCTURE OF CEMENT BINDING COMPOSITION ON ELECTROLYTE ACQUEOUS SOLUTIONS ACTIVATED BY MECHANOMAGNETIC METHOD

Abstract. In the present paper, the issues of studying the influence of complex activation of grouting fluid on the structure and properties of the hardened cement paste and concrete are considered. The problem is relevant for manufacturing of building materials. In the paper, there was used the method of applying in the concrete mix composition of the elementary chemical substances undergone special physical treatment by means of mechanomagnetic activation. For more profound study of the structure formation processes in the hardened cement paste, the method of differential thermo gravimetric analysis has been used. As the research results have shown, the concrete samples on the activated electrolyte solutions are characterized by improved strength. In addition, on the base of differential thermo gravimetric analysis, it was proven that in the studied samples of the hardened cement paste on the electrolyte solutions activated by the method of mechanomagnetic treatment, the less calcium hydroxide and the more hydrated calcium silicate with amorphous and fine crystalline is formed. The obtained results for cement composites could be applied when manufacturing effective binder for concretes and mortars in the production of building materials and structures.

Key words: Cement compositions, mechanomagnetic activation, electrolyte aqueous solutions, differential thermo gravimetric analysis, compressive strength, structure formation of binders, sodium thiosulphate, calcium chloride.

Introduction. Nowadays, construction industry in CIS countries and Kazakhstan is gaining momentum that leads to the increasing demand for building materials and structures. Thus, development of structural and thermal insulating materials based on the effective cement binders is regarded as a pressing challenge. Manufacturing of cement-based concretes remains the key direction of the construction industry. Along with that, the large focus is given not only to the issues of cost price lowering but also to the problems of quality enhancement of the obtained concretes. In the most cases, the alteration of concrete properties is achieved by application of chemical substances introduced into the concrete mix as modifying additives. Along with that, the priority is placed on the nano-additives' direction, in particular, fulleroid materials [1-21].

However, it is worth mentioning that carbon nanotubes are considered effective but very costly modifiers [20, 21]. Application of elementary chemical substance in the concrete mix composition undergone special physical treatment – activation – is seen as an alternative method. The most widely spread is activation of solid components of concrete: fine milling of cement clinker, grinding of the

aggregate part. Recently, liquid-phase activation is gaining momentum when grouting fluid and the containing concrete additives are exposed to external effects (magnetic, electrical, mechanic, acoustic, etc.) Liquid-phase activation is possible at the rates by one order lower than required for solid-phase activation; therefore, grouting fluid activation is more cost-effective. It is commonly known that adding the electrolyte molecules to water distorts its supramolecular structure and increases the total number of ice-like structural formations [20]. From the other side, during high-speed water mixing in the rotor-impulse apparatus, the phenomenon of cavitation appears accompanied by the ionization of the part of H_2O molecules, and the radicals H^o are formed [21].

Mechano-impulse impact leads to the transformation of the hydrogen-bonds grid. Thus, both factors (chemical and mechanical activation) act in one direction – they facilitate the formation of the large number of water clusters of smaller size that preconditions the increase in activity of aqueous solutions treated mechanically. This activity is manifested not only in the temperature rise followed activation but also the change of pH factor, electrical conductivity and oxidation-reduction potential. The use of activated water for cement grouting should lead to the rise of cement degree of hydration and, consequently, to the change of the series of physical and mechanical properties of the hardened cement paste and concrete.

Materials: The following materials and solutions have been used for the research purpose: Portland cement, grade 500, produced by Chimkent cement plant (All-Union Standard (GOST) 10178-85, 30515-97), sand (GOST 8736-93) with the fineness modulus 1.8÷2, mains water (GOST 23732-79), calcium chloride (GOST 450-77), sodium thiosulphate (GOST 244-76).

Methods. The properties of initial and activated cement binder were evaluated in compliance with the All-Union Standard GOST 30515-97, GOST 31108-2003 and GOST 7473-2010. Limit of ultimate compressive and bending strength for cement compositions was determined on the test beams with the dimenstions 40x40x160 mm on the apparatus IP-2710. Before cement paste grouting, water with additives has undergone mechanomagnetic treatment. For this purpose, there was used the laboratory unit comprising rotor-pulsation apparatus, with the constant consumer magnet located at its output, with coercitive force 140 mcA/m, water container and connecting hoses [21]. The treated fluid was circulating in a close loop circuit, exposed to the magnetic field periodically. Along with that, there was provided the required destruction degree of supramolecular water structure, ultra dispersal of the additive, and repositioning of water dipoles in the magnetic field. During the activation process, the rotational frequency of the rotor accounted for 4000 rotations per minute, the time of treatment – 120…150 seconds, the amount of additive is 0.08% of cement mass for sodium thiosulphate and 0.1% of cement mass for calcium chloride. The given values of technological parameters were selected experimentally by the method of measurement planning [1-21].

Results. Having completed the strength tests of concretes based on activated and non-activated electrolyte solutions, it was stated that the concrete samples on 0.1% solution of calcium chloride and 0.08% sodium thiosulphate, treated at the rotor frequency of 4000 rotations per minute during 120…150 seconds, are characterized with the best strength properties. Application of the mechanomagnetic activation has led to the rise in ultimate compressive strength by 25% and 20%, for the compositions with calcium chloride and sodium thiosulphate respectively, if compared with the test composition. Bending strength has increased by 29% for calcium chloride and 27% for sodium thiosulphate, correspondingly. The results of strength tests of the hardened cement paste are given in the table 1.

Table 1 – The results of strength tests of the hardened cement paste

Type of additive	The amount of additive, % cement mass	Rotational frequency of the rotor, rotations per minute	Activation time, seconds	Ultimate strength, MPa	
				compressive	bending
-	-	-	-	41.7	5.9
-	-	4000	150	44.3	6.2
Calcium chloride	3	-	-	45.6	7.0
Sodium thiosulphate	0.3	-	-	44.5	6.8
Calcium chloride	0.1	4000	120	48.4	7.8
Sodium thiosulphate	0.08	4000	150	46.8	7.5

The block diagrams of ultimate compressive and bending strength demonstrating the efficiency of grouting fluid mechanomagnetic activation are presented in figures 1 and 2. The block diagrams of water absorption by the samples of the fine grain concrete are demonstrated in figure 3.

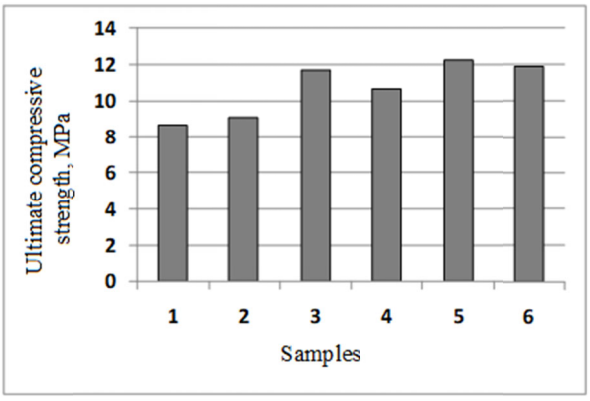

Figure 1 - Ultimate compressive strength of the fine grain concrete samples:
1-reference sample (no-additives and non-activated); 2-on the water activated by mechanomagnetic method, no additives; 3-on the solution of calcium chloride (3% of cement mass); 4-on the solution of sodium thiosulphate (0.3% of cement mass); 5-on the calcium chloride solution activated by mechanomagnetic method (0.1% of cement mass); 6-on the sodium thiosulphate solution activated by mechanomagnetic method (0.08% of cement mass)

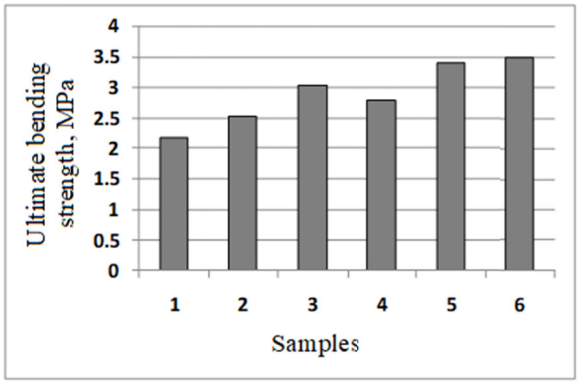

Figure 2 - Ultimate bending strength of the fine grain concrete samples:
1-reference sample (no-additives and non-activated); 2-on the water activated by mechanomagnetic method, no additives; 3-on the solution of calcium chloride (3% of cement mass); 4-on the solution of sodium thiosulphate (0.3% of cement mass); 5-on the calcium chloride solution activated by mechanomagnetic method (0.1% of cement mass); 6-on the sodium thiosulphate solution activated by mechanomagnetic method (0.08% of cement mass)

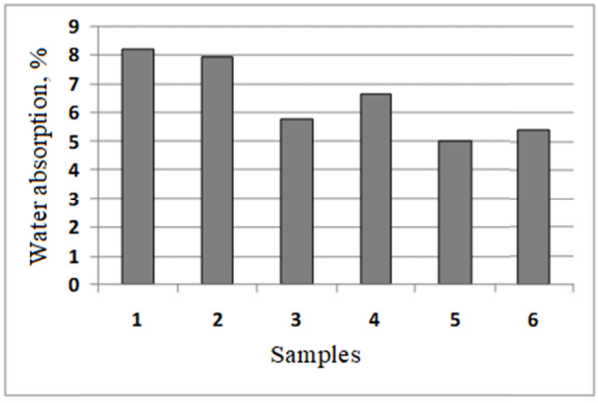

Figure 3 - Water absorption of fine grain concrete samples:
1-reference sample (no-additives and non-activated); 2-on the water activated by mechanomagnetic method, no additives; 3-on the solution of calcium chloride (3% of cement mass); 4-on the solution of sodium thiosulphate (0.3% of cement mass); 5-on the calcium chloride solution activated by mechanomagnetic method (0.1% of cement mass); 6-on the sodium thiosulphate solution activated by mechanomagnetic method (0.08% of cement mass)

Discussion. As a matter or record outlined in the table 1, we can conclude that mechanomagnetic activation could lower the content of calcium chloride by factor of 30 and sodium thiosulphate by factor of 5, not experiencing any strength loss. It is worth noting that mechanomagnetic activation of the grouting fluid with no additives cannot ensure significant gain in strength of the hardened cement paste. Evidently, when electrolytes solutions are activated even at lower concentration, synergetic effect takes place.

Comparing the graphs 1, 2 and 3, it can be observed the present correlation between concrete strength and the lowering of water absorption. Thus, concrete samples on the non-activated water with no additives had the highest water absorption, while the values of ultimate compressive and bending strength were recorded at their minimum.

The decrease in water absorption by the concrete samples on the solutions activated by mechanomagnetic method could indicate the formation of dense concrete structure due to the change of porous volume, i.e. in the modified concrete, more closed microscopic pores and less capillaries are formed. Redistribution of pores increasing the presence of microscopic ones is also evidenced by the rise of frost resistance of concretes on activated solutions, for calcium chloride – by 45 cycles and for sodium thiosulphate by 50 cycles respectively, in comparison with the reference sample, that withhold 250 cycles of freezing and thawing.

Conclusions. Having implemented the comparative analysis of the tested samples, we can conclude that in the hardened cement paste on the electrolyte solutions activated by mechanomagnetic method, there has been formed the greater amount of calcium hydro silicates and the lesser amount of calcium hydroxide with amorphous or fine crystal structure. Thus, mechanomagnetic activation of aqueous electrolyte solutions enables to obtain fine grain concretes characterized by homogeneous monolithic structure and enhanced strength properties and frost resistance. The performed research will allow direct planning of the production of the effective binder for concretes and mortars in manufacturing building materials and structures.

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МЕХАНОМАГНИТТІК ТӘСІЛМЕН БЕЛСЕНДІРІЛГЕН ЭЛЕКТРОЛИТТЕРДІҢ СУЛЫ ЕРІТІНДІЛЕРІНДЕГІ ЦЕМЕНТТІ ТҰТҚЫШ КОМПОЗИЦИЯЛАРДЫҢ ҚАСИЕТТЕРІ МЕН ҚҰРЫЛЫМЫН ЗЕРТТЕУ

Аннотация. Мақалада құрылыс материалдарын өндіруде өзекті мәселе болып табылатын цемент тасы мен бетонның құрылымы мен қасиеттеріне сұйықтықтың кешенді белсенділігінің әсерін зерттеу жөніндегі мәселелер қаралады. Жұмыста механомагниттік белсенділік жолымен арнайы физикалық өңдеуге ұшыраған қарапайым химиялық заттарды бетон қоспасы ертінділерінің құрамында пайдалану әдісі қолданылды. Жұмыс барысында цемент тастарындағы құрылымдық түзілу процестерін тереңірек зерттеу үшін дифференциалды-термогравиметрлік талдау әдісі қолданылды. Зерттеу нәтижесінде, электролиттердің белсендірілген ерітінділеріндегі бетон үлгілерінің жоғары беріктік сипаттамаларға ие болғаны анықталды. Сондай-ақ дифференциалды-термогравиметрлік талдау негізінде механомагниттік өңдеу әдісімен белсендірілген электролиттердің ерітінділерінде зерттелетін цемент тасының үлгілерінде кальций гидроксидінің аз мөлшерде және аморфты немесе ұсақ кристалды құрылымы бар кальций гидросиликаттарының көп мөлшері пайда болатыны анықталды. Цемент композиттарінің алынған нәтижелерін құрылыс материалдары мен конструкцияларын даярлау өндірісінде қолданылатын тұтқыр бетондар мен ерітінділер дайындау үшін пайдалануға болады.

Түйін сөздер: цементтік композициялар, механомагниттік белсенділік, электролиттердің сулы ерітінділері, дифференциалды-термогравиметрлік талдау, тұтқыр, натрий тиосульфаты, кальций хлоридінің құрылымы, қысу кезіндегі берік.

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ИССЛЕДОВАНИЯ СВОЙСТВ И СТРУКТУРЫ ЦЕМЕНТНЫХ ВЯЖУЩИХ КОМПОЗИЦИЙ НА ВОДНЫХ РАСТВОРАХ ЭЛЕКТРОЛИТОВ, АКТИВИРОВАННЫХ МЕХАНОМАГНИТНЫМ СПОСОБОМ

Аннотация. В статье рассматриваются вопросы по исследованию влияния комплексной активации жидкости затворения на структуру и свойства цементного камня и бетона, которые является актуальным в производстве строительных материалов. В работе применялся метод использования в составе бетонной смеси простых химических веществ, подвергшихся специальной физической обработке путем механомагнитной активации. Для более глубокого изучения процессов структурообразования в цементном камне применили метод дифференциально-термогравиметрического анализа. В результате исследований установлено, что образцы бетона на активированных растворах электролитов обладали высокими прочностными характеристиками. Также на основании дифференциально-термогравиметрического анализа установлено, что в изучаемых образцах цементного камня на растворах электролитов, активированных методом механомагнитной обработки, образуется меньшее количество гидроксида кальция и большее количество гидросиликатов кальция, который имеет аморфную или мелкокристаллическую структуру. Полученные результаты цементных композитов можно использовать при изготовлении эффективного вяжущего для бетонов и растворов в производстве строительных материалов и конструкции.

Ключевые слова: цементные композиции, механомагнитная активация, водные растворы электролитов, дифференциально-термогравиметрический анализ, прочность при сжатии, структурообразования вяжущих, тиосульфата натрия, хлорида кальция.

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