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USE OF NANOMODIFIED CLINOPTILOLITE AS ADDITION TO BUILDING MATERIALS

G.P. Tsintskaladze[1], V.G. Tsitsishvili[1], P.E. Tskhvitaridze[2], B.F. Keshelava[2], G.Sh. Tatarashvili[2], T.V. Sharashenidze[1]

[1]Melikishvili Institute of Physical and Organic Chemistry of Georgia
5 Jikia Street, Tbilisi 0186, Georgia, physorgchem@pochta.ru
[2]Zavriev Institute of Structural Mechanics and Earthquake Engineering
8 M. Alexidze Street, Tbilisi 0193, Georgia, irakl85i@yahoo.com

Natural zeolite clinoptoline from Georgian origin and its nanomodified forms have been used for modification of structures of the composite building materials. Characteristics of this zeolite have been studied by thermal analysis, IR spectroscopy, and adsorption methods. The testing results of the zeolite-containing cement have shown that introduction of zeolite (treated at high temperature) into the composition of cement improves its physical-mechanical properties and whole nanomodification of zeolite with plasticizers significantly decreases water-cement ratio improves its mechanical properties and quickens the setting time.

INTRODUCTION

The forming of durable structure composite materials of high quality is the main problem of modern construction materials science. The same is the basis of production prime cost decrease, as well as of its quality improvement. According to scientific prognosis, in XXI century, the nanotechnologies become one of the most perspective in material production. The investigations of properties of materials with nanoparticles and nanostructure, development of theoretical conception, elaboration of concrete technology of the new material production are the priority directions of nanotechnology. In modern materials science, basically, the fine-disperse silica and alumina of different origin are used as nanomodifier additions. The zeolite, particularly the natural one, can be one of interesting mineral additions [1].

EXPERIMENTAL

Georgia is rich by natural zeolites, hence, their use in production of modern building materials, is quite perspective. As an addition into cement, we had used zeolite – clinoptilolite of Kaspi district Upper-Khandak origin. The chemical composition of examined zeolite has the following appearance [2]: $0.14K_2O{\cdot}0.32Na_2O \cdot 0.51CaO \cdot 0.27MgO \cdot 0.11Fe_2O_3 \cdot Al_2O_3 \cdot 8.28SiO_2 \cdot 6.1H_2O$.

The experiments have shown that the particle sizes of additions to cement are in direct connection with diffusion properties of obtained substance. The more the molecule sizes of addition, the more the viscosity, and the diffusion velocity is not changed. The additions with small size molecules slow down the ionic diffusion.

RESULTS AND DISCUSSION

As far as the zeolites are distinguished by adsorption properties, their bringing into cement composition increases the water charges what is undesirable in concrete production. Therefore, our goal was creation of such a nanomodifier addition where water absorption is decreased. Unlike other mineral additions, zeolites are characterized by low thermal stability therefore due to treatment to certain temperature, the partial destruction of zeolite structure is expectable. This is expressed by break of long chains of zeolite structure and, in some cases, by decrease in porosity and increase in surface volume. All the above stated testifies a partial amorphization of zeolite, i.e., a "thermal nanomodification" of zeolite has place. By the method of IR spectroscopy and thermal analysis there were examined the structural changes of specimen under investigation after heating at different temperatures. The data of thermal analysis have shown that the total mass loss consists of 14.8%; initial specimen after heating at 300°C fills up 89% of lost water; at heating up to 500°C – 63% are filled up, at 600°C – 37%, and at heating up to 700°C – only 3% of lost water are filled up.

After specimen thermal treatment, by the method of IR spectroscopy, the containment of zeolite phase has been found.

Table 1. Dependence of initial zeolite phase containment (%) on treatment temperature

°C	$D\frac{630}{460}$	%
20	0.401	100.0
300	0.400	99.0
500	0.250	60.0
600	0.201	50.1
700	0.112	28.1
750	0.024	6.0

The data of IR spectroscopy are almost in full accordance with those of thermography. For improvement of the quality of different building structures – floors, foundations, columns – there are used successfully plasticizers and superplasticizers, those are the special liquid additions, produced on the basis of modified polymers. When they are brought into concrete composition, they decrease the water charge, simplify the treatment process, and increase the strength and homogeneity of the concrete. All the above stated contribute to concrete economy. After dehydration of dispergated zeolite at 400°C, its nanomodification in fluid plasticizers – Sikamen-MO-50 and Sikamen-32 N was conducted. After nanomodification, the changes in crystal lattice of clinoplitolite were examined, that after nanomodification being not changed substantially, however, a structural deformation is present. The results of adsorption have shown the existence of water on both initial and after nanomodification specimens of clinoplitolite. Results of adsorption have shown as well that, when the adsorption of initial specimens is of 4.75 mmol/g, after nanomodification the adsorption decreases significantly: in one case it consists of 1.84 mmol/g, and in the second – 1.53 mmol/g. This has confirmed that the organic plasticizers after nanomodification partially block entrances into channels what is the reason of a decrease in water steam adsorption.

Table 2. Results of testing of zeolite containing cements

N	Cement Composition				Grind fineness Remainder N 008	Relative surface according to Blein g/cm^2	Water for paste of normal thickness	Solution characteristics		Mechanical strength			
										Bending		Compression	
	Clinker	Gypsum	Zeolite 200^0	Zeolite 600^0				w/c	Extension, cm	3 days	28 days	3 days	28 days
1	90	5	-	-	5	3300	25.7	0.38	115	54	55	340	550
2	80	5	15	-	5	4000	26.3	0.4	115	49	61	220	510
3	75	5	20	-	5	4600	27.3	0.4	112	40	70	210	505
4	75	5	-	20	4,5	4300	27.0	0.4	115	47	69	235	485
5	60	5	35	-	5	4400	31.3	0.4	105	26	59	170	475
6	60	5	-	35	5	5900	31.0	0.4	112	33	60	180	460

Table 3. Results of testing of zeolite-containing cements treated by plasticizers

Series	Cement Composition				Grind fineness remainder N 008	W/C	Terms of hardening hour-second		Limit strength on compression kg/cm^2 28 days
	Clinker	Gypsum	Zeolite 400^0	Plasticizer			Beginning	End	
I	75	5	20	-	10	30.0	2-40	4-00	300
II	75	5	20	1%Sikament MR-50	10	26.7	2-00	3-20	360
III	75	5	20	1%Sikament 32N	10	26.7	2-25	3-50	370

The results of zeolite containing cement testing (Table 2) have shown that the addition of dry and particularly burned zeolite into cement composition improves its physical-mechanical properties. The addition of 20% zeolite, if it is dried out, allows production of M400, D20, and M500 D20 Portland cement. If adding a composition of 35% thermally treated nanomodified zeolite into the cement, the production of pozzolatic (sulphate resistant) Portland cement becomes possible. The burned zeolite increases the cement solidification velocity.

The testing of zeolite containing cements after zeolite nanomodification by plasticizers has shown (Table 3) that the zeolite nanomodification by plasticizers significantly decreases the water/cement ratio and terms of solidification, and increases its mechanical characteristics.

The analysis of data given has shown that use of plasticizers significantly decreases the water-zeolite ratio, improves their mechanical indices, and increases terms of hardening.

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Можливість використання наномодифікованого клиноптилоліту як добавки до будівельних матеріалів

Г.П. Цінцкаладзе, В.Г. Ціцішвілі, Р.Є. Схвітарідзе , Б.Ф. Кешелава , Г.Ш. Татарашвілі , Т.В. Шарашенідзе

Інститут фізичної та органічної хімії ім. П. Мелікішвілі
вул. Джикія 5, Тбілісі 0186, Грузія, physorgchem@pochta.ru
Інститут будівельної механіки і сейсмостійкості ім. К. Завр'єва
вул. М. Алексідзе 8, Тбілісі 0193, Грузія, irakl85i@yahoo.com

Модифікуванням структури природного цеоліту клиноптилоліту грузинського родовища одержано добавку для цементу. Вивчено її властивості методами термічного аналізу та ІЧ-спектроскопії. Тестування цеолітовмісних цементів свідчить, що введення цеоліту до складу цементу покращує його фізико-механічні властивості, а наномодифікування цеолітів пластифікаторами істотно знижує водоцементне відношення, поліпшує його механічні характеристики та прискорює терміни схоплювання.

Возможность использования наномодифицированного клиноптилолита в качестве добавок к строительным материалам

Г.П. Цинцкаладзе, В.Г. Цицишвили, Р.Е. Схвитаридзе, Б.Ф. Кешелава, Г.Ш. Татарашвили, Т.В. Шарашенидзе

Институт физической и органической химии им. П. Меликишвили
ул. Джикия 5, Тбилиси 0186, Грузия, physorgchem@pochta.ru
Институт строительной механики и сейсмостойкости им. К. Завриева
ул. М. Алексидзе 8, Тбилиси 0193, Грузия, irakl85i@yahoo.com

Модифицированием структуры природного цеолита клиноптилолита грузинского месторождения получена добавка для цемента. Изучены её свойства методами термического анализа и ИК-спектроскопии. Тестирование цеолитсодержащих цементов показывает, что введение цеолита в состав цемента улучшает его физико-механические свойства, а наномодифицирование цеолитов пластификаторами существенно понижает водоцементное отношение, улучшает его механические характеристики и ускоряет сроки схватывания.