Influence of Nanoscale Barium Hydrosilicates on Composition of Cement Stone

GRISHINA Anna N.^{a*}, KOROLEV Evgeniy V.^b

Moscow State University of Civil Engineering 129337, Yaroslavskoje hw., 26, Moscow, Russian Federation ^aGrishinaAN@mgsu.ru, ^bKorolevEV@mgsu.ru

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Abstract. The development of new types of composite materials is an important aim for construction. Nanoscale admixtures allow efficient control of the composition and properties. Results of experimental investigations concerning effect of admixture of nanoscale barium hydrosilicates to the chemical composition of hydrated portland cement are discussed in the present work. It is shown that several key processes are taking place during nanomodification. Amount of portlandite in cement stone decreases, and there is also quantity growth of different calcium hydrosilicates CSH (I), CSH (II), riversideite and xonotlite. Influence of composition and storing time of barium hydrosilicates to the ratio of different portland cement hydration products is examined. It is found that admixture of barium hydrosilicates with gross formula BaO•26.47SiO₂•nH₂O stored for 28 days leads to both reduction of portlandite and accretion of hydrated phase.

Introduction

Currently, one of the requirements in Russian construction industry is to develop effective concrete with required parameters of quality. The essence of improving the technical and economical efficiency of cement concrete is to increase the value of an integral parameter which characterizes consumption of cement per unit strength:

CR = C/Rc,

(1)

where C – consumption of portland cement, kg/m³; Rc – compressive strength of concrete, MPa. Such increase can be achieved in various ways. The most common are: admixture of chemical

and / or mineral supplements; preparation of aggregates; using of portland cement with high activity. There are also combined methods.

Methods of control of structure formation at the atomic and molecular levels are subjects of design in nanotechnology. Such methods are currently in active development; they can be implemented in various ways. There is a feasible and well-studied technique which allows to implement the nanotechnology. The technique of nanomodification can be implemented on existing production lines, and the essence of the technique is the introduction of nanoscale modifiers (so-called "primary nanomaterials"). Such materials include various nano-carbon objects, sols, ceramic or oxidic compounds, etc. [1-5]. For cement systems, the nanoscale barium hydrosilicates can be used as modifiers. Their application is promising partially because of low-temperature sol-gel synthesis technology of relatively low cost.

Nanoscale barium hydrosilicates are products of interaction between barium hydroxide and silicic acid synthesized in system with nanoscale particles of iron hydroxide (III) [6]. It is known [7] that nanosized barium hydrosilicates are reactive additives which are capable of changing the rate of structure formation and the influencing the chemical composition of the reaction products [8]. This, in turn, determines the physical-mechanical and operational properties of the cement stone.

Experimental setup

Several informative methods of structural analysis were used during the study of nanomodified cement stone. Differential thermal analysis was carried out on the HDSC PT1600/1400 device. X-ray analysis was performed on the ARL EXTRA device (Bragg angles 4-70[°], Cu anode and Ni filter, goniometer rotation rate was 1.2 deg/min).

The samples were prepared according to the requirements of the aforementioned instruments.

Experimental results and discussion

To study the influence of nanoscale barium hydrosilicates on the chemical composition of nanomodified cement stone it is necessary to use informative methods of research, including infrared spectroscopy, differential thermal analysis and X-ray analysis.

Differential thermal analysis allows to quantify the variation of the main phases of cement stone. Studies show (Fig. 1) that composition of artificial stone changes during nanomodification: the degree of hydration of portland cement is increases, while amount of carbonate portlandite phase decreases.



Figure 1. Thermograms of reference (1) and nanomodified cement stones (2)

Examination of phase composition of nanomodified cement stone by means of X-ray analysis indicates a decrease in the amount of portlandite by 27...28% (Fig. 2). Admixture of nanoscale hydrosilicates barium leads to an overall increase in the intensity of peaks corresponding to calcium hydrosilicates CSH (I) and CSH (II). The amounts of riversideite and xonotlite in the cement stone are minimal.

However, by means of X-ray analysis it often impossible to accurately determine the changes in the concentrations of components. It was shown during studies of changes in the chemical composition of hydration products with the admixture of nanoscale barium hydrosilicates that chemical composition of barium hydrosilicates and their age are influencing the chemical composition of the resulting artificial stone (Fig. 3, Table. 1).



Figure 2. Results X-ray analysis of nanomodified cement stone: P - riversideite; T - tobermorite; I - calcium hydrosilicate CSH (I); II - calcium hydrosilicate CSH (II); Π - portlandite



Figure 3. IR spectra of cement stone modified by nanoscale barium hydrosilicates based on precursor with silicic acid of composition: $1-BaO \cdot 24,86SiO_2 \cdot nH_2O$; 2 - reference cement stone; 3 - fresh $BaO \cdot 26,47SiO_2 \cdot nH_2O$; 4 - $BaO \cdot 26,47SiO_2 \cdot nH_2O$; at age of 28 days

Analysis of hardened products by means of infrared spectroscopy shows that for all tested compounds bands are observed at the same wavelength, but these bands are of different intensities. Therefore, to identify the underlying processes it is possible to examine alternation of phases or areas of the observed peaks. Area values of anomalies are shown in Table. 1.

As it follows from Table 1 and Fig. 3, for all examined samples there are peaks at same wavelengths. But these peaks are of different intensities. Therefore, identification of underlying processes is possible if we examine the alternation of concentration of phases and areas of observed peaks.

Anomalies in the spectrogram are observed at wavelengths 3638, 1414, 1100, 950 and 871 cm⁻¹. Intensive band at 3638 cm⁻¹ is due to vibrational degrees of freedom of OH groups. Therefore, the response may be caused by portlandite, xonotlite or another hydrosilicates with similar structure relative to the position of the hydroxyl group. It is known that the admixture of nanoscale hydrosilicates considerably reduces the amount of portlandite in the cement stone. Therefore,

reduction of the area near the 3638 cm^{-1} peak in 1.19...12.1 times (depending on the concentration and duration of storing of the colloidal solution) is probably due to decreased concentration of portlandite.

Composition	Wavenumber, cm^{-1}				
	3638	1414	1100	950	871
Reference cement stone	0.121	9.054	0.581	4.153	0.700
Cement stone nanomodified by fresh BaO·26,47SiO ₂ ·nH ₂ O	0.102	11.709	1.103	4.447	0.970
Cement stone nanomodified by BaO·26,47SiO ₂ ·nH ₂ O at age of 28 days	0.010	16.980	2.004	3.328	1.620
Cement stone nanomodified by fresh BaO·24,86SiO ₂ ·nH ₂ O	0.020	12.235	1.007	2.533	1.14

Table 1. Areas of anomalies

Peaks in range of 800...1100 cm⁻¹ are typical for calcium hydrosilicates. In particular, line at 1100 cm⁻¹ corresponds to spanning vibrations of Si–O–Si skeleton, vibrations of symmetrical and asymmetrical Si–O bonds typical for tobermorite-like structures. Admixture of nanoscale barium hydrosilicates increases the content of such silicates. It must also be noted that during storing for up to 28 days activity of nanoscale barium hydrosilicates (as nanomodifiers) grows.

Peaks at 1414 cm⁻¹ corresponds to bending vibrations of hydroxyl groups in vertices of the silicon-oxygen tetrahedral. These peaks can also be caused by calcium carbonate, thus indicating presence of any mentioned components. Furthermore, combination of peak at 1414 cm⁻¹ with broad peak in range 3300...3500 cm⁻¹ indicates presence of submicrocrystalline tobermorite-like calcium hydrosilicates. The above indicates further formation of tobermorite-like calcium hydrosilicates. A similar effect is observed when nanoscale additives is used, based on barium hydrosilicates and stored for 28 days. This indicating the possibility of long-term storing of nanoscale barium hydrosilicates.

Peak at 950 cm⁻¹ corresponds to stretching vibrations of Si(OH) (there are three types of such vibrations), as well as vibrations of calcium hydrosulfoaluminates. Admixture of nanoscale barium hydrosilicates in most cases reduces the intensity of this peak. Accordingly, it belongs to calcium hydrosulfoaluminates and not to calcium silicates. Increase of content of calcium hydrosilicates was already confirmed by X-ray diffraction and by increased intensity of peaks on IR spectrograms at 1100 cm^{-1} and 1414 cm⁻¹.

Weak maximum at 871 cm⁻¹ is typical for $-(Si_4O_{10})\infty$ and ettringite. Response of ettringite is weakly expressed on X-ray diffractograms. Thus, the admixture of nanoscale barium hydrosilicates leads to increase of hydrosilicates in reaction products.

Conclusion

It is revealed that admixture of nanoscale barium hydrosilicates changes the chemical composition of cement stone. Content of portlandite reduces. Amount of hydrosilicate phases grows (was clearly identified phases CSH (I), CSH (II), riversideite and xonotlite). It is found that reduction of portlandite and increasing of the hydrosilicates content are observed for barium hydrosilicates with chemical composition described by gross formula BaO•26,47SiO₂•nH₂O. It also revealed that shelf life of nanoscale barium hydrosilicates exceeds 28 days; this simplifies production of the nanomodified cement composites.

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References

[1] A.F. Khuzin, M.G. Gabidullin, R.Z. Rakhimov, A.N. Gabidullina, O.V. Stoyanov, Modification of Cement Composites with Carbon Nanotubes, News of KGASU (in Russian). 5 (2013) 115-118.

[2] N.I. Makridin, V.N. Vernigorova, I.N. Maksimova, Microstructure and Strength of Cement with Additives of Calcium Hydrosilicates, News of High Educational Institutions. Construction (in Russian). 8 (2003) 37-42.

[3] E.G. Matveeva, Improving the Efficiency of Concrete by Nanosized Silica Additive, BGTU after name of V.G. Shuhov, Belgorod (in Russian), 2011.

[4] D.S. Starchukov, D.P. Mandritsa, Yu.F. Vilchinskiy, Development of High-strength Heavy Concrete on the Basis of a Sol Containing Admixture of Iron Hydroxide (III) of Elevated Activating and Plasticizing Effect, Technology of Concrete (in Russian). 2 (2013) 10-11.

[5] L.B. Svatovskaya, V.Ya. Solovyeva, I.V. Stepanova, D.S. Starchukov, Nanoscale Additives Based on Silicon- and Iron (III) Sol for Heavy Concrete on Ordinary Cements, Nanotechnologies in Construction: A Scientific Internet-Journal (in Russian). 5 (2010) 61-68.

[6] A.N. Grishina, E.V. Korolev, Nanoscale Barium Hydrosilicates: Choosing the Synthesis Technology, Nanotechnologies in Construction: A Scientific Internet-Journal (in Russian). 4 (2013) 111-119.

[7] A.N. Grishina, A.B. Satuykov, E.V. Korolev, Early Structure Formation of Cement Stone Modified with Nanoscale Barium Hydrosilicates, Scientific Review (in Russian), 7 (2014) 134-139.

[8] E.V. Korolev, A.N. Grishina, A.B. Satuykov, Chemical Composition of Nanomodified Composite Binder with Nano- and Microsized Barium Silicate, Nanotechnologies in Construction: a Scientific Internet-Journal (in Russian). 4 (2014) 90-103.