ISSN 0020-1685, Inorganic Materials, 2019, Vol. 55, No. 10, pp. 1079–1085. © Pleiades Publishing, Ltd., 2019.
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Structuring Behavior of Composite Materials Based on Cement, Limestone, and Acidic Ash

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Received July 13, 2018; revised February 11, 2019; accepted March 19, 2019

Abstract—We have studied structure formation of cement stone with the use of silica-containing and inert additives and mechanochemical activation. Rational compositions and the particle size composition of composite binders have been determined by X-ray diffraction, differential thermal analysis, and microstructural analysis, which makes it possible to obtain preset physicomechanical characteristics of cement stone and related concrete. The synergistic effect of pozzolanic and inert additives has been shown to activate hydration processes, densifying the microstructure of newly formed phases.

Keywords: solubility, hydrated calcium silicates, structuring, hydration, mechanochemical activation, carbonation, X-ray diffraction

DOI: 10.1134/S0020168519100042

INTRODUCTION

The structuring of cement stone during the cement hydration process has been the subject of extensive studies [1–6]. Nevertheless, there is still no unified theory of hydrated calcium silicate phase formation during mixing with water. The existing theories—crystallization (Le Chatelier), colloidal (Mikhaelis), and crystallization–colloidal (Baikov) interpret cement hydration mechanisms from different points of view.

On the whole, all of these theories agree in that cement stone hardening is accompanied by the formation of coagulation, conventionally coagulation, and crystallization–condensation structures and that the contribution of each structure to the strength of the composite depends on the water-to-cement ratio, the chemical and mineralogical compositions of the hydrating material, and the hardening conditions and duration [7–11]. The formation of a high-strength structure of cement stone is also influenced by the contact zone between the hydrates and starting cement grain residues. Therefore, cement stone structure formation depends on a number of factors, which can be influenced by using various technological approaches and adjusting the binder composition.

Thus, an important issue is the ability to control cement stone structure formation by using silica-containing and organic additives, activating the binder, and reducing the water-to-cement ratio.

THEORETICAL ANALYSIS

The facts that the contribution of the cement industry to global greenhouse gas (especially CO_2) emissions amounts to 7–10% and that this is the third most energy consuming sector [12, 13] pose serious environmental concern regarding the industrial environment. In particular, the production of 1 t of clinker is accompanied by emission of 0.97 t of carbon dioxide into the atmosphere [14]. Partial replacement of cement by various additives allows greenhouse gas emission into the atmosphere to be reduced.

Composite binders (CBs) are a mixture of a hydraulic binder, silica-containing component, and various modifiers that help to optimize particular characteristics of final products. To date, a considerable range of various CBs have been developed and tested: unique from the viewpoint of environment safety, beneficial from the viewpoint of capital investments, and fabricated and approved on a commercial scale. At the same time, because of the effect of various factors, such composites have no deserved volume of production facilities at cement or concrete plants or target markets [15].

Strength characteristics of composite materials can be enhanced, first of all, by mechanochemical activation of their binding system. There is a variety of approaches for activating binders, the simplest of which is milling. Moreover, from the environmental point of view, mechanochemical activation offers the possibility of obtaining the most stable material with-

Table 1. Chemical composition of CEM I Spassk Portland cement, %

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO_{bound}	LoI
66.2–67	20.2–20.9	6.0–6.7	3.5–4.0	1.4–2.0	≤ 1.2	0.18

out carbon dioxide emissions into the atmosphere. Stability of properties of an activated material is due to the release of internal free energy, which is determined by the structural perfection of the material.

Besides, the engineering performance of cement stone can be improved as a result of the formation of fine grains of additives, located in the contact zone of the cement [16–18]. At the same time, this "microfiller effect" cannot be accounted for only by the formation of additional crystallization centers, primarily because their direct effect shows up as an increase in the rate of the first chemical hardening step. The "microfiller effect" is based on not only chemical interaction of cement with hydration products but also physicochemical phenomena, in particular, on the influence of the surface energy of binder nanoparticles.

The use of a CB in concrete enhances the strength of the contact zone between the cement stone and filler. In conventional Portland cement concretes without active mineral additives, the contact zone is typically less dense than the cement paste and contains numerous platelike $Ca(OH)_2$ crystals, whose longitudinal axis is perpendicular to the filler surface. Accordingly, it is more susceptible to microcracking under tension, which shows up as a result of changes in temperature and humidity. The above indicates that the contact zone has the weakest structure in concrete and therefore has the strongest effect on its strength characteristics. Reducing the particle size of the binder drastically the capillary porosity of the contact zone as a result of the considerable decrease in the total calcium hydroxide concentration.

The purpose of this work was to study the structuring behavior of cement stone in the presence of different additives and during mechanochemical activation.

EXPERIMENTAL

To confirm theoretical concepts, we designed CBs with different compositions: 55–100% Portland cement, 0–45% fly ash, and 0–10% limestone.

Our samples contained CEM I 42.5N Spassk commercial cement, whose composition is given in Table 1. As an active additive to CBs, we used fly ash from the largest thermal power plants in Primorskii krai: Artemovskaya combined heat power plant, Primorskaya regional power plant, and Partizanskaya regional power plant (Table 2).

In designing the CB, we used screening dust of ground limestone from the Dlinnogorskoe deposit (Table 3).

Table 2. Chemical composition of ash from thermal power plants in Primorskii krai

Components	Percentage of elements in terms of oxides		
	Primorskaya regional power plant	Artemovskaya combined heat power plant	Partizanskaya regional power plant
	Luchegorskii brown coal (Bikinskoe field)*	Primorskii brown coal (Pavlovskii open pit mine)*	Neryungrinskii hard coal*
SiO_2	55.3	48.1	75.7
TiO_2	0.5	0	0.9
Al_2O_3	12.6	24.3	16.0
Fe_2O_3	10.7	6.5	3.8
CaO	12.5	14.7	1.0
MgO	3.5	1.8	0.4
K_2O	1.0	1.2	1.2
Na_2O	0.4	0.2	0.3
SO_3	3.4	2.3	0.2
P_2O_5	1.0	<0.1	0.1
ZrO_2	<0.1	<0.1	0.1
MnO	<0.1	<0.1	0.2
LoI	2.3	0.6	1.4

* Predominant type of coal.

Table 3. Chemical composition of the limestone powder, %

CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	LoI
44.21	2.57	7.49	3.33	0.24	0.24	38.71

Table 4. Effect of specific surface area on the activity of the CB

Hardening, days	Activity					
	500*	550*	600*	700*	800*	900*
3	46.1	47.4	47.2	46.0	45.6	45.5
7	50.3	54.2	54.1	49.1	48.6	48.4
28	68.1	77.3	70.2	65.8	55.0	65.0

* S, m^2/kg.

We compared the efficiency of the mechanochemical activation of the CB in different mills: vibratory, vario-planetary, and ball mills. Depending on the type of milling device, the specific surface area of the resultant fine powder varied from 300 to 900 m^2/kg. The largest specific surface area for a given composition, 550–600 m^2/kg (Table 4), was only obtained with a Pulverisette 4 vario-planetary mill.

The composition of the newly formed cement stone was determined by X-ray diffraction, and microstructures were examined by scanning electron microscopy.

RESULTS AND DISCUSSION

The strongest technical effect was achieved through a synergistic action of technogenic pozzolanic additives (fly ash) and natural sedimentary materials (limestone) at the composition 55 wt % cement, 5 wt % limestone, and 40 wt % ash. At this composition of the composite, after joint milling to a specific surface area of 550 m^2/kg the samples had a compressive strength of up to 77.3 MPa, whereas that of a control material (pure CEM I 42.5N) was 47.5 MPa (Table 5) [13].

The cement stone formed is a microscopically inhomogeneous disperse system (Figs. 1b, 1d). The cement grains that have not yet entered into the hydration reaction act as a microfiller, with gel-like and crystalline newly formed phases on its surface. The main performance parameters of cement stone depend on the ratio of the gel-like and crystalline phases, which differ in particle size, morphology, and physicomechanical properties.

On the other hand, cement stone based on pure Portland cement characteristically has a matrix with a high density of pores and microcracks, and most of the material consists of poorly crystallized, X-ray amorphous newly formed phases, in combination with hexagonal portlandite plates (Figs. 1a, 1c).

According to electron microscopy results, the addition of mineral fillers to the composition of the binder leads to the formation of a high-density grain packing in the structure of the composite of ash, limestone, and clinker in the total array of newly formed phases. The microstructure is pierced with crystalline hydrated silicates, hydrated aluminates, and hydrated calcium ferrites, which form a dense matrix on mineral filler grains (Figs. 1b, 1d).

Thus, the binder hydration products have good adhesion to grains of the silica-containing component owing to the high defect density in the silica crystals produced by the mechanochemical activation of the CB. The mechanochemical processing of the binder components makes it possible to activate clinker mineral hydration processes, favors the formation of large amounts of newly formed phases, and helps to raise the strength of the cement stone. The denser structure

Table 5. Compositions and properties of the CBs

Sample no.	Weight percent				Compressive strength, MPa		
	cement	fly ash		limestone			
		Vladivostokskaya combined heat power plant 2	Artemovskaya combined heat power plant		3 days	7 days	28 days
1	100	–	–	–	17	32.5	47.5
2	30	–	50	20	30.2	40.1	50.4
3	35	45	–	20	34.2	43.1	53.2
4	40	–	45	15	36.6	48.2	56.6
5	45	45	–	10	39.2	50.1	59.2
6	50	–	40	10	45.1	54.9	65.8
7	55	40	–	5	47.2	54.1	77.3
8	100	–	–	–	60.3	81	103.2

Control sample 1 (without remilling); samples 2–8 were milled to $S = 550\ m^2/kg$.

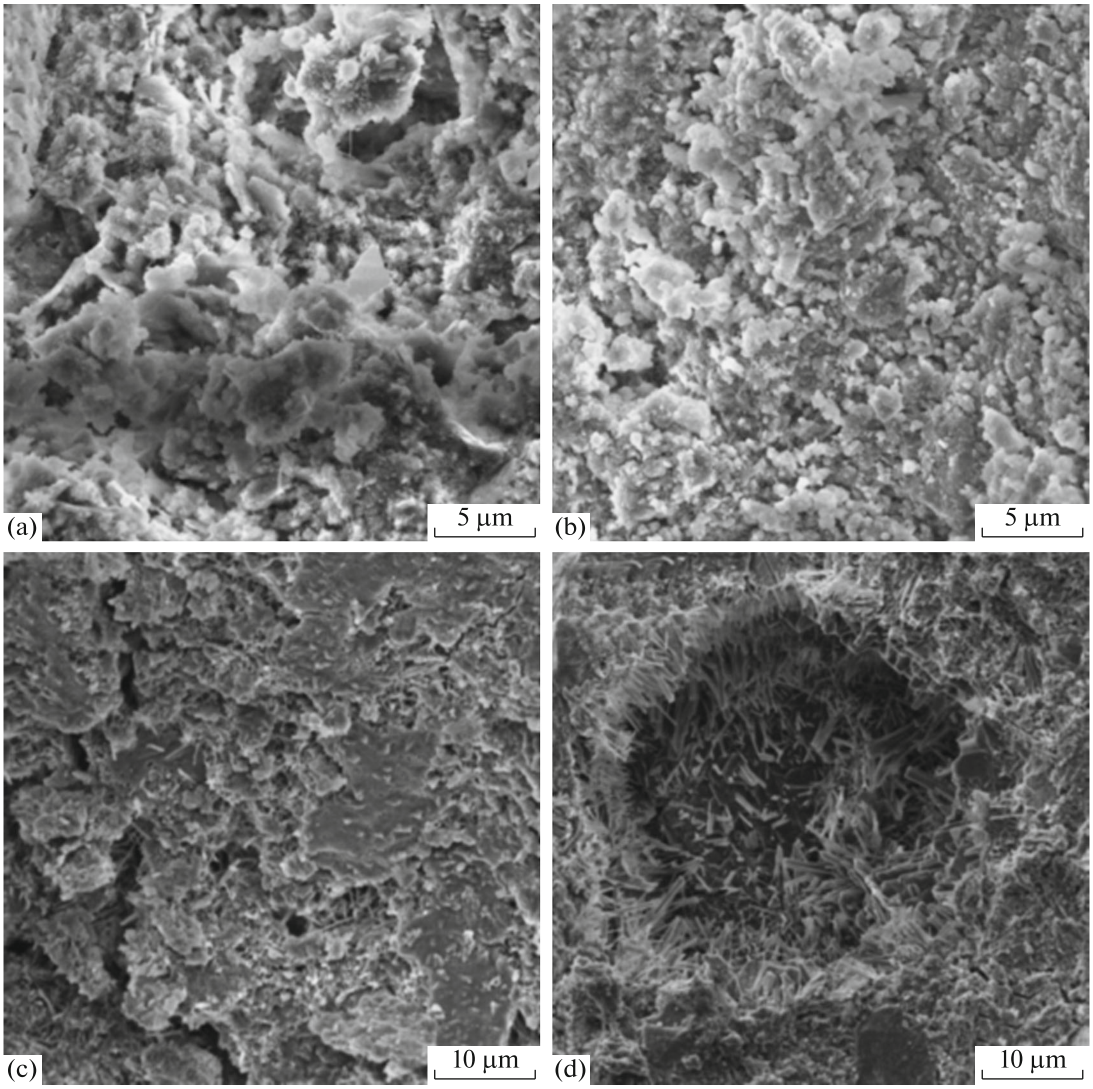

Fig. 1. Microstructure of the newly formed phases: (a, c) pure cement stone, (b, d) CB-based cement stone.

of the CB in comparison with the control sample is due to the increased hydration activity of the fine fractions of the mineral filler. The combined effect of the large specific surface area, the mechanochemically activated surface layers of the filler and cement grains, and the amorphous surface of the shells (on the order of 2 μm in thickness) produced on the grains during the hydration process ensures advantageous physicomechanical properties of the proposed binders.

In the X-ray diffraction pattern of cement stone based on the proposed CB (Fig. 2), the peaks corresponding to the clinker minerals C_3S with d/n = 3.04, 2.97, 2.78, 2.74, 2.75, 2.61, 2.18, and 1.77 Å and C_2S with d/n = 2.89, 2.67, 2.72, 2.76, 2.75, 2.78, and 1.77 Å have reduced intensity, indicating that the use of the CB activates hydration processes. In addition, the CBs reduce the intensity of reflections from portlandite with d/n = 4.93, 2.63, and 1.93 Å.

Differential thermal analysis (DTA) of additive-free and CB-based cement stones showed three main endothermic peaks (Fig. 3). The first of them (at a temperature of 160°C) is due to the removal of adsorbed water from the gel-like hydration products. The smaller area of this peak in the DTA curve of the CB-based cement stone indicates a reduction in the content of the gel-like newly formed phases as a result of their crystallization.

The next endothermic peak (at a temperature on the order of 475°C) corresponds to calcium hydroxide dehydration. The larger area of this peak in the DTA curve of the additive-free cement stone indicates that it contains more portlandite.

The last endothermic peak (at a temperature in the range 525–650°C) is attributable to calcium carbonate decomposition.

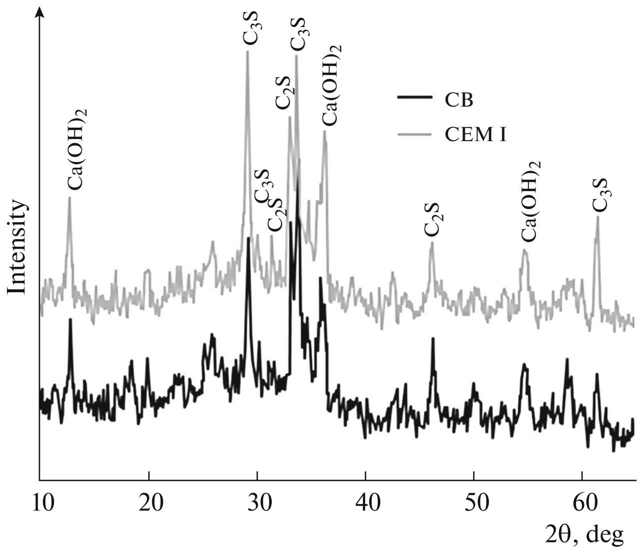

Fig. 2. X-ray diffraction pattern of the newly formed phases.

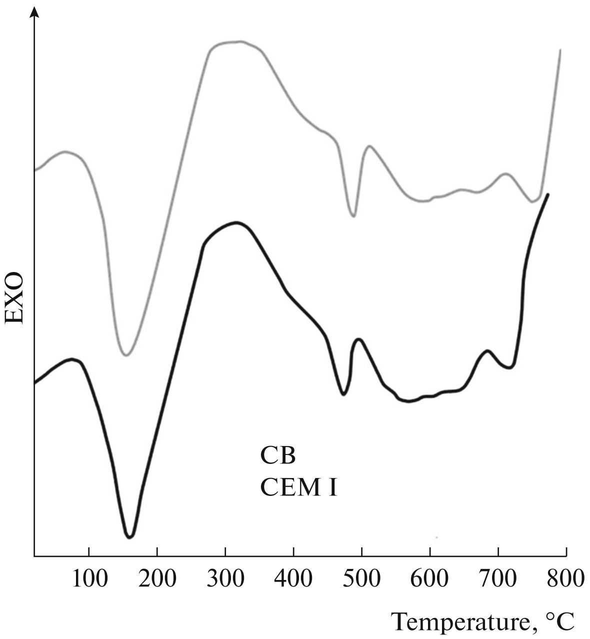

Fig. 3. DTA results for pure and CB-based cement stones.

The combined effect of mechanical and chemical activation (the presence of limestone particles) was found to lead to an increase in the pozzolanic activity of the acidic ashes. As shown by microstructural analysis, the ash and limestone particles are surrounded by gel shells. Individual particles are linked to each other to form clusters. Characteristically, such cement stone contains needle-like newly formed hydrated silicate particles 2 μm in length and about 0.2 μm in diameter.

The microstructure of concrete in the CB-based cement stone samples differs from that in the control (additive-free) sample. In these cases, we observe not only a decrease in total porosity but also changes in pore structure. The number of capillary pores decreases and that of gel pores rises, which is a direct consequence of a pozzolanic reaction and the formation of an additional amount of the C–S–H phase. This zone is very porous and is characterized by an increased $Ca(OH)_2$ content. The pozzolanic reaction in the contact zone influences $Ca(OH)_2$ binding, as a consequence of which we observe a decrease in the density and thickness of the contact zone and, hence (subsequently), a rise in the adhesion of the hardened cement stone to the filler and reinforcement.

Note the presence of secondary hydrated silicates, which are formed as a result of calcium hydroxide binding with the active silica of the CB (Fig. 4).

Limestone powder helps to control cement stone structuring processes at early age. The limestone filler in the form of CaO binds calcium hydroxides and hydrated calcium aluminates. The binding of $Ca(OH)_2$, which is present in CB-based cement stone in considerable amounts, contributes to the formation of the C–S–H phase. The percentage of capillary pores less than 2 nm in average size decreases. Thus, tending to exhibit hydraulic properties, the ash filler forms weakly basic hydrated calcium silicates in the

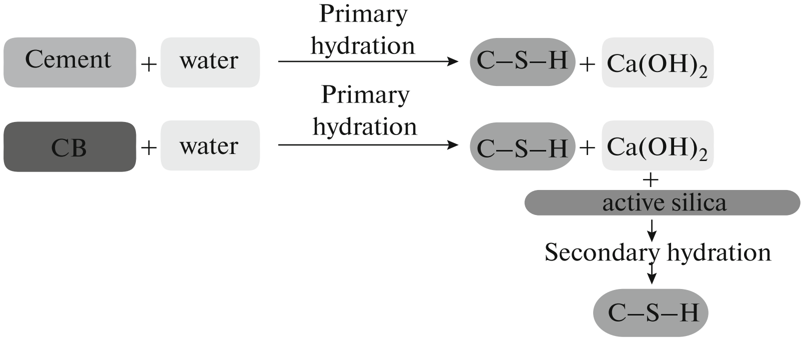

Fig. 4. Mechanisms of hydration.

Table 6. Effect of the composition of the CB on the porosity of cement stone

Composition (according to Table 5)	Percent porosity			
	technological pores (macroscopic level)	capillary pores (microscopic level/submicroscopic level)	gel pores (supramolecular level)	total
1	1.2	4.6/2.3	8.2	16.3
2	2.6	1.7/4.5	1.6	10.4
3	1.3	1.1/5.0	3.5	10.8
4	1.4	1.9/2.3	4.4	9.6
5	3.6	1.7/2.5	1.6	9.4
6	3.2	1.1/1.0	3.5	8.8
7	1.0	0.9/1.8	4.4	8.1

cement matrix and, reacting with the limestone microfiller, it forms hydrated tricalcium monocarboaluminates: $3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$.

Varying the amount of added ash, we can control the number and size of ettringite crystals, which subsequently determines the properties of cement and concrete. The carbonates have tight contacts with the cement stone, which can be accounted for by the formation of epitoxic bonds between the cement hydration products and limestone. Thus, the addition of finely ground limestone is a chemical factor activating reaction between ash and sand. It has a catalytic effect on the surface reactivity of ash and sand during mechanical processing in a vario-planetary mill. Mineral additives in cement activate the hydration process. The crystalline phases in the composition of the CB hydration products—not only the unhydrated clinker minerals (C_3S, C_2S, and C_4AF), quartz, and calcite, but also the hydration products (CH (portlandite) and $3C_3A \cdot 3CaSO_4 \cdot 32H_2O$ (ettringite))—undergo a redistribution.

As pointed out above, the hydrate structure of the CB is represented by two varieties: primary and secondary. The primary structure is represented by amorphous products located in interpore spaces and formed by a through solution mechanism. Note that the composition of the products in pore space depends on the chemical composition of the large particles surrounding the pore.

The paramount issue in designing dense concrete for covering polystyrene foam heat insulation is to rationally configure and optimize the pore space structure. On the whole, it is worth noting the overall decrease in the porosity of the composites modified with industrial waste by more than a factor of 2 (from 16.3 to 8%). In addition, we observe variations in pore diameter, depending on the nature of pore formation (Table 6).

The presence of a large amount of hydrated silicate compounds is confirmed by the decrease in gel porosity in the crystalline binder at a molecular level of the modified composites, with the maximum decrease by more than a factor of 5 (Table 6). Despite the maximum strength (77.3 MPa) of the optimal binder composition (after grinding to $S = 550$ m^2/kg), the gel porosity of this composite decreased almost twofold. The high strength achieved in this case is due to a combined effect: a decrease in capillary porosity due to the activation of the growth of primary crystalline hydrated silicate phases, possible recrystallization, and the formation of secondary crystals, which fill space on a microscopic and a submicroscopic level of the structural organization of the composite, in combination with a decrease in technological porosity by 17% due to the formation of a dense packing of the grain composition at a macroscopic level with the participation of finely dispersed spherical components of the fly ash and screening dust of ground limestone.

The present results demonstrate a clear synergistic effect of the binder components on the mineralogical composition of the hydration products and the rate of the interaction of clinker minerals with water, as well as on the morphology of the hydration products and the microporosity of the stone.

The use of a CB with an increased specific surface area accelerates hydration processes and leads to the formation of new products that contribute to an increase in the density of the cement stone and, as a consequence, to an increase in strength and impermeability.

An important feature of cement systems based on such binders is a significant retardation of structuring processes during the first 4–8 h after mixing with water, followed by active crystallization and hardening processes. The induction period of CB-based cement paste decreases with increasing clinker content in its composition. Advantages of these CBs include prolonged activity and a rapid increase in the strength of cement stone and related concrete at different hardening times, including early age.

CONCLUSIONS

We have demonstrated the possibility of controlling the structure formation of cement stone and related concrete by designing a rational composition and mechanochemical activation technology.

The strongest technical effect can be achieved through a synergistic action of technogenic pozzolanic additives (fly ash) and natural sedimentary materials (limestone) at the composition 55 wt % cement, 5 wt % limestone, and 40 wt % ash. At this composition of the composite, after joint milling to a specific surface area of 550 m^2/kg the material has a compressive strength of up to 77.3 MPa.

Milling to a smaller particle size causes no improvement in strength characteristics of cement stone (concrete). By contrast, some of the unhydrated cement grains should persist in concrete, which react during the service of a concrete structure (many years later), thereby "healing" the cracks formed.

The synergistic effect of pozzolanic and inert additives activates hydration processes, densifying the microstructure of newly formed phases. Besides, silica-containing additives favor the formation of secondary hydrated silicates.

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Translated by O. Tsarev