Investigation of Structure Formation in Complex Binder

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This study deals with the particularities of structure formation and hydration of the complex binder, which consists of liquid glass, metallurgical slag and high aluminate cement (Al_2O_3 > 70 %). According to the ultrasonic and exothermal temperature results, it was determined that due to the reaction between liquid glass and dicalcium silicate the highest hardening intensity was found in the first 20 minutes; however, the hydration of cement takes place much later, i.e. in the hardened structure. SEM investigations of the complex binder showed that its structure is dominated by areas where cement particles are joined by nanostructures (<50 nm) of the products formed during the reaction between liquid glass and hardener, and that the surface of most cement particles is coated by layers of nanoparticles sized from 30 nm up to 100 nm, i. e. the products of cement hydration.
Keywords: complex binder, high aluminate cement, liquid glass, ultrasonic wave velocity, SEM, nanostructures.
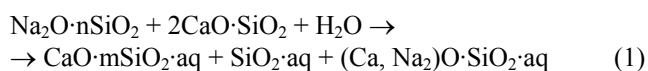
INTRODUCTION

For production of refractory concretes, various binding materials are used. According to the type of binding, they are classified into hydraulic (various cements), chemical (phosphates, liquid glass), organic (resin) and ceramic (clay) [1]. In order to improve the properties of refractories [2] composite binding materials can be used.

One of such kind of compositions consists of high aluminate cement (HAC), liquid glass (solution of sodium silicate) and hardener of liquid glass (metallurgical slag) [3]. It was established that in concretes with complex binder, after hardening, drying and firing at temperature of $500\,°C-600\,°C$, the compressive strength is up to 3 times greater than that of concrete with traditional liquid glass-based binder. The thermal shock resistance of concrete with complex binder increases up to 45 cycles (that of traditional equal to 16). The deformation properties of concretes undergo considerable changes: the samples of traditional concrete expand at temperature of $800\,°C-1000\,°C$, while for concrete with complex binder shrinkage is characteristic [4].

Up to now it is not fully clear why the properties of concretes with complex binder change so markedly. It is believable that these changes are influenced by structure formation during process of hardening and reaction between separate binding components (liquid glass + hardener and HAC + water).

During the process of hardening, the reaction between liquid glass and dicalcium silicate (γ-C_2S – main component of metallurgical slag) is as follows [5]:

$$Na_2O·nSiO_2 + 2CaO·SiO_2 + H_2O \rightarrow$$
$$\rightarrow CaO·mSiO_2·aq + SiO_2·aq + (Ca, Na_2)O·SiO_2·aq \qquad (1)$$

The final products of this reaction are silicium oxide gel, calcium and sodium-calcium hydrosilicates (CSH).

The generated CSH phases are amorphous hydrosilicates with low content of Na_2O, which influence on the properties of hydrosilicates is insignificant [6].

CSH is also the main hydration product and primary amorphous binding phase in Portland cement. Over the past two decades, investigations of Portland cement compositions have provided a reasonably clear picture of CSH structure on the nano scale, and it is widely accepted that CSH is composed of nanoparticles [7–9]. However, it is difficult to identify the products of hardening in liquid glass binder. For example X-ray analysis (XRD) indicates only not reacted γ-C_2S minerals and other admixtures of metallurgical slag (MgO, Mg(Al, Cr)$_2$ O$_4$, Cr$_2$O$_3$), which practically do not participate in the reaction with liquid glass [6, 10].

The main products of hydration of HAC in the reaction with water are crystalline hydrate CAH_{10} ($CaAl_2O_{14}H_{20}$) (formed at temperature lower $20\,°C$), crystalline hydrate C_2AH_8 ($Ca_2Al_2O_{13}H_{16}$) and amorphous AH_3 ($Al(OH)_3$) ($20\,°C-35\,°C$), crystalline hydrate C_3AH_6 (Ca_3Al_2 (OH)$_{12}$) and amorphous AH_3 (>$35\,°C$). CAH_{10} and C_2AH_8 are metastable and, subjected to temperature, time and moisture of environment, turn into gibbsite of crystalline structure [11]. The Table 1 provides the characteristics of crystalline hydrates [12].

In cement stone produced under normal conditions, formation of both crystalline hydrates CAH_{10} and C_2AH_8 in typical [12]. They may be easily identified by X-ray and are visible by microscope. The size of hexagonal prisms of hydrates can grow up to 1 μm-20 μm [13, 14]. However, when the water-cement ratio is low (in pastes of normal consistence), the structure of cement stone has high density (dominated by gel phases); it is difficult to separate structural elements [14].

In the complex binder the mechanism of hydration of HAC is quite different. One of the components (liquid glass and dicalcium silicate) of the composite binding material consisting of liquid glass, metallurgical slag and

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HAC hardens during first 20 min – 30 min [15], while the reactions of hydration of other component (cement) performs in hardened material. The last reaction was obviously observable by heat release (temperature of exothermal reaction) [15], though by XRD tests [16] the reaction products formed during hardening were not identified.

Table 1. Characteristics of crystalline hydrates of aluminate cement [12]

Minerals	Chemical composition, %			Shape of crystal	Density of crystal, g/cm^3
	CaO	Al$_2$O$_3$	H$_2$O		
CAH$_{10}$	16.6	30.1	53.3	Hexagonal prism	1.72
C$_2$AH$_8$	31.3	28.4	40.3	Hexagonal prism	1.95
C$_3$AH$_6$	44.4	27.0	28.6	Cubic	2.52
AH$_3$	–	65.4	34.8	Monocline prism	2.42

It is supposed [1, 17] that the limited amount of water released after the reaction between sodium silicate and dicalcium silicate creates conditions for formation of only initial nanoclusters and nanolayers of amorphous hydrates of HAC, inhibiting the generation of coarse crystalline hydrates of cement. Namely this formed structure of composite binding material exerts a great influence on properties of the material. However, that is only presumptions.

The aim of this investigation was to confirm suggestion that during complex binder's hardening process different structures in different structural levels are formed.

EXPERIMENTAL

The materials used in this investigation included module 3.3 (SiO$_2$/Na$_2$O) sodium liquid glass of 1250 kg/m^3 density; HAC produced by the enterprise GORKA, Trzebinia, Poland; waste of metallurgical slag (MS) from the Cheliabinsk Electrometallurgic Plant, Russia. Main properties of these materials are presented in Table 2.

Three binders have been investigated: HAC with water, metallurgical slag with liquid glass and composition binder in which the ratio of slag to HAC was 1 : 3 (Table 3). The ratio of water to dry component in all binders was constant (up to 0.29 wt. %). The amounts of sodium silicate (% Na$_2$O + % SiO$_2$) and water in liquid glass were calculated using the empirical formulas [18].

For investigation of ultrasonic wave velocity in binder samples, the Schleibinger Geräte GmbH datalogger with the Pundit 7 ultrasonic pulse indicator was used. Binder paste was set between two ultrasonic transducers operating at 10 pulses per second and frequency of 54 kHz. The temperatures during exothermal reaction of binders were established according to the methodology devised by the company Alcoa [19].

The surface (in the fracture zone) of binder sample, which has been matured for 3 days, was scanned by the electron microscopes FEI, QUANTA 200F and JEOL JSM-7600F.

Table 2. Properties of HAC and metallurgical slag

Property	Material	
	HAC	MS
Surface area, m^2/kg	420	250
Bulk density, kg/m^3	1100	990
Chemical composition (wt. %)		
Al$_2$O$_3$	70.5	4.33
CaO	28.7	54.3
SiO$_2$	0.35	29.6
Fe$_2$O$_3$	0.1	1.34
TiO$_2$	0.05	–
MgO	–	6.7
Cr$_2$O$_3$	–	1.4

Table 3. Compositions of binders

No.	Composition, wt. %				
	Dry component of binder		Liquid glass components		Water
	MS	HAC	Sodium silicate	Water	
N1	–	77.5	–	–	22.5
N2	71.7	–	7.4	20.9	–
N3	17.9	53.8	7.4	20.9	–

RESULTS AND DISCUSSION

The changes in structure of binders during hydration where the complicated processes such as water redistribution, initiation of germs of gel and crystalline hydrates, growth of crystalline hydrates are taking place can be analyzed and interpreted by variations of ultrasonic pulse velocity changes determined during hardening of the material.

The measurements of ultrasonic pulse velocity (UPV) of hydraulic binder (in the composition of HAC with water, N1) show (Fig. 1, curve N1) that for the structure of such binder formation four stages is characteristic. In the first stage after molding of paste UPV starts rising immediately. When it reaches ~300 m/s, the second stage begins and during it UPV practically does not change during period of 13 hours.

In the third stage where cement crystalline hydrates are generating, UPV greatly increases from 300 m/s up 3300 m/s. In the fourth stage the main processes of hydration are finished and after ~20 hours UPV curve shows plateau amounting to ~3500 m/s.

During hardening of the composition of liquid glass and metallurgical slag (N2) for 24 h, two stages in formation of structure are observed. The first stage occurs immediately after mixing of components when the chemical reaction between sodium silicate and dicalcium silicate (Fig. 1) begins and UPV of sample rises up in first 20 minutes from 0 m/s up to 1500 m/s. The second stage starts after one hour and after it UPV only slightly increases (not bigger than to 10 % in 24 h).

For the complex binder (Fig. 1, curve N3) the structure formations during 24 h perform in three stages, which, as believable, are subject to hardening of separate binding components. In the first stage, similarly to the binder N2, the increase in UPV (from 0 m/s to 1200 m/s) during first 20 min is caused by the reaction between sodium silicate and dicalcium silicate. During this period the products of hydration are formed and the material hardens up. In the second stage, i. e. after 8 hours, UPV jumps from 1700 m/s up to 2800 m/s. The reason of this process can be the phase of crystallization in the process of hydration of cement. In the third stage (after ~14 h), UPV is growing slowly (by ~13 %) only up to 3200 m/s. In this stage the inhibited process of hydration of HAC is still continuing.
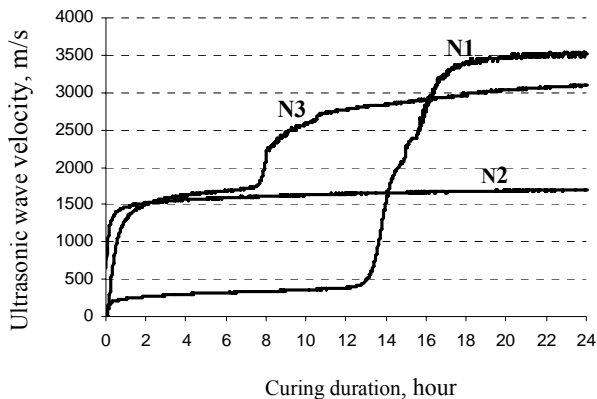
Fig. 1. Ultrasonic pulse velocity in the samples of binder compositions during hardening: N1, N2, N3 – number of binder composition

The process of hydration of binders is accompanied by heat release, which indicates the information about formation of structure. The results of investigation of exothermal reaction (EXO) shows (Fig. 2, a, curve N1) that in the composition N1 after mixing of HAC with water, the exothermal temperature in the sample increases by 2 °C and does not changes during ~ 7.5 h. This interval corresponds to the inductive period of cement hydration [14], during which a high ion concentration is achieved. In 8 h the temperature starts rising rapidly and after 12 h it reaches 99 °C. During this period, ions are settled down on a mass scale, crystalline hydrates form, the binding takes place and the binder hardens up (the most expressive third stage of UPV variation is observable, Fig. 1). Upon reaching the maximum, the EXO temperature starts to decrease.

During the reaction of liquid glass and hardener a certain amount of heat is released as well. As can be seen from Fig. 2, b, the exothermal temperature of sample starts rising up immediately after mixing of composition, however, the temperature reached in 20 min is as low as 24 °C. At this moment the material hardens up, and UPV after the achieved maximum changes but only insignificant (Fig. 1).

The variations of EXO temperature in the composite material (Fig. 2, a, curve N3) are running oppositely to the traditional binders. We can see two characteristic periods of temperature variation. In the first period, due to the reaction between sodium silicate and slag, heat is released and the temperature of sample rises up by ~2 °C. The

second stage starts after 7.5 hours and during it the EXO temperature in the sample reaches 36 °C. When comparing this temperature with the value achieved in the composition N1 (99 °C), it is believable that in the complex binder the stage of crystallization during the hydration of HAC is inhibited and runs under special conditions: the binder hardens up after the reaction between liquid glass and dicalcium silicate, the water, not used fully because of diffusion, is redistributed and adsorbs on surface of cement particles, the growth of cement crystalline hydrates is restricted in the structure of solid material.
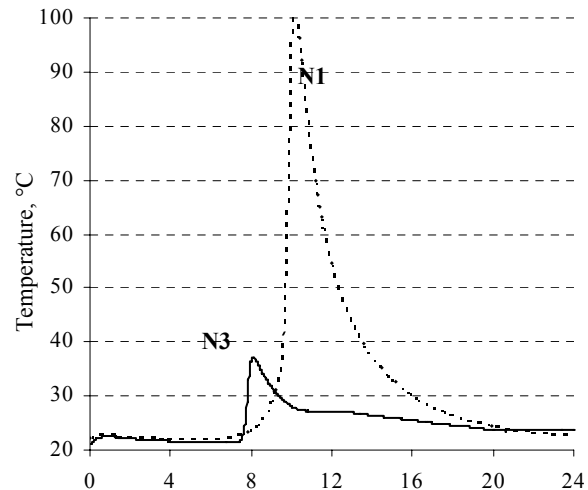

a
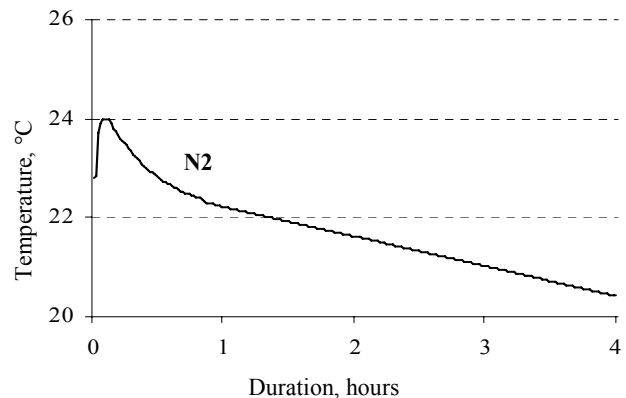
b

Fig. 2. Exothermal temperature during hardening of binders: a – composition N1 and N3, b – N2

SEM tests show type of structure formed in the binder after 3 day of hardening. As the water and cement ratio in the HAC composition N1 was low (0.29) and the gel phase AH_3 joined all structural elements of cement into a very dense structure, we failed to see any classic coarse hexagonal structures of crystalline hydrates CAH_{10} and C_2AH_8 (Fig. 3, a). The minor crystalline hydrates were observable only in the areas of pores of this material (Fig. 3, b) where they could grow unrestrictedly and fill the pores.

The SEM investigations of liquid glass binder (N2) demonstrated that its structure is composed from conglomerates (Fig. 4, a, b), i. e. partially dissolved particles of dicalcium silicate and other admixtures of metallurgical slag, which were coated by clusters of products formed during hardening of liquid glass and dicalcium silicate. In
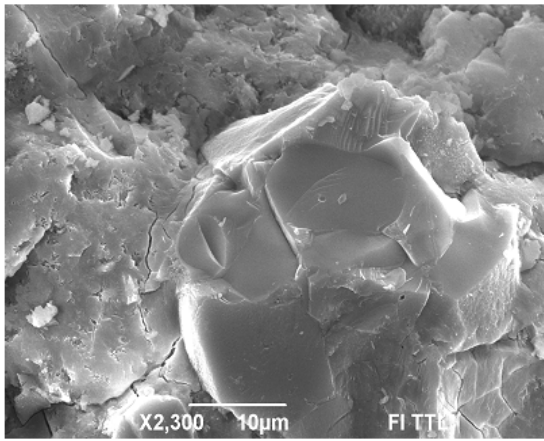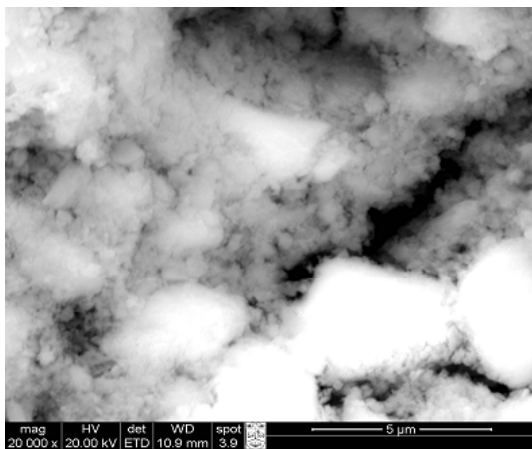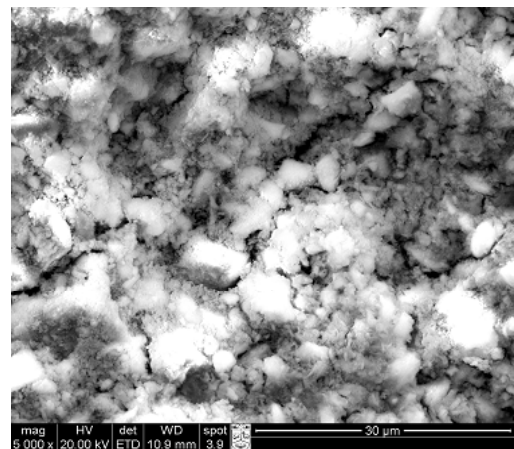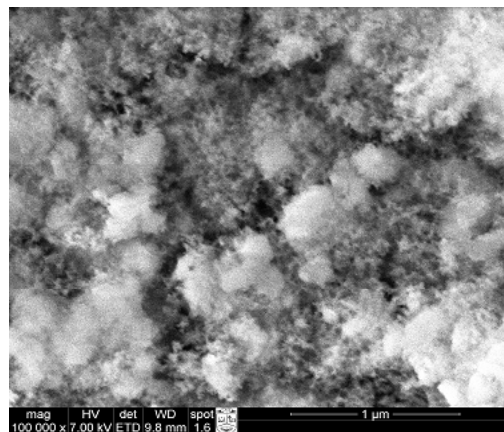
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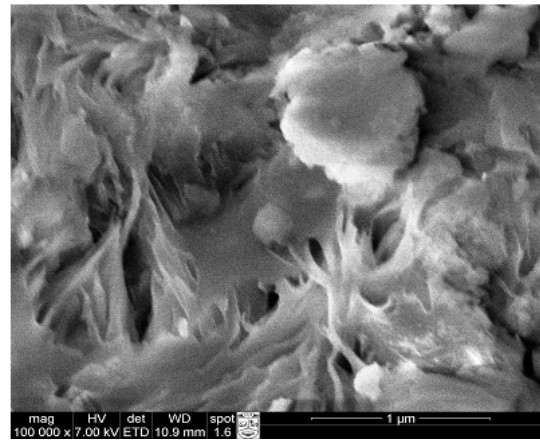
b

Fig. 3. Structure of aluminate cement stone: a – general view, b – minor crystalline hydrates

a

b

c

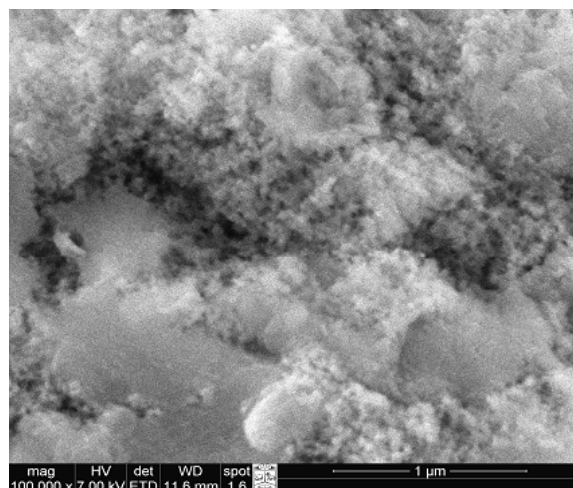**Fig. 4.** Structure of liquid glass binder: a – magnification ×5 000, b – ×20 000, c – ×100 000

Fig. 4, c, we can clearly see that among the amorphous products of hardening the nanosized structures are dominating (< 50 nm), supposedly CSH. One can observe that these particles form certain networks with a great number of voids.

The structure of complex binder (Fig. 5, a) versus that of one-component binder of liquid glass (Fig. 4, a) is more compact and not so "glassy" versus that of cement stone (Fig. 3, a). In separate zones of structure we see that in the
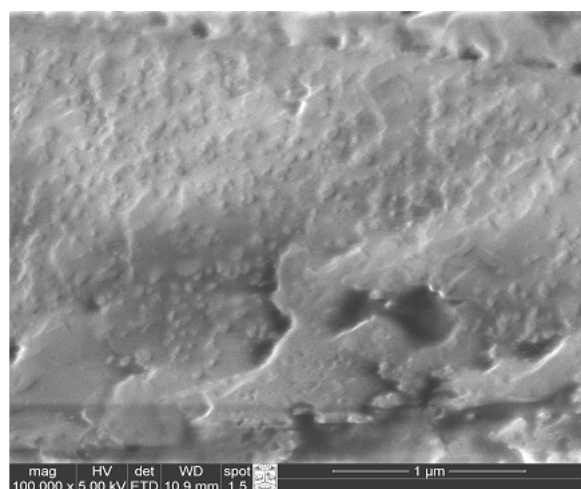
composition the particles of metallurgical slag and cement are joined by nanostructures (Fig. 5) of products of reaction between liquid glass and its hardener. In the contact zones and pores of cement particles neither coarse nor minor crystalline hydrates of HAC are observable. None-theless, one can distinctly observe that the surface of cement particles is very typically coated by nanostructures of a certain orientation and with particles sized from 30 nm up to 100 nm (Fig. 5, c, d). According to the obtained
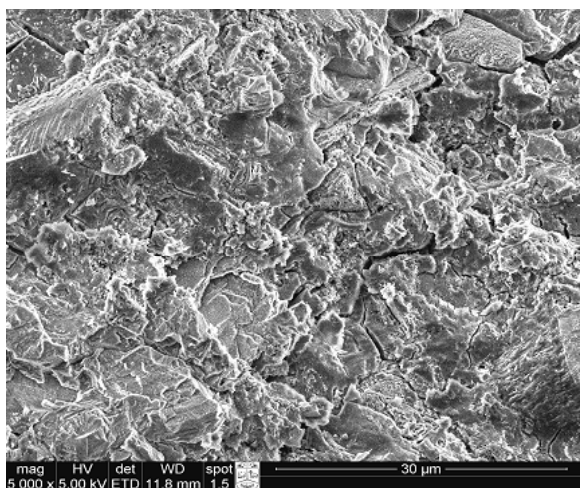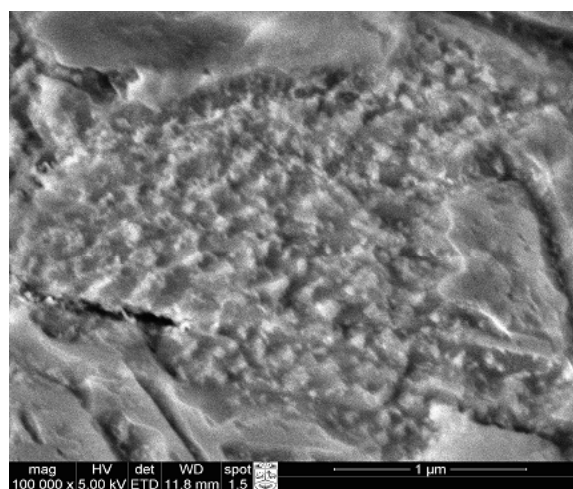
Fig. 5. Structure of complex binder: a – concerted view; b – reaction products between liquid glass and slag; c, d – surface of alumina cement particle

results it can be stated that this study proved the above mentioned assumption that a limited amount of water (released after the reaction between sodium silicate and dicalcium silicate) creates the conditions for formation of only initial nanoclusters and nanolayers of amorphous hydrates of aluminate cement in the hardened structure of complex binder, inhibiting the generation of coarse crystalline hydrates of cement.

CONCLUSIONS

1. The complex binder from liquid glass, metallurgical slag and high aluminate cement (Al_2O_3 >70 %) hardens up already during the first 20 min. Due to the reaction between liquid glass and dicalcium silicate: the ultrasonic pulse velocity in the sample sharply rises up from 300 m/s to 1500 m/s, the exothermal temperature increases by 2 °C. After 7.5 h due to cement hydration the second densification of structure takes place: the ultrasonic pulse velocity and exothermal temperature increases by ~65 % (amounting to 2800 m/s and 36 °C, respectively).

2. The structure of complex binder is dominated by the areas where cement particles are joined by nanostructures of products formed in the reaction between liquid glass and its hardener (supposedly, clusters CSH) and the surface of most cement particles is coated by layers of nanoparticles sized 30 nm – 100 nm – cement hydration products.

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