Study of the Hydration Kinetics of Cement Paste by Measuring Electrical Conductivity

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Abstract. The hardening cement paste is a highly concentrated polyelectrolyte that changes over time. From this point of view, the main electrochemical characteristics of the hydration process of cement paste can be the electrical conductivity and electrode potentials of metals lowered into cement pastes. In the process of setting and hardening of cement dough, complex physical and chemical processes of interaction of clinker minerals with water occur. In this case, new chemical compounds are formed, the concentration of Ca²⁺, Mg²⁺, Al³⁺, Si⁴⁺, Na⁺, H⁺, OH⁻ ions in the liquid phase changes, and the amount of free water decreases. Therefore, the electrical conductivity of the cement paste will change during the hydration of Portland cement minerals. The kinetics of hydration of cement paste is studied by measuring the electrical conductivity depending on the water-cement ratio and in the presence of additives SP C-3 and PDO-M. The parameter of electrical resistance of cement paste was studied using a digital voltmeter of type B7-27A/1. In experimental studies, we used additive-free sulphate-resistant Portland cement with an activity of 41.0 MPa with a normal density of 0.24 and pure clinker minerals – C₃S и β-C₂S. After preparation, the cement paste was placed in the assembled cell and compacted by vibration. Graphs of changes in the complex electrical resistance of cement pastes are obtained, which show that the curves have an oscillatory character. It was found that with an increase in the water-cement ratio, the vibrational nature of the interaction of water with Portland cement minerals weakens. When the water-cement ratio is equal to 0.42, there are no fluctuations in electrical conductivity. This can be explained by the fact that when the amount of water in the cement paste increases, the influence of cations on the degree of its ordering decreases. Curves of changes in the electrical conductivity of cement pastes obtained at W/C=0.26, without additives, as well as in the presence of SP C-3 and PDO-M additives. It can be seen that in the presence of SP C-3, fluctuations in electrical conductivity are weakly expressed. It can be assumed that SP C-3 has a disordering effect on the water in the cement paste. The addition of PDO-M, on the contrary, orders the structure of water, there are fluctuations in electrical conductivity. It is shown that in the CaO–SiO₂–H₂O system, a state of instability develops at certain ratios of the rate constants of individual stages of the hydration process. SP C-3, adsorbed on the adsorption centers of polysilicon acid, slows down some processes, which accelerates others, and the difference between the speed constants of individual stages increases.
1. Introduction
Currently, one of the most dynamic building materials markets in construction is the market for consumption of concrete based on cement binder. The development of new types of them is constantly expanding. To date, concretes have been developed based on new binders, modifiers, and intensive technologies [1-14]. A cement composite material is an inhomogeneous capillary-porous body, the structure of which depends on the water-cement ratio, the volume concentration of the filler and cement, their grain composition, etc. According to modern concepts, the setting and hardening of cement-water systems is a set of sequential processes associated with the formation of hydrates and the appearance of the structure. The formation of the structure of hardening systems based on Portland cement is a Central issue of physical and chemical mechanics [15]. The properties of concrete are largely determined by cement stone.

The hardening cement paste is a highly concentrated polyelectrolyte that changes over time. From this point of view, the main electrochemical characteristics of the hydration process of cement paste can be the electrical conductivity and electrode potentials of metals lowered into cement pastes. In the process of setting and hardening of cement dough, complex physical and chemical processes of interaction of clinker minerals with water occur. In this case, new chemical compounds are formed, the concentration of ions Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), Na\(^{+}\), H\(^{+}\), OH\(^{-}\) in the liquid phase changes, and the amount of free water decreases. Therefore, the electrical conductivity of the cement paste will change during the hydration of Portland cement minerals. In addition, it depends on changes in the water structure and temperature [16].

2. Relevance and scientific significance of the issue
Modern research on the processes of hydration and hardening is characterized by a deep insight into the mechanism of the elementary stages of the above-mentioned processes, and the study of the reaction of hydration of binders at the ion level is the most fruitful and relevant direction [17].

Conventional cement clinker contains 70-80 % anhydrous calcium silicates, hydrolysis and hydration of which are accompanied by the appearance of free calcium hydroxide, Ca(OH)\(_2\), which interacts with SiO\(_2\) and determines the binding properties of cement. The resulting synthetic calcium hydrosilicates (SCH) are the main binding component and carrier of mechanical strength of composite materials based on a cement dispersion system.

The question of the interaction of the binder with water has been covered in numerous works of domestic and foreign researchers, which show that since the closing of the components of the concrete mixture with water, a number of complex chemical, physico-chemical and physico-mechanical transformations occur in parallel in it, which are closely related to each other and have a direct impact on the formation of the phase composition and structure of concrete [16, 18-26].

The physical and chemical processes occurring in cement pastes strongly depend on the structural changes in water. Water molecules are bound together by hydrogen bonds. As a result, it has specific proton transfer mechanisms that are not present in other liquids. Water is a low-dissociating substance, but in the presence of adsorbents and catalysts such as Portland cement minerals, water not only dissociates into hydrogen ions H\(^{+}\) and hydroxyl ions OH\(^{-}\), but also breaks down into free hydrogen atoms H\(^{•}\) and free radicals OH\(^{•}\) [27]. The resulting hydrogen ions H\(^{+}\) and free H\(^{•}\) atoms approach the chain of water molecules connected by a hydrogen bond on one side and cause the appearance of a free proton on the other side of the chain. This results in the highest proton mobility in water (U\(_{\text{H+}}\) = 349 Ohms\(^{-1}\)-g-EQ\(^{-1}\)-cm\(^2\)), which suggests that the electrical conductivity of cement pastes is due solely to proton transport and their mobility.

3. Theoretical part
Cement stone hardening is a complex phenomenon associated with a complex of chemical and physical processes. Physical and chemical processes occurring during the hardening of binders lead to the formation of a strong crystalline junction, which is naturally accompanied by destructive phenomena caused by violations of the fusion contacts during the development of individual components of the
structure [28]. The resulting synthetic calcium hydrosilicates (SCH) are the main binding component and carrier of mechanical strength of composite materials based on a cement dispersion system. The concrete hardening process is a set of complex and diverse physical and chemical transformations that result in a significant change in the structural and mechanical state of the cement dispersion system. H. Taylor notes that the study of chemical hydration of pure cement (without filler) is almost always more appropriate [29]. From the schematization of the hardening mechanism, it follows that the chemical reaction is the primary cause of the development of subsequent physical changes and transformations of the hardening material: the products of hydration and hydrolysis are like "semi-finished products" capable of subsequent structure formation [30]. With further interaction of the chemically active dispersed phase and the dispersion medium, the chemical and physical binding of moisture continues – the accumulation of reaction products, which is identified with an increase in the strength of the hardening system.

The electrical conductivity of cement pastes is caused by proton transfer and their mobility. The mobility of protons significantly depends on the order of water molecules. It can be stated unequivocally that the mobility of protons is related to the degree of ordering of water molecules and increases with the increase of this ordering. In turn, the structure of water depends on the amount and nature of the substances dissolved in the cement paste. Thus, the ions $\text{Al}^{3+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{CO}_3^{2-}$, $\text{OH}^-$ are ordered around the water structure. Near these ions, the translational movement of water molecules is weakened: they become less mobile than in pure water. If the degree of ordering of water depends on the concentration of reagents with which it reacts, and on the products of this reaction, as well as on the temperature, then self-oscillating processes are possible in the cement paste. Indeed, at first, the reaction rate of water interaction with Portland cement minerals increases due to the increase in the order of the water structure, but with increasing speed, heat release also increases. When the heat release becomes greater than the heat sink, the temperature starts to rise. As the temperature increases, the degree of order of the water decreases, which causes the reaction to slow down and stop. As a result of heat transfer, the temperature decreases again, the order of the water increases, and the reaction of water interaction resumes. Its structure in the cement paste is constantly changing.

In the initial period of hydration, when cement particles come into contact with water on the contact surface, the dissolution reactions of crystals of anhydrous minerals immediately begin and the result of their flow is saturation of the water of the closure with $\text{Ca}^{2+}$, $\text{SO}_4^{2-}$, $\text{OH}^-$, $\text{K}^+$, $\text{Na}^+$, etc. During the first few minutes, the water contained in the pores of the molded cement dough is supersaturated with $\text{Ca}^{2+}$ ions and saturated with $\text{SO}_4^{2-}$, $\text{K}^+$, $\text{Na}^+$ ions small amounts of aluminum, iron, and silicon ions also pass into the solution [31].

4. Problem statement
The aim of the study was to study the kinetics of hydration of cement paste by measuring electrical conductivity.

Research objectives:
1. Examine the parameter of electrical resistance of cement paste using a digital voltmeter type B7-27A/1.
2. to Investigate the dependence of the electrical conductivity of cement pastes on the water-cement ratio.
3. Investigate the dependence of the electrical conductivity of cement pastes depending on the introduced plasticizing additives.

5. Materials and methods
In experimental studies, we used additive-free sulphate-resistant Portland cement with an activity of 41.0 MPa with a normal density of 0.24 and pure clinker minerals – $\text{C}_3\text{S}$ and $\beta$-$\text{C}_2\text{S}$. The mineralogical composition of Portland cement was (%) $\text{C}_3\text{S} – 50$; $\text{C}_2\text{S} – 24$; $\text{C}_3\text{A} – 5$ and $\text{C}_3\text{AF} – 17$. Start of setting – 3 h 50 min, end – 5 h 10 min. Additives for concrete – SP S-3 in accordance with the normative document TU 6-36-020429-625 and PDO-M [32]. When conducting studies of the electrical conductivity of
cement systems, a rectangular measuring cell with dimensions of 10×10×50 mm was used. The electrodes were side walls along the length of the cell made of 12X18H10T alloy. The remaining parts of the cell were made of fluoroplast-4. After preparation, the cement paste was placed in the assembled cell and compacted by vibration.

6. Results and discussion

The kinetics of changes in the complex electrical resistance of cement paste is shown in figures 1-3.

Figures 1 show the curves of changes in the electrical conductivity of cement pastes with different water-cement ratios. It can be seen that all curves have an oscillatory character, low-frequency vibrations. At first, the water interacts energetically with the minerals of Portland cement. Heat is released, the temperature increases, translational movements of water molecules increase, and its order decreases. The proton mobility, which depends on the order of the water, decreases, and the electrical conductivity of the cement paste decreases. The reaction is suspended. The dissipation decreases, the temperature decreases, the order of water increases the mobility of protons increases, and the conductivity again increases. It can be seen that with an increase in the water-cement ratio, the vibrational nature of the interaction of water with Portland cement minerals weakens. When the water-cement ratio is equal to 0.42, there are no fluctuations in electrical conductivity. This can be explained by the fact that when the amount of water in the cement paste increases, the influence of cations on the degree of its ordering decreases.

The curves of changes in the electrical conductivity of cement pastes obtained at W/C=0.26, without additives, as well as in the presence of SP C-3 and PDO-M additives, are shown in figure 2. It can be seen that in the presence of SP C-3, fluctuations in electrical conductivity are weakly expressed. It can be assumed that SP C-3 has a disordering effect on the water in the cement paste. The addition of PDO-M, on the contrary, orders the structure of water, there are fluctuations in electrical conductivity.

Figure 1. Kinetics of changes in the electrical conductivity of the cement mixture at different water-cement ratio.

The curves of changes in the electrical conductivity of cement pastes obtained at W/C=0.26, without additives, as well as in the presence of SP C-3 and PDO-M additives, are shown in figure 2. It can be seen that in the presence of SP C-3, fluctuations in electrical conductivity are weakly expressed. It can be assumed that SP C-3 has a disordering effect on the water in the cement paste. The addition of PDO-M, on the contrary, orders the structure of water, there are fluctuations in electrical conductivity.
Figure 2. Kinetics of changes in the electrical conductivity of a cement composition with various additives.

Figure 3 shows the curves of changes in the electrical conductivity of cement dough at W/C=0.3, without additives and in the presence of superplasticizer C-3 (1.0 %) and PDO-M (1.5 %), as well as the curves of changes in the electrical conductivity of pastes prepared from pure monomineral binders β-bicalcium silicate β-2CaO·SiO₂ and tricalcium silicate 3CaO·SiO₂.

From the graphs shown in figure 3, it follows that fluctuations in electrical conductivity in the cement test at W/C=0.3 in the presence of SP C-3 are also absent. There are no fluctuations in electrical conductivity and hydration of these clinker minerals. During hydration of tricalcium silicate pastes, the electrical conductivity is greater than the hydration of dicalcium silicate. In a highly concentrated suspension of tricalcium silicate, water dissociation is more intense and the concentration of hydrogen ions is greater. Calcium cations Ca²⁺ have an ordering effect on water, but are inferior to the cations Al³⁺ and Mg²⁺, which are present in the minerals of Portland cement. Therefore, the process of hydration of the minerals β-2CaO·SiO₂ and 3CaO·SiO₂ does not have an oscillatory character.

Thus, the curve \( \theta = f(r) \), depending on the concentration of cement paste (W/C) and the type of additive, is clearly identified by the time of occurrence of fluctuations and their nature. In General, \( \theta \) changes over time along a curve that logarithmically tends to the limit value \( \theta_0 \). At the same time, in the process of approach in \( \theta_0 \), periodic changes \( \theta \) are attenuated.

Based on the conducted experiments, a spontaneous self-oscillating process of changing its electrical resistance was registered in the hardening cement system. This indicates the manifestation of self-organizing processes that accompany structuring when hardening concentrated cement systems.

Earlier in [27, 33, 34] it was shown that in the CaO–SiO₂–H₂O model system, as well as in hardening cement systems, the phenomenon of self-organization is observed. Comprehensive work has confirmed this phenomenon. In the presence of SP C-3, the self-organization of the structure is more pronounced in these systems. Self-oscillations occurring in the CaO–SiO₂–H₂O system and hardening cement paste indicate the extreme complexity of these systems, as well as the nonlinear nature of the processes occurring in them.
Figure 3. Kinetics of changes in the electrical conductivity of cement and monomineral compositions in the presence of superplasticizers C-3 and PDO-M.

\[ \text{W/C}=0.30 \quad \text{PDO-M 1.5\%} \]

\[ \text{W/C}=0.30 \quad \text{C-3 1.0\%} \]

\[ \text{W/C}=0.30 \quad \text{W/C}=0.30* \]

\[ \text{W/C}=0.30** \]

Physical and chemical processes in the above-mentioned systems proceed at different speeds. If at least one of them develops much faster than all the others, then the others seem to "freeze" in comparison with it. This leads to the emergence of self-oscillation in the systems under consideration, that is, to the phenomenon of self-organization of the structure. In the presence of SP C-3, the speed of one of the processes increases, and the self-oscillation increases.

The effect of SP C-3 on the absorption of calcium cations by polysilicon acid in the CaO–SiO\textsubscript{2}–H\textsubscript{2}O system was investigated. CaO and SiO\textsubscript{2} were taken in a molar ratio equal to 1. Water-solids ratio was equal to 60. The synthesis of calcium hydroxides were at room temperature. SP C-3 was introduced into the system in the amount of 0.1; 0.2; 0.5 and 2.0 % of the solid phase mass. The results of experiments obtained by complexometric titration are shown in figure 4 [35].

In [35] it is shown that in the CaO–SiO\textsubscript{2}–H\textsubscript{2}O system, a state of instability develops at certain ratios of the velocity constants of individual stages of the hydration process. SP C-3, adsorbed on the adsorption centers of polysilicon acid, slows down some processes, which accelerates others, and the difference between the speed constants of individual stages increases. The system develops a state of instability.

As can be seen from the graphs of figure 4 [36], the process of absorption of calcium cations by polysilicon acid has an oscillatory unstable character. From the graphical dependencies, it follows that fluctuations with large amplitudes alternate with fluctuations of small amplitude, which depends on the amount of SP entered.

As it increases, the oscillation amplitude decreases, and the vibrations become attenuated. After 28 days of synthesis, the fluctuations are insignificant. The oscillation amplitude is small.
Figure 4. Kinetics of absorption of calcium cations by polysilicon acid in the \( \text{CaO} - \text{SiO}_2 - \text{H}_2\text{O} \) system in the presence of C-3 superplasticizer in various concentrations [36].

7. Summary
1. Research has been carried out to establish the physical and chemical processes that occur during the hydration of cement pastes by measuring electrical conductivity.
2. Based on the conducted experiments, a spontaneous self-oscillating process of changing its electrical resistance was registered in a hardening cement system, which indicates the manifestation of self-organizing processes that accompany structuring when hardening concentrated cement systems.
3. In the study of cement pastes with different water-cement ratio, it was found that the electrical conductivity curves have an oscillatory character, and the vibrations are low-frequency, and with an increase in the water-cement ratio, the vibrational character of the interaction of water with Portland cement minerals weakens.
4. When introducing a superplasticizer based on naphthalene sulfonic acid, fluctuations in the electrical conductivity of compositions are less pronounced compared to the additive-free prototype, and the addition of PDO-M, on the contrary, orders the structure of water and increases fluctuations.
5. It is shown that in the \( \text{CaO} - \text{SiO}_2 - \text{H}_2\text{O} \) system, a state of instability develops at certain ratios of the rate constants of individual stages of the hydration process. SP C-3, adsorbed on the adsorption
centers of polysilicon acid, slows down some processes, which accelerates others, and the difference between the speed constants of individual stages increases. The system develops a state of instability.

8. References

[1] Erofeev V, Kalashnikov V, Karpushin S, Rodin A, Smirnov V, Smirnova O, Moroz M, Rimshin V, Tretiakov I and Matvievskiy A 2016 Physical and mechanical properties of the cement stone based on biocidal Portland cement with active mineral additive Solid State Phenomena 871 28-32 DOI: 10.4028/www.scientific.net/MSF.871.28

[2] Erofeev V, Kalashnikov V, Emelyanov D, Balathanova E, Erofeeva I, Smirnov V, Tretiakov I and Matvievskiy A 2016 Biological resistance of cement composites filled with dolomite powders Solid State Phenomena 871 33-9 DOI: 10.4028/www.scientific.net/MSF.871.33

[3] Erofeev V, Kalashnikov V, Emelyanov D, Balathanova E, Erofeeva I, Smirnova O, Tretiakov I and Matvievskiy A 2016 Biological resistance of cement composites filled with limestone powders Solid State Phenomena 871 22-7 DOI: 10.4028/www.scientific.net/MSF.871.22

[4] Erofeev V, Bobryshev A, Lakhno A, Shafigullin L, Khalilov I, Sibgatullin K and Igtisamov R 2016 Theoretical evaluation of rheological state of sand cement composite systems using topological dynamics concept Solid State Phenomena 871 96–103 DOI: 10.4028/www.scientific.net/MSF.871.96

[5] Erofeev V, Rodin A, Rodina N, Kalashnikov V and 2016 Irina E Biocidal binders for the concretes of unerground constructions Procedia Engineering 165 1448-54 DOI: 10.1016/j.proeng.2016.11.878

[6] Bobrishev A A, Shafigullin L N, Erofeev V T, Treshchev A A, Sotnikov M I and Vyacheslav A 2016 Study of effects of redispersable latex powders on hardening kinetics of cement-sand composites Research Journal of Pharmaceutical, Biological and Chemical Sciences 7 7 795-802

[7] Travush V I, Karpenko N I, Erofeev V T, Rodin A I, Smirnov V F and Rodina N G 2017 Development of biocidal cements for buildings and structures with biologically active environments. Power Technology and Engineering 51(4) 377-84 DOI: 10.1007/s10749-017-0842-8

[8] Erofeev V T, Rodin A I, Yakunin V V, Bogatov A D, Bochkin V S and Chegodajkin A M 2018 Alkali-activated slag binders from rock-wool production wastes Magazine of Civil Engineering 82(6) 219-27 DOI: 10.18720/MCE.82.20

[9] Kalashnikov V I 2012 What is powder-activated concrete of the new generation Construction Materials 10 70-1 (In Russian)

[10] Maksimova I N, Makridin N I, Erofeev V T and Skachkov Yu P 2015 Strength and Parameters of Destruction of Cement Composites (Monography) (Saransk: Publ. H. of the Mordovian University) 360 p (In Russian)

[11] Bazhenov Yu M, Chernyshov E M and Korotkikh D N 2014 Construction of structures of modern concrete: defining principles and technological platforms Construction Materials 3 6–14 (In Russian)

[12] Komokhov P G, Latypov V M, Latypova T V and Vagapov R F 1998 Durability of Concrete and Reinforced Concrete (Ufa: Belaya reka) 216 p (In Russian)

[13] Kaprielov S S, Travush V I, Karpenko N I, Shejnfel’d A V, Kardumyan G S, Kiseleva Yu A and Prigozhenko O V 2008 Modified high-strength concrete classes C80 and C90 in monolithic structures Construction Materials 3 9–13 (In Russian)

[14] Bazhenov Yu M, Fedosov S V, Erofeev V T, Matviyevsky A A, Mitina E A, Yemelyanov D V Yudin P V 2011 Cement Composites Based on Magnetically and Electrochemically Activated Mixing Water (Monography) (Saransk: Publ. H. of the Mordovian University) 127 p (In Russian)

[15] Segalova E E and Rebinder P A 1960 Modern physical and chemical representations of the processes of hardening of mineral binders Construction Materials 1 21-6 (In Russian)

[16] Akhverdov I N 1981 Fundamentals of Concrete Physics (Moscow: Stroyizdat) 464 p (In Russian)
[17] Vernigorova V N 2001 Physico-Chemical Bases of Formation of Modified Calcium Hydrosilicates in Composite Materials Based on the System CaO-SiO₂-H₂O (Penza: PGUAS) 394 p (In Russian)

[18] Bazhenov Yu M, Demyanova V S and Kalashnikov V I 2006 Modified High-Quality Concrete (Moscow: ASV) 368 p (In Russian)

[19] Bazhenov Yu M 2002 Technology of Concrete (Moscow: ASV) 500 p (In Russian)

[20] Grushko I M, Ilyin A G and Chikhladze E D 1986 Increasing the Strength and Endurance of Concrete (Kharkiv: Vyssha Shkola) 147 p (In Russian)

[21] Desov A E 1956 Vibrated Concrete (Moscow: Stroyizdat) 227 p (In Russian)

[22] Lhermitte R 1959 Problems of Concrete Technology (Moscow: Stroyizdat) 292 p (In Russian)

[23] Mchedlovy-Petrosyan O P 1988 Chemistry of Inorganic Building Materials (Moscow: Stroyizdat) 304 p (In Russian)

[24] Babkov V V, Mokhov V N, Kapitonov S M and Komokhov P G 2002 Structure Formation and Destruction of Cement Concrete (Ufa: Ufa polygraph-combine) 376 p (In Russian)

[25] Shestoperov S V 1977 Technology of Concrete (Moscow: Stroyizdat) 429 p (In Russian)

[26] Yambor Ya Ya 1976 Structure of the phase composition and strength of cement stones VI international Congress on cement chemistry vol 2 book 1 (Moscow: Stroyizdat) pp 315-21 (In Russian)

[27] Vernigorova V N and Taube P R 1979 Concentration self-oscillations in the CaO–SiO₂–H₂O system in the presence of additives J. of physics and chemistry vol 53 4 966-8 (In Russian)

[28] Yudenfreund M, Odler I and Brunauer S 1972 Hardened portland cement pastes of low porosity I. Materials and experimental methods Cement and Concrete Research 2 313-30 DOI: 10.1016/0008-8846(72)90073-7

[29] Taylor H F U 1969 Chemistry of Cements (Moscow: Stroyizdat) 501 p (In Russian)

[30] Stackelberg D I 1984 Thermodynamics of Structure Formation of Water-Silicate Dispersed Materials (Riga: Zinatne) 200 p (In Russian)

[31] Kuznetsova T V, Kudryashov I V and Timashev V V 1989 Physical Chemistry of Binding Materials (Moscow: Higher school) 384 p (In Russian)

[32] Kalashnikov V I (et al.) 1989 Recommendations for the Use of Accelerating Plasticizing Additives PDO-M in the Production of Precast and Monolithic Reinforced Concrete (Moscow-Penza: Penza ISI, NIIZHB Gosstroy of the USSR) 16 p (In Russian)

[33] Bobryshev A N, Makridin N I Solomatov V V 1990 The Phenomenon of Self-Organization in Hardening Cement Systems (Penza) 34 p (In Russian)

[34] Vernigorova V N and Makridin N I 1998 Mathematical modeling of oscillatory processes in the CaO–SiO₂–H₂O system Izvestiya Yuzov. Construction Series 1 38-41 (In Russian)

[35] Vernigorova V N 1977 Thermodynamic properties of the system J. Of Physics and Chemistry vol 51 6 1498-9 (In Russian)

[36] Makridin N I and Vernigorova V N 1990 Physico-Chemical Aspects of the Influence of Superplasticizer C-3 on the Structure Formation of Cement Systems (Penza: PDNTP) 24 p (In Russian)