Influence of Chemical Additives on Modification of the Structure of Hydrosilicates of Cement Systems

V T Erofeev1#, N I Makridin2, I N Maksimova3 and I N Burnaykin1

1Department of Building Materials and Technologies, National Research Ogarev Mordovia State University, 68 Bolshevistskaya St., Saransk 430005, Russia
2Department of Technology of Building Materials and Woodworking, State University of Architecture and Construction, 28 German Titov St., Penza 440028, Russia
3Department of Quality Management and Construction Production Technologies, Penza State University of Architecture and Construction, 28 German Titov St., Penza 440028, Russia

E-mail: al_rodin@mail.ru

Abstract. The article provides information on the study of the influence of aprotic acid (AA) additives on the electrophysical properties of calcium hydrosilicates (HSCs), which allow us to better understand their physical and chemical nature, the type of chemical bond, and the effect of impurities on the structure. The measurements showed that the specific electrical conductivity of HSCs is within $10^{-7}$–$10^{-8}$ Ohms$^{-1}$·cm$^{-1}$. This suggests that HSCs are more "bad" semiconductors than dielectrics. Specific electrical conductivity of HSCs obtained without additives is 10 times greater than with additives. Experimental data shown that the activation energy of the intrinsic conductivity is less than for the impurity conductivity due to imperfections of the crystal lattice, cations and anions of AA additives. The exception is HSCs obtained with the additives BaCl$_2$, CrCl$_3$ and CoCl$_2$ at a concentration of 50 mg/l. For true semiconductors, on the contrary, $E_a > E_{a_{AA}}$. Both without additives and with AA additives, the temperature of the beginning of its own conductivity is the same ~ 50 °C. The decrease in the specific electrical conductivity of HSCs with all the listed AA additives allows us to assert that it is due not so much to the presence of an ordered covalent crystal lattice, but mainly to the covalent interaction of atoms within the near order, as is observed in melts and glasses.

1. Introduction

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. Currently, there is a wide range of technological techniques that allow purposefully regulating the structure and properties of cement composites [1-11].

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. It is appropriate to note that the formation of the structure of hardening systems based on Portland cement is a Central issue of physical and chemical mechanics [12].

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
(HSCs) are the main binding component and carrier of mechanical strength of composite materials based on a cement dispersion system. Formed on the basis of the dispersed system $\text{CaO} - \text{SiO}_2 - \text{H}_2\text{O}$, HSCs is the main binder and carrier of mechanical strength in cement and lime-silica concretes. At the same time, the phase composition and structure of HSCs determine all the qualitative characteristics of the latter.

Numerous studies have shown that the phase composition and structure of HSCs change during synthesis. The main role in such a system, taking into account the low solubility of silica, which, as is known, does not exceed 15-30 mg/l, is played by adsorption processes occurring on the surface of silica particles. Therefore, by influencing them, you can change the structure and properties of HSCs.

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 [13].

2. Problem statement

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 it in parallel, which are closely related to each other and have a direct impact on the formation of the phase composition and structure of concrete [14-23].

So, the hardening process is a set of complex and diverse physical and chemical transformations, the result of which is a significant change in the structural and mechanical state of the cement dispersed system. H. Taylor notes that the study of chemical hydration of pure cement (without filler) is almost always more appropriate [24].

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 [25].

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 [20, 26, 27].

This paper provides information on the study of the effect of aprotic acid additives on the electrophysical properties of HSCs, which allow us to better understand their physical and chemical nature, the type of chemical bond, and the effect of impurities on the structure.

3. Materials and methods

During the research, sulphate-resistant Portland cement with an activity of 41.0 MPa was used for the formation of cement systems, as well as modifying additives $\text{BeCl}_2$, $\text{BaCl}_2$, $\text{CrCl}_3$, $\text{CoCl}_2$, and $\text{FeCl}_3$ to study the effect of additives on the specific electrical conductivity of HSCs were pressed into tablets and the specific resistance of samples was measured on a four-probe compensation unit.

4. Results and discussion

The most sensitive to changes in the composition, structure, nature and concentration of defects is the specific electrical conductivity. The conductivity mechanism, type and concentration of carriers (especially in the region of self-conductance) are determined by the conditions of their own generation, which in turn depend on the nature of the chemical bond between atoms in a crystal, from its strength, the type of crystalline structure, concentration and type of defects. The study of the specific electrical conductivity ($\sigma$) of HSCs plays a particularly important role in estimating the concentration and behavior of impurities in the crystal lattice.

Table 1 shows the results of experimental studies of the effect of additives AA $\text{BeCl}_2$, $\text{BaCl}_2$, $\text{CrCl}_3$, $\text{CoCl}_2$, and $\text{FeCl}_3$ at 30, 50 and 75 °C on the specific electrical conductivity of polycrystalline samples
of HSCs and on the activation energy of this process, since the temperature course of the mobility of electric current carriers is affected by the nature of the chemical bond.

The measurements shown in table 1 showed that the specific electrical conductivity of HSCs is within $10^{-7} - 10^{-8}$ Ohms$^{-1}$·cm$^{-1}$. This suggests that HSCs are more "bad" semiconductors than dielectrics. From the data table 1 it can be seen that the specific electrical conductivity of HSCs obtained without additives is 10 times greater than with additives. Analysis of experimental data shows that HSCs obtained with additives do not have the properties characteristic of true semiconductors, in contrast to which the specific electrical conductivity of HSCs does not increase with increasing temperature. It either does not change, or decreases, and if it increases, it is insignificant. The exception is HSCs obtained with the addition of FeCl$_3$ at a concentration equal to 50 mg/l. Introduced into the structure of a true semiconductor, additives always significantly increase their electrical conductivity. Aprotic acid additives introduced into the HSCs structure do not meet these conditions.

### Table 1. Specific electrical conductivity of HSCs $\sigma$, Ohms$^{-1}$·cm$^{-1}$.

| No | Additive | Concentration, mg/l | Temperature, °C | 30 | 50 | 75 |
|----|----------|---------------------|-----------------|----|----|----|
| 1  | Without additives | – | | 2.3 $\cdot 10^{-7}$ | 0.9 $\cdot 10^{-7}$ | 1.0 $\cdot 10^{-7}$ |
| 2  | BeCl$_2$ | 50 | | 9.1 $\cdot 10^{-8}$ | 5.7 $\cdot 10^{-8}$ | 8.0 $\cdot 10^{-8}$ |
| 3  | 250 | | | 5.8 $\cdot 10^{-8}$ | 4.7 $\cdot 10^{-8}$ | 4.75 $\cdot 10^{-8}$ |
| 4  | BaCl$_2$ | 50 | | 3.6 $\cdot 10^{-8}$ | 4.0 $\cdot 10^{-8}$ | 3.7 $\cdot 10^{-8}$ |
| 5  | 250 | | | 2.3 $\cdot 10^{-8}$ | 7.0 $\cdot 10^{-8}$ | 5.6 $\cdot 10^{-8}$ |
| 6  | CoCl$_2$ | 50 | | 4.1 $\cdot 10^{-8}$ | 4.0 $\cdot 10^{-8}$ | 4.3 $\cdot 10^{-8}$ |
| 7  | 250 | | | 4.6 $\cdot 10^{-8}$ | 4.0 $\cdot 10^{-8}$ | 3.6 $\cdot 10^{-8}$ |
| 8  | CrCl$_3$ | 50 | | 2.7 $\cdot 10^{-8}$ | 3.0 $\cdot 10^{-8}$ | 1.9 $\cdot 10^{-8}$ |
| 9  | 250 | | | 2.7 $\cdot 10^{-8}$ | 3.0 $\cdot 10^{-8}$ | 2.6 $\cdot 10^{-8}$ |
| 10 | FeCl$_3$ | 50 | | 4.2 $\cdot 10^{-8}$ | 5.3 $\cdot 10^{-8}$ | 6.6 $\cdot 10^{-8}$ |
| 11 | 250 | | | 6.0 $\cdot 10^{-8}$ | 6.5 $\cdot 10^{-8}$ | 8.0 $\cdot 10^{-8}$ |

Table 2 shows the impurity and intrinsic specific electrical conductivity of HSCs per carrier and the activation energy of the specific electrical conductivity, as well as the radii of AA cations.

### Table 2. Activation energy of the impurity and its own specific electrical conductivity of HSCs.

| No | Additive | Concentration, mg/l | $\sigma_{0}$ impurity | $\sigma_{0}$ own | $E_{a1}$, kJ/K | $E_{a0}$, kJ/K | Radius of the cation AA, Å |
|----|----------|---------------------|----------------------|-----------------|----------------|----------------|------------------------|
| 1  | Without additives | – | 2.25 $\cdot 10^{-7}$ | 1.78 $\cdot 10^{-8}$ | +1.93 $\cdot 10^{-20}$ | -0.24 $\cdot 10^{-20}$ | – |
| 2  | BeCl$_2$ | 50 | 9.12 $\cdot 10^{-8}$ | 4.37 $\cdot 10^{-8}$ | +1.0 $\cdot 10^{-20}$ | -0.69 $\cdot 10^{-20}$ | 1.13 |
| 3  | 250 | | 5.76 $\cdot 10^{-8}$ | 4.57 $\cdot 10^{-8}$ | +0.44 $\cdot 10^{-20}$ | 0 | |
| 4  | BaCl$_2$ | 50 | 3.55 $\cdot 10^{-8}$ | 4.22 $\cdot 10^{-8}$ | -0.19 $\cdot 10^{-20}$ | +0.96 $\cdot 10^{-20}$ | 2.20 |
| 5  | 250 | | 2.25 $\cdot 10^{-7}$ | 8.4 $\cdot 10^{-8}$ | +1.93 $\cdot 10^{-20}$ | +0.24 $\cdot 10^{-20}$ | |
| 6  | CoCl$_2$ | 50 | 3.98 $\cdot 10^{-8}$ | – | – | 0 | +0.25 $\cdot 10^{-20}$ | 1.62 |
| 7  | 250 | | 4.68 $\cdot 10^{-8}$ | 3.72 $\cdot 10^{-8}$ | +2.76 $\cdot 10^{-20}$ | +0.14 $\cdot 10^{-20}$ | |
| 8  | CrCl$_3$ | 50 | 3.98 $\cdot 10^{-8}$ | 6.31 $\cdot 10^{-8}$ | +0.096 $\cdot 10^{-20}$ | +0.39 $\cdot 10^{-20}$ | 1.45 |
| 9  | 250 | | 3.98 $\cdot 10^{-8}$ | 3.16 $\cdot 10^{-8}$ | +2.49 $\cdot 10^{-20}$ | +0.39 $\cdot 10^{-20}$ | |
| 10 | FeCl$_3$ | 50 | 4.47 $\cdot 10^{-8}$ | 1.00 $\cdot 10^{-8}$ | +2.49 $\cdot 10^{-20}$ | -2.76 $\cdot 10^{-20}$ | 1.63 |
| 11 | 250 | | 6.31 $\cdot 10^{-8}$ | 1.26 $\cdot 10^{-8}$ | -0.96 $\cdot 10^{-20}$ | -2.96 $\cdot 10^{-20}$ | |

The experimental data shown in table 2 show that the activation energy of the intrinsic conductivity is less than for the impurity conductivity due to imperfections of the crystal lattice, cations and anions.
of AA additives. The exception is HSCs obtained with the additives BaCl₂, CrCl₃ and CoCl₂ at a concentration of 50 mg/L. For true semiconductors, on the contrary, \(E_{a0} \gg E_{a1}\). Both without additives and with additives, the temperature of the beginning of its own conductivity is the same – 50 °C. The activation energy of the intrinsic conductivity \(E_{a0}\) determines the thermal width of the band gap. From the table 2 it can be seen that the smallest width of this zone is in HSCs obtained with additives BeCl₂ (50 mg/l) and FeCl₃.

The difference between hydrosilicates-semiconductors and true semi-semiconductors is explained by the presence and state of water in the structure of HSCs.

The impurity conductivity of HSCs is caused by hydrogen ions (protons). Protons are the main carriers of current in the structure of HSCs. Water itself is a low-dissociating compound, but in the structure of HSCs it is chemically bound by both donor-acceptor and hydrogen bonds with other atoms of the structure. High effective charges of atoms, especially the Si atom, for which the effective charge \(q_{\text{eff}} = +1.97\), with which water is bound, increase the degree of dissociation of water, resulting in increased proton concentration. Without additives, the current carriers in the HSCs structure are mainly hydrogen protons. The activation energy of proton mobility as a carrier is significant and is explained by the effect on proton mobility of non-stoichiometry of the chemical composition of HSCs, dislocations, and other structural imperfections. When the temperature increases, the mobility of protons decreases and the impurity conductivity passes into its own electron-hole. This is due to the scattering of protons as carriers on dislocations, impurity ions, and thermal vibrations of the lattice. The semiconductor properties of HSCs are determined by the nature of the Si–O. Chemical bond Si–O is predominantly covalent, pair-electron, and tetrahedral. When the temperature rises, the covalent bonds Si–O deformed. If one of the electrons of the pair leaves its place and goes to the internode, then current carriers appear in the form of electrons and holes and their own electron-hole conductivity. The most easily self-conductivity occurs with the addition of FeCl₃.

It can be assumed that Fe³⁺ cations replace silicon atoms in SiO₄ tetrahedra. Since the Fe³⁺ atom has three valence electrons, the formation of four bonds with silicon atoms is accompanied by the capture of one electron from a neighboring covalent bond. This act of electron capture forms a hole when some energy is transmitted, which is the energy of activation of acceptors. The resulting holes serve as current carriers, and the HSCs becomes a hole semiconductor. The act of electron capture is the excitation of the entire crystal, in which the electron is transferred from the valence band to the impurity level of the acceptor. The cations Be²⁺, Ba²⁺, Co²⁺, Cr³⁺ and Cl⁻ ions are located in the internodes of the HSCs crystal lattice, forming a solid solution of the solution. Cations behave as electron acceptors, and Cl⁻ ions behave as donors. Therefore, with the listed additives, HSCs exhibit their own electron-hole conductivity. Embedded cations Be²⁺, Ba²⁺, Co³⁺, Cr³⁺, Fe³⁺ and anions Cl⁻ deform the covalent bond Si–O, and the degree of deformation depends on what kind of conductivity HSCS exhibit: n-type or p-type.

In liquid water, the cations Be²⁺, Ba²⁺, Co³⁺, Cr³⁺ and Fe³⁺ interact with water molecules in such a way that they reduce the speed of their translational movement, constrain the self-diffusion of molecules and increase the viscosity of water. In the HSCs structure, water is in a more or less connected ordered state. Protons in such a structure move in a relay, along a chain of hydrogen bonds. Introduced into the HSCs structure, the cations and anion Cl⁻ of the reduced AA break the chains of hydrogen bonds, increase the structure’s defectiveness, and Cl⁻ ions even in HSCs increase the speed of translational movement of water molecules, resulting in both the concentration and mobility of current carriers – protons-decreases.

The decrease in the specific electrical conductivity of HSCs with all the listed AA additives allows us to assert that it is due not so much to the presence of an ordered covalent crystal lattice, but mainly to the covalent interaction of atoms within the near order, as is observed in melts and glasses. AA supplements have an effect on the Si–O only within the near order, within a single tetrahedron, at the atomic level. In silicon-oxygen tetrahedra, silicon atoms are in the sp³-hybrid state and, in addition to the covalent bond between Si–O, between silicon and oxygen atoms, there is an additional \(d_{\sigma–p_{\pi}–}\)
binding, which reduces the length of the Si–O bond. This compacts the silicon-oxygen motif as a whole and brings the $3sp^3$-hybrid valence band closer to the $4s$-conduction band, meaning that the width of the band gap $\Delta E$ decreases. When the concentration of additives BaCl$_2$ and CrCl$_3$ increases, the cations Ba$^{2+}$ and Cr$^{3+}$ destroy the additional $d_s-p_b$-binding between silicon and oxygen atoms, the bond length Si–O increases, as a result of which the width of the band gap increases and a large activation energy is required for the electron to pass from the valence band to the conduction band. The decrease in the specific electrical conductivity of $\sigma$ HSCs with AA additives allows us to assert that cations and anions, having penetrated into tetrahedral voids, destroy additional $d_s-p_b$-binding, increase the length of the Si–O bond, resulting in an increase in the width of the forbidden energy zone. AA additives loosen the silicon-oxygen tetrahedral motif of HSCs, which leads to changes in the structure and properties of calcium hydrosilicates.

5. Summary

1. Analysis of ionization radiographs of hydrated samples $\beta$-C$_3$S and C$_3$S in the presence of SP C-3 and NF relative to control samples without SP showed the following:
   - In samples of the mineral $\beta$-C$_3$S without SP C-3 and with SP C-3, two phases – C$_2$SH (A) and C$_3$SH (B) are formed, and without SP C-3 in approximately equal quantities, and with SP C-3, the C$_2$SH (A) phase prevails. At the same time, the relative intensity of the lines of these phases in the presence of SP C-3 is less, i.e. SP C-3 prevents the crystallization of these phases; in the presence of SP NF, 3 phases are formed, this is due to the fact that NF, embedded in the crystal lattice $\beta$-C$_3$S, creates greater steric difficulties than C-3, while the C$_2$SH (A) phase prevails.
   - 3 phases are present in samples of the C$_3$S mineral hydrated both without SP additives and with additives, but the relative intensity of the lines of the released phases C$_2$SH (A), C$_3$SH (B) and C$_3$SH (C) is less in the presence of SP C-3 and NF due to the lower degree of crystallization of the formed phases.
   - The role of SP C-3 and NF is reduced to the dispersion of C$_3$S and $\beta$-C$_3$S particles and to the creation of steric difficulties in the formation of phases of variable composition. By introducing SP molecules into the crystal lattices of minerals, we make them more active and reactive.

2. in the hardening cement paste, a spontaneous self-oscillating process of changing its electrical resistance was registered, which indicates the manifestation of self-organizing processes that accompany structure formation during the hardening of concentrated cement systems. The manifestation of self-organizing processes is noted both when calcium cations are absorbed by polysilicon acid, and when the pH of the cement test is measured in the first hours after closing, when the most intense chemical reactions occur between cement minerals and water. The registered spontaneous self-oscillating process is significantly influenced by chemical additives.

3. Self-oscillations occurring in the hardening cement paste indicate the extreme complexity of these systems, the nonlinear nature of the processes occurring in them and their dependence on chemical additives of water-reducing action. The phenomenon of self-organization of the structure in the cement-water system is the basis of the well-known from practice position on a faster deterioration of the workability of concrete mixes prepared with the use of SP.

4. The main binding substance and the carrier of the mechanical strength in cement concrete are HSCs. By influencing the adsorption processes, it is possible to change the structure and properties of HSCs. Additives of various chemical nature loosen the silica tetrahedral motif of HSCs, which leads to modification of their structure and properties.

6. References

[1] 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)

[2] Chernyshov E M, Potamoshneva N D, Stepanova M P and Lesovik R V 2014 Clinkerless composites with portlandite matrix Research Journal of Applied Sciences vol 9 12 1109-13
[3] Kaprielov S S, Travush V I, Karpenko N I, Shejnfel’d A V, Kardumyan G S, Kiseleva Yu A and Prigozenko O V 2008 Modified high-strength concrete classes C80 and C90 in monolithic structures Construction Materials 3 9–13 (In Russian)

[4] Makridin N I, Kalashnikov V I, Maksimova I N, Tarakanov O V and Polubarova J V 2016 Inner friction and dynamic modulus of elasticity of structural concrete Journal of Engineering and Applied Sciences vol 11 7 1545-8

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

[6] 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) p 360 (In Russian)

[7] 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

[8] 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

[9] 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

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

[11] 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 4 795-802

[12] 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)

[13] 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)

[14] Akhverdov I N 1981 Fundamentals of Concrete Physics (Moscow: Stroyizdat) 464 p (In Russian)

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

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

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

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

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

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

[21] 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)

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

[23] 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)

[24] Taylor H F U 1969 Chemistry of Cements (Moscow: Stroyizdat) 501 p (In Russian)
[25] Stackelberg D I 1984 Thermodynamics of Structure Formation of Water-Silicate Dispersed Materials (Riga: Zinatne) 200 p (In Russian)

[26] Locher V F and Richartz W 1976 Investigation of the mechanism of hydration of cement VI international Congress on cement chemistry vol 2 book 1 (Moscow: Stroyizdat) pp 123-33 (In Russian)

[27] Sychev M M 1978 Chemistry of hardening and formation of strength properties of cement stone Cement 9 4-6 (In Russian)