Виконано термодинамічні дослідження утворення гідросилікатів кальцію при використанні в вапняно-кремнеземистої суміші гідроксиду та оксиду кальцію. Найбільшу термодинамічну ймовірність мають реакції з оксидом кальцію, реакції екзотермічні. Використання гідроксиду кальцію – причина ендотермічних реакцій. Помічено синергетичний ефект при одночасній дії на суміш механічної і хімічної активації. Гідросилікати кальцію утворюються без автоклавної обробки

Ключові слова: силікатна цегла, ентальпія реакцій, оксид кальцію, гідроксид кальцію, активація, енергозбереження

Выполнены термодинамические исследования образования гидросиликатов кальция при использовании в известково-кремнеземистой смеси гидрооксида и оксида кальция. Наибольшую термодинамическую вероятность имеют реакции с оксидом кальция, реакции экзотермические. Использование гидрооксида кальция – причина эндотермических реакций. Замечен синергетический эффект при одновременном действии на смесь механической и химической активации. Гидросиликаты кальция образуются без автоклавной обработки

Ключевые слова: силикатный кирпич, энтальпия реакций, оксид кальция, гидрооксид кальция, активация, энергосбережение

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THEORETICAL AND EXPERIMENTAL RESEARCH INTO MANUFACTURING OF SILICATE PRODUCTS WITHOUT THERMAL TREATMENT

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1. Introduction

Silicate brick is manufactured from the most widespread material on Earth – sand, with the addition of small amounts of lime and water. For the first time in 1880 [1], the first artificial stone was obtained from the mixture of sand and lime, after exposure for 8 hours in an autoclave under pressure of 8 atmospheres in the medium of saturated vapor. Since then the technology of silicate brick practically has not changed. It consists of several stages: preparation of lime-silica binder by grinding a mixture of lime and sand, exposure of this binder in the capacities for providing the most complete lime hydration, molding the articles by pressing from the mixture of the binder and unground sand and thermal treatment in autoclaves.

Under the action of temperature, in the medium of saturated water vapor, physical-chemical processes occur in the autoclave between components of the mixture, as a result of which calcium hydrosilicates form, which provide for the strength of silicate brick.

Autoclave technology is characterized by considerable consumption of thermal energy. Decrease in the expenditures for thermal energy in the process of production of silicate materials is becoming very relevant.

2. Literature review and problem statement

At present, efforts of many scientists are directed toward reducing power costs in the course of autoclave treatment or replacing autoclave treatment by steaming in a pit steaming chamber.

Two basic directions of reduction in power expenditures in the course of autoclave treatment are known: chemical activation and mechanical activation. Chemical activation is accomplished with the aid of additives of natural and artificial origin [2]. The obtained effect manifests itself in the decrease of temperature of thermal treatment, vapor pressure or reduction of exposure time in an autoclave [3]. It is also potentially possible to improve performance properties of the articles, obtained from the chemically activated silicate mixtures [4].

Mechanical activation is an increase in reactivity of the surface of components, which enter into reactions between each other. It is achieved by mechanical actions of different nature on the processed material. The most widespread method of activation is processing the material in the mills (usually, ball-type) [5] at different regimes and size of balls. In this case, an increase in dispersiveness of the processed powder is observed. Mechanical activation is an increase in reactivity of the surface of components, which enter into reactions between each other. However, the increase in dispersiveness is not the main purpose of such a treatment. Because the effect from mechanical activation of the mixtures, applied in construction sector, is achieved owing to the entire complex of modifications. They include deformation of crystals, formation of defects, aggregation of crystallites, heat release, local rise in temperature and pressure, phase transformations, amorphization, break of chemical bonds, acceleration of the processes of diffusion, formation of active centers. In the course of activation of concrete (including silicate) mixtures), important is reaching optimum granulometric composition from the point of view of the best laying to achieve maximum density [6]. In addition to the increase in strength of the finished product, rheological properties of construction mixtures after processing (activation) also change [7].

The disintegrator [8] was among the very first machines, widely utilized for activating the moistened silicate mixture in the production of silicate brick. The action of disintegrator on the material is based on high rates (about 100 m/s) of blows of the working organ against particles of the mixture. One of the shortcomings of this technology of activation is rapid wear of the working organs and high operating costs associated with this. One more technical complexity in this technology is severe consequences for the equipment in the case a large uncrushable inclusion enters the working organs. There are other principles of action on a lime-silica binder for the purpose of its activation [9]. The course of reactions of structure formation can start directly in the activator [10]. It is obvious that a large volume (big layer) of the particles that simultaneously contact each other will ensure higher productivity and efficiency.

A drum-roll machine is proposed (Fig. 1) that is principally different from the known equipment for activating a silicate mixture [11]. The processed material is repeatedly rolled between the surfaces of drum 1 and roll 3; it is loosened by knife 6 after each rolling. The material is removed from the drum through discharge tray 7. The processing of the material occurs in thick layer (thickness of layer of the material between drum 1 and roll 3 considerably exceeds particle size in the processed mixture). The machine depicted in Fig. 1 works in the continuous regime. There are also constructions of periodic action. Increase in the intensity of action may be reached by vibration of the roll 3 [12].

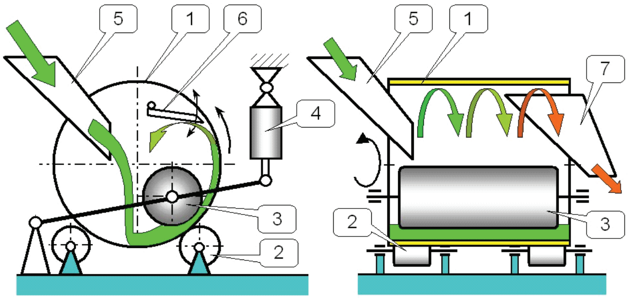

Fig. 1. Schematic of a drum-roll machine (activator) of continuous action: 1 – drum, 2 – rollers, 3 – roll, 4 – device for roll clamping to the internal drum surface, 5 – loading tray, 6 – knife, 7 – discharge tray

Fig. 2 demonstrates processes, which accompany the process of activation in a drum-roll machine.

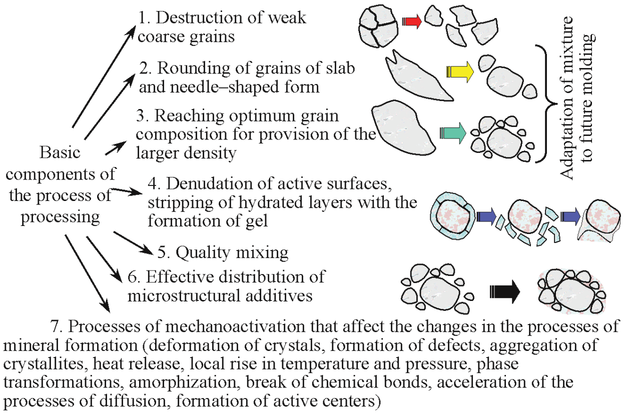

Fig. 2. Paths of change in the state of mixture in drum-roll activators

By the traditional method of manufacturing silicate brick, a lime-sandy (lime-silica) mixture is quenched in silos or reactors where active calcium oxide CaO mixeds with water and passes into slaked lime $Ca(OH)_2$. Under standard conditions, CaO hydration is accompanied by energy release: per 1 kg CaO – 269,5 kcal. This energy is not used (it is dissipated through heat exchange into the environment). The process of preliminary hydration of lime, at which its capability for hydration hardening is not realized, may be considered irrational. That is why of interest is the preparation of mixture for molding without preliminary hydration of calcium oxide. This is possible because of a very effective mixing and active passage of reaction of hydration in the drum-roll activator. Furthermore, this direction of research became possible owing to paper [13] and others, in which it is proven that lime in the unslaked form under certain conditions is capable of hydration hardening.

Significant contribution to the development of theory of silicate systems was made by scientists from Kharkov [14, 15]. The known methods of thermodynamics are developed with their participation. They also proposed new methods, which made it possible to conduct theoretical analysis of power expenditures in any chemical production, based on chemical reactions. In particular, it is possible to carry out analysis of power costs for the variants of traditional hydration hardening (at which the hydration energy is dissipated) and of the hardening that involves energy of lime hydration. Experimental confirmation of this, more energy-efficient, method of obtaining construction (silicate) brick is possible with the use of a drum-roll activator (Fig. 1).

3. Aim and objectives of the study

The aim of the study is theoretical and experimental substantiation of technological solutions of obtaining the lime-silica articles of non-autoclave hardening.

To achieve the set aim, the following tasks were to be solved:

– to determine, from an energy-saving point of view, thermodynamic expediency of applying calcium oxide in the lime-silica mixture instead of calcium hydroxide;

– to examine influence of the presence of amorphous silica dioxide in the lime-silica mixture on the energy of reactions of formation of hydrosilicates;

– to carry out comparative experimental research into separate and combined influence of mechanical and chemical activation on the strength indices of the samples of silicate brick.

4. Methods of thermodynamic analytical studies and experimental research into non-autoclave technology of silicate brick

4. 1. Method of thermodynamic analytical studies

Thermodynamic analysis makes it possible to determine direction and duration of the course of reactions, stability of the formed compounds and ways of suppressing undesirable directivity of the processes [15].

The necessary condition for correct comparison of thermodynamic sequence of reaction in one and the same system is consideration of the stoichiometry of reactions. The latter may be realized based on the so-called principle of calculation ΔG (the Gibbs free energy) by compositions [15]. The essence of this principle consists in the fact that the identical amount of starting substances is taken for all reactions in one system in the left sides of the equation. Then each of the possible reactions will be related to one and the same amount of starting substances and, therefore, the corresponding values ΔG will prove to be comparable.

In [15], in the system $Ca(OH)_2$–SiO_2–H_2O, they examined reactions of formation of nine calcium hydrosilicates: hillebrandite, afvillite, foshagite, xonotlite, riversideite, tobermorite, plombierite, oceanite and gyrolithe from $Ca(OH)_2$, β-quartz and water for the ratio $Ca(OH)_2$ and SiO_2, equal to 1:2, 2:3, 5:6, 1:1, 4:3, 3:2, 2:1.

For the comparative thermodynamic analysis, the paper's authors comprised equations of reactions of formation of calcium hydrosilicates in the systems $Ca(OH)_2$–SiO_2–H_2O and CaO–SiO_2–H_2O at the ratio of $Ca(OH)_2$ and SiO_2, CaO and SiO_2, equal to 5:95. The original data, used in the calculations, are borrowed from [15]. From the point of view of search for the most rational directions of reducing power costs when manufacturing silicate brick, it makes sense to analyze thermodynamic indices of the above-mentioned systems.

It is known that the reaction of interaction of quicklime with water is exothermic and is accompanied by significant heat release, which is completely lost into the environment and is not at all used in the traditional technological process of manufacturing silicate brick. It is also known that the formation of calcium hydrosilicates may occur not only in the course of autoclave treatment but also at room temperature [15]. Therefore, it is expedient to carry out comparative analysis of the energy of chemical reactions in two variants: with the use of calcium oxide (formulas (3)–(11)) in the lime-silica mixture and hydroxide (formulas (12)–(20)) depending on temperature.

Thermodynamic calculations are performed by the method, presented in [15]. The effect of temperature on the change in the Gibbs energy ΔG_T^0 and the enthalpy ΔH_T^0 of chemical reactions were determined by dependencies:

$$\Delta G_T^0 = \Delta H_0 - \Delta a \cdot \ln T - 0{,}5\Delta b \cdot T^2 - 0{,}5\Delta C \cdot T^{-1} + yT, \qquad (1)$$

$$\Delta H_T^0 = \Delta H_0 + \Delta a \cdot T + 0{,}5\Delta b \cdot T^2 - \Delta C \cdot T^{-1}, \qquad (2)$$

where ΔH_0, y are the constants of integration; Δa, Δb, Δc are the coefficients in equation of dependence of heat capacity on temperature; T is the temperature of the course of reaction, K.

4. 2. Method of experimental research into the proposed technology of silicate brick

To confirm the possibility of obtaining brick with the non-autoclave technology with the use of reactions in the system CaO–SiO_2–H_2O, we prepared a mixture with the help of the activator (Fig. 1). The time of activation composed 10 min, pressure under the roll – 1 MPa. After that, the samples of size 50×50×28 mm were formed from the mixture on a hydraulic press. Compacting pressure was 25 MPa.

Composition of the mixtures:

1) quicklime CaO (activity about 80 %) – 8 % of the sum of dry components; quartz sand – 92 % of the sum of dry components; mixture humidity – 8 %;

2) quicklime CaO (activity about 80 %) – 8 % of the sum of dry components; quartz sand – 87 % of the sum of dry components; phosphogypsum (additive for chemical activation) – 5 % of the sum of dry components; mixture humidity – 8 %.

The molded samples were kept at room temperature in wet environments not less than 72 hours. Compressive strength was determined by the crushing of samples on a hydraulic press. We carried out 4 series of experiments:

1) without activation and without adding phosphogypsum (mixture 1 without activation);

2) without activation with adding phosphogypsum (mixture 2 without activation);

3) with activation and without adding phosphogypsum (mixture 1 with activation);

4) with activation with adding phosphogypsum (mixture 2 with activation).

The number of samples for each series comprised 15 pieces, which ensured reliable probability of the values of strength about 92 %.

5. Results of examination of the process of hydration and mineral formation

5. 1. Comparative thermodynamic analysis of the energy of reactions in the systems $Ca(OH)_2$- SiO_2-H_2O and CaO-SiO_2-H_2O

Possible reactions of the formation of calcium hydrosilicates with participation of CaO (energy-efficient variant):

$$5CaO+95SiO_2+5{,}5H_2O= \\ =5/2(2CaOBSiOB1{,}17H_2O)+ \\ +92{,}5SiO_2+2{,}575H_2O, \qquad (3)$$

$$5CaO+95SiO_2+5{,}5H_2O= \\ =5/3(3CaOB2SiOB3H_2O)+275/3SiO_2+0{,}5H_2O, \qquad (4)$$

$$5CaO+95SiO_2+5{,}5H_2O= \\ =5/4(4CaOB3SiOB1{,}5H_2O)+ \\ +91{,}25SiO_2+3{,}625H_2O, \qquad (5)$$

$$5CaO+95SiO_2+5{,}5H_2O= \\ =5/6(6CaOB6SiOBH_2O)+90SiO_2+28/6H_2O, \qquad (6)$$

$$5CaO+95SiO_2+5{,}5H_2O= \\ =5CaOB6SiOB3H_2O+89SiO_2+2{,}5H_2O, \qquad (7)$$

$$5CaO+95SiO_2+5,5H_2O= \\ =5CaOB6SiOB5,5H_2O+89SiO_2, \quad (8)$$

$$5CaO+95SiO_2+5,5H_2O= \\ =5CaOB6SiOB10,5H_2O+89SiO_2, \quad (9)$$

$$5CaO+95SiO_2+5,5H_2O= \\ =CaOB2SiOB2H_2O+93SiO_2+3,5H_2O+4CaO, \quad (10)$$

$$5CaO+95SiO_2+5,5H_2O= \\ =2CaOB3SiOB2,5H_2O+92SiO_2+3H_2O+3CaO. \quad (11)$$

Possible reactions of the formation of calcium hydrosilicates with the participation of $Ca(OH)_2$ (conventional variant, applied in industry):

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5/2(2CaOBSiOB1,17H_2O)+ \\ +92,5SiO_2+2,575H_2O, \quad (12)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5/3(3CaOB2\ SiOB3H_2O)+91,7SiO_2+0,5H_2O, \quad (13)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5/4(4CaOB3SiOB1,5H_2O)+ \\ +91,25SiO_2+3,625H_2O, \quad (14)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5/6(6CaOB6SiOBH_2O)+ \\ +90SiO_2+28/6H_2O, \quad (15)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5/6(6CaOB6SiOB3H_2O)+89SiO_2+2,5H_2O, \quad (16)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =6CaOB6SiOB5,5H_2O+89SiO_2, \quad (17)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =5CaOB6SiOB10,5H_2O, \quad (18)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =CaOB2SiOB2H_2O)+ \\ +CaO+3,5H_2O+93\ SiO_2, \quad (19)$$

$$5Ca(OH)_2+95SiO_2+0,5H_2O= \\ =2CaOB3SiOB2,5H_2O+ \\ +3CaOH+3H_2O+92\ SiO_2. \quad (20)$$

Based on the calculations by dependencies (1) and (2), we built dependencies of the Gibbs energy on temperature for the variants of application CaO (Fig. 3) and $Ca(OH)_2$ (Fig. 4).

Negative values of ΔG^o_T in the course of formation of calcium hydrosilicates from quicklime (CaO calcium oxide) (Fig. 3) testify to the possibility of formation of all nine calcium hydrosilicates in temperature interval from 273 to 473 K in this sequence: plombierit, tobermorite, riversideite, foshagite, xonotlite, hillebrandite, afvillite, gyrolithe and oceanite.

In the reactions of formation of calcium hydrosilicates from slaked lime ($Ca(OH)_2$ calcium hydroxide) (Fig. 4), the formation of hydrosilicates is most probable in this sequence: plombierite, tobermorite, riversideite, hillebrandite, afvillite.

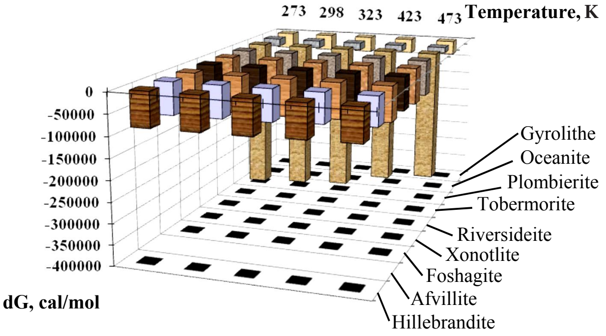

Fig. 3. Dependency of the Gibbs energy of the formation of calcium hydrosilicates on temperature when using calcium oxide in the mixture

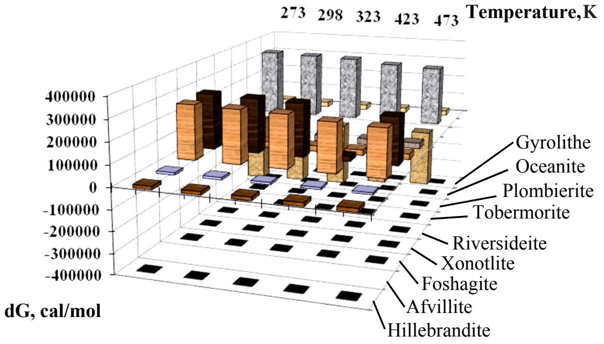

Fig. 4. Dependency of the Gibbs energy of the formation of calcium hydrosilicates on temperature when using calcium hydroxide in the mixture

A distinctive feature of realization of the reactions with the use of quicklime (Fig. 3) in the lime-silica mixture is the fact that thermodynamically all nine hydrosilicates are represented by the probable reaction products in the above-mentioned sequence (including low-basic hydrosilicates, which is important).

Thus, at temperature from 273 to 323 K, more probable for hillebrandite is its obtaining from quicklime, and at a temperature of 423 and 473 K – only from slaked lime.

Foshagite, xonotlite, oceanite and gyrolithe are formed only in the reactions with quicklime in the entire examined temperature range.

Riversideite, tobermorite and plombierite in the entire temperature interval are more probable in the reactions with quicklime.

Therefore, upon analyzing the obtained data, it is possible to draw the conclusion that thermodynamically it is more expedient to apply quicklime for the production of silicate brick.

Notable are also the results of calculation of enthalpy of the formation of calcium hydrosilicates depending on the application of slaked lime and quicklime. Fig. 5 displays a change in enthalpy of reactions of the formation of calcium hydrosilicates with the use of calcium hydroxide in the lime-silica mixture.

In the course of formation of hydrosilicates xonotlite, foshagite, gyrolithe, oceanite, the enthalpy of reactions is positive. And the formation of such hydrosilicates as plombierite, tobermorite, riversideite, afvillite hillebrandite is accompanied by a change in the enthalpy of reactions to the side of negative values. It should be interpreted in the following way. It is accepted to assume as positive the heat, absorbed by system in this process, and as negative – the heat, released by the system [15]. Examining in this context the values of a change in the enthalpy of chemical reactions in the case of using slaked lime in the mixture, it is possible to state that the formation of hydrosilicates plombierite, tobermorite, riversideite, afvillite, and hillebrandite is possible only when the power is supplied to the system. When applying quicklime CaO in the lime-silica mixture, the picture changes (Fig. 6). Enthalpy of all reactions (Fig. 6) is negative, which indicates the passage of reactions of the formation of all nine named hydrosilicates with the heat release. Furthermore, in the course of reactions of the formation of the same hydrosilicates, the heat release is much larger at applying quicklime as the lime component.

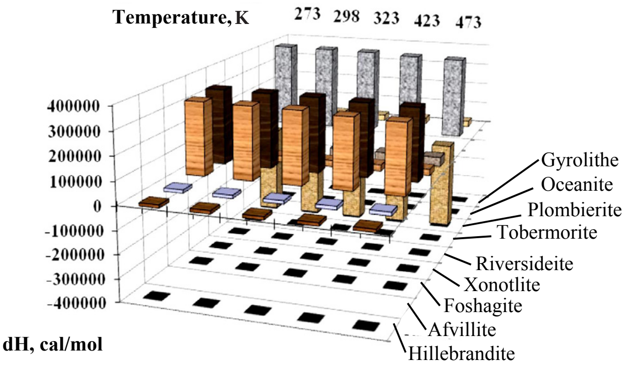

Fig. 5. Dependency of enthalpy of the formation of calcium hydrosilicates on temperature in the reactions with the use of slaked lime (calcium hydroxide) in the lime-silica mixture

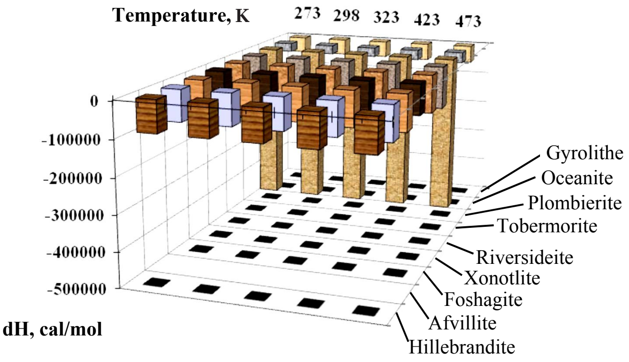

Fig. 6. Dependency of enthalpy on temperature in reactions of the formation of calcium hydrosilicates with the use of quicklime (calcium oxide) in the lime-silica mixture

Thus, as a result of conducted thermodynamic analysis of the change in enthalpy of chemical reactions with the use of slaked lime as the lime component in the mixture, it is possible to say that the formation of calcium hydrosilicates is possible only when the power is supplied to the system.

When applying quicklime, the formation of all nine hydrosilicates occurs with the heat release, which means that from an energy point of view, it is most expedient to use quicklime in the production of silicate brick.

5. 2. Influence of amorphous SiO_2 on thermodynamics of reactions of the lime-silica mixture

Mechanical activation is not simple decreasing of particle dimensions. This is a complicated physical-chemical process of increasing potential energy of a substance and increasing its chemical activity as a result of the increase in surface energy and energy of its internal structure [16].

Mechanical processing of the components renders significant influence on the character and course of chemical reactions; as a result, in many cases, the reaction products differ considerably from the same products, obtained in the traditional course of reactions. Moreover, at mechanical processing chemical reactions most intensively occur directly in the period of mechanical treatment with gradual attenuation after its removal. The indicated circumstance determines special interest in the study of energy state of mineral substances immediately after termination of mechanical action.

Activated solid substances are characterized by thermodynamic instability as a result of disturbance in a stable arrangement of structural elements (ions, atoms, molecules and their elementary groupings), which comprise a solid body. Compared to ideal single crystals, the substance activated by crushing is characterized by other values of standard free energy of formation [16].

The physical essence of the process of mechanical activation does not have a clear definition and is expressed by the totality of physical and chemical changes, connected with the accumulation of surface and internal energy, i. e., a substance acquires excess energy. The changes, occurring in this case with mineral substances, are accompanied by transition to the state, which is characterized by a higher enthalpy. Thus, the transition quartz – amorphous silica is accompanied by the increase in enthalpy by 2,5 kcal/mole [8]. Energy, accumulated during mechanical activation of substance, manifests itself in an increase in chemical activity in the subsequent processes of processing [16]. In the course of mechanical activation, 3 % of crystalline silicon oxide SiO_2 is transferred into a soluble state [8]. Below we examined reactions that are most probable in the course of hydration of lime-silica mixture with the presence of 3 % amorphous silica (SiO_2) in the mixture (reactions, analogous to reactions (3)–(11), but with the presence of soluble SiO_2).

Equations of reactions of the formation of calcium hydrosilicates with the presence of amorphous SiO_2 in the mixture:

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5{,}5H_2O= \\ =5/2(2CaOBSiO_2(glass)B1{,}17H_2O)+ \\ +92{,}5SiO_2(\beta\text{-quartz})+2{,}575H_2O,\end{gathered} \tag{21}$$

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5{,}5H_2O= \\ =5/3(3CaOB2SiO_2(glass)B3H_2O)+ \\ +275/3SiO_2(\beta\text{-quartz})+0{,}5H_2O,\end{gathered} \tag{22}$$

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5{,}5H_2O= \\ =5/4(4CaOB3SiO_2(glass)B1{,}5H_2O)+ \\ +91{,}25SiO_2(\beta\text{-quartz})+3{,}625H_2O,\end{gathered} \tag{23}$$

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5{,}5H_2O= \\ =5/6(6CaOB6SiO_2(glass)BH_2O)+ \\ +90SiO_2(\beta\text{-quartz})+28/6H_2O,\end{gathered} \tag{24}$$

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+ 3SiO_2(glass)+5{,}5H_2O= \\ =5CaOB6SiO_2(glass)B3H_2O+ \\ +89SiO_2(\beta\text{-quartz})+2{,}5H_2O,\end{gathered} \tag{25}$$

$$\begin{gathered}5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5{,}5H_2O= \\ =5CaOB6SiO_2(glass)B5{,}5H_2O+ \\ +89SiO_2(\beta\text{-quartz}),\end{gathered} \tag{26}$$

$$5CaO+92SiO_2(\beta\text{-quartz})+3SiO(glass)_2+5,5H_2O= =5CaOB6SiO_2(glass)B10,5H_2O+ +89SiO_2(\beta\text{-quartz}), \quad (27)$$

$$5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5,5H_2O= =CaOB2SiO_2(glass)B2H_2O+ +93SiO_2(\beta\text{-quartz})+3,5H_2O+4CaO, \quad (28)$$

$$5CaO+92SiO_2(\beta\text{-quartz})+3SiO_2(glass)+5,5H_2O= =2CaOB3SiO(glass)B2,5H_2O+ +92SiO_2+3H_2O+3CaO. \quad (29)$$

Based on the obtained data, we built dependencies of the Gibbs energy on temperature (Fig. 7).

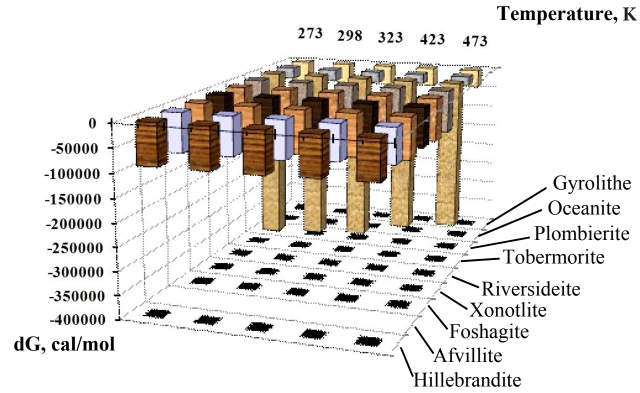

Fig. 7. Dependency of the Gibbs energy of the formation of calcium hydrosilicates on temperature from quicklime with the presence of amorphous SiO_2 in the mixture

During the analysis of influence of amorphous SiO_2 on the course of reactions (21)–(29) in comparison with reactions (3)–(11) (Fig. 3), we note an increase in the Gibbs energy in the entire examined temperature interval.

We built dependencies of enthalpy of the formation on temperature without amorphous SiO_2 (Fig. 8) and with amorphous SiO_2 (Fig. 9).

With the presence of amorphous SiO_2 in the mixture, an increase in the heat of formation for hillebrandite is noted, for example, at a temperature of 273 K $\Delta=-6815,93$ cal/mol, 298 K $\Delta=-6812$ cal/mol, 323 K $\Delta=-6810,31$ cal/mol, 423 K $\Delta=-6787,83$ cal/mol, 473 K $\Delta=-6751,84$ cal/mol.

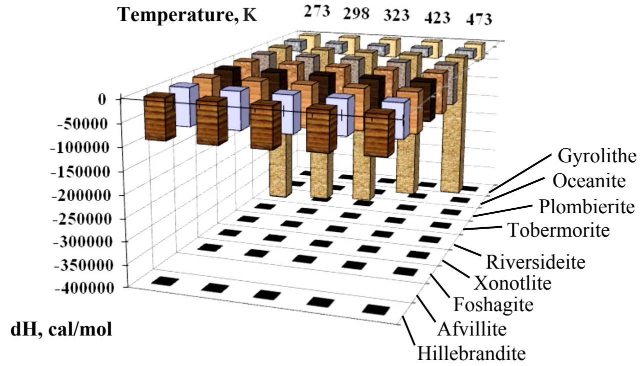

Fig. 8. Dependency of enthalpy of the formation of calcium hydrosilicates on temperature without amorphous SiO_2

By the value of change in the enthalpy of reaction it is possible to judge the strength of substances – the less the value of enthalpy of formation, the steadier the connection, the more durable the chemical bond [15]. Therefore, it is possible to assume that activated materials will possess higher strength since the negative values of enthalpy grow.

Thus, the obtained data confirm the possibility of increasing enthalpy (on the average $\Delta=-6800$ cal/mol) by the action of mechanical activation, which contributes to the occurrence of amorphous SiO_2.

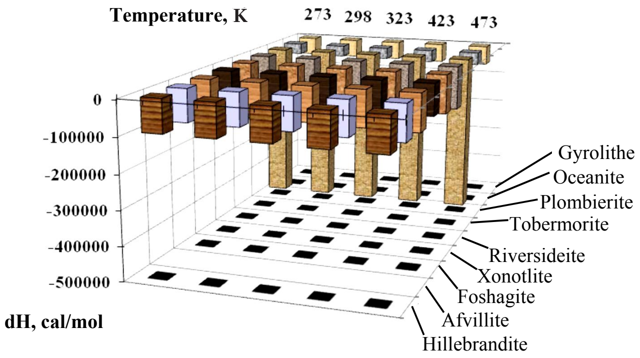

Fig. 9. Dependency of enthalpy of the formation of calcium hydrosilicates on temperature with the presence of amorphous SiO_2 in the mixture

5. 3. Influence of mechanical and chemical activation on the strength of the samples at compression

Employing the procedure, presented in chapter 4.4, we evaluated the strength of the samples, obtained based on the system $CaO-SiO_2-H_2O$:

1) without activation and without adding phosphogypsum;
2) without activation with adding phosphogypsum;
3) with activation and without adding phosphogypsum;
4) with activation and with adding phosphogypsum.

The strength of the obtained samples is illustrated in Fig. 10.

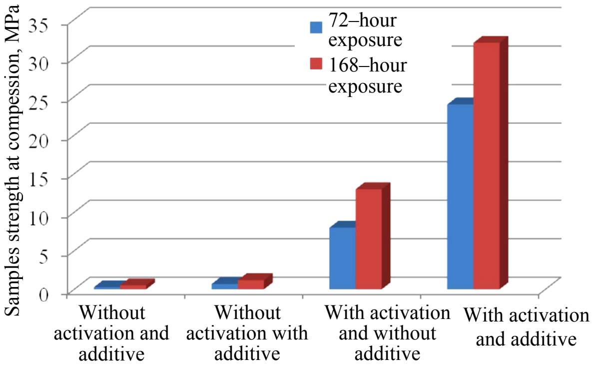

Fig. 10. Strength at compression, MPa, 72-hour and 168-hour exposure

Strength of the samples "with activation and with adding phosphogypsum" at a week-long exposure guarantees brick brand 200 by strength, which is not inferior to the classical technology with the use of an autoclave.

The obtained samples were examined with the aid of X-ray diffraction, infrared spectroscopy, thermogravimetry and electron microscopy methods of physical-chemical analysis. It is established that calcium hydrosilicates are formed without the application of thermal treatment at room temperature in wet environment in the samples, manufactured with the use of mechanochemical activation. The results of physical-chemical research are presented in papers [17, 18].

6. Discussion of results of thermodynamic analytical studies and experimental research into non-autoclave technology of silicate brick

The conducted thermodynamic studies with a sufficient degree of certainty make it possible to determine the probability of the course of reactions, as well as energy costs at the stage of analytical studies, without conducting experiments. This allows us to simplify substantially and to reduce in time the entire research process as a whole.

The technique of thermodynamic studies may be also used for analysis of other inorganic processes.

Promising is the possibility of obtaining calcium hydrosilicates with the use of calcium oxide in the reaction instead of hydroxide. Positive is the fact that when using calcium oxide, there is the formation, to a considerable extent, of the low-basic calcium hydrosilicates, which in the traditional technology are formed insufficiently.

Obtained data testify to a significant influence of mechanical and chemical activation on the strength of the samples of silicate brick. Combined application of calcium oxide (instead of hydroxide), as well as mechanical and chemical activation, provides for a synergetic effect and it makes it possible to obtain brick of non-autoclave hardening of strength up to 24 MPa at a three-day age. Subsequent growth is observed, thus the strength reached 32 MPa in a week.

The possibility of obtaining silicate non-autoclave samples, confirmed experimentally, gives the prospect of creating the technology of non-autoclave silicate brick. The limiting factors now are a too long time of activation, high energy intensity of activation and a long period (in comparison to the autoclave treatment) of exposure for hardening. It is planned, in further experimental studies, to search for the ways of reducing the time of activation and the period of hardening due to the choice of a rational composition and amount of activating additive.

7. Conclusions

1. We conducted comparative thermodynamic analysis of the course of chemical reactions in the lime-silica mixture with the use as a silica component of calcium oxide and hydroxide. It is demonstrated that the change in the Gibbs energy of all reactions of the formation of hydrosilicates with the use of calcium oxide testifies to the possibility of their passage under standard conditions. It is established that the character of reactions is exothermic, i. e., in the system $CaO-SiO_2-H_2O$, reactions of formation of calcium hydrosilicates release heat.

2. It is demonstrated that the application of amorphous silica dioxide is energetically expedient for intensification of reactions of the formation of hydrosilicates.

3. Comparative experimental studies were conducted of separate and combined influence of mechanical and chemical activation of lime-silica mixture on strength indices of the samples of silicate brick. It is found that the joint action of mechanical and chemical activation considerably increases strength at compression of the silicate samples. The conducted theoretical and experimental research confirms a possible prospect of creating the technology of silicate brick without autoclave treatment, which will make it possible to considerably decrease thermal energy consumption, to simplify and to reduce the cost of technological equipment.

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