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Study of structuring processes in liquid glass compositions based on inorganic polymers under microwave irradiation in the production of heat-insulating materials

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The structure formation processes in liquid glass compositions with modifying additives exposed to microwave field were studied. It is shown that under microwave irradiation,the rapid coagulation and crystallization of liquid glass occur under the influence of semi-aqueous gypsum with the formation of $CaSiO_3$. This increases the crystallinity of partitions, the strength of thermal insulation materials and water resistance, since calcium acts as a modifier of the glassy matrix, replacing sodium and forming water-insoluble silicates. Moreover, the formation of $CaSiO_3$ under microwave irradiation at temperatures of 110–120°C occurs more intensively than during traditional convective heating even at a temperature of 600°C. The catalytic function of $CaSO_4 \cdot 0.5H_2O$ modifier in the contact-condensation and colloid-coagulation mechanisms of hardening of the liquid glass composition has been established. The formation of ($CaSiO_3$) under microwave irradiation contributes to the formation of an inhomogeneous structure, which provides increased strength and water resistance of heat-insulating materials.

Keywords: thermal insulation materials, liquid-glass compositions, modifying additives, microwave radiation, convective heating, X-ray diffraction phase analysis.

Дослідження процесів структуроутворення рідинноскляних композицій під впливом нвч випромінювання при виробництві теплоізоляційних матеріалів на основі неорганічних полімерів. *Т.Римар, О.Суворін, Л.Родін*

Проведено дослідження процесів структуроутворення в рідинноскляних композиціях у присутності модифікуючих добавок при їх НВЧ опроміненні. Показано, що в умовах НВЧ випромінювання спостерігається швидка коагуляція і кристалізація рідинного скла під впливом напівводного гіпсу з утворенням $CaSiO_3$, що призводить до підвищення кристалічності перегородок і міцності теплоізоляційних матеріалів, надає їм більшу водостійкість, оскільки кальцій виступає як модифікатор склоподібної матриці, заміщуючи натрій і утворюючи нерозчинні у воді силікати. Причому утворення $CaSiO_3$ під дією НВЧ випромінювання за температури 110–120°C відбувається інтенсивніше ніж при традиційному конвективному нагріві, навіть за температури 600°C. Таким чином, встановлена каталітична функція модифікаторів в контактно-конденсаційному і колоїдно-коагуляційному механізмах твердіння рідинноскляних композицій, що забезпечують формування нових фаз, які в свою чергу під дією НВЧ випромінювання сприяють утворенню гетерогенної структури підвищеної міцності та водостійкості.

1. Introduction

Improving energy efficiency is one of the main tasks of industry not only in Ukraine but also all around the world due to the constant rise in the prices of energy sources. In this regard, an effective way to save energy is the thermal modernization of buildings, industrial equipment, and utility systems with thermal insulation materials (TIM) [1].

Most common thermal insulation materials used in the heating industry cannot fully meet the standards of heat loss. Asbestos-lime siliceous materials for thermal insulation of power equipment are not used due to the Ministry of Health's ban on the use of asbestos. During the operation of mineral wool and basalt insulation materials, phenolic binders burn out at a temperature of 190–200°C, thus leading to material destruction and, consequently, heat loss. Polyurethane foam operates at temperatures up to 120°C, as its structure is destroyed. Foam rubber insulation material can withstand temperature up to 90–110°C, high-temperature rubber — up to 175°C. Liquid glass (LG) materials can operate at temperatures up to 600°C. Their main advantage is stable properties at high temperatures and environmental friendliness.

Currently, thermal insulation materials based on liquid glass are manufactured mainly in the form of granules. Large-scale manufacturing of composite TIM in the form of plates and other configurations is not used due to the difficulty of heating the inner layers of a liquid glass composition (SGC) using traditional convective heating. An alternative source of heat treatment in manufacturing TIM is microwave irradiation, which ensures volume heating of SGC internal layers to obtain high-quality TIM.

The use of new and non-traditional types of energy has recently become very relevant. Microwave radiation undoubtedly refers to such types of energy. In recent decades, there has been growing interest in the possibility of its application in the field of silicate materials.

Work [2] shows the possibility of obtaining solutions of alkaline silicates from silica-containing rock formations (perlite, diatomite, quartzite, etc.) at temperatures of 90–200°C, i.e., lower compared to the traditional technology. It is shown that the use of microwave energy allows significantly intensifying hydrothermal treatment of diatomite, perlite, and quartzite in comparison with the usual heating method.

Studies of microwave heating on the curing of the liquid glass molding mixtures are described in [3–4], where a significant effect of this heating method on improving the strength properties of products as well as reducing the curing time, is noted.

Obtaining hydrogel-based foam materials by acid heat treatment and subsequent rapid foaming with microwaves is studied in [5]. This paper shows that microwave exposure ensures a hierarchical pore structure, low hygroscopicity, and excellent thermal insulation properties of these foams.

The technology of silicate materials uses microwave radiation mainly for drying semi-finished or finished products to improve their properties [6]. This also applies to manufacturing thermal insulation materials. Some technologies of manufacturing silicate thermal insulation materials use microwave radiation for drying or heat treatment of finished products [7], and their swelling [8].

Unfortunately, despite the prevalence of small microwave devices, the field of application of microwave radiation for manufacturing materials is poorly studied. Therefore, this paper studies the structure formation in the liquid glass compositions with modifying additives under exposure to microwave fields. Microwave (MW) radiation can interact with substances that are in gaseous, liquid, or solid states [9] (Fig. 1).

2. Experimental

In any experiments on microwave heating, one should take into account the following properties of the substance being heated, namely, electronic and ionic conductivity, dielectric constant and dielectric loss factor, and thermal conductivity [10].

Silicate glasses are substances characterized by ionic conductivity, so they have a high ability to absorb microwave radiation. Despite the fact that ions are much heavier than electrons and therefore less mobile, heating of the substance due to the flow of ionic currents plays a significant role in the microwave processing of such materials. Application of a low-frequency electromagnetic field of causes the ions to move to vacant positions, which leads to the appearance of a space charge in the substance. The application of a higher frequency field leads to the excitation of oscillations of alkali metal ions in the silicate lattice. The efficiency of the substance heating due to ionic conductivity practically does not depend on the frequency of microwave radiation but

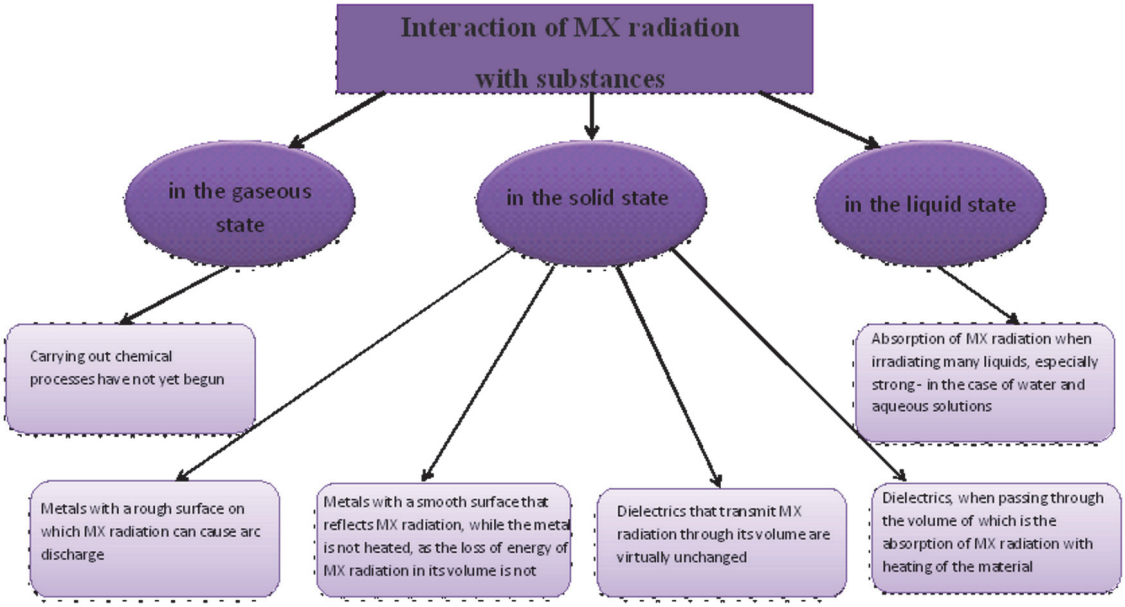

Fig. 1. Interaction of microwave radiation with substances. a) microwave radiation (power 500 W), b) microwave radiation (power 650 W), c) convective heating (T = 100°C), d) convective heating (T = 200°C), e) convective heating (T = 400°C), f) convective heating (T = 600°C).

strongly depends on the temperature, since with its increase the mobility of ions also increases [11].

Moreover, since water has a very high dielectric constant, alkali silicate solutions will have a high absorption capacity, since they are about 50 % water. Under exposure to microwaves, water molecules (dipoles) perform oscillatory and rotational movements. The motion of molecules is thermal energy. The more water is in the given volume, the more molecules are involved in this movement, and the more heat energy is released. Thus, the entire volume of the sample is heated, and more humid areas receive more energy [12].

Electronic conductivity plays a decisive role in microwave heating of metallic materials and semiconductors. The efficiency of heating substances due to electronic conductivity slightly depends on the frequency of the applied electromagnetic field and is determined primarily by its chemical nature. Thus, materials with reduced conductivity (semiconductors, dielectrics) are heated by the MW field more efficiently than good conductors (metals). This is due to the fact that the value of the dielectric loss factor at room temperature is low in insulators, so they are not heated efficiently enough, despite the fact that the MW field penetrates deeply into their volume. Metal oxides, hydroxides, and crystal hydrates of salts have the optimal range of electronic conductivity providing the most effective interaction of the substance with the microwave field, so they can be used as modifying additives in the SGC. When passing through the volume of such an SGC, the absorption of MW radiation is accompanied by heating of the sample.

Due to the increase in the absorption capacity of the substance with increasing temperature, there is usually observed local overheating and hot spots when treating substances with low thermal conductivity. This happens because the heat released does not have time to be evenly distributed over the volume of the treated substance. For uniform heating of a substance by microwave radiation, this substance must have a sufficiently high thermal conductivity [10]. The initial SGC subjected to microwave treatment has a high average density and, consequently, high thermal conductivity, so the sample is heated evenly.

The SGC used for manufacturing composite thermal insulation materials contains sodium liquid glass as the main component, and zinc oxide and semi-aqueous gypsum as modifiers of coagulation and crystallization. liquid glassfor building purposes with a silicate modulus of 2.7-3.3 and an average density of 1.36-1.5 g/cm3 was chosen, in which the mass fraction of silicon dioxide is 24.8-36.7%, since concentrated aqueous solutions sodium silicates of module above 2 contain, in addition to oligomers, silica with

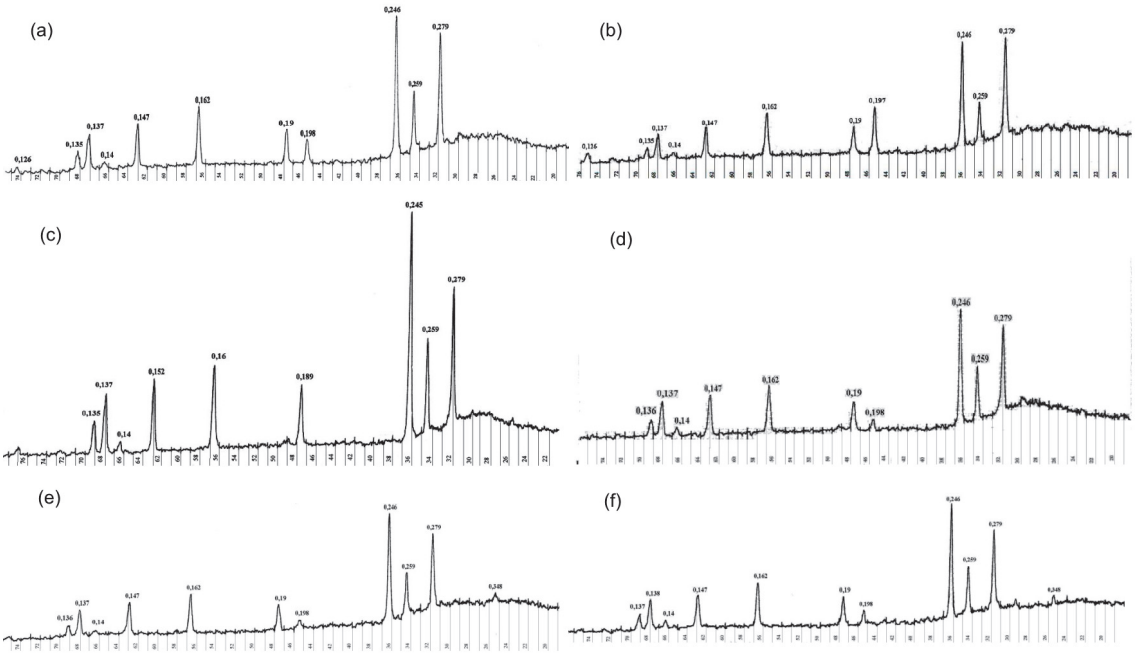

Fig. 2. X-ray diffraction patterns of composite thermal insulation materials obtained by microwave and convective heating. a) ZnO, b) $CaSO_4 \cdot 0.5H_2O$, c)ZnO + $CaSO_4 \cdot 0.5H_2O$, d) granulated thermal insulation materials (microwave radiation power 650 W), e) liquid glass is cured by microwave heating, f) liquid glass is cured by convective heating.

a high degree of polymerization and a high degree of cohesion. Soluble glasses with a low value of the silicate modulus (2 - 3) are characterized by the greatest multiplicity of swelling, which increases with a decrease in its value, but to obtain porous materials with satisfactory physical and mechanical characteristics, it is necessary to use liquid glasswith a silicate modulus of ~ 3, since such soluble glasses are characterized maximum level of binding properties. It shows that the addition of ZnO helps to slow down gelation SGC, thus requiring more time to reach equilibrium, and provides optimal viscosity of the suspension for further porization. Non-swelling granules based on LG and zinc oxide are used as granular fillers. Manufacturing of thermal insulation materials has been carried out according to the technology described in [13–15].

3. Results and discussion

To study the synthesis of the newly formed structures and the nature of the crystalline phases, thermal insulation materials were studied using X-ray phase analysis on a DRON-2-0 diffractometer using an X-ray tube with a copper anode (Cu–K_α radiation). Measurement conditions were as follows: time constant S = 2.5 count/s, range = $2 \cdot 10^3$. To analyse the diffraction patterns, "Handbook of X-ray diffraction analysis of polycrystals" (ed. Prof. Ya.S.Umansky) was used as well as the database of powder diffraction data based on PDF2 files.

Diffraction patterns from TIM produced at different power of microwave radiation and different temperatures of convective heating in comparison with diffraction patterns of initial materials are shown in Fig. 2 and 3.

The results of X-ray phase analysis indicate that LG cured by both microwave and convective heating (Fig. 3e, f) consists mainly of X-ray amorphous phase with a slight degree of order in the structure. The crystalline phase is present in a small amount. Identification of interplanar distances d/n = 0.296 and 0.235 nm makes it possible to predict the presence of SiO_2 in the form of α-tridymite (2Θ = 30.3° and 38.1°). The granular materials (Fig. 3d) containing a small amount of ZnO (1.5 parts by weight) the amorphous phase also predominates; as a result, granules exhibit plastic-deformation properties giving the samples greater strength. The reflections observed on the diffraction pattern correspond to ZnO, their intensity is low due to the low content of the substance in granules. The reflections corresponding to ZnO in samples

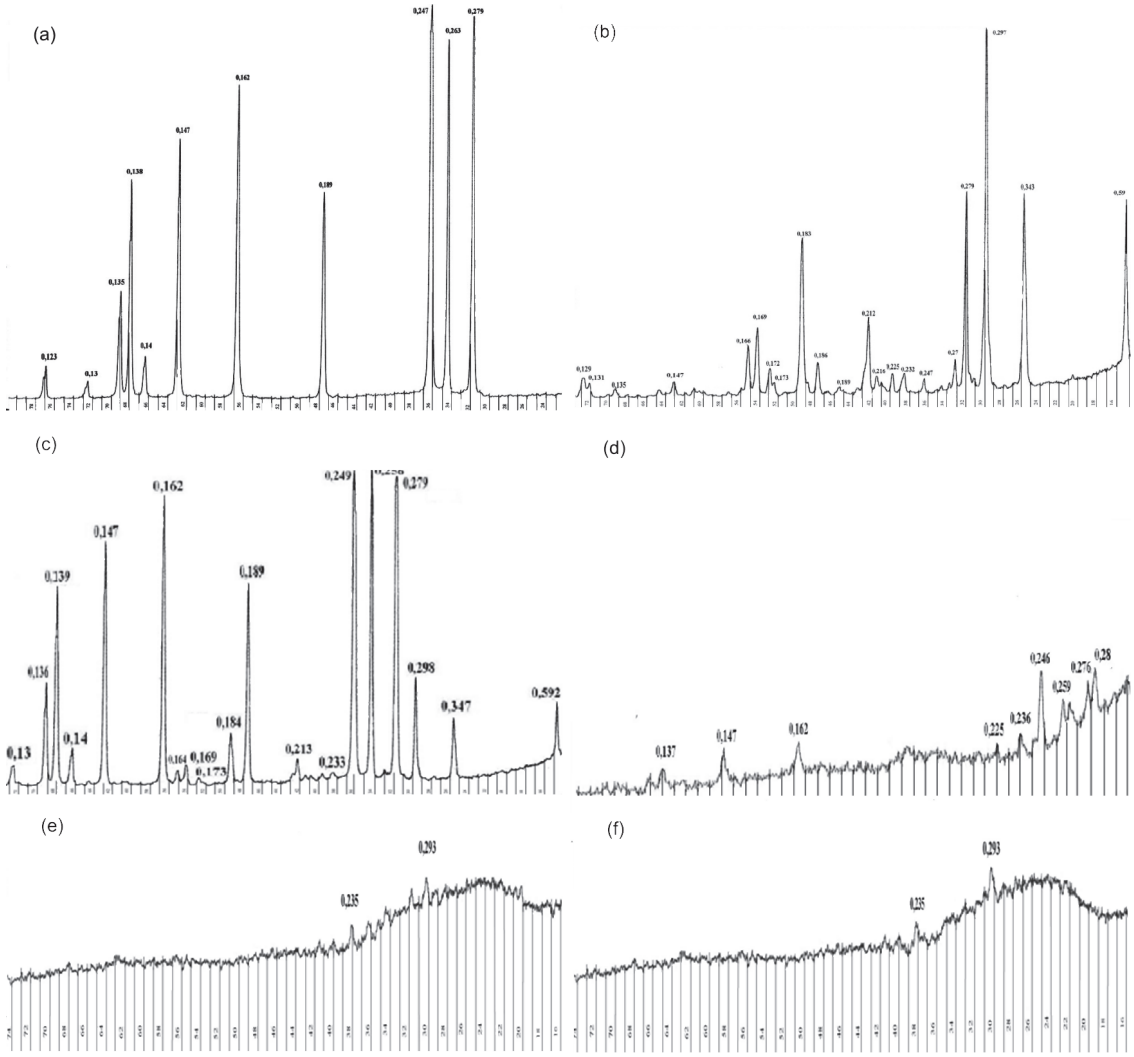

Fig. 3. X-ray diffraction patterns of composite thermal insulation materials obtained by microwave and convective heating starting substance.

of composite materials (Fig. 2) are more intense due to its higher content in these materials (10 pts.wt.). The halo-like maximum at $2\Theta = 20...30°$ indicates the formation of X-ray amorphous glassy phases and is observed in all samples of composite TIM. This causes their higher deformation properties; they are not subject to brittle fracture but mainly deform with a decrease in volume during compression. The amorphous phase is observed to a lesser extent in the samples obtained at 600°C, which is explained by the rapid crystallization of silicate at high heating temperatures.

Comparing the diffraction patterns of the composite TIM with the diffraction patterns of the starting materials, it can be noted that most of the reflections correspond to zinc oxide, and some of them such as at the angles $2\Theta = 31.94–31.98°$ (d/n = 0.279 nm), $2\Theta = 47.64–47.9°$ (d/n = 0.19–0.189 nm), $2\Theta = 62.94–63.12$ (d/n = 0.147 nm) and $2\Theta = 69.14–69.44°$ (d/n = 0.135 nm) probably overlap with the reflections corresponding to $CaSO_4 \cdot 0.5H_2O$.

On the diffraction patterns of the composite TIM, a reflection atypical for the initial material is observed at $2\Theta = 45.58–45$ (d/n = 0.197–0.198 nm), indicating the formation of a new phase. It can be identified as calcium silicate $CaSiO_3$ (wollastonite), which is formed due to the interaction of semi-aqueous gypsum $CaSO_4 \cdot 0.5H_2O$ and Na_2SiO_3 (LG). Apparently, due to the rapid dehydration of the SGC under microwave irradiation, the complete dehydration of the silicate and the formation of wollastonite occur. In this case, the greater the intensity of this reflection, the lower the intensity of

the adjacent reflection corresponding to the interplanar distance $d/n = 0.19$ nm, which is typical for semi-aqueous gypsum. This fact indicates its expenditure for the formation of a new phase. For the samples exposured to microwave radiation (Fig. 2a,b), these reflections are much more intense than in the case of convective heating (Fig. 2d–e), indicating a higher content of the new phase. This reflection is absent in the samples obtained by convective heating at a temperature of 100°C (Fig. 2c). That is, the interaction of $CaSO_4 \cdot 0.5H_2O$ and Na_2SiO_3 does not occur at the same temperature for microwave and convective heating in the latter case. With a further increase in temperature, both in the case of microwave irradiation and in the case of convective heating, the intensity of these reflections somewhat increases, which indicates an acceleration of crystallization of the samples and an increase in the size of crystallites. Thus, under microwave irradiation, the size of crystallites is 163–173 nm, and under convective heating, they are 124, 141, 155 nm at the corresponding temperatures of 200, 400, 600°C.

The reflection intensity corresponding to the $CaSiO_3$ interplanar spacing $d/n = 0.197–0.198$ nm is 100 % (according to PDF2 files, No. 31036), and the reflection intensity corresponding to the interplanar spacing $d/n = 0.28$ nm is 60 %. This reflection corresponds to $d/n = 0.279$ nm, typical for zinc oxide. Under microwave exposure, reflections in the range of interplanar distances $d/n = 0.123–0.126$ nm account for 20–10 % of the intensity of $CaSiO_3$ reflections; this fact indicates a greater degree of order in the structure of the samples obtained by microwave irradiation. During convective heating, these reflections are absent, but at temperatures of 400–6000°C, a reflection with 20 % intensity is observed, corresponding to the interplanar distance $d/n = 0.348$ nm, which is characteristic of $CaSiO_3$. That is, a higher degree of structure ordering during convective heating is observed only at high temperatures. Thus, the spectral studies of the composite TIM obtained by microwave and convective heating show that under microwave irradiation, rapid coagulation and crystallization of liquid glass occurs under the action of semi-aqueous gypsum with the formation of $CaSiO_3$. This increases the crystallinity of partitions, TIM strength, and water resistance, since calcium acts as a modifier of the glassy matrix replacing sodium and forming water-insoluble silicates [16–17]:

$$Na_2SiO_3 + CaSO_4 + nH_2O \rightarrow \rightarrow Na_2SO_4 + CaSiO_3 + nH_2O. \quad (1)$$

The results of X-ray phase analysis in [17] showed that in samples of liquid-glass suspensions with calcium-containing hardeners, including gypsum, there are no new crystalline phases, and intense peaks correspond to unreacted crystalline phases of hardeners at ambient temperature. The same study showed the formation of a new crystalline phase of calcium silicate under microwave irradiation at temperatures of 110–120°C. Under traditional convective heating even at a temperature of 600°C, the formation of this phase occurs much less intensively.

Thus, the following mechanism of coagulation of the liquid glass composition can be proposed: coagulation occurs due to its aggregative instability and tendency to reduce free energy under the influence of temperature and modifying additives. That is, colloidal particles stick together when they collide in thermal (Brownian) motion, mixing, or directional motion in an external force field. The ability to coagulate depends on the diffusion of reactants and temperature. During gelation with increasing temperature, there is a transition from small particles to larger agglomerates. However, the formation of bonds between silica particles during gelation is not always dependent on additives and temperature increase. It is largely intensified by microwave irradiation and contributes to a significant increase in the rate of formation of siloxane bridging bonds between particles. The interaction of water-soluble silicates in the liquid glass solution with modifiers of coagulation and crystallization (zinc oxide, semi-aqueous gypsum) occurs through two types of silanol groups, namely hydrogen-bound and so-called "free", and reduces the overall potential of the system, thereby accelerating gelation. Low-active additives form coagulative structures due to the biding of particles with weak van der Waals forces through thin residual layers of the (dispersion) medium and are not at all waterproof. In contrast to them, the first modifiers contribute to the formation of a coagulation structure with reduced liquid interlayers between the parts of the material. Under the action of microwave radiation, the liquid phase is completely removed from the sys-

tem and this structure condenses into a solid stone that is not destroyed by water, since in this case the coagulation structure becomes new, namely contact-condensation. In accordance with the work of Runova R.F. [18–19] such structures are formed under the action of external physical factors such as external pressure (pressing) to ensure stronger contacts between the particles of binders during their condensation. The hardening in such systems occurs instantly at the moment of contact of the binder particles. Microwave radiation may be such an external factor, which will promote stronger contacts between microparticles of an amorphous or unstable crystalline structure without changing its chemical composition as a result of physical surface phenomena such as polarization.

4. Conclusions

Thus, as a result of the study, the catalytic function of the $CaSO_4 \cdot 0.5H_2O$ modifier in the contact-condensation and colloid-coagulation mechanisms of hardening of the liquid glass composition were established. This ensures the formation of new phases ($CaSiO_3$) under the action of microwave radiation, which contribute to the formation of an inhomogeneous structure of heat-insulating materials with increased strength and water resistance. At the same time, the formation of $CaSiO_3$ under the action of microwave radiation at temperatures of 110–120°C occurs more intensively than with traditional convective heating even at a temperature of 600°C.

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