

Investigation of the modifying additives influence on the porosity of granular liquid-glass compositions in the process of obtaining ecological thermal insulators

T. Rymar

Volodymyr Dahl East Ukrainian National University, Ukraine, Kyiv,
Ioanna Pavla Druhoho, 17, 01042

Received December 7, 2024

In this work we study the effect of modifying additives on the porosity of granular liquid-glass compositions under the influence of microwave radiation. It was found that to ensure a high-quality granulation process of liquid-glass compositions, its dynamic viscosity should be 0.5-0.7 Pa·s, which allows forming granules of the correct round shape and maintaining the stability of liquid-glass composition during the granulation process. To preserve the porosity, the transition of the liquid-glass composition to a viscous state must be achieved with maximum preservation of the original structure of the liquid glass. For this purpose, the chemical exchange interaction at the stage of composition formation in the presence of a modifier must be minimal. ZnO meets this requirement, since Zn^{2+} ions have optimal cation exchange capacity and provide a strong coagulation structure of the composition. ZnO acts as a modifier of coagulation and crystallization processes, helps to slow down gelation; this increases the time to reach an equilibrium state and ensures optimal viscosity of the suspension for its further porization, and also allows preserving the polymer structure of liquid glass, which has a positive effect on the physical and mechanical properties of granulated thermal insulation materials.

Keywords: granular thermal insulation materials, liquid-glass compositions, modifiers, porosization, viscosity, gel formation, microwave radiation.

Дослідження впливу модифікуючих добавок на поризаційну здатність гранульованих рідинноскляних композицій, в процесі отримання екологічної теплоізоляції. Т.Е. Рymar

В роботі проводилось дослідження впливу модифікуючих добавок на поризаційну здатність гранульованих рідинноскляних композицій під дією НВЧ випромінювання. На підставі проведених досліджень було встановлено, що для забезпечення якісного процесу гранулювання рідинноскляних композицій їх динамічна в'язкість повинна складати 0,5-0,7 Па·с, яка дозволяє сформувати гранули правильної круглої форми та зберегти стабільність композиції в процесі грануляції. З метою збереження поризаційної здатності необхідно, щоб перехід рідинноскляної композиції у в'язкий стан досягався при максимальному збереженні вихідної структури рідинного скла. Для цього необхідно, щоб хімічна обмінна взаємодія на етапі формування композиції у присутності модифікатора була мінімальною. Цій вимозі задовольняє ZnO, іони Zn^{2+} виявляють оптимальну катіонообмінну здатність та забезпечують міцну коагуляційну структуру композиції. ZnO виконує роль модифікатора коагуляційно-кристалізаційних процесів та сприяє сповільненню гелеутворення, що збільшує час досягнення рівноважного стану і забезпечує оптимальну в'язкість суспензії для подальшої її поризації, та дозволяє зберегти полімерну структуру рідинного скла, що позитивним чином відбивається на фізико-механічних властивостях гранульованих теплоізоляційних матеріалів.

1. Introduction

The development and implementation of innovative, environmentally friendly thermal insulation materials is an important step towards energy-efficient and sustainable construction. This will significantly reduce greenhouse gas emissions, reduce heating costs and contribute to the preservation of the environment.

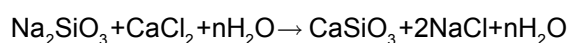
Thermal insulation materials based on liquid glass can be a promising environmentally friendly solution compared to traditional organic foams. Liquid glass (LG) is an inorganic polymer, non-flammable and non-toxic material, which significantly increases its environmental safety compared to organic polymeric insulators; such materials are characterized by high resistance to aging, moisture, fungi and pests, which ensures the durability of thermal insulation; due to its high fire resistance, liquid glass-based thermal insulation increases the fire safety of the building.

A liquid glass is a material consisting of alkaline silicates $R_2O \cdot nSiO_2$, where R_2O is an alkaline oxide. Liquid glass belongs to strong electrolytes that are in a dissociated state. It is characterized by the presence of alkali metal cations and anions in water in the form of associated silica-oxygen complexes, which give glass properties typical of inorganic polymers. These properties are manifested in its low tendency to crystallize, ability to swell, and high viscosity of the solutions formed. The manifestation of binding properties by solutions of alkali-silicate glasses when water is removed during the hardening process causes high strength of materials based on them, so the scope of their application is quite wide. The binding properties of alkali-silicate glasses are used to produce a number of composite materials, including thermal insulation materials [1].

The solidification of the liquid glass system can be achieved in three ways: 1) moisture loss by evaporation at normal temperatures; 2) loss of moisture by the system upon subsequent heating above 100°C; 3) transition to a solid state by introducing special reagents called hardeners [2]. All three processes are used in combination in the production of granular thermal insulation materials, since the surface increases rather quickly during swelling and the polymer framework should be fixed to prevent its destruction and the breakthrough of water vapor through the shell during heat treatment.

Granular liquid-glass materials can be produced by spraying a liquid-glass mixture in a tower dryer (silipor technology). In this case the stages of granulation and swelling are combined in one operation: swelling of crushed siolite in a fluidized bed (siphoning technology) [3-4]; granulation of a gel-like liquid-glass composition (LGC) using an extruder with a hole nozzle, when the liquid glass is pre-coagulated with active additives (acids, alcohols, acid salts, etc.) by reducing the pH of liquid glass (glass breaker technology); liquid granulation of LGC by coagulating liquid glass droplets in a medium of calcium chloride ($CaCl_2$) solution [5]. The advantages of this method are higher strength and water resistance of the granules.

In dilute solutions, the interaction of concentrated sodium silicate with calcium chloride is characterized by the very rapid formation of a silicic acid film separating $CaCl_2$ from the soluble glass. Two parallel processes are allowed to occur: the adsorption of calcium oxide on SiO_2 gel formed due to excessive meta-silicate and silica disilicate, and the formation of calcium silicate as a result of an exchange reaction between $CaCl_2$ and silica, which is part of sodium meta- and disilicate according to the total equation [6]:

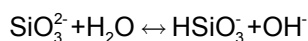
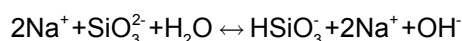
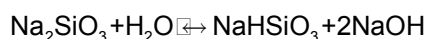


When liquid glass is added to a concentrated $CaCl_2$ solution, a hydrolysis reaction prevails at the interface between the two liquid phases due to the difference in pH of the solutions. The neutralization of the anion charge leads to immediate coagulation of surface bonds. If the concentration of silicates is high enough, a membrane is formed with a negative charge on the side of the silicate and a positive charge on the side of the calcium chloride solution. When the viscosity of the silicate solution is high, the membrane gradually transforms into a gel-like shell with coagulated silicate with a low concentration gradient created by the walls of calcium from the $CaCl_2$ solution and sodium from the silicate solution. After drying the surface of wet granules, which is waterproof, a partially calcined layer is formed, which is not vapor- and moisture-impermeable (due to the formation of microcracks during shrinkage) [7]. The pre-formed granules are then thermally expanded to form a gas-impermeable, water-resistant surface layer.

The curing of liquid glass with special reagents is based on increasing its modulus by

neutralizing part of the alkali. This is achieved by introducing various acids, salts, and buffer systems with a pH lower than that of liquid glass. Organic compounds capable of reacting with hydroxyl ions, such as esters, proteins, silicic acid esters, etc., are also used.

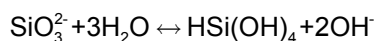
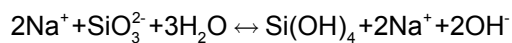
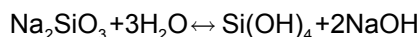
The polymeric state of silica in an aqueous solution depends on the alkalinity of the latter. Thus, in an alkaline environment at a pH above 10, there is practically no polymerization of orthosilicic acid. The hydrolysis of sodium silicate results in the formation of sodium hydrosilicate, the medium becomes alkaline (pH > 10) and no polymerization occurs:



Changing the pH of the medium significantly affects the gelation of silicic acid. When binding hydroxide ions, i.e. acidifying the sodium silicate solution, the proportion of polymer structures increases. The feature of silica polymerization is that even at a low degree of polymerization, cyclic forms of ions occur, cross-linked in parallel planes into dense three-dimensional structures with a minimum number of silanol (Si-OH) groups; already at pH < 9-10, subnanometer particles are formed - centers (embryos) for further deposition of silica.

Reducing the alkalinity of the solution leads to a shift in the hydrolysis equilibrium of sodium silicate toward the hydrolyzed form; in this case, silicic acid gel is released. The release of silicic acid gel begins at pH below 10.

At pH below 6, liquid glass undergoes hydrolysis to form orthosilicic acid:



Polymerization is most energetic at pH = 5-6. In an acidic environment at pH = 2-3, orthosilicic acid is most stable. Outside this range, its stability decreases [8-9].

Thus, at pH ≤ 6, neutralized silicate molecules polymerize at a very high rate, which is inconvenient for use in binder systems. At higher pH, up to 10, the process of silica coagulation prevails. After the bulk of the silica is coagulated and its concentration in the solution is significantly reduced, an opaque gel is formed.

The composition for granulation must be in a stable state; if it coagulates prematurely, the granulation process becomes impossible, as it clogs the granulator filters. To obtain a time-stable RSC, it is necessary that the modifying additives do not reduce the pH of the medium and do not cause its rapid gelation. Therefore, when producing swollen granular materials based on RS, it is very important to choose mineral additives that will contribute to its curing. It is necessary to use low-activity additives, since when forming granules with the introduction of such modifying additives, pH values > 10 are used. In this case, the initial stage of granular material formation will be the aggregation of individual silica particles into short chains, followed by spatial condensation of silicates to form branched clusters characteristic of an alkaline environment. Further, with an increase in temperature during swelling, due to water evaporation, the silicate coagulates and further polycondensation occurs, with the formation of a higher degree of polycondensation.

Compounds of alkaline earth and polyvalent metals can be used as hardeners for liquid glass compositions. However, in the case of low-active forms, the difference between filler and hardener of the system is purely conditional. The interaction of alkaline silicate solutions with compounds of polyvalent metals, such as zinc, iron, aluminum, etc. is similar to the interaction with alkaline earth metal compounds. Thus, the introduction of a filler, such as SiO_2 , Al_2O_3 , Fe_2O_3 , which can change the pH locally in the solution-grain contact, results in the formation of surface compounds [2].

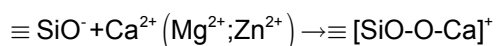
The components of raw material compositions are divided into a number of groups in relation to liquid glass: 1) passive: mica, titanium whitewash, cadmium oxide pigments, feldspar, they do not send their ions into the silicate solution, and the cured liquid glass film is water-soluble; 2) low activity: calcium carbonate, ferrous antimony, aluminum oxide, various aluminosilicate rocks; 3) active: zinc oxide, magnesium carbonates, dolomite, aluminum powder; 4) highly active: lime, portland cement components, magnesium oxide [10].

The use of additives that are chemically active in relation to liquid glass not only causes rapid gelation, but also reduces the pore size or even suppresses pore formation during swelling of the LGC. Substances of reduced activity and active substances form slowly hardening systems and can be used as modifying additives in

the production of granular swollen liquid glass materials to ensure the manufacturability of the composition.

Thus, low-activity additives and active additives were used for the manufacture of granules, namely oxide compounds: iron (III) oxide, zinc oxide, kaolin, and carbon dioxide salts: dolomite, calcium carbonate. When these additives are used, the pH of LGC is in the range of 10-11 and these compositions have a viability of about one day, which is sufficiently technological.

When such substances are added to the LGC, ions of calcium, magnesium, zinc, etc. interact with the ionic forms of liquid glass. As a result of the interaction, insoluble silicates are formed, complete or partial recharging of the particles occurs, which causes their enlargement with subsequent coagulation, and substances of lower activity form coagulation bonds more slowly in the dispersion medium:



The scientific and technical literature notes a positive effect when liquid glass is modified with substances containing polyvalent metal ions (Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} , Fe^{3+} , Ba^{2+}). Paper [11] presents a comparative analysis of some metal-containing compounds and the peculiarities of their interaction mechanisms with liquid glass. The analysis of the work shows that the interaction between oxides and hydroxides of Ca^{2+} , Mg^{2+} , Zn^{2+} , Al^{3+} with aqueous alkaline solutions of sodium silicates leads to the formation of water-insoluble silicates, hydrosilicates, and sodium hydrosilicates of the corresponding metals. At the initial stages, the formation of structure and properties of such compositions occurs due to exchange reactions depending on the chemical activity of metal cations and technological parameters (method of combination, order of mixing of components, etc.). The work shows that zinc oxide is the most effective in the manufacture of alkali-silicate foamed materials at low temperatures of 120-130 °C. Aluminum and magnesium oxides are used primarily in the manufacture of fireproof coatings, and they require composition aging; calcium oxide worsens the physical and mechanical parameters of composites due to the high rate of hydration [12]. In the interaction of alkaline silicate solutions with various calcium-containing compounds, the transfer of Ca^{2+} into the solution may precede the formation of calcium silicates. In other cases, the deposition of silica

on calcium surfaces of the solid phase is the first stage, and then the interaction of the reagents is limited for a long time to a narrow zone of phase contact, and the limiting stage is the diffusion of calcium ions. Some calcium- and magnesium-containing compounds hold these ions so tightly in their structure that they are practically inert, and only the surfaces of minerals have an affinity for silica [1]

The influence of modifying additives on the characteristics of swelling and structure formation processes of alkali-silicate compositions has been studied by many foreign researchers [13-16]. However, as noted above, the ways of producing granular liquid glass materials are different, and additives that are relevant for one method do not give positive results for another, so the choice of modifying additives is always a pressing task.

The aim of this work is to study the effect of modifying additives on the porosity of granular liquid-glass compositions under the influence of microwave radiation. To achieve this goal, the effect of modifying additives on the viscosity of liquid glass compositions and their ability to swell was studied.

2. Experimental

Based on previously studies [19], the compositions of liquid glass compositions were determined, which include sodium liquid glass as the main component. Liquid glass for construction purposes with a silicate modulus of 2.7-3.3 and an average density of 1.36-1.5 g/cm³ was selected, in which the mass fraction of silicon dioxide is 24.8-36.7%, since concentrated aqueous solutions of sodium silicates with a modulus higher than 2 contain, in addition to oligomers, silica with a high degree of polymerization and a high degree of cohesion. Iron (III) oxide, zinc oxide, kaolin, dolomite, calcium carbonate were selected as modifying additives. These additives have a reduced activity and are active in relation to liquid glass and are introduced to increase the strength and ensure the manufacturability of the composition.

The processes of thermal porosification of such granular liquid-glass compositions under the influence of microwave radiation were studied in the works [17-20].

For successful porosization, the LGCs must be able to deform irreversibly without breaking continuity. The porosity of the material and the structure of the pores formed during swelling depends on the amount of gas phase retained

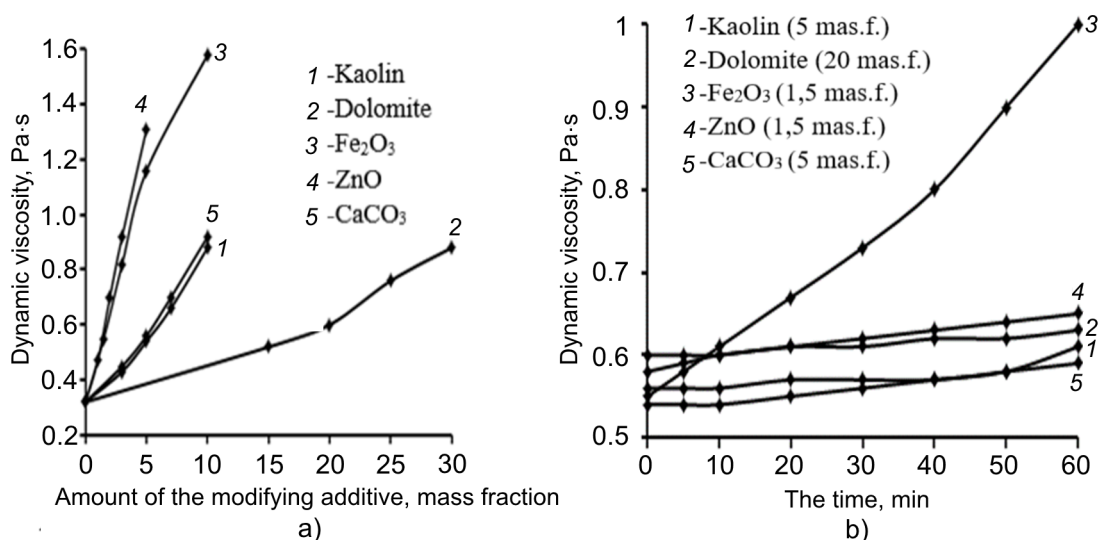


Fig. 1. The dependence of the viscosity of the composition on: a) the type and amount of the modifying additive; b) the time of its action

by the mass. In this process, it is necessary to control the main rheological parameter for these systems, namely their viscosity. The need to control the rheological properties of silicate compositions in the production of granular materials by their liquid granulation in a calcium chloride medium is explained by the fact that they must have a strong coagulation structure and maintain stability during the granulation process.

The dynamic viscosity of the samples was determined using a Brookfield DV-II+Pro rotational viscometer in the spindle loading range of 25-85%. The viscosity measurement is carried out by recalculating the torque required to rotate the spindle of the device at a constant speed when it is immersed in the test medium.

3. Results and discussion

The dependences of the viscosity of the compositions on the type and amount of the modifying additive and its exposure time are shown in Fig. 1.

For the composition to pass through the filter efficiently, its dynamic viscosity should be 0.5-0.7 Pa·s, so that it drips when passing through the filter, and there is no free flow of the mixture, which allows the formation of granules of the correct round shape. When determining the change in viscosity of the composition over time, the optimal amount of the modifying additive was used.

The viscosity of the LGC depends to the greatest extent on the adsorption and cation exchange capacity of the modifying additive and on the size of its particles. As can be seen

from Fig. 1, the highest viscosity value is observed for compositions containing iron (III) oxide with fairly large particles of 0.7 μm or more. Thus, the viscosity of such a composition increases from 0.55 to 1.58 Pa·s (with 1.5 and 10 mass fractions of the additive, respectively). Measuring the viscosity of a composition containing iron (III) oxide is complicated by the fact that without intensive mixing, such an additive instantly precipitates, forming insoluble iron silicates. Apparently, Fe₂O₃ locally changes the pH at the solution-grain contact, resulting in the formation of surface compounds. Such a composition is unstable in time, so its use in the production of granular LGC is impossible.

The peculiarity of using dolomite is determined, first of all, by the largest particle size among the above-mentioned additives - more than 1 μm . Dolomite is a coarse mineral, so to achieve the required viscosity of the liquid-glass mixture, it is necessary to introduce the largest amount of this additive. If the dolomite content is less than 15 mass fractions, the finished LGC cannot be used for granulation due to its low viscosity and high fluidity. The viscosity of such compositions increases in the optimal range from 0.5 to 0.7 Pa·s at 15 to 23 mass fractions of dolomite.

Finely dispersed modifying additives, such as kaolin and calcium carbonate, with a particle size of 0.2-0.4 μm and 0.4-0.6 μm , respectively, are introduced in a much smaller amount, since they thicken the composition well. Thus, to ensure an optimal viscosity of 0.5 to 0.7 Pa·s, they should be added in an amount of 5-7 mas.f.

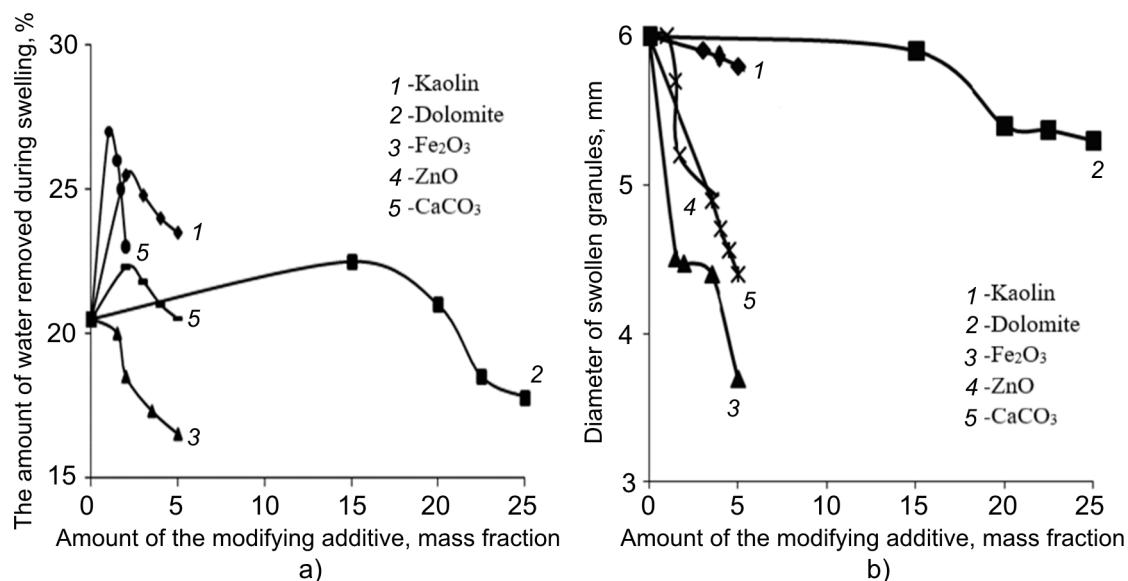


Fig. 2. The effect of modifying additives on: a) the amount of water removed during swelling; b) the granules diameter

Calcium- and magnesium-containing compounds such as calcium carbonate and dolomite firmly retain Ca^{2+} (Mg^{2+}) ions in their structure, so they are practically inert in relation to LG, and their mixtures with liquid glass can remain without visible changes for a long time (about a day). Kaolin is more active in relation to LG than dolomite and calcium carbonate, because it forms coagulation bonds more quickly in the dispersion medium due to the presence of Al^{3+} ions in addition to Ca^{2+} ions, which has a greater cation exchange capacity. However, mixing of the composition with kaolin is complicated by its reduced wettability by LG, since kaolin has a low adsorption capacity, and before using this composition, it should be kept for 10-15 minutes to make the mixture homogeneous, which is not technological. The compositions with kaolin, as well as with the above modifying additives, are stable in time during the day.

Zn^{2+} ions exhibit the greatest cation exchange capacity, since to achieve the required viscosity they should be introduced in the smallest amount of 1.5-2 mass fractions. The composition using zinc oxide with a particle size of 0.4-0.6 μm is unstable in time, because this filler is the most active in relation to LG and causes its gelation faster than other additives. The maximum amount of zinc oxide in the composition, at which it can be passed through a granulating filter, is 5 mass fractions, and such a composition should be used within 1-2 min. after preparation, since it subsequently turns

into a gel-like state. The use of a small amount of zinc oxide (1.5-2 mass fractions) allows obtaining a composition that is stable over time (within 1-2 hours) and provides the optimal viscosity of the LGC for its subsequent liquid granulation, amounting to 0.5-0.67 Pa·s. The gelation of LGC is due to the amphoteric nature of zinc oxide, which is capable of exhibiting acidic properties. The products of interaction of zinc oxide with LG are a mixture of hydroxides, silicates and basic salts in an amorphous state. The interaction of alkaline silicate solutions with polyvalent metal compounds, such as zinc, easily causes the formation of precipitates of poorly soluble metal hydroxides. The resulting zinc hydroxide has the appearance of a gelatinous precipitate, since at the points of contact between the phases the pH changes sharply due to the absorption of hydroxide ions by zinc cations, which promotes the polymerization of silica. The surface of gelatinous precipitates is more developed and more prone to adsorption and co-precipitation of various ions. For example, zinc oxide precipitates silica from liquid glass solutions, and an increase in the concentration of SiO_2 in the solution accelerates its polymerization.

Thus, ZnO acts as a modifier of coagulation and crystallization processes and slows down gelation, which increases the time to reach the equilibrium state and provides optimal viscosity of the suspension for its further porosization, as can be seen from Fig. 2.

The process of swelling of granular materials was carried out at an output power of 650 W, which corresponds to a sample temperature of 110-120°C.

Fig. 2 (a) shows that for all types of modifying additives, the amount of water removed during swelling increases with increasing amount of the additive. At small amounts of additives (1.5-2 mass fractions ZnO, 2-3 mass fractions of kaolin and CaCO_3), the inter-pore walls in the granule structure are strengthened. Such an additive serves as a scaffolding element and the removal of adsorption water is prevented by the reinforced walls, while free water is easily removed at room temperature, and only bound water is involved in swelling, which has a positive effect on both the resulting porous structure and the duration of the process. The increased amount of the mineral additive has a disorderly effect on the macrostructure of the material, destroying it, as a result, chemically bound water becomes free and can be removed even at low heating temperatures.

The lowest amount of water converted to steam during swelling is characterized by granules containing iron (III) oxide, since the specific surface of this additive is small (13.82 m²/g) for uniform distribution of the liquid phase in the LGC. Thus, with an additive amount of 1.5-5 mass fractions, this amount is 17-20%. The use of iron (III) oxide helps to strengthen the internal framework in the granule to such an extent that pore formation is almost impossible. Calcium carbonate is finely dispersed, with a specific surface area of 20 m²/g, and, as noted above, this additive was used in small quantities to achieve the required rheological characteristics of the original LGC. However, at the above calcium carbonate content, the original LGC undergoes such a modification that the amount of solid phase formed prevents free pore formation and at an additive content of 3-5 mass fractions, the amount of water removed is 20.5-21.8%. Dolomite is a coarse mineral, so its content in the initial LGC is the highest, which leads to the destruction of the colloidal structure of the liquid glass and the transition of part of the molecular water to free water, resulting in a high moisture removal rate of 21-22.5% at 15-20 mass fractions of the additive.

Granules with kaolin are characterized by a rather high amount of water removed during swelling; at a content of 3-5 mass fractions of the additive, the amount of water removed

is 23.5-24.8 %, due to the rather large specific surface area of kaolin, which is 29 m²/g. Kaolin contributes not only to the formation of a strong outer crust on the surface of the granules after drying the material, but also to a strengthened inner framework that prevents the formation of large pores and intense evaporation of bound water.

For the granular material containing zinc oxide, the amount of water removed is the highest, so with an increase in the content of the modifying additive from 1 to 2 mass fractions, the indicator slightly decreases from 27 to 23%. This indicates the high viscosity of the initial LGC due to the coagulation of liquid glass and the formation of a sufficient solid phase content, which led to the most complete release of molecular water during swelling. In addition, it is characterized by the largest specific surface, which is 35 m²/g. This fact allows us to conclude that zinc oxide is generally the most optimal modifier in terms of the ability of LGC to swell, since in order to preserve the porosity of LGC, it is necessary that the transition of the original LGC to a viscous state is achieved with maximum preservation of the original LG structure. For this purpose, it is necessary that the chemical exchange interaction at the stage of LGC formation is minimal. This requirement is met by ZnO, as Zn^{2+} ions exhibit optimal cation exchange capacity and provide optimal viscosity of the suspension for its further porosization.

As can be seen from Fig. 2 (b), the values of the granule diameter are consistent with the viscosity of the LGC. The diameter of the granules decreases with an excessive amount of the modifying additive; in the case of zinc oxide, this is due to the gelation of the LG, but its content in the composition is so small that the gelling effect is not so noticeable. The average diameter of zinc oxide granules is 6-7 mm. The largest diameter is ~8 mm, the granules with kaolin content have practically no gel-forming effect on the LGC and do not interfere with its porosity. The small diameters of granules containing iron (III) oxide, 3-5 mm, can be explained by the low ability of such LGC to swell. Thus, the viscosity of the initial mixtures with different amounts of iron (III) oxide is the highest among other compositions, so the formation of pores in the structure of the material is practically not observed..

4. Conclusions

It was found that to ensure a high-quality granulation process of LGC, its dynamic viscosity should be 0.5-0.7 Pa·s, which allows forming granules of the correct round shape and maintaining the stability of LGC during the granulation process. In order to preserve the porosity, it is necessary that the transition of the LGC to a viscous state is achieved with maximum preservation of the original structure of the liquid glass. For this purpose, it is necessary that the chemical exchange interaction at the stage of composition formation in the presence of a modifier is minimal. This requirement is met by ZnO, as Zn^{2+} ions exhibit optimal cation exchange capacity and provide a strong coagulation structure of the composition. ZnO acts as a modifier of coagulation and crystallization processes and helps to slow down gel formation, which increases the time to reach the equilibrium state and provides optimal viscosity of the suspension for its further porosity; it also allows preserving the polymer structure of the LG, which has a positive effect on the physical and mechanical properties of granular thermal insulation materials.

References

1. Dvorkin L.I. Budivelni viazhuchi materialy. Rivne, NUVHP, 622 p. (2019) [in Ukraine].
2. Vail J.G. Soluble Silicates. New York, V 1, 2 (1952).
3. Sobchenko V.V. Rozrobka enerhozberihaiuchoi tekhnolohii vyrobnytstva porystykh zapovniuvachiv iz hidrosylikativ v aparatakh psevdozridzhenoho sharu. Avtoref. dys. Kyiv, 26 p. (2006) [in Ukraine].
4. Pshynko A.N., Savytskyi N.V., Koretskaia S.A., Honcharenko A.A., *Visnyk DNUZT*. № 4, 200, (2004) [in Russian].
5. Storozhenko D., Dryuchko O., Jesionowski T. *International Journal of Engineering & Technology*, **7** (3.2), 692, (2018).
6. Tykhomyrova Y.N., Skoryna T.V. XVIII Mendelevskoho syezda po prykladnoi y obshei khymii. T. 2, P. 550, (2007)
7. Yvanov M.Iu. *Systemy. Metody. Tekhnolohyy*, **2** (22), 102, (2014) .
8. Svensson I.L., Sjoberg S., Ohman L. O. *J. Chem. Soc, Faraday Trans.*, **82**, 2635, (1986).
9. Ailer R. Khymia kremnezema. Moskva: Myr. Ch. 1, 416 p., (1982).
10. Ryzhkov Y.V., Tolstoi V.S. Fyzyko-khymicheskye osnovy formirovaniya svoistv smesei s zhydkym steklom. Kharkov: Yzd-vo Kharkovskoho in-ta, 136 p, (1975).
11. Lebedeva E.Iu., Kazmyna O.V. Materyaly mezhd. nauchno-prakt. konf. «Aktualnye problemy sovremennoho mashynostroeniya». Materyalovedenye, mekhanika y obrabotka metallov v mashynostroyeniye, P. 262 – 265, (2013).
12. Kocherhyna M.P. Strukuroobrazovanye y svoystva stroytelnykh kompozitov na osnove sylykatnatryevykh svyazuiushchykh, modyfytsirovannykh tsynksoderzhashchymy rastvoramy. Dys. Kand. Tekh. Nauk, Saratov, 213 p., (2017)
13. Pat. US EP 1803693 A1 Unated States, (2007).
14. Pat. CA 2332797 A1 Unated States, (1999).
15. Zhang Z.; Provis J.L.; Reid A.; Wang H. *Cem. Concr. Compos.*, V. 62, P. 97–105, (2015).
16. Bai C.; Colombo P. *Ceram. Int.* V. 44, 16103–16118, (2018).
17. Rymar T.E. Zbirnyk naukovykh prats Ukr-DUZH. Kharkiv, **196**, 6-16, (2021) [in Ukraine].
18. T.Rymar, O.Suvorin, L.Rodin., *Functional materials*. **29**, 364, (2022).
19. Rymar T.E. Pytannia khimii ta khimichnoi tekhnolohii. Dnipro, DDKhTU, № 2 (123), P. 112-120, (2019).
20. Rymar T. E., Kryuchkova, E.Ju., Pinchukova, N.A., Voloshko, A.Y., Chebanov, V.A., *Functional materials*. **26**, 478, (2016)