PREPARATION AND PROPERTIES OF SILICATE INORGANIC EXTERNAL WALL INSULATION MATERIALS BASED ON HEAT STORAGE

by

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In this article, the foaming slurry after the reaction of silicate inorganic gelling material sodium silicate and foaming agent azodicamide is taken as the main investigation object, and the mechanism of bubble nucleation and the effect of physical parameters such as temperature, time, viscosity and surface tension on the structure of bubble pores are analyzed. As well as the influence of processing technology such as foiling temperature, heating rate, holding time and various kinds of modifiers on the structure and properties of the material, the appropriate processing technology conditions and modifiers are screened out, and an inorganic foiling insulation material with light weight, high strength, heat preservation, fire prevention, no pollution, low cost, simple process and easy to use is prepared. The experimental results show that, although the properties of the prepared material are better with the increase of azodicarbonamide (ADC) content and viscosity, the maximum amount of ADC added is only 1%. When the ADC content in the system is greater than 1%, the foaming slurry will appear gel, which is not conducive to the late high temperature foaming and the uniformity of the final product. Therefore, the optimal amount of ADC is 1% of the mass of sodium silicate.

Key words*: thermal energy storage, silicate, inorganic external wall, thermal insulation material, foaming foam material*

Introduction

In the world, with the progress of society and the development of economy, people's demand for energy is increasing. At the same time, the deterioration of the environment is becoming more and more severe. Energy saving and emission reduction has become a global investigation issue. At present, energy saving in buildings is the most direct and effective way with the greatest potential. The energy consumption of buildings mainly occurs in the heating, cooling, electrical and lighting aspects of buildings, among which the heating and cooling energy consumption of buildings is the largest, accounting for the total energy consumption of the country, and is rising year by year with the continuous heating of real estate. Therefore, we must attach great importance to the production of thermal insulation materials for building heating and cooling, so as to reduce building energy consumption, save resources and alleviate energy crisis [1].

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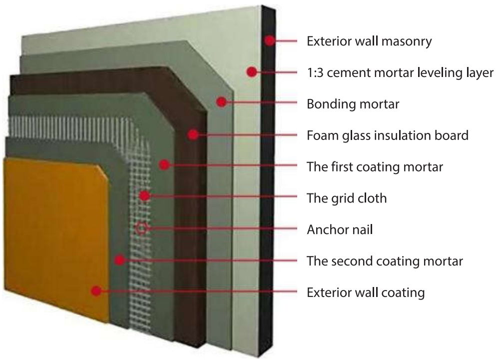

Figure 1. Insulated wall

Thermal insulation has been around for thousands of years. In primitive times, humans have been building caves and houses to keep out the cold by using earth, rocks and vegetation. At the beginning of the Industrial Revolution in the 1760, the traditional handicraft industry gradually shifted to large-scale machine production. The arrival of the industrial era also led to the development of thermal insulation materials in the modern sense [2]. In the early 1970's, the emergence of the global energy crisis made the rapid development of thermal insulation materials, a large number of new varieties emerged in succession, at the same time, the traditional thermal insulation materials are gradually retiring from the stage of history. Energy-saving thermal insulation materials have become the mainstream of development in today's world. The thermal insulation wall is shown in fig. 1.

Thermal insulation materials are usually light, loose, porous materials with low thermal conductivity. When the average temperature of thermal insulation materials is not greater than 623 K (350 °C), the thermal conductivity should be less than 0.14 W/mK. Thermal insulation materials prevent heat transfer from high temperature to low temperature by slowing the rate of heat flow generated by conduction, convection and radiation, and isolate the effects of solar radiation and high temperature [3]. There are many kinds of classification methods for thermal insulation materials. According to the different materials, they can be divided into organic thermal insulation materials and inorganic thermal insulation materials. According to the different state and structure, it can be divided into foam heat insulation materials (that is, solid matrix continuous and stomatal discontinuous), powder heat insulation materials (that is, solid matrix discontinuous and stomatal continuous), fibrous or multilayer heat insulation materials (that is, solid matrix and stomatal continuous). According to the different shape, it can be divided into plate heat insulation material and slurry heat insulation material [4].

Literature review

Composite silicate wall insulation material is a non-toxic, pollution-free, lightweight inorganic heat preservation, heat insulation powder material. It is made of silicone Cambuddy fiber, expanded perlite powder and other optimal heat insulation compound refined, with heat preservation, cold insulation, sound insulation, flame retardant, fire prevention functions. Its outstanding characteristics are: high strength, fast setting, no cracking, convenient and durable, it not only consolidated the thermal insulation performance, but also emphasized the characteristics of construction, its compressive strength is 5-8 times of traditional materials. This ensures that the large area of construction does not crack, not empty drum. At the same time, it solves the difficulties caused by the complicated construction of similar products, slow dry and solid time, and complicated technology for engineers. Production is not affected. Small apparent density, low thermal conductivity, good integrity, no gap, stable material, no oxidation, no degradation, no decomposition, no weathering, good durability. Construction is convenient, the whole stability is good and it is easy to bond with brick, concrete and other basic wall, especially suitable for the insulation of irregular wall. Good waterproof performance, no combustion, meet the requirements of fire prevention, even in the open flame does not burn, no deformation.

Natural materials up to 98%, non-toxic, tasteless, no pollution, no radiation freeze-thaw resistance, good weather resistance, insulation layer and protective surface layer by exposure to the sun, weathering, degradation, its comprehensive effect has met the design requirements [5].

Application analysis of composite silicate external wall insulation materials

Moisture and water resistance of composite silicate external wall insulation materials

The water absorption rate of the material is an important factor to be considered when choosing insulation materials. The thermal conductivity of water at room temperature is 23 times that of air. After absorbing water, the thermal insulation material will not only greatly reduce its thermal insulation performance, but also accelerate the corrosion of metal, which is very harmful. The gap structure of thermal insulation materials can be divided into connected type, closed type and semi-closed type. Except for a few organic foam Spaces, most of them are closed type. Regardless of the gap structure, the material itself absorbs water, and the capillary permeates water through the connected space, so the overall water absorption rate is very high. Composite silicate external wall insulation material is non-connected hole structure, hydrophobic material, which can be very good moisture and waterproof [6].

Investigation on composite silicate external wall insulation materials

Heat conduction, or heat conduction, refers to the phenomenon of heat transfer to the surface of an object after contact with the object. It is a diffusion process associated with the disorderly random motion of atoms, molecules, free electrons and other microscopic particles, that is, the process of high level particles transferring energy to low level particles. Heat conduction can occur in solids, liquids and gases, but only solids can conduct pure heat conduction. Metals conduct heat conduction through the movement of free electrons, non-conductive solids mainly rely on the transfer of free electrons and lattice vibration phase superposition for heat conduction, while liquids mainly rely on the vibration of molecules and atoms near the equilibrium position, namely the transfer of elastic waves [7]. Gas is mainly composed of molecules in the process of thermal motion, by colliding with each other to generate heat conduction. Among the three forms of solid, liquid and gas, gas has the smallest thermal conductivity, which is due to the large distance between molecules when substances exist in gaseous form, thus its average free travel is longer and the probability of contact and collision is smaller.

Fourier's law establishes the heat flow rate equation of thermal conductivity, which reflects the quantitative relationship between the temperature field of an object and the heat flux of thermal conductivity:

$$\Phi = -kA\frac{\mathrm{d}t}{\mathrm{d}x} \text{ or } q = \frac{\Phi}{A} = -k\frac{\mathrm{d}t}{\mathrm{d}x} \tag{1}$$

where Φ is the heat flow, q – the heat flux, and k [$\mathrm{Wm^{-1}K^{-1}}$] – the thermal conductivity.

Heat convection refers to the heat transfer caused by the temperature difference between hot and cold in the fluid. This heat transfer mode only exists in the fluid [8].

The heat flow rate equation caused by convective heat transfer conforms to Newton's cooling law:

$$q = a\left(t_1 - t_2\right) \text{ or } q = a\left(t_2 - t_1\right) \tag{2}$$

where coefficient a [$\mathrm{Wm^{-2}K^{-1}}$] is called surface heat transfer coefficient.

All objects are capable of absorbing or emitting radiant energy, with varying abilities. When the radiant energy emitted by one object is transmitted to another object, part of the radiant energy passes through the interior of the object and is absorbed by the object, while the rest is reflected. If an object has a strong ability to absorb and transmit radiant energy without considering other forms of heat transfer, its thermal insulation performance is poor. On the contrary, if the object's ability to reflect radiant energy is strong, its heat insulation performance is better. An object that can absorb all the radiant energy radiated to the object is called an *absolute black body*, whose radiant heat density flow is:

$$q = KT^{-4} \tag{3}$$

The energy of thermal radiation emitted by the surface of all real objects is lower than that of black bodies at the same temperature. The radiation energy of real objects is given by Stephen Boltzmann's law:

$$q = \varepsilon KT^{-4} \tag{4}$$

where ε is the amount of the blackness of the object, namely the emissivity, whose value is between 0 and 1, K [$5.67 \cdot 10^{-8}$ Wm^{-2}K^{-4}] – the Boltzmann's constant, and T – the thermodynamic temperature of the radiant surface of the object.

Experimental methods

The IR test

Test instrument: ALPHA Fourier infrared spectrometer test conditions: wave number range 4000-400 cm^{-1}.

Sample preparation method with a resolution of 4 cm^{-1}: Firstly, the prepared inorganic foaming material was ground into powder. Secondly, the ground solid powder sample and KBr were mixed evenly by grinding, and then the sample was prepared by tablet pressing method [9].

The DSC-TG Test

Testing instrument: STA449C thermogravimetric analyzer.

Test conditions: Nitrogen atmosphere, temperature range 25-800 °C.

Heating rate: 10 °C per minute.

Sample preparation method: Grind the sample into powder, use the balance to accurately weigh the sample of about 10 mg, and put it into the sample room.

The NMR Test

Test instrument: AV300(CP/MAS type nuclear magnetic resonance spectrometer).

Test conditions: ^{29}si MAS-NMR resonance frequency 596 MHz, pulse power 20 dB, pulse width 4.0 μs, cyclic delay time 1.5 seconds, the reference sample was tetramethylsilane.

Sample preparation method: Fully grind the sample into a uniform powder with an agate mortar.

The SEM Test

Test instrument: S250MK3 scanning electron microscope.

Test conditions: Magnification of 30-100 times.

Sample preparation method: Cut the sample into small pieces, stick them on the test table with conductive adhesive, and spray gold [10].

Preparation of foaming materials

The inorganic foaming material prepared in this experiment is to evaporate the water in the foaming slurry by increasing the temperature, decompose the substance that can release the gas, and make the slurry expand. At the same time, accompanied by the condensation and solidification of the slurry, the foaming material with a large number of pores is formed. Only when the gas expansion process is matched with the condensation and solidification process, the foam material with uniform structure and stable performance can be prepared. Therefore, it is necessary to investigate the ratio of raw materials and processing technology (temperature, heating rate*, etc.*).

Influence of ADC addition amount on properties of foaming materials

The ADC will react with sodium silicate, which will accelerate the hydrolysis of sodium silicate and the polymerization of silicic acid, thus changing the viscosity of the foaming slurry. As one of the important properties of the foaming slurry, the viscosity of the foaming slurry directly affects the formation and stability of the bubble structure of the material. In addition, the regulation of foaming slurry viscosity is the most effective control link in the whole preparation process [11].

The ADC raw powder with different weight percentages was mixed with sodium silicate. After full reaction, the foam slurry was poured into the mold, and the temperature was raised to 500 °C for 2 hours at a heating rate of 5 °C per minutes. The foam was calcined at high temperature. The performance of the foaming materials prepared with different ADC additions was tested, and the test results are shown in tab. 1.

Table 1. Effect of different ADC additions on the properties of foaming materials

ADC content [%]	Dynamic viscosity [Pa·s]	Flowering rate	Density [kgm^{-3}]	Compressive strength [Mpa]	Resistance strength [Mpa]	Thermal conductivity [Wm^{-1}k^{-1}]	Water absorption [%]	Porosity [%]
0.0	0.098	8.62	131.48	0.51	0.27	0.048	35.06	72. 13
0.2	0.106	5.41	209.58	1.27	0.36	0.051	30.06	55.58
0.4	0.141	4.61	245.72	1.54	0.48	0.053	28.39	47.92
0.6	0.315	4.45	255.01	1.75	0.63	0.061	27. 88	45.95
0.8	0.690	4.29	263.84	1 89	0.82	0.067	27.46	44.08
1.0	1.020	4.13	274.22	2.03	1.07	0.081	26.37	41.88

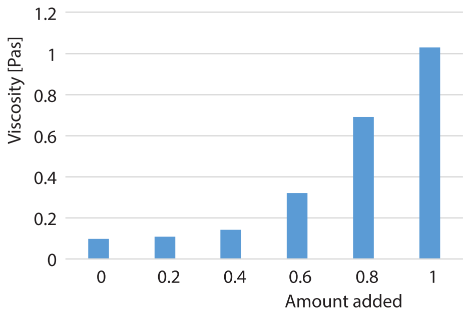

Figure 2. Relationship between ADC content and foaming slurry viscosity

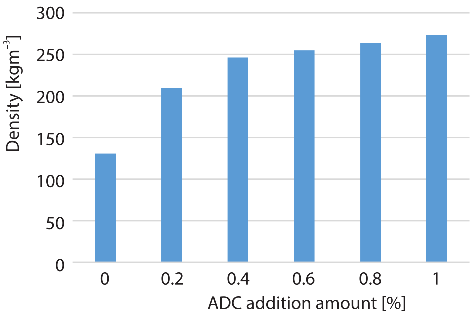

Figure 3. Relationship between ADC content and foaming material density

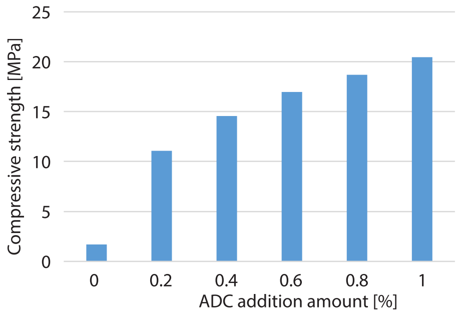

Figure 4. Relationship between the ADC content and the compressive strength of the foaming material

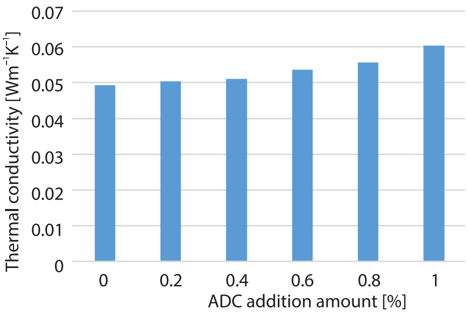

Figure 5. Relationship between the ADC content and the thermal conductivity of the foaming material

The ADC reacts with sodium silicate during the mixing process, and this reaction helps the polymerization of silicate acid in sodium silicate, thus improving the viscosity of the foaming slurry. As shown in figs. 2-5, with the increase of ADC content, the viscosity of foaming slurry gradually increases, which can inhibit the bubble rising rate and prevent the gas from being wrapped by the crack of the gas-liquid interface film, so that the prepared material becomes relatively uniform and dense. Therefore, the density, strength and thermal conductivity increase with the increase of ADC content [12].

During the experiment, the foaming material prepared by pure water glass has a large number of irregular large bubble holes, and the defects in the material where the bubble holes are gathered are very large. The overall comprehensive performance of the material is very poor, and it has no practical application value. When the viscosity of foaming slurry is greater than 0.3 Pa·s, inorganic foaming materials with low density, high strength and low thermal conductivity can be prepared. Although with the increase of ADC content and viscosity, the properties of the prepared material will be better, the maximum amount of ADC added is only 1%. When the ADC content in the system is greater than 1%, the foaming slurry will appear gel, which is not conducive to the high temperature foaming in the later stage and the uniformity of the final product. Therefore, the optimal amount of ADC is 1% of the mass of sodium silicate.

Influence of nucleating agent on properties of foaming materials

The effect of the addition of ADC on the bubble structure and performance of foaming materials is very similar to that of nucleating agents in the foam forming process. Therefore, we selected several commonly used nucleating agents for comparison further analyze the effect of ADC on materials.

After mixing one part of different kinds of nucleating agent with 100 parts of sodium silicate, it was poured into the mold, heated to 500 °C at a heating rate of 5 °C per minute, calcined, and released to prepare inorganic foaming materials [13].

It can be seen from figs. 6 and 7 that the foaming materials prepared with the foaming slurry added with ADC and the foaming slurry added with other nucleating agents have the same performance change compared with the materials prepared with pure water glass. According to the action mechanism of nucleating agent in foam molding process, according to the hot spot nucleation theory, after nucleating agent is added, due to the expansion effect of polymer grout during heating process, the grout will expand with the increase of temperature, so that the temperature will drop and the energy balance will be maintained [14]. However, because the nucleating agent does not expand, it will rise with the increase of temperature and become a local hot spot, gath-

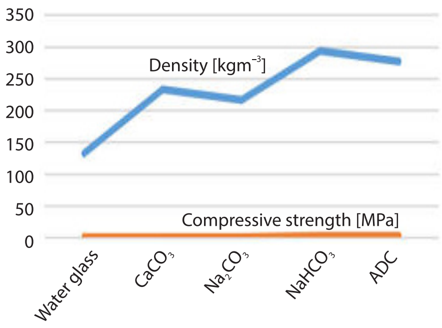

Figure 6. Relationship between the ADC content and the compressive strength of the foaming material

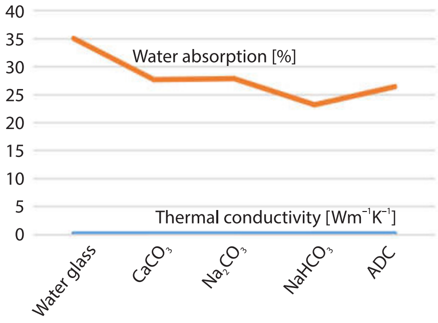

Figure 7. Relationship between the thermal conductivity and the water absorbance of the materials prepared by different nucleating agents

ering a lot of gas. Therefore, the addition of nucleating agent will increase the number of bubble nuclei, improve the density of bubble nuclei, reduce the size of bubbles, so that the strength of the prepared foam material can be improved. During the experiment, with the increase of ADC content, the performance of the material was similar to that of the nucleating agent. It can be seen that in addition increasing the viscosity of the foaming slurry after the reaction of ADC with sodium silicate, the product Na_2CO_3 generated after the reaction can act as a nucleating agent, making the comprehensive properties of the prepared foaming material excellent.

Nucleating agents Na_2CO_3 and $CaCO_3$ can both prepare foaming materials with better performance than pure water glass. However, compared with the materials prepared by adding ADC, the foaming materials prepared by these nucleating agents have larger and uneven pore size, lower compressive strength, and are easy to be damaged in the demoulding process. In the heating process, nucleating agent NaHCO will decompose into CO_2 acid gas, which can react with sodium silicate hydrolysis to produce NaOH, thus accelerating the hydrolysis of sodium silicate, promoting the polymerization of silicic acid, and improving the strength of the material. However, the foaming slurry with $NaHCO_3$ is easy to form local gel, and it is difficult to prepare uniform foaming slurry. After comprehensive analysis, the foaming slurry of ADC fully reacted with sodium silicate can produce relatively superior foaming materials without the addition of other nucleating agents [15-17].

Conclusion

Under the strong alkaline condition of sodium silicate, ADC will undergo alkali decomposition reaction, which can promote the hydrolysis of sodium silicate, accelerate the polymerization of silicic acid, and improve the viscosity of the slurry. In addition, the product Na_2CO_3 after the reaction can play the role of nucleating agent. However, when the content of ADC is higher than 1%, gel will be formed, affecting the performance of the material. Therefore, the optimal amount of ADC is 1% of the mass of sodium silicate.

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