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Elucidation of the technological conditions for the formation of alkali silicates heat-insulating products based on ash-removal of thermal power plants and liquid glass

The raw material mixture from the silicon-like techno genic component the ash-removal of thermal power plants and the preparation methods of waterproof porous heat-insulated materials wide usage for raw mass hot foaming powdered two-stage technology are developed. The development uses the polyfunctional properties of liquid glass as a) the binder component; c) breeder; c) the speed regulator of the clamping mass hardening. Its optimized version begins to solidify at its usual temperature from the moment its "reproduction" is soluble glass and forms a paste-shaped cake with a set of properties necessary for the next fragmentation. The proposed formulation allows compositions processing in various ways, with the formation of granular heat-insulating fillers, materials for thermal insulation in complex structures, slab and shell-like types of thermal insulation materials. The task is set, depending on the goals and features of the tasks being solved; it is possible to conduct several different methods at the final stages of their obtaining. Two stages of the recycling process determine the character and behavior of the rare-glass composite systems constituent components during heat treatment, their strong adhesion to most structural materials and the need to solve billets easy removal problem from the molding unit. Study results can be used in the field of building materials production, in particular porous artificial products, in obtaining granular insulating material and light aggregate for concrete industrial and civil construction, in thermal engineering as thermal insulation, etc.

Keywords: alkaline-silicate heat-insulation composite materials; ash removal; liquid glass; thermal foaming.

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Introduction

Alkali-silicate porous materials obtained by means of thermal or cold foaming of alkali metals silicates aqueous solutions (soluble glass) or solid alkali silicate hydrogels [1 – 6], are referred to the present-day, efficient inorganic insulates, promising due to the ability to achieve low values of the relative density and thermal conductivity while maintaining sufficient structure strength and easy handling of foaming and induration processes within a wide range of composition formulations. The above benefits are based on the equilibrium and homogeneity of the main raw mixture component: soluble glass and hydrogels based on it.

Composite alkaline-silicate porous thermal-insulating materials, both granulated and block type, contain significant amounts of the gas phase. There are various technological approaches to obtaining such materials at gas development directly in the strata of the formed composition. Moreover, the process of gas development at high temperatures can be based both on the special additives reactions, and on the crystallization and chemically bound water vapors liberation.

Identification of Previously Unsettled Parts of the General Problem

Analysis of the existing suggested raw mixtures formulations and methods of obtaining thermal insulating materials proves that introducing a significant gel formers amount has a serious drawback: the gelling agent breaks the soluble glass structure to form hydro silicic acid gel, which is capable of retaining less water than soluble glass. This adversely affects the porosity of the resulting rare glass compositions. Therefore, there is a need to introduce such substances that are inert to soluble glass at the normal temperature.

In addition, a significant drawback of the known methods is performing air-entrainment at fixed temperatures in the furnace within the range of 300 – 700 °C. Such a mode of heat treatment reveals several contradictory trends. At relatively low temperatures, the air entrainment process is complicated due to the low warming up rate of the raw mass internal areas, resulting in the increased duration of its air-entrainment process. At the same time, the slow warming up of rare-glass mixtures also leads to significant losses of chemically bound water, due to which air-entrainment of the mixtures occurs. The high rate and unevenness of their heating is manifested in the size, regularity of the pores and the strength of the entire porous structure, in the internal ten-sons of the products. Therefore, an important prerequisite for obtaining the expanded material possessing a set of required properties and their reproduction, is compliance with the principle of correspondence between the rate of crystallization and chemically bound water isolation and the rate of new solid silicate structures formation.

In all of the above-described methods, the first stage is to obtain a solid or plastic composition from soluble glass which can then be subjected to heat treatment. At the same time it is not necessary to use different additives that cause coagulation of silicates. It is possible to obtain a plastic composition using soluble glass simply by means of adding an inert disperse component.

The purpose of the Work

The study performed is aimed at the search and development of an optimized raw material mixture variant of the silicon oxide containing techno genic component: fly ash of thermal power plants and methods of obtaining the fly ash based porous alkaline-silicate composite thermal insulating materials of extended application, differing from the analogues by their composition, the content of the starting raw mass, the sequence and modes of the target product formation, the applied technological equipment.

Experimental part

Raw Materials and Regulations for Composite Alkaline-Silicate Insulation Materials Preparation Development

The proposed development is an option for interconnected, interdependent choice of composition combining and complex practical implementation, content of raw material based on techno genic origin liquid glass and a method for utilization an ash-making coal-energy complex by creating wide usage water-resistant, porous, thermal-insulating material.

In the raw mixture, the industrial soluble glass, thermal power plants fly ash of the mixed chemical composition (see Table 1), sticky Portland cement and, additionally, a thickener (pre-staged partially dehydrated hardened "dry glass") are used.

Table 1- Chemical composition of the thermal power plants fly ash, mass. %

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	SO_3
51,68	16,75	14,47	0,88	4,38	0,35	2,58	0,86	4,24

In the prepared samples, the fly ash is manifesting good reinforcing properties, high thermal stability, sufficient resistance to aggressive media, has a small bulk density.

At the same time, the results of the authors' studies [5, 6] (on the ability of alkaline-silicate systems with Al_2O_3 in alkaline media to form insoluble products of $Na_2O{\cdot}Al_2O_3{\cdot}2Si_2O_3{\cdot}nH_2O$) permit to consider aluminum oxide contained in ash to be a modifying component that provides the raw mix with the properties necessary for the targeted product formation.

In forming the raw mix, the results were taken into account on improving the water resistance of alkali silicate composition by means of replacing the two-calcium silicate (belt) hydrophobia components with the sticky Portland cement; the results are presented in [6].

The "setting" rate control of the suggested raw mix during the formation of hydro silicic acid aerogel (depending on the executed tasks purposes) was performed by means of varying properties of the thickener used and by means of regulating the hardened processed mass fragmentation in the further processes and its subsequent hot foaming.

In the present project, the set task of making the targeted porous thermal insulating material is achieved by means of the raw mass hot foaming technology, which procedure includes the four main stages:

1) preparation of the starting raw mixture components and homogenization of the latter;

2) the composite system "gaging" by soluble glass and formation of a persistent gel; fragmentation of the hardened raw mass and placement of the granulate into lined dismountable molds;

3) heating and transferring of the work pieces' substance into the pyro plastic state (110 – 115 °C); 4)

further hot foaming and reproduction of the regular porous macrostructure of composite systems (130 – 220 °C) and formation of the targeted processed product's properties (500 – 550 °C).

The blowing agent in this case is water (mainly silanol or molecular, strongly bound by hydrogen bonds with unbridged oxygen atoms), which is released during heat treatment of composite systems.

Study Results and Their Discussion

The raw mix prepared according to the optimized formulation, in contrast to the previously considered analogues, starts hardening at the usual temperature from the moment of its "gaging" with soluble glass and forms a plastic cake with the properties necessary for further fragmentation.

The suggested raw mix also permits to overcome the difficulties associated with drying of viscous rare-glass mix to remove a large output amount of water (56 – 62 %) to the water content of 33 – 38 % needed to obtain a rigid hydrogel capable of thermal blowing.

The optimized formulation of the raw mix allows processing of the compositions in various ways, with the formation of thermal insulating materials of extended application. An important prerequisite for their reproduction with the necessary properties system is strict compliance with the regulatory requirements established by the previous empirical studies.

In parallel with the formulation development, the technology of samples manufacturing was being tried. Thereat, the decisive factor, in contrast to the regulations [4], the exclusion of the raw mix granulation stage after heat treatment 110 – 115 °C and the use of sealed closed forms at their temperature annealing.

The suggested hot air entrainment of the silicate compositions structure "blowing" of the systems in a aerogel form passes quickly, avoiding the viscous-adhesive state. The determining factor in the process of the systems thermal activation was the technical performing of their heating reproduced rate [see 7].

The conscious choice of its optimal mode is motivated by empirical data to determine the thermal foaming features of composite systems obtained by the method of differential-thermal analysis (DTA) presented in Fig. 1.

The air entrainment process includes the three main stages, the duration and nature of which depends on the type and amount of water containing the raw mix:
– within the range of 100 – 110 °C, the hardened composite system partially transforms into the pseudopyroplastic state and begins to deform with increasing volume;
– within the range of 130 – 147 °C, an intensive release of free and adsorbed water and intensive air entrainment of the sample mass occurs;
– at the temperature values above 147 °C, the removal of constitutional moisture, the completion of restructuring, physical and chemical transformations of composite systems are observed.

Based on the analysis of the thermo graphic data and the macrostructure of the samples obtained, it can be concluded that the greatest contribution to the formation of the product's structure with maximum homogeneity is made by the constitutional water, while removal of the excess adsorption moisture at the initial stages leads to the formation of large through pores and capillary channels in the raw mass. Therefore, the initial rare-glass composition should contain a minimum amount of free and adsorbed water.

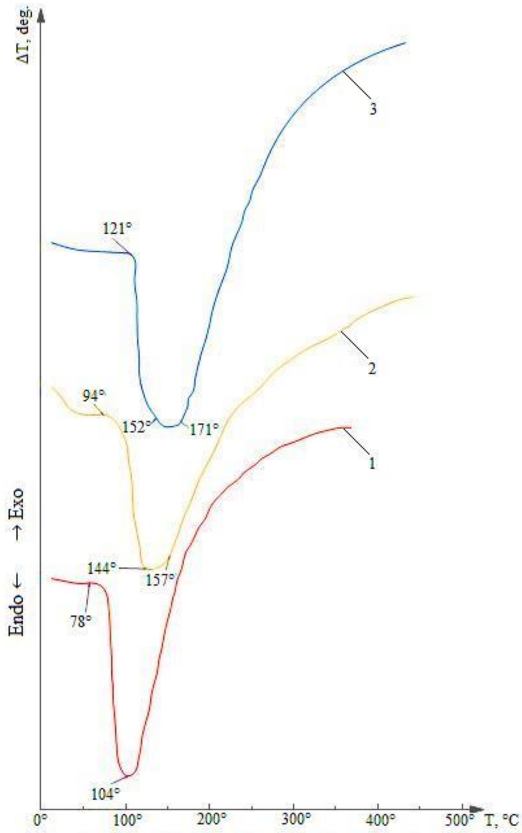

Figure 1 - DTA thermo grams of sodium rare-glass composites aerogels in coordinates ΔT – T, recorded at heating the samples in adequate conditions at different rates: curve 1 – 4 deg. / min.; curve 2 – 7 deg. / min.; curve 3 – 20 deg. / min.

As the efficient ways to reduce the free water's effects, the following ones can be recommended:
– direct thermal dehydration and transformation of soluble glass into aerogel (the basis of the present variant of the suggested technical solution);
– liquid granulation of composite systems (for example, in Al, Ca, Zn, Mg chlorides solutions or their mixtures);
– introducing of mineral fillers or chemical additives into the rare-glass composite system, which leads to the development of gelation processes.

According to the results of the study [6], alkaline-silicate compositions in solutions at heating form a number of hydrated associates with differing properties (see Fig. 2). This permits modifying the properties of the raw mix thickener - grated "dry glass" – by means of the partial unwatering of the purchased product in a liquid state at different temperature values, in the conditions of the technological cycle for the target product formation, simultaneously with the same equipment, without the use of additional equipment.

Meanwhile, the empirically determined physicochemical behavior of composite silicate systems, the features of unwatering and the viscosity state passing, strong adhesion of the intermediate transformation products to

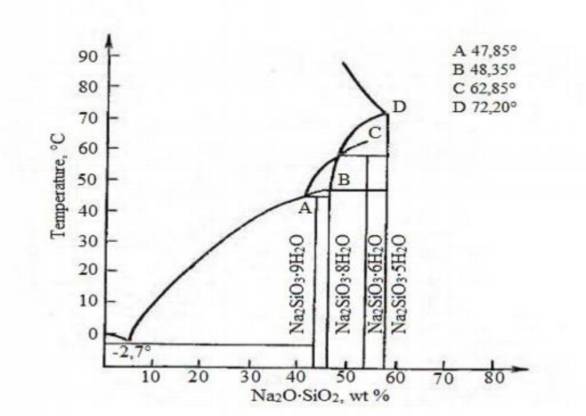

Figure 2 - Solubility in the $Na_2O – SiO_2 – H_2O$ system

metals, ceramics, glass allow to suggest technological regulations, stages, sequence of operations during processing, development and selection of the equipment materials, variations in the methods of obtaining and using porous targeted composites.

Laboratory practice proves that the excess amount of the soluble glass introduced in a liquid state during the "gaging", on the one hand improves the rheological properties, the plasticity of the treated raw mix, and on the other hand, during the subsequent heat treatment, causes additional viscosity of the system, deteriorates the heat transfer conditions, requires more prolonged temperature holding at higher temperature values and leads to the increased energy costs. Therefore, a necessity arises to find an efficient way of regulating the rate of gelling, using the method of shifting the equilibrium of physical and chemical processes of the disperse systems dehydration by adding less hydrated forms of the dried soluble glass; with the degree of the grated "dry glass" dispersion, with its dosage and regulating the processes of the hardened processed mix fragmentation during the granulate formation and the subsequent hot air entrainment.

The improved formulation of the raw mix preparing allows processing compositions in various ways with the formation of insulating materials of extended application: granular insulating filler (Fig. 3, [8]), materials for thermal insulation for the structures complicated in the form (Fig. 4, [9]), the plate and film-like types of insulating materials (Fig. 5, [10]). This task (depending on the purpose and features of the performed tasks) is solved by the capability of performing the final stages by means of several different ways of the products obtaining.

The use of the two stages procedure of the suggested renovation in the technology of preparing the porous thermal insulating materials determines:

1) the nature and the behavior peculiarities of the rare-glass composite systems components during the heat treatment, their strong adhesion manifestation related to most structural materials;
2) the necessity to solve the problem of easy work pieces removal from the formation molds;
3) the choice of the method for lining the internal surfaces of dismountable equipment molds;
4) thermo physical and chemical properties of the used lining material.

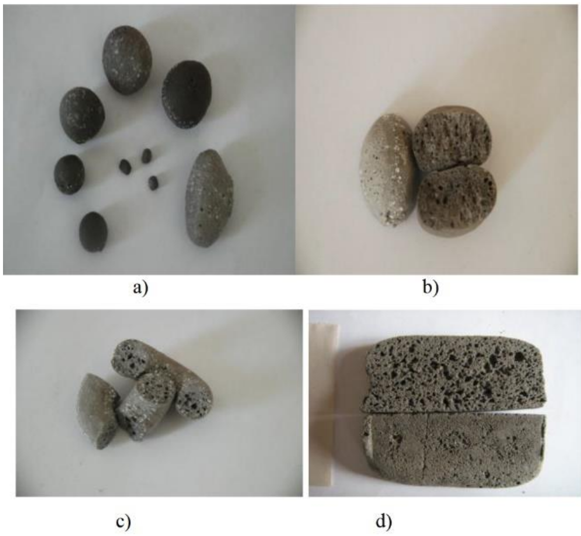

Figure 3 - Illustration of the granular thermal insulating fillers' samples, obtained in the lined molds without limitation of formation volume: a), b) - cutting of iso-sized elements; c) - cutting elements of plastic hardened raw cake of the set preformed thickness; d) –of work pieces, formed in separate dismountable molds.

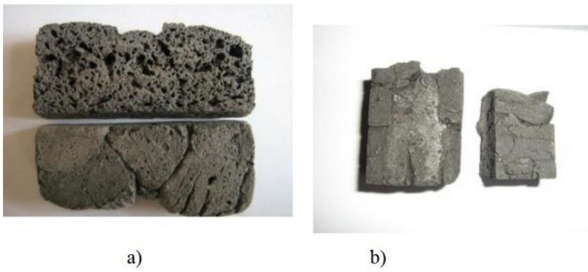

Figure 4 - Illustration of fragments of thermal insulation zones sections in complicated form structures performed by the working zone filling with fragmented elements and the subsequent heat treatment in dismountable equipment of varying complexity: a) - without limiting the free volume of formation; b) - with restriction of formation space

Figure 5 - Illustration of the items fragments formed: a) – in the form of plates; b) – in the form of films

Developed step by step circuit forming composite alkaline silicate porous insulating materials based on soluble glass and fly ash thermal power plants include:

1) the preparation of initial components of raw mix grinding, milling sifting through a sieve (80-315 microns), fly ash thermal power plants, sticky Portland cement, partially dehydrated "dry glass", dried at the given temperature, in accordance with the proposed regulations for the processing of the composition system (105, 190 °C);
2) preparation constituent raw powder components and dosed amount of soluble glass according to proven recipes optimized;
3) homogenization of the of the raw material mixture powder components by thorough mixing (for example, using a mixer);
4) "formation" of raw material by soluble glass and mixing to thickening of the stable gel composition and formation under standard conditions;
5) mechanical fragmentation hardened plastic cake into individual elements (rolling perforated thorn, punching, cut-ting, cutting and other methods) defined size, shape and configuration of the coefficient swelling (depending on the characteristics of tasks,
6) placing the fragmented elements in lined shape with unlimited volume on a heat-resistant pallet separately, without touching the neighbors;
7) heating at a speed of 4-7 degrees. / min and transferring granular material blanks in pyro plastic state (110-115 °C, 15 min exposure, may seal) followed by a two-stage heat treatment hot foaming and play regular porous structure of the body pellet (130-220 °C, 20 min exposure) non sticky carrying blanks to form resistant lined pan and then heating to 500-550 °C and their exposure (to give them satisfactory water and vapor resistance), cooling and receiving the end products.

The features of the suggested project are:

– ease and availability of obtaining components and preparing the raw mix;

– formation of the raw mix directly at its “gaging” with soluble glass under the normal conditions;

– the thermal insulation method is fast;

– the possibility of easy formation and fragmentation of the raw work pieces, their inherent properties makes it possible to spread in time and space separate stages of thermal insulation: the stage of preparation, formation of granulate (possibly, in a specialized site); storage; transportation; technological packing in the working area complying with the increased resistance requirements to the heat transfer (possibly, in the construction site);

– processing of complicated working areas: selection of the raw mix cake thickness, the size and shape of the starting fragmented elements (depending on the target task and in order to provide more tight packing);

– the versatility of the thermal insulation method (based on the manifestation of significant adhesion ability of alkaline-silicate composite systems in relation to most structural materials: metals, ceramics, glass, wood);

– low shrinkage with the suggested formulation of the raw mix and the method of treatment;

– indifference to most components and stability of the thermal insulation material properties, high thermal and chemical resistance, no combustibility, ability to withstand significant temperatures;

– combination of the valuable properties set: low thermal conductivity factor, thermal stability, incombustibility, durability, low cost.

Conclusions

The raw mix of silica-containing techno genic component - fly ash of thermal power plants - and the methods of preparing waterproof porous thermal insulating materials of extended application on its base according to the powder low-temperature technology has been developed using multifunctional properties of soluble glass as: a) a binding component; b) blowing agent; c) the raw mix hardening rate regulator. The physical and chemical, technological aspects of obtaining and using the suggested alkaline-silicate compositions have been considered.

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З′ясування технологічних умов для формування лужно-силікатних теплоізоляційних виробів на основі золи-винесення теплових електростанцій і рідкого скла

Розроблено сировинну суміш із кремнеземвмісної техногенної складової – золи-винесення теплових електростанцій та способи приготування водостійких пористих теплоізоляційних матеріалів широкого призначення за двостадійною технологією гарячого спінювання порошкоподібної сировини. У розробці використовуються полі функціональні властивості рідкого скла як а) зв'язуючого компонента; б) пороутворювача; в) регулятора швидкості твердіння сирцевої маси. Сирцева маса, приготовлена за оптимізованою рецептурою, починає тверднути за звичайної температури вже з моменту її «за творення» розчинним склом й утворює пастоподібний корж з набором властивостей, необхідних для наступної фрагментації. Оптимізована рецептура приготування сирцевої суміші дозволяє перероблення композицій різними способами з формуванням термоізоляційних матеріалів широкого призначення: гранульованих теплоізоляційних наповнювачів, матеріалів для термоізолювання у складних за формою конструкціях, плитного і оболонко подібного видів термоізоляційних матеріалів. Така поставлена задача в залежності від цілей і особливостей вирішуваних завдань досягається можливістю проведення декількома відмінними способами завершальних стадій їх отримання. Двох стадійність процесу перероблення визначають характер і поведінка складових компонентів рідко-скляної композитної системи під час термічної обробки, їх міцна адгезію до більшості конструкційних матеріалів і необхідність вирішення проблеми легкого видалення заготовок із розбірних форм оснащення. Результати досліджень можуть бути використані у галузі виробництва будівельних матеріалів, зокрема пористих штучних виробів, при отриманні зернистого ізоляційного матеріалу та легкого заповнювача для бетону промислового та цивільного будівництва, у теплотехніці як теплоізоляція тощо.

Ключові слова: лужно-силікатні теплоізоляційні композиційні матеріали; видалення золи; рідке скло; термічне спінювання.

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