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Organo-mineral additives based on oil and gas complex waste to building materials

Органоминеральные добавки к строительным материалам на основе отходов газовой и нефтяной промышленности

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Ключевые слова: здания; органоминеральные добавки; нефтесодержащие отходы; отработанные сорбенты; утилизация отходов; экологическая безопасность; вторичные ресурсы; керамзит

Abstract. The use of waste and products of their utilization as secondary raw materials is promising and rational way for their disposal. The addition of waste to mixtures provides either high-quality products or improvement some of the physical and mechanical characteristics. Organo-mineral additives are produced by oil-contaminated waste and spent sorbents utilization meet environmental safety requirements and are suitable for use as an additive in building materials, for example, expanded clay and asphalt mixtures. The aim of the paper is to develop technology for producing organo-mineral additives that is aimed at the elimination of environmental pollution with wastes, their involvement into resource circulation and ensures rational nature management with reducing the consumption of reagents and receiving high quality ecologically safety products. It is established the minimum necessary quantity of quicklime (calcium oxide reagent) required to transfer viscous sludge in bulk and obtain organo-mineral additives. In order to achieve the most important technical parameters of building materials in particular expanded clay – a bulk density and strength, it is used various additives. Application of the complex additives can increase the swelling clay factor up to 3 times and get the required strength of concrete block with less energy consumption, which significantly reduces the cost of the products. It is carried out the research to develop formulations of puddle clay with organo-mineral additives and choose burning conditions for preparing expanded clay. It's established the optimal temperatures and a thermal presintering for producing products that meet the requirements of the standards, with minimal energy consumption. The impact of the percentage of organo-mineral additive on the coefficient of clay swelling is determined. In the process of burning poor swelling clay with using organo-mineral additive at temperature 1050 °C constructive quality factor is increased by 70–97 % in comparison with the expanded clay obtained from raw materials without additives. Proposed technology for production of expanded clay with organo-mineral additives allows getting high-quality environmentally friendly products and disposing in its composition oil and gasing complex waste, involving them into resource management, and satisfies best available techniques due to encouraging re-use of waste.

Аннотация. Использование отходов и продуктов их переработки в качестве вторичного сырья является перспективным и рациональным способом их утилизации. Добавление отходов в смеси обеспечивает и высокое качество продуктов, и улучшение некоторых физико-механических характеристик. Органоминеральные добавки, получаемые при обезвреживании отработанных сорбентов и нефтесодержащих отходов, отвечают требованиям экологической безопасности и пригодны для использования в качестве добавки в строительные материалы, например, керамзит и асфальтобетонные смеси. Целью работы является разработка технологии получения органоминеральных добавок, которая направлена на ликвидацию загрязнения окружающей среды отходами, их вовлечение в ресурсооборот и обеспечение рационального природопользования через уменьшение потребления реагентов и получение высококачественной экологически безопасной продукции. Установлено минимальное необходимое количество негашеной извести (реагента оксида кальция), требуемое для перевода вязкотекучего шлама в сыпучее и получения органоминеральных добавок. Для достижения наиболее важных технических характеристик строительных материалов, в частности, керамзита – насыпной плотности и прочности, применяют

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различные добавки. Органические добавки улучшают вспучивание глины и снижают насыпную плотность керамзита. Кремнеземсодержащие добавки помогают увеличить прочность готового продукта. Применение комплексных добавок способствует увеличению коэффициента вспучивания глины до 3х раз и получению требуемой прочности бетонного блока с меньшим потреблением энергии, что значительно снижает себестоимость продукции. Было проведено исследование по разработке составов глинистого теста с органоминеральными добавками и выбору режима обжига для получения керамзита. Были установлены оптимальные температуры и режим предварительной термоподготовки для производства продукта, отвечающего требованиям стандартов, с минимальным потреблением энергии. Определено влияние процентного содержания органоминеральной добавки на коэффициент вспучивания глины. В процессе обжига слабовспучивающейся глины с использованием органоминеральной добавки при температуре 1050 °C коэффициент конструктивного качества увеличивается на 70–97 % по сравнению с керамзитом, полученным из сырья без добавок. Таким образом, предлагаемая технология для производства керамзита с органоминеральными добавками позволяет получить высококачественные экологически безопасные продукты и утилизировать в своем составе отходы нефтегазового комплекса, вовлекая их в ресурсооборот, и отвечает требованиям наилучших доступных технологий, стимулируя повторное использование отходов.

Introduction

The current situation in the field of formation, accumulation and disposal of oil and gas complex waste leads to dangerous contamination of all components of the environment – surface water and groundwater, vegetative ground cover, air, as well as unsustainable use of natural resources, significant economic damage and poses a real threat to health current and future generations of the country. At the enterprises of the oil and gas industry oily waste are generated during the construction of oil and gas wells, commercial exploitation, transportation and processing of oil and gas, treatment of waste water containing oil products and cleaning of tanks and other equipment. The accumulation of large masses of waste is due to objectively existing level of technology for the processing of raw materials and lack of its complex use.

For the oil industry it is characterized formation of oil-contaminated liquid and solid waste - waste water and sludge. Most of the refinery waste is oil sludge generated in the wastewater treatment process; scales and deposits on equipments. Output of oil sludge is up to 10 kg per 1 ton of crude oil processed [1]. Among the solid waste of oil refining let us note the spent adsorbents used for wastewater treatment and spent catalysts used in the catalytic oil processing. Considering the gas industry, there is spent adsorbent formed by the dehydration of natural gas. Every year during the extraction of fuel and energy minerals it's generated about 2000 million tons of oil sludge, including in Krasnodar Territory – to 12000 tons [2].

The use of oil-containing waste as secondary raw materials is one of the most efficient methods for their treatment and disposal. Oil sludge has been used in road construction, building materials, fuel industry, oil and gas industry. Adding sludge in mixtures allows obtaining high-quality products that comply with regulatory requirements, to improve some of the physical and mechanical characteristics similar products. Areas of oil sludge use are chosen both by technological, technical and sanitary requirements for products, as well as on performance standards for raw materials. Suitability oil waste as technogenic raw materials is determined during their complex analysis.

Thus, it is topical and essential the development of effective methods of oil and gas complex waste disposal and the best available techniques of their utilization for the elimination of air, water, soil pollution by waste of hazard classes II to III and environmental remediation. Along with this it is important resource-using waste and products of their disposal as complex additives in building materials, involving at the same time waste into resource management.

The possibility of using oil sludge in the production of building materials are determined by the type of the products (brick, concrete block, aggregates) and the role of waste in the process (burn-out additive or softener).

Oil-contaminated waste is widely used as the organic binder in the manufacture of waterproofing materials. Using the oil waste can not only reduce the consumption of bitumen or oil, but also obtain materials with high physical and mechanical properties [4–7].

It is worth noticing an insulating material [8] that can be used in the disposal of toxic industrial waste of hazard classes III to IV, including municipal solid waste. The material contains clay (10–60 mass.%), sediment of staked lime or sludge of chemical water purification in quality of used lime

waste material (15–40 mass.%), bottom, floating oil-slime or soil polluted with mineral oils in quality of oil-slime (25–50 mass.%).

It is used oil waste solidification techniques that allow to get products in the form of blocks for it use as structural elements in the construction and waterproofing of landfills for the disposal of waste. Method of detoxifying petroleum-containing wastes includes adding 10-% aqueous emulsion of waterproofing liquid and resultant mixture is solidified by mixing with cement. The quantity of oil waste in the composition ranges from 20.8 to 41.6 mass.% [9].

In research papers [10–14] it is suggested the use of oil sludge for production of expanded clay. According to the mineral composition of oil sludge waste are similar to the components of the raw mixture, and according to the fractional composition of the organic part they are similar to expansion admixture.

In order to improve the quality of expanded clay it is commonly used various additives. Organic additives can improve distension clay, resulting in a reduction in the bulk density of expanded clay. Silica-containing supplements help to increase the strength of the finished product due to the saturation of silicium ions and increase the proportion of vitreous component. It is used organo-mineral and alkaline additives to reduce the burning temperature. Powdering the pellets with refractory powders surface, in particular limestone, ground quartz sand, gypsum causes blistering expansion slot. Application of the complex additives can increase the swelling clay factor of up to 3 times and get the required strength of concrete block with less energy consumption which significantly reduces the cost of the product.

At the Department of oil and gas technology it is developed technologies of oil-contaminated waste disposal by reagent method with introducing quicklime and adsorbing additives based on industrial waste, including oil and gas industry (waste siliceous adsorbents: silica gels, ODM-2F, diatomite, C-sorbents, the products of pyrolysis of used tires, rice husk) [15–23]. The composition of waste utilization products is suitable for use as complex additives in building materials, for example, in the production of expanded clay and asphalt concrete [24–29]. Patented technologies take into account the requirements for BAT [30, 31]. One of the criteria for inclusion to the BAT is encouraging re-use of waste. Application of BAT in the oil and gas industry is a comprehensive solution to the problem of waste management, including the transition to energy-efficient, resource-saving technologies to the improvement of the environment and citizens' health. Using BAT in the field of waste management will eliminate the environmental pollution by waste [32–34].

The composition of oil utilization products by reagent method includes calcium oxide, silicon oxide and conversion products, calcium hydroxide, encapsulated hydrocarbons from oil-sludge and organic compounds from the spent silicious sorbents. Consequently, those products are organo-mineral additives and in fact are complex additives for increasing the coefficient of clay swelling, reduction the bulk density and maintaining granule strength. The introduction of neutralized oil sludge makes it possible to mix clay mass without contamination of working area, eliminating the release of hydrocarbons and other harmful substances from waste. Organic components stimulate porization of expanded clay and intensify processes occurring during the clay swelling including the transition clay into pyroplastic state. By reducing the bulk density of expanded clay it is important to ensure an optionally strength because increasing the pore size causes a sharp decline in the strength of the pellets due to the reduction of wall thickness and then enhance stress concentrations. Not only volume and pore size affect on the strength of porous materials. The structure and composition of the solid phase component of the vitreous play a great role. The strength of the vitreous increases by the saturation of aluminum and silicium ions. Therefore, silica-containing additives, including the siliceous spent sorbents, help to increase the strength of the finished product.

Following the research the objectives of this study are to develop technology for producing organo-mineral additives for the elimination of environmental pollution with wastes, to involve wastes into resource circulation and to ensure rational nature management with reducing the consumption of reagents and to receive high quality ecologically safety products.

Methods

Method of obtaining organo-mineral additive to building materials consists in mixing oil-contaminated sludge with quicklime, preliminarily milled to a finely dispersed condition, and exhausted silica gel, which represents the gas industry waste product at the stage of natural gas drying, with the following introduction of water. As for exhausted silica gel it contains more than 90 mass % silicon oxide, 2.4 mass % coke deposits, 3.6 mass % organic components and the remaining metal oxide [35–36], and

it's used as the hydraulic additive in manufacture of waterproof concretes on the basis of calseal-puzzolane binding agent [37–40].

The necessary quantity of water for slaking is determined stoichiometrically including water, present in the oil-contaminated sludge, and wateradsorption of exhausted silica gel. The obtained organo-mineral additive is exposed until the process of calciumsilicate structure formation is finished. First, the quantity of oil components in the oil-contaminated sludge is determined, which is then used to calculate the necessary quantity of quicklime (1).

$$y = (0.023x - 0.001) \cdot m\,, \tag{1}$$

where y – necessary quantity of quicklime, kg;

x – quantity of oil components in the oil-contaminated sludge, mass. %;

m – quantity of oil-contaminated sludge, kg;

0.023 – empirically determined coefficient;

0.001 – empirically determined coefficient.

The obtained data are used to calculate the necessary quantity of exhausted silica gel (2).

$$\mathrm{z} = 1.1 \cdot \mathrm{y}, \tag{2}$$

where z – necessary quantity of exhausted silica gel, kg;

1.1 – empirically determined coefficient, taking into account the quantity of silicon oxide in exhausted silica gel.

Before mixing powdered quicklime it's treated with waterproofing additive in the form of a solid technical fat, heated to a temperature of 28–40 °C, taken in an amount calculated by equation 3:

$$\mathrm{n} = 0.05 \cdot \mathrm{y}, \tag{3}$$

where n – necessary quantity of waterproofing additive, kg;

0.05 – empirically determined coefficient.

The obtained by this method organo-mineral additive meets ecological safety requirements and is suitable for use as a complex additive in construction materials.

Results and Discussion

For the rational disposal of oil-contaminated waste and production effective organo-mineral additives to building materials it's important to determine necessary quantity of quicklime taking into account oil components in waste. The dependence of oil-sludge neutralization efficiency from quantity of quicklime (Fig. 1) is obtained by experimental research of the effectiveness of oily waste neutralization with different quantity of organic components.

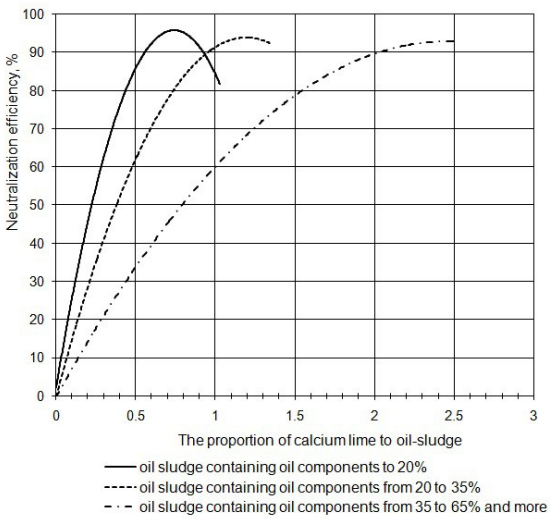

Figure 1. The dependence of oil-sludge neutralization efficiency from quantity of quicklime

It is established the minimum necessary quantity of quicklime (calcium oxide reagent) required to transfer viscous sludge in bulk and obtain organo-mineral additives. To achieve neutralization efficiency of 85–95 % the proportion of calcium lime to oil-sludge varies widely the average from 0.4 to 1.7 and higher. Thus further increase quicklime leads to decrease in the efficiency of neutralization, which is associated with an excess of the reagent.

With a minimum quantity basic reagent (quicklime) environmental safety of organo-mineral additives is achieved by increasing the quantity of silica component in neutralizing composition – exhausted silica gel, the main part of which is silicon oxide.

So, considering the composition of organo-mineral additive it is a complex additive, for example, for increasing the coefficient of clay swelling, reduction the bulk density and maintaining granule strength.

Formulation of puddle clay for preparing expanded clay with additives deals with the selection the optimum percentage of additive in the raw mix to achieve the requirements of standards for the products. It is carried out the research to develop formulations of puddle clay with organo-mineral additives and choose burning conditions for preparing expanded clay.

Method of preparing expanded clay involves mixing clay raw material, an additive and water, granulation of the obtained mixture, drying and burning. Mixing is carried out in two steps. At the first step clay raw material is mixed with the additive (1–5 mass %). At the second step water is added in an amount sufficient for obtaining a mixture with water content of 18–20 %. In accordance with the composition of the raw materials it's characterized by quantity of silicon oxide 67.84 % and quantity of organic components 0.40 %, so it refers to moderately ductile raw materials. With adding organo-mineral additive in quantity from 1 to 5 mass. % the clay composition will be included in the regulated Russian technical specifications TU 21-0284739-12-90 value.

Selecting the mode of burning raw granules is to establish the optimal temperatures and a thermal pre-sintering for producing products that meet the requirements of the standards, with minimal energy consumption. Test results of obtained expanded clay samples showed that optimum temperature conditions are rapid and gradual thermal treatment at temperatures of 200, 300, 400 °C with the addition of 1–3 % OMD in the burning temperature range from 1050 to 1110 °C.

The impact of the percentage of organo-mineral additive on the coefficient of clay swelling is expressed by the following relationship (Fig. 2).

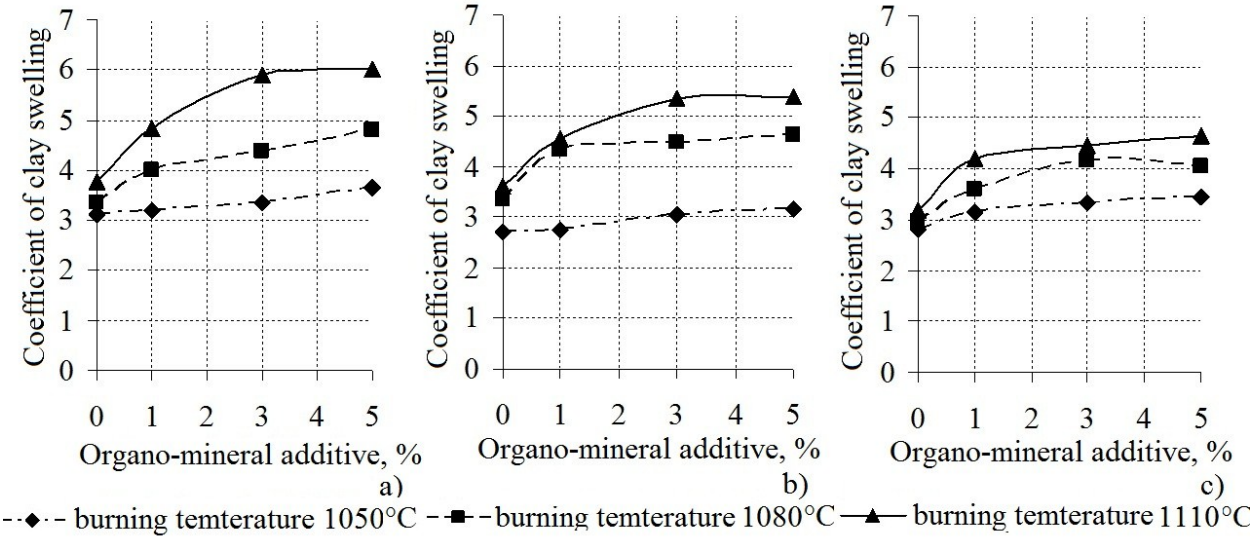

Figure 2. The impact of the percentage of organo-mineral additive on the coefficient of clay swelling at various burning temperatures and rapid thermal treatment at 200 °C (a), 300 °C (b), 400 °C (c)

In the range of raw materials burning from 1050 to 1110 °C adding organo-mineral additive in quantity 1 mass. % increases the coefficient of swelling from 3 to 40 % in comparison with pure raw materials. Adding organo-mineral additive in quantity 3 mass. % increases the coefficient of swelling from 5 to 45 % and in quantity 5 mass. % – from 12 to 50 %. However, the use 5 % of organo-mineral additive limits the narrow swelling range in 30 °C and surface glazing at a lower temperature 1110 °C due to the increase the organic components in the clay composition.

Thus, in the process of burning poor swelling clay with using organo-mineral additive at temperature 1050 °C constructive quality factor is increased by 70–97 % in comparison with the expanded clay obtained from raw materials without additives. Therefore, developed method is energy-saving, environmentally friendly and technologically appropriate technology of expanded clay production.

Conclusions

1. The research results can be used in the oil and gas industry to utilize the accumulated and annually produced at the enterprises technogenic waste for minimization environmental pollution, while reducing air, water and soil pollution by waste of hazard classes II to III; as well as in the building industry, reducing the consumption of natural resources and energy.

2. The developed technology for production of expanded clay with organo-mineral additive provides preparing high-quality environmentally friendly expanded clay and disposed in its composition oily waste and meets BAT requirements.

3. The use of complex additives OMD increases coefficient of clay swelling up to 3 times and obtaining the required strength of expanded clay with lower energy consumption, which significantly reduces the cost of the product due to the use raw materials of poor quality.

4. It is established the optimal temperatures and a thermal pre-sintering for producing products that meet the requirements of the standards, with minimal energy consumption.

5. The impact of the percentage of organo-mineral additive on the coefficient of clay swelling is determined. In the process of burning poor swelling clay with using organo-mineral additive at temperature 1050 °C constructive quality factor is increased by 70–97% in comparison with the expanded clay obtained from raw materials without additives.

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