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POSSIBILITY OF TUFF WASTE APPLICATION IN THE PRODUCTION OF THERMAL INSULATION MATERIALS

Possible methods of dust, sand and gravel waste involvement during tuff mining for production of modern thermal-insulating construction materials using energy-efficient technologies are presented. The possibility of using the valuable properties of these wastes for the production of modern competitive materials and products, particularly clinkerless binders, artificial porous fillers, foam concrete, etc is described. The volcanic rocks, which have a glass-like structure, i.e. easily modified, give the system sufficient energy potential, which is accumulated in the rock, allowing work to be performed through chemical reaction. The possibility of increasing rock reactivity both by mechanical (crushing, grinding) and chemical methods (creation of basic, sulfate environments) is presented.

It has been theoretically substantiated and practically confirmed that by using the waste materials it is possible to obtain artificial construction conglomerates of various structures using resource-saving technologies and the activities of rocks endowed with nature. The composition of concrete with a cellular structure has been developed and its physical and mechanical characteristics have been brought forth.

Keywords: *tuff waste, energy-efficiency, rock activity, inner energy, specific surface, lime-sand binder, environmental issues, low-basic hydrosilicates and hydroaluminates, heat resistance.*

Introduction

Armenia has large resources of different types of mountain rocks, which, however, are limited; it is necessary to look for ways to use them rationally and effectively. Mining and processing of mountain rocks generate large amounts of waste, which creates serious environmental problems that are constantly intensifying. In particular, the mining and processing of tuff rock generate a large amount of waste, the disposal of which is of great economic and environmental importance [1].

About 60-80% of the mined tuff mass turns into waste, which is due to the cracks of natural tuffs. As a result, a large amount of waste, such as dust, sand and gravel accumulates around the mine, which pollutes the environment and causes serious environmental problems. These wastes are subjected to alkalinization under the influence of atmospheric factors and become a constant pollution source for air, underground water and surface water. Irrigation of land by these waters leads to salinization of land, the regeneration of which requires considerable costs. This wastes are very cheap, but valuable raw materials for the production of modern competitive materials and products, especially clinkerless binders, foam concrete of solid and cellular structure, artificial porous fillers, etc. [2-4].

Main Part

The complex use of mineral raw materials, particularly tuffs, has been and remains a very relevant problem, which is connected with the large amounts of waste generated.

Our republic has a rich raw material base for the production of effective thermal insulation materials, but up to this day such materials are imported from abroad, resulting in a significant increase in their cost. Moreover, the properties of thermal insulation materials and products deteriorate during transportation due to their low strength or fragile structure, and the load-carrying capacity of the vehicle is not fully utilized, as these materials have low average density. Therefore, it is necessary to find ways to organize the production using material and energy-efficient technologies involving various types of industrial waste, which are available in the country in millions of cubic meters and are dangerous in their nature. By involving this waste as the main raw material for the production of thermal-insulating materials and products, it will be possible to reduce the mining of precious mountain rocks, by making the use of natural resources more rational. Thermal-insulating materials are used not only in construction, but also in various areas - for insulation of pipelines, chemical machinery, thermal units, which increases their productivity.

It should be noted that special attention should be paid to the thermal insulation of refrigerators, since the cost of a refrigeration unit is approximately 20 times more expensive than the cost of the corresponding thermal unit [5,6].

Thus, the one effective way of scientific and technological progress is to involve wastes into circulation, which are one of the sources of environmental pollution.

The use of industrial wastes and secondary materials as the main raw material in the production of various construction materials and products contributes to the creation of low-waste or waste–free technologies and at the same time solves social problems, particularly of environmental protection.

On the basis of the above mentioned, the task was set to study the possibility of obtaining effective competitive thermal-insulating materials and products from tuff waste by energy-efficient technological schemes.

The tuff rocks have a glass-like structure, that is, there are crystalline enclosures in the amorphous body, and when these enclosures leave the center, the regular structure is gradually disrupted, giving the rock sufficient energy potential. Thus, rocks with volcanic glass structures are mutable (amorphous), i.e. they can be easily changed, which gives the system sufficient energy potential to work through chemical reactions. Mechanical methods (crushing, grinding) and chemical methods (creating basic sulfate environments) can be used to increase the reactivity of the rocks.

Mountain rock crushing severely disrupts the surface of the particles, resulting in a large number of unsaturated surface bonds. These surface disruptions significantly increase the activity of the materials compared to the original. As the specific surface of the material increases, surface energy also increases, but over time the surface charges neutralize, which leads to a decrease in surface energy and an increase in the inertia of the rock.

Although, according to the Gibbs-Curie principle, an increase in the degree of the material grinding leads to an increase of its solubility and chemical activity [1, 2, 7], the energy potentials increase so much from a certain index of grinding fineness, that a spontaneous aggregation of particles takes place, which leads to a reduction in the specific surface area of the original material. Similar phenomena have been observed in the study of disperse systems based on volcanic rocks [1, 2, 8], and those phenomena have been explained by the fact that with a high degree of grinding fineness, the regulation degree of the volcanic glass structure increases: the mutable state shifts to a metastable (changing-stable) and to a more stable crystalline form (Table 1). Limitations must therefore be imposed on rock grinding and to determine the fineness of grinding each type of volcanic rock experimentally. The optimum grinding rate depends on the chemical activity of the rock: the higher the activity index, the lower the rate of optimum grinding degree of the powder-like material, that is, in the case of a smaller specific surface area of a material, the aggregation of its particles begins.

Under certain conditions, rock energy can be used to synthesize waterproof conglomerates at relatively low temperatures. The criterion of reaction heat is enthalpy, and in case of exothermic reaction the reduction the enthalpy of the system, i.e. free energy is the driving force of the chemical reactions, and entropy increases, i.e., the disorder in the system decreases, which requires additional energy consumption. During the reactions in volcanic aluminosilicate rocks such disorders occur to some extent, which contribute to the production of silicate construction materials by energy-efficient technology.

The specific surface of the original materials together with the hydrothermal treatment regime can have a decisive impact on the phase composition of the new formations, which are crystallizing at the first phase of the synthesis. In the case of small dispersions of original material, low basic hydrosilicate of C-S-H (I) type is formed in two stages. In the first stage, bibasic calcium hydrosilicates are crystallized, which synthesize until all lime is bound, followed by the second stage, during which bibasic calcium hydrosilicates are dissolved and stable low-basic calcium hydrosilicate crystals are formed. At high dispersion rates of the silica-soil component, due to the high activity of its surface, high-basic hydrosilicate is not synthesized even at the stage of temperature increase.

Table 1. Evaluation of tuff rock activity by the amount of absorbed lime (mg/g)

Types of tuffs	Specific surface, m^2/kg		
	200	400	700
Ani	74.6	140.4	57.3
Artik	54.5	73.8	56.1
Aghavnatun	78.1	155.4	56.5
Kosh	79.4	146.4	55.7
Jrvezh	80.2	153.3	55.2
Armavir	70.8	136.6	52.5

The kinetics of silicate formation and the phase composition of new formations are strongly influenced by various additives, for example, mixtures containing aluminium. In this case, there is an increase in strength, which is explained by an increase in the density of the monolith and in the number of new formations. If there is clay soil in the system, the mechanism of silica formation changes. In this case, first hydroaluminates are synthesized, then calcium hydrosilicates [2, 8].

The synthesis of calcium hydrosilicates by the CaO-SiO_2-H_2O system is well covered in the reference. Scientific works by Yu.M. Butt, A.N. Rashkovich, Yu.P. Gorlov and Armenian scientists M.H. Badalyan, L.G. Kalashyan and others are dedicated to it. Similar systems are R_2O-SiO_2-H_2O slug-alkaline systems, which were developed in Ukraine by Glukhovsky V.D. [5, 6, 9, 10].

On the basis of all the developed scientific concepts it has been established that synthetic processes in the earth's crust are similar to processes in industrial conditions, but differ in activation of output components, which, without changing the essence of mineral formation, affects only the duration.

During structural operation, energy efficiency should be taken into account as well. One of the biggest consumers of fuel and energy resources is the utility-household sector. In Armenia, from 2 to 3 times [2] more conventional fuel is spent on heating buildings than for the same purposes in developed countries, and the reason is the non-strict thermal physical requirements for wall materials. Even in new buildings wall materials do not meet strict requirements for thermal resistance.

The traditional wall materials used in Armenia were blocks of mountain tuff rocks for decades, which are not expedient for use as wall material today, as the requirements for thermal resistance have become stricter in modern building standards - HHShN II-7.02-95 [11]. The normative indicators of thermal resistance can be provided only in case of 0.9… 1.2 *m* thick tuff wall. The triple increase in the wall mass, together with the drastic increase in the construction cost, will lead to a significant deterioration of the seismic resistance of the objects under construction.

Products and structures made of autoclaved aerated concrete meet these requirements most. Thanks to the long-term hard work of the Armenian scientists, the technologies for obtaining autoclaved aerated concrete from local raw materials have been developed [12]. Since Armenia is located in a seismically active zone, products made of light autoclaved aerated concrete will increase the seismic resistance of structures by reducing the weight of buildings and structures.

In addition to the technical and economic indicators, wall materials are also evaluated on other indicators, for example, comfort. According to the classification of wall materials in terms of comfort, wooden walls are in the first place, houses with autoclaved aerated concrete walls are in third place, walls of silicate and ceramic brick are in 6-9 places, and reinforced concrete is in last place [4]. Autoclaved aerated concrete house is very close to a wooden house in its operation, but does not burn. It is a material with a great perspective, as it has sufficient strength (5MPa), is easily processed and it is possible to get products of any geometric shape and size [13].

The cellular structure improves the sound insulation properties, which is very important for residential building construction. Besides these important parameters, autoclaved aerated concrete "breathes", it can be sawn, it is able to regulate humidity in the apartment, eliminates the possibility of fungus growth, does not rot, because it is produced from mineral raw material, is environmentally friendly and does not contain dangerous chemical compounds. All these characteristics give reason to consider aerated concrete as one of the best building materials of the 21st century [13]. Aerated concrete is widely used in the West and CIS, where most of them are produced with German equipment [4, 5].

Raw material for the production of building materials should be widespread and environmentally friendly. In nature it is water, carbonate rocks (limestone, chalk, marl) and products of their processing - lime concrete, etc. Comprehensive analysis of radiation safety of raw materials and construction products showed the advantages of using silicate products in residential construction.

Aerated concrete blocks are often produced of lime-sand binder (such as quartz sand) and are reinforced in autoclaves. If the aluminosilicate component is active, the reinforcement process can be performed using energy efficient technology in a heat-moisture processing chamber [2, 8]. Taking into account the requirements for the strength of the blocks and the fact that the Portland cement blocks still have higher strength, during the study it was envisaged to use a mixed lime-cement binder, i.e., partially replace the expensive Portland cement with less energy-consuming lime-sand binding (240 *kg* of conventional fuel is used to obtain 1 ton of Portland cement, and 160 *kg* of conventional fuel for 1 ton of lime) [2, 14].

The binding powder obtained as a result of joint grinding of crystalline silicate component and lime, with a certain ratio is considered clinkerless, because without an aluminosilicate component, lime is an air-binder. Kosh mine tuff wastes have been used for studies, as this type of tuff is highly active (Table 1). Mixed binder compositions have been developed, where the ratio of binder-aluminosilicate component is 1:3, not taking into account that the fraction of sand dust is in the composition of the lime-sand binder. The obtained results are presented in Table 2.

The heat-moisture treatment was carried out with steam heating up to 95 $°C$ in the following mode: 3 hours of temperature increase, 8 hours of isothermal treatment and 3 hours of temperature decrease. After heat-moisture treatment, the samples were dried in laboratory conditions and tested.

Table 2. Physical and mechanical parameters of autoclaved aerated concrete based on quicklime and Kosh mine tuff

Quicklime, %	Cement, %	Gypsum, %	Aluminium powder, %	Physical and mechanical properties	
				density, kg/m^3	Compressive strength limit, MPa (class)
10	10	-	0.02	916	2.2 (B1.5)
10		2.5		940	7.2 (B 5)
15		2.5		938	7.8 (B 5)
15		5.0		944	8.4 (B 5)
10		-	0.03	876	1.9 (B1.5)
10		2.5		890	6.2 (B 5)
15		2.5		894	6.5 (B 5)
15		5.0		895	7.1 (B 5)

Gypsum in the system is an additive or sulphate activator, the presence of which sharply increases the process of hydrolysis of volcanic rock, alkaline extraction of the soluble alkali component, which leads to a drastic increase in condensation of the system.

The alkali, being electrolytes, increase the ionic potential of the solution, enriching it with OH- ions, thereby increasing the solubility of the system's original materials, contributing to the formation of silica gel.

Conclusion

The high strength of lime-aluminosilicate binding material is conditioned by physical and chemical processes that occur in the system and lead to the formation of cement stone. The composition of these new formations depends on the CaO and SiO_2 ratio, the fineness of the grinding, the structure of the aluminosilicate component and the temperature of reinforcing.

Low basic calcium hydrosilicates and hydroaluminates are mainly formed by heat-moisture treatment. Calcium hydrosilicate from hydrolysis of cement alite mineral - $Ca(OH)_2$, can also be involved in the formation process of structure-forming by chemically binding to the active silica soil and alumina soil in the system, bringing forth new formations of tobermorite and hydrogranate type. The structure of the aluminosilicate component is very important, because the temperature of the chemical binding capacity of lime depends on the structure.

Autoclaved aerated concrete is one of the wall materials with the best properties of the 21st century, which can meet the requirements of thermal resistance, reducing the mass of the structure. It can be produced with various binders, including clinkerless, mixed, cement, which can be produced with the involvement of tuff waste as the main component, present in large quantities in our country. In addition, the cellular structure contributes to the improvement of sound insulation properties, which is very important for residential construction.

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