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Physico-Chemical Processes for the Production of Agloporite From Industrial Waste in Uzbekistan

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Abstract: The possibility of obtaining high-quality porous agloporite material with high physical and mechanical properties based on local clay raw materials and industrial waste from the Tashkent industrial region has been established. The effect of chloride roasting, whose components are phosphogypsum industry waste and alkaline soda waste, on the mechanism and kinetics of mineral formation during agglomeration of agloporite gravel, is studied. It was established that the used waste - mineralizers accelerate the process of glass formation during chloride firing, reducing the temperature of agglomeration and pressing by 50-80 ^{o}C, while obtaining a durable porous material. The regularities of the influence of physicochemical features, used clay materials and flotation waste of the Almalyk mining and smelting complex on the mechanism of mineral and pore formation during agglomerate agglomeration are revealed..

Keywords: agloporite, physicochemical properties, mechanism, kinetics, expansion, chloride firing.

Introduction

During the enrichment of metallurgical ores, a huge amount of waste is generated. No other type of human industrial activity affects the environment as extensively and destructively as mining. In the sphere of its direct influence are the water and air basins, the earth's surface, subsoil, fauna and flora - all elements of the natural environment. On the other hand, in the process of mining and processing of minerals, a significant amount of various wastes of direct production is generated, which often significantly exceeds the mass of marketable products. Therefore, their integrated use is not only the basis of waste-free production, but also serves as a radical means of reducing the technogenic load on the natural environment and an important source of saving labor and natural resources.

The economic significance of the problem of using secondary material resources lies in the fact that its correct solution allows: increasing the types of raw materials, reducing the use of natural raw materials; to prevent the loss of a large amount of land, including those important for agricultural production, which are occupied by dumps for waste and by-products; avoid high costs for the creation of warehouses, storage facilities, dumps; improve the technical and economic indicators of industries.

The use of waste and by-products in the building materials industry gives a great economic effect due to a reduction in the cost of production, fuel, electricity and capital costs. Raw materials or components that are made from waste are cheaper than raw materials that are made specifically from natural materials. Current investments in the use of certain types of waste are reduced by (30–50%). In addition, it should be remembered that the known reserves of natural raw materials are increasingly depleted and moving away from industrial regions.

At present, much attention is paid to energy saving issues. One of these areas is the use of building materials with thermal insulation properties. Agloporite is widely used as a heat-insulating material for the manufacture of lightweight concrete and heat fillings.

Agloporite is a porous granular material of a cellular structure obtained by swelling of clay rocks during their firing. Complex physical and chemical processes occur in the fired clay material in different temperature ranges: dehydration, burnout of organic impurities, interaction between clay components, redox reactions, and others, which causes gas evolution, melt formation, softening of the material. With rapid firing, the temperature intervals approach, shifting to the region of high temperatures, which makes it possible to combine the process of gas formation with the softening of the material and the achievement of a certain viscosity, at which the clay swells. In this case, it is important that by the time of intense gas evolution, the surface layer of the granules should be sintered with the formation of closed pores. Otherwise, the gases are easily removed through the layer of material without swelling it.

According to the degree of swelling, weakly, medium, and well-swelling clayey rocks are distinguished with a swelling coefficient of at least 2.5, respectively, or from 2.5 to 4.5 and higher.

The existence of different opinions about the causes of swelling and pore formation in clay raw materials during its high-temperature heat treatment to obtain agloporite and the inconsistency of some of these opinions indicate insufficient knowledge of the main factors of swelling and pore formation (1-4).

In this paper, we studied the possibility of obtaining a heat-insulating material - agloporite based on the use of technogenic products, by recycling various industrial wastes, as well as overburden clayey rocks and studying the effect of their physical and chemical properties on the mechanism and patterns of formation of porous agloporite.

For this purpose, clay materials and flotation wastes of the Tashkent industrial region were considered as raw materials in the production of aggloporite.

Research methods and materials used

According to the results of preliminary studies, it was found that the most accessible and suitable materials for these purposes are overburden clay rocks of the Akhangaran deposit of loess and gray unenriched kaolin of the Angren coal basin, and as the main aluminosilicate component, the flotation tailings of the lead and copper processing plants of the Almalyk Mining and Metallurgical Plant (5,6) . As mineralizers of agglomeration and swelling processes, and as a chlorinator of residual metals contained in tailings, solid alkaline waste from soda production and phosphogypsum - waste from phosphoric acid production were used.

Table 1. The chemical composition of the materials used

Names	SiO_2	Al_2O_3	Fe2O3	CaO	MgO	Na2O	K2O	SO3	Ppp
Floating waste MOF	59,32	13,86	9,31	1,16	0	2,31	3,14	6,02	4,18
Flotation waste SOF	45,7	8,72	7,1	14,59	7,10	2,00	0.98	2,98	8,83
Unenriched kaolin	58,6	18,95	1,87	3,91	0,53	0,12	1,11	0,12	14,72
Less	49,29	11,66	4,41	13,97	3,28	1,44	0,80	1,30	13,29
Phosphogypsum	10,43	0,420	0,15	28,32	-	0,04	0,04	40,51	19,64
Waste TOSP	1,1	0,4	-	47,1	4,2	-	-	3,8	42,40

The study of the used components of raw mixtures was carried out by a number of physical and chemical methods of analysis: X-ray phase, petrographic and infrared - spectroscopic, mineralogical.

X-ray phase analysis of the materials used showed differences in their chemical and mineralogical composition, which certainly indicates a completely variable effect on the processes of solid-state transformations occurring during firing, the temperature of the onset of the formation of the liquid phase and swelling of aggloporite, on the degree of swelling and a number of other physicochemical processes occurring during the agglomeration of silicate mixtures.

The flotation waste from the copper concentrating plant (MOF) - dark gray in color, is formed during the enrichment of copper-bearing ore, it is an aluminum-iron silicate substance. The results of chemical analysis of flotation waste samples showed their little changeable chemical composition. The samples are characterized by a high content of silica, reaching 63% and its melting point is 1220-1240 ^oC.

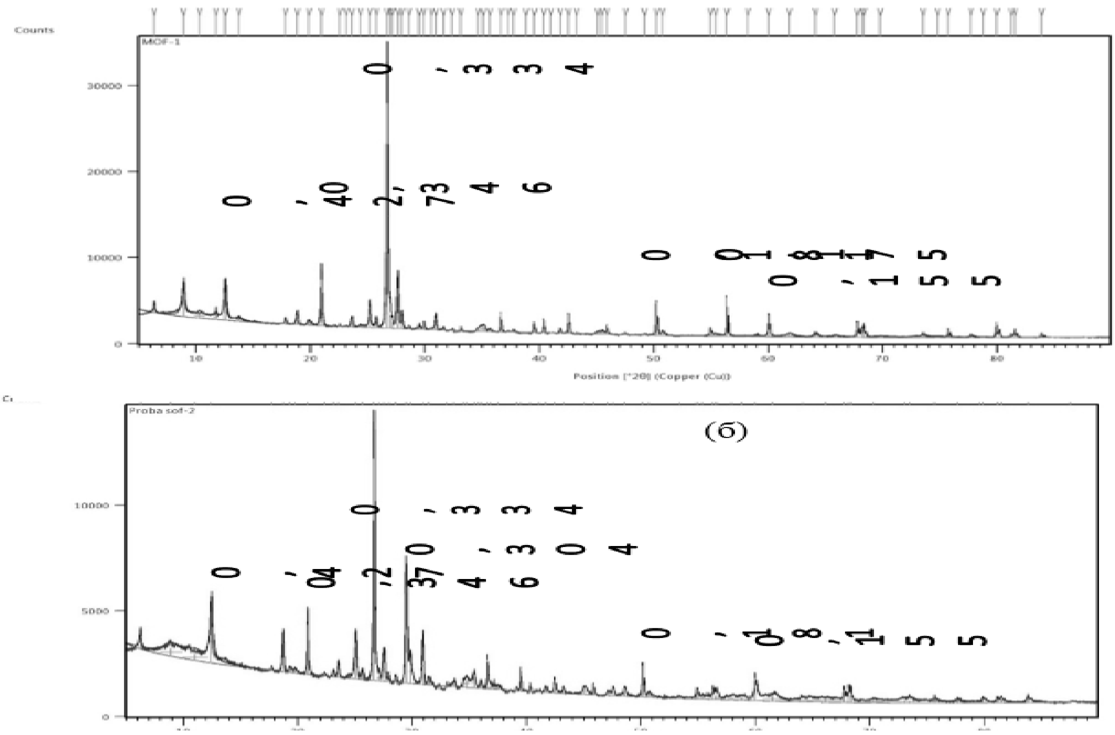

Figure 1. X-ray patterns of flotation wastes: a) MOF-copper-concentrating and b) SOF of the lead concentrator

The main minerals are quartz (up to 40%), feldspar (10%), hydromica (23%) and a small amount of calcium and magnesium carbonates. X-ray patterns of the MOF flotation waste burned at different temperatures show characteristic maxima of quartz d=0.3344; 0.181; 0.153 nm, feldspar d=0.200; 0.166 nm, hydromicas d=0.441; 0.254; 0.148 nm, hematite d=0.370; 0.471; 0.499 nm, gelenite d=0.247; .284; 0.364 nm.

Dump tailings of the lead concentration plant (SOF) of the Almalyk Mining and Metallurgical Combine are formed during the flotation enrichment of lead-containing ore and are a free-flowing, sandy material of gray color, with a grain size of 1-3 mm and a moisture content of 3-5%. The main constituents of tails are; oxides of silicon, calcium, aluminum and magnesium with the following mineralogical composition: quartz, calcite, dolomite, feldspar. As noted in a number of studies (7-10), clays containing silica in an amount exceeding 65% are in most cases unsuitable for the production of agloporite and expanded clay. As the content of SiO_2 increases and the content of Al_2O_3, Fe_2O_3, MgO, Na_2O K_2O decreases, the swelling of clayey rocks decreases. A feature of the chemical composition of the studied clays is a low content of iron oxide - up to 5%. The granulometric composition of the clays of these deposits are similar and are characterized by a low content of large particles (1-0.005 mm), a high content of silty particles (0.05-0.005 mm) and a low content of particles of fine fractions. At the same time, the granulometric composition of flotation tailings differs in particle size from the natural clays used. The degree of swelling is greatly influenced by all oxides contained in clays and flotation tailings, so the optimal content should be, according to some studies, in the range of 17-22%, as the alumina content decreases, the swelling of clays decreases sharply. Also in the works (7,8) it was found that as the ability to swell in clay materials decreases, the content of MgO decreases markedly, the introduction of which in the composition of alkaline waste from soda production causes, as shown further, their swelling during chloride firing. In addition, it is known that an increase in the CaO content above 3-4% sharply worsens the sintering of granules during firing, and the content of alkaline oxides of potassium and sodium above 3-4% increases the swelling of the granules. A number of scientific data (9, 10) have shown the dependence of the physicomechanical parameters of aggloporite on the physicochemical properties of the raw materials used, when the optimal chemical and mineralogical composition of the raw mixture makes it possible to greatly reduce the temperature of formation of the liquid phase and firing and increase pore formation and strength characteristics. Summarizing the above, it should be noted the possibility of using the proposed rocks and waste as a raw material for the production of agloporite.

Experimental Raw materials were first dried and ground in a laboratory ball mill to a specific surface area of 1300-1500 g/cm2. Then the components were weighed in the required quantities and mixed dry. After that, water was added to the dry mixture. Granules 10-15 mm in diameter were made from the resulting mixture and fired in an electric muffle furnace with silicate heaters to temperatures of (1000, 1100, 1200) °C.

Physical and chemical studies have established that raw mixtures with MOF flotation waste have a higher swelling ability compared to mixtures based on SOF flotation waste, while at the same time, from clay materials, kaolin from the Angren deposit is also preferable in comparison with the forest of the Akhangaran deposit in terms of its chemical and mineralogical properties. characteristics. The temperature of the beginning of the formation of the glass phase and the completion of the agglomeration of raw mixtures based on the flotation wastes of MOF and SOF with the addition of wood and kaolin clay as an intumescent material, without mineralizers and with their participation, was determined, as a result of which the regularities of the influence of the physicochemical properties of the components on the agglomeration process were established. It is shown that the temperature of the beginning of swelling of aggloporite, and this process itself is directly dependent on the chemical and mineralogical composition of the initial components, so unenriched kaolin significantly increases the swelling of aggloporite. Therefore, further studies were carried out in mixtures with unenriched kaolin (Table 2).

Table 2. Compositions of the studied raw mixes for agloporite

Raw mix №	Kaolin	HMOF waste	SOF waste	Coal	Phosphogypsum
1	10,0	85,0	-	5,0	20,0
2	15,0	80,0	-	6,0	30,0
3	20,0	73,0	7,0	30,0	30,0
4	10,0	-	5,0	15,0	30,0
5	15,0	-	80,0	6,0	30,0
6	20,0	-	73,0	7,0	30,0

Chloridny objig syrevyx smesey providolsya v temperaturennom intervale 1000-1200 oS, c dobavkoy ot 10 do 30% phosphogypsa i schelochnogo othoda, v vide granule 10-15mm mixed v corundum tygli. In the case of conducted experiments, it was established that the temperature of the appearance of the glass phase and the final agglomeration of 50-100 °C in the sulfochlorite objige occur, and the resulting material has a pronounced porosity.

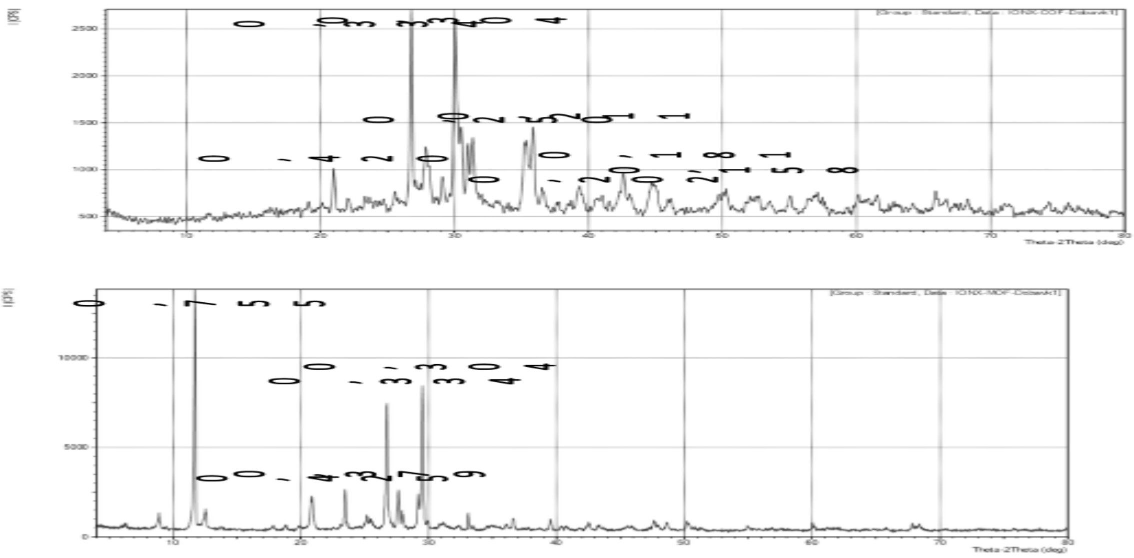

Figure 2. X-ray patterns of obtained aggloporites a) based on SOF flotation waste, b) based on flotation waste MOF with sulfochloride additive 30% alkaline waste + 30% phosphogypsum

X-ray phase and petrographic methods have been used to study the effect of sulfochloride roasting on the mechanism and kinetics of agglomeration of agglomeration crushed stone, and it has been shown that at a temperature of 800-900 ^{o}C in raw mixtures, decomposition of the initial minerals - feldspars with d=0.200; 0.166 nm, hydromica with d=0.441; 0.254; 0.148 nm, $CaCO_3$ with d=0.303; 0.191; 0.187 nm with the formation of new mineral phases in mixtures with MOF tails at Tobf=950-1100 ^{o}C mullite with d=0.211; 0.220; 0.339 nm, gelenite c d=0.285; 0.243 nm, calcium aluminate with d=0.297; 0.252 nm, in agloporite with SOF tails additionally okkermanite with d=252 nm, wollastonite with d=0.329 nm (Fig. 2).

When determining the temperature range of sintering and swelling for mixtures of unenriched kaolin with flotation waste from a copper concentrating plant, the best results were obtained for samples from Angren unenriched kaolin with the addition of alkaline waste from soda production and phosphogypsum in various amounts; Tobzh 1160-1190 ^{o}C and with the addition of 30% alkaline waste and 30% phosphogypsum, there is a decrease in T obzh. up to 1100-1140 ^{o}C, and the swelling coefficient of agloporite increases from 2.5 to 3.5 (Table 3). The coefficient of swelling of clay raw materials without additives and with additives is determined as the ratio of the volume of an expanded granule to the volume of a semi-finished product granule. The volume of each grain of a semi-finished product of stone-like raw materials, expanded clay crushed stone and gravel is determined according to GOST 9758 and calculated by the formula $V = (\pi D^2 / 4)h$.

The coefficient of swelling of clay raw materials is determined by the formula

$$K_{всп} = \frac{\sum_1^n V_2}{\sum_1^n V_1}$$

where is the $\sum_1^n V_1$ sum of the volumes of granules (grains) of the semi-finished product supplied for expansion, cm; $\sum_1^n V_2$ - the sum of the volumes of expanded granules of expanded clay gravel and expanded clay crushed stone, see.

Table 3.The swelling temperature of optimal formulations

Compounds №	Composition of components in%						T°C	Coefficient To, swelling
	Kaolin	HMOF waste	SOF waste	Coal	SHOSP	Phosphogypsum		
1	10	85	-	5	20	20	1130	2,9
2	15	80	-	7	30	30	1110	3,6
3	20	75	-	6	20	30	1120	3,2
4	10	-	85	5	20	20	1150	2,7
5	15	-	80	7	30	30	1140	3,1
6	20	-	75	6	20	30	1145	3

Presumably, on the basis of the physical and chemical studies carried out, the reaction mechanism during the synthesis of agloporite with flotation waste MOF and SOF proceeds according to the following scheme, at a temperature of 900-1000 ^{o}C, dehydration of clay minerals and iron hydroxide and crystallization of hematite and gelenite occur. At these temperatures, processes occur in the material, the most important for the formation of the structure of agloporite.

Inside the layer, with a lack of oxygen, the environment is reducing, therefore ferrous oxides are reduced to FeO, which contributes to the intensive formation of the liquid phase, in addition, a sulfochloride additive serves as a smooth decrease in the temperature of the formation of the liquid phase, resulting in a decrease in the agglomeration completion temperature by 50-80 ^{o}C. Sintering occurs inside the granules and at their contacts. The loose layer turns into sintered, but porous due to the suction of gases. Clay and mica impurities partially swell, causing the formation of a certain proportion of closed pores in the material.

It has been established that the used mineralizers accelerate the process of glass formation during sulfochloride firing, reducing the agglomeration temperature by 50-80 ^{o}C, obtaining a durable porous material. Regularities of the influence of physical and chemical features of the used clay materials and flotation tailings of the Almalyk Mining and Metallurgical Plant on the mechanism of mineral and pore formation during sulfochloride roasting are revealed. As a result of the experiments, materials were identified that meet the requirements for chemical and mineralogical composition to obtain aggloporite with such properties as a high degree of pore formation, strength and low agglomeration temperature. Raw mixtures of unenriched kaolin and flotation waste from a copper processing plant (MOF) with the integrated use of phosphogypsum agglomeration process and alkaline waste from soda production as a mineralizer, which, as established by a complex of physicochemical methods, positively affect the kinetics of agglomeration and pore formation of aggloporite crushed stone.

It has been established that raw mixtures based on MOF flotation waste have a higher swelling capacity compared to mixtures based on SOF flotation waste.

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