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Features of chemical-mineralogical composition and processing properties for medium-ferrous bauxites

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Abstract. The features of chemical-mineralogical composition and processing properties of bauxites from Iksinsk and Severoonezhsk deposits are investigated in the paper. It is found that the studied bauxites are coarsely dispersed and low-dispersive, high-alumina clay raw materials with a high content of colouring oxides. According to their mineralogical composition, Iksinsk and Severoonezhsk bauxites are boehmite-hydrargillite-kaolinite clay bauxites. Moreover, Iksinsk bauxite samples are characterized by the total absence of quartz impurities. The samples of plastic molding based on Iksinsk bauxites are fully sintered at 1500 °C with the formation of strong structures with a compressive strength of 70-120 MPa (depending on the variety of bauxites). The samples based on Severoonezhsk bauxites are fully sintered at 1450 °C, and they are characterized by a compressive strength to 70 MPa in the sintered state.

1 Introduction

Currently, oil and gas industry has faced a serious problem of keeping up the achieved level of oil production, which can be stabilized by intensification of old well operation. In this regard, Russian oil and gas industry pays much attention to the prospects of using hydraulic fracture for oil-and gas-bearing formations. These operations cannot be conducted without using a granular material – a proppant. It acts as a proppant agent and prevents a fracture closure in the process of fluid extraction [1].

Numerous studies and practical applications have allowed giving preference to the ceramic technology in proppant production, as far as ceramic proppants combine a high strength, low bulk density, chemical resistance, and high conductivity. Granular materials of the high and medium strength can be used as ceramic proppants. On a large scale, they have the alumina or silica-alumina composition of natural raw materials, mainly, bauxites or refractory clays and kaolins [2].

Production of ceramic proppants is connected with high energy costs, which can be cut by using inexpensive local aluminosilicate clay raw materials.

Therefore, the aim of this work is a comprehensive study of the bauxites from Severoonezhsk (mark GB-1) and Iksinsk deposits (marks GIO-2 and GIO-5) of

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Arkhangelsk region in order to use them in the technology of aluminosilicate ceramic proppants.

2 Chemical and mineralogical features of studied bauxites

Severoonezhsk bauxite area is formed with the bauxites of a sedimentary origin. Three largest deposits in Severoonezhsk bauxite area are: Iksinsk, Plesetsk, and Denislavsk. Iksinsk deposit is situated in the north-west of the European part of Russia, Plesetsk district of Arkhangelsk region. It is represented by six deposits, and it is located on both banks of the Onega. The total area of the deposit is about 120 km^2 with a thickness of a layer from 0.8 to 16.0 m [3]. The distinctive feature of Iksinsk bauxite deposit is a high content of alumina along with a high content of silica and relatively low amounts of iron oxides. It is not typical for the other bauxite deposits in the world [4].

The analysis of granulometric composition for the tested samples of bauxites defined in accordance with GOST 21216.2-81 shows that the samples of Iksinsk clay bauxites are low-dispersive materials, and Severoonezhsk bauxites are coarsely dispersed raw materials (Table 1).

Table 1. Granulometric composition of studied bauxites

Sample code	Content,%, fraction size, mm				
	1-0,06	0,06-0,01	0,01-0,005	0,005-0,001	< 0,001
Bauxites of Iksinsk deposit					
GIO-2	9,97	27,99	7,76	25,28	29,00
GIO-5	14,79	37,65	7,52	19,08	20,96
Bauxites of Severoonezhsk deposit					
GB-1	28,45	68,65	0,96	-	1,94

Initial visual inspection of raw bauxite samples indicates that tested sample GIO-2 of Iksinsk bauxite contains the lowest amount of iron oxide, as far as it has a creamy colour. Tested sample GIO-5 has a red color, GB-1 is a light brown one, indicating the higher Fe_2O_3 content in their gross chemical composition. This fact is confirmed by the chemical analysis (Table 2).

Table 2. Chemical composition of studied bauxite in calcined state

Type of raw materials	Content of oxides, wt. %								
	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	MnO
Bauxites of Iksinsk deposit									
GIO-2	11,70	77,14	4,60	3,94	0,22	1,53	0,65	0,19	0,04
GIO-5	25,91	59,92	4,33	7,34	0,52	1,19	0,57	0,20	0,04
Bauxites of Severoonezhsk deposit									
GB-1	20,84	62,26	1,75	10,45	0,05	4,39	0,07	0,03	0,16

It is observed that both investigated samples of Iksinsk bauxite deposit are high alumina rocks (Al_2O_3 content – 60-77 wt.%) with a low content of alkaline and alkaline-earth oxides, and also with a high content of Fe_2O_3 (from 3.94 to 7.34 wt.%) and TiO_2 (from 4.33 to 4.60 wt.%) colouring oxides.

Severoonezhsk bauxite belongs to the ferrous type of bauxite with a high content of silica (20.84 wt.%), a high alkaline oxide content (the total content of 0.1 wt.%), and alkaline-earth oxides (the total content of 4.44 wt.%). In addition, this material belongs to high-alumina raw materials due to Al_2O_3 content of 62 wt. %.

In order to determine the mineralogical composition of the studied bauxite rocks, X-ray and integrated thermal analyses have been carried out.

The analysis of the results obtained while processing the diffraction patterns of Iksinsk bauxite samples indicates their qualitative identity. The difference is in the intensity of corresponding X-ray reflections, which allow making indirect conclusions about the quantitative content of minerals identified (Figure 1).

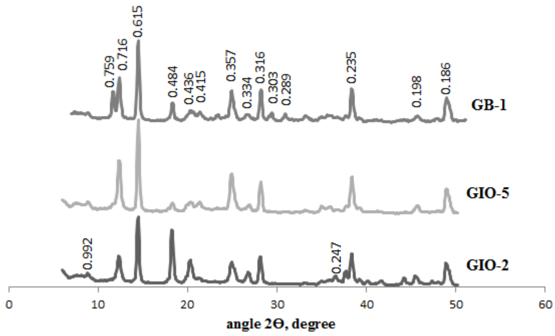

Figure 1. X-ray diffraction patterns of bauxites from Iksinsk (GIO-2, GIO-5) and Severoonezhsk (GB-1) deposits

The studied Iksinsk bauxites are polymineral clay-containing rocks, which are formed with a mixture of such clay minerals as kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (reflections with the interplanar distances of 0.717 - 0.720, 0.356, and 0.247 nm), with a low content of hydromica of an illite type $0.2 \cdot K_2O \cdot Al_2O_3 \cdot 3SiO_2 \cdot 1{,}5H_2O$ (0.992; 0.440 nm). X-ray kaolinite reflections are well-defined and rather intense, and this fact confirms its dominant content in the mixture with hydromica (illite) and its high crystallinity.

The mineralogical composition of Iksinsk bauxites has a special feature: it is the presence of aluminous minerals in the form of alumina hydrates of different water content – hydrargillite (gibbsite) $Al_2O_3 \cdot 3H_2O$ (differential peaks with the interplanar distances of 0.484 and 0.316 nm), and boehmite $Al_2O_3 \cdot H_2O$ (differential peaks with the interplanar distances of 0.615 and 0.185 nm), with a prevalence of the latter in both samples. In the case of GIO-5 sample, the prevalence of boehmite is particularly high (Figure 2). It means that the sample of bauxite will have less mass loss on calcination, and the fired samples based on GMO-5 will be characterized by lower shrinkage values.

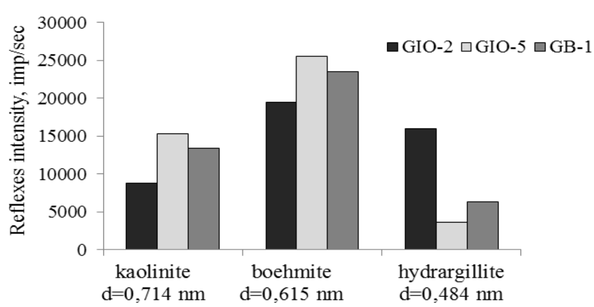

Figure 2. Intensity of X-ray reflections for basic minerals (kaolinite, d – 0.714 nm, boehmite, d – 0.615 nm, and hydrargillite, d – 0.484 nm) in X-ray diffraction patterns of Iksinsk and Severoonezhsk bauxites

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The X-ray diffraction pattern of Severoonezhsk bauxite GB-1 is almost identical to the diffraction patterns of Iksinsk bauxites (Figure 1), and this confirms the closeness of their mineralogical composition.

The conclusions concerning the features of the mineralogical composition in Iksinsk and Severoonezhsk bauxites (according to the X-ray analysis) are consistent with the results of a complex thermal analysis for the investigated raw materials. The presence of kaolinite in the mineralogical composition of the studied clay bauxites is confirmed by the endothermic effect in DSC curves at 520 °C, and exothermic effect at 970 °C. The endothermic effect is associated with the removal of chemically bound water from a kaolinite lattice. The exothermic effect is caused by decomposition of the kaolinite lattice (Figure 3, 4). The high intensity of the endothermic effect with a minimum at 270-290 ° C caused by decomposition of hydrated aluminous minerals, DSC curve (Figure 3, 4) and GIO-2 samples confirm that its mineralogical composition has a large amount of watery alumina hydrate in the form of $Al_2O_3 \cdot 3H_2O$ hydrargillite, in comparison with sample GIO-5.

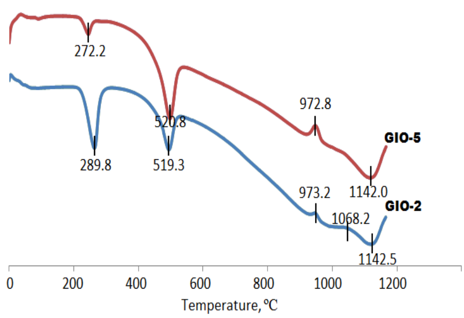

Figure 3. DSC curves of Iksinsk bauxite deposit

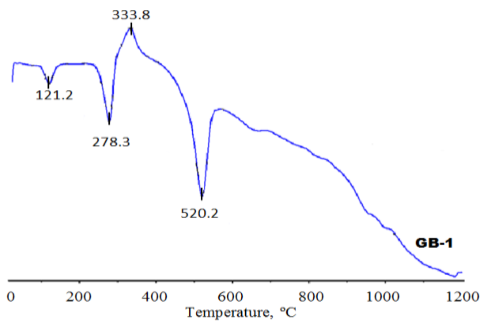

Figure 4. DSC curves of Severoonezhsk bauxite deposit

Thus, both Iksinsk and Severoonezhsk bauxite samples are varieties of a clay bauxite boehmite-kaolinite hydrargillite-type, and this agrees well with the data of their chemical composition.

3 Behaviour of studied bauxites at firing and sintering

Chemical and mineralogical characteristics of the investigated bauxites influence their behaviour at firing. So, sintering both samples of Iksinsk deposit is fully completed at the temperature of 1500 °C, which is proved by achieving water absorption values of less than 2% in the samples (Figure 5).

Moreover, the strength characteristics of the sintered samples of plastic molding from test sample GIO-5 (115-120 MPa) is almost 2 times higher than the strength characteristics of the samples from test sample GIO-2 (53-70 MPa). This feature may be associated with the difference in the ratio of minerals synthesized at firing.

Severoonezhsk clay bauxite (GB-1) is fully sintered at 1350 °C, providing the formation of sufficiently strong structures with mechanical properties (a compressive strength) at the level of 60-70 MPa (Figure 5).

Investigations of phase formation processes at Iksinsk bauxite heating from 1100 to 1400 ° C show that in the process of firing corundum is synthesized as a product of thermal decomposition of alumina hydrates, which are present in the initial samples in the form of boehmite and hydrargillite. In addition, the synthesis of mullite from kaolinite is observed, which is present in the mineralogical composition (Figure 6). A greater amount of mullite is found in the fired products of test sample GIO-5, and this mullite contributes into glass phase reinforcement. This fact could explain the higher strength characteristics of the fired samples based on the given bauxite.

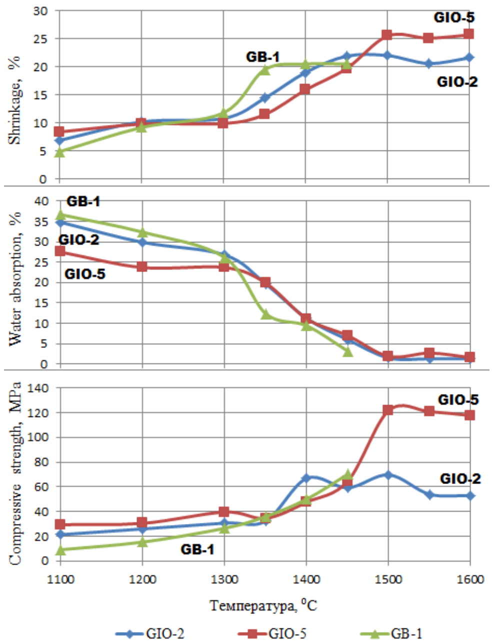

Figure 5. Sintering curves of Iksinsk and Severoonezhsk bauxites

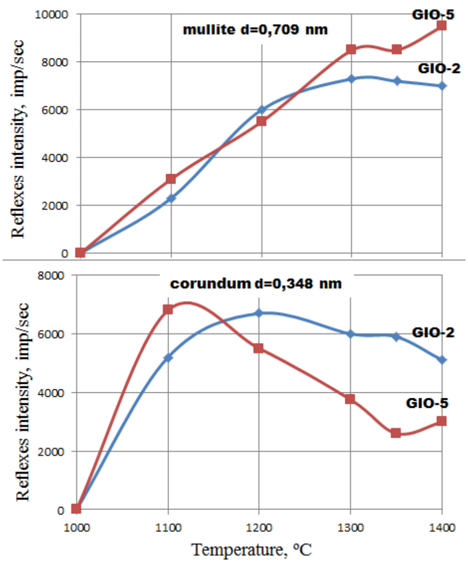

Figure 6. Intensity of X-ray reflections of main crystalline phases (mullite and corundum) in the sintered Iksinsk bauxite samples

It is necessary to take into consideration the fact that during the mullite synthesis from kaolinite amorphous silica is released, which can partially dissolve in the melt, and, partially, it is crystallized in the form of cristobalite. Consequently, the decrease of corundum reflection intensity at temperature increase up to 1400 °C (especially, with test sample GIO-5) is caused, probably, by its binding with this silica into the secondary mullite. A total absence of the fired Iksinsk bauxites with a silica component in the diffraction patterns can also be explained by the formation of the secondary mullite from the decomposition products of alumina hydrates and kaolinite.

4 Conclusion

Investigations of physical-chemical and structural-mineralogical characteristics of medium-ferrous bauxite rocks from Iksinsk and Severoonezhsk deposits (GIO-2, GIO-5, and GB-1), and high strength characteristics of plastic molding samples on their basis show that this raw material has a potential for its application in the technologies for aluminosilicate ceramic proppants of a high strength, which can withstand the pressure of 70 MPa.

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