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A. A. Biryukova[1, 2], T. D. Dzhienalyev[1], A. V. Boronina[1]

[1]JSC «Institute of metallurgy and ore benefication», Almaty, Kazakhstan,
[2]NJSC «The Kazakh National Research Technical University after K. I. Satpaev».
E-mail: biryuk.silikat@mail.ru

OVERBURDEN ROCKS OF KEMPIRSAI DEPOSITS OF CHROMITE ORE – RAW MATERIALS FOR PRODUCTION OF CERAMIC PROPPANT

Abstract. The aim of this work is to estimate the overburden rocks formed during the development of Kempirsai chromite deposits as a raw material for the production of ceramic proppants. The chemical-mineralogical composition of overburden rocks of Kempirsai chromite deposits was studied using chemical, microscopic and X-ray diffraction analyzes. It is established that the main mineral of overburden rocks is serpentine, present in the form of fibrous chrysotile and lamellar antigorite. In the impurities are iron oxides and hydroxides, carbonates, quartz. Technological assessment of the use of overburden rocks as a raw material for the production of ceramic proppants was carried out. The interval of sintering of overburden rocks was determined at 1280-1300 °C. The optimum temperature of sintering firing of ceramics based on this type of raw material is 1300 °C. The effect of preliminary heat treatment of raw materials on the properties of magnesium silicate ceramic proppants was studied. A positive effect of heat treatment of the raw material at a temperature of 1000 °C on the formation of the structure and hardening of magnesian-silicate composition samples was established. Magnesium silicate proppants based on overburden rocks were obtained with the following properties: apparent density – 1.6 g/cm^3, strength resistance (52 MPa) – 14%, sphericity and roundness – 0.8; chemical resistance (hydrochloric acid) – 98%, static strength of the fraction 16/20 – 72-118 N/granule. The field of application is oil and gas production, metallurgy and ceramic industries.
Keywords: ceramic magnesium silicate proppant, overburden, minerals, phases, serpentine, chrysotile, antigorite, porosity, water absorption, strength, structure, apparent density.

Introduction. Hydraulic fracturing to increase the productivity of oil wells is ever more used in global practice of oil and gas production. Hydraulic fracturing is a technique of creating artificial fractures in the rock. An essential attribute of hydraulic fracturing are proppants - natural or artificial ones.

The process involves injection of fracking fluid with proppants into well. Proppants hold the fractures open and create a permeable proppant pack. It results with significantly increase of oil recovery due to involvement to development weakly drained zones and interlayers.

Aluminosilicate proppants are mainly used among all ceramic proppants [1-10]. However, there are difficult to develop oil fields with their own characteristics, which require using of proppants with a specific given set of properties. Therefore, the compositions, properties and technologies of ceramic proppants are constantly being improved. Currently, applied research of magnesium silicate proppants is being actively carried out [11-17]. Prospectivity of such proppants is that the main raw materials for their production are the available natural magnesium silicate rocks (dunites, olivinites, talc, serpentinites), wastes from mining, refractory and metallurgical industries [11-12, 14].

During the mining and processing of Kempirsai chromite deposits (Kazakhstan), a large amount of overburden and ore enrichment tailings is formed. Involving all these types of raw materials in production will make it possible to use the mineral resources of the region with minimal losses of mineral components at the same mining costs.

The aim of this work is to estimate the overburden rocks which have magnesium silicate composition as a raw material for the production of ceramic proppants.

Experimental methods. The chemical-mineralogical composition of raw materials and structural-phase transformations during heat treatment of ceramic compositions has been investigated by means of chemical, X-ray diffraction and microscopic methods of analysis. Ceramic samples were molded by using techniques adopted in the technology of ceramic and refractory materials.

Technical properties of ceramics were determined according to the following GOSTs: 2409-80 "Refractory materials and products. Method for determination of water absorption, apparent density, open and general porosity", 4071-80 -"Refractory products. Method for determining the compressive strength limit ", GOST R 51761-2013" Magnesium-silicate proppants".

Chemical analysis of raw materials was carried out in a specialized laboratory for certified methods.

X-ray diffraction analysis of the raw materials and synthesized compositions was carried out on a diffractometer D8 Advance (BRUKER).

Thermal analysis of samples overburden was conducted using simultaneous thermal analyzer STA 449 F3 Jupiter. Heating was carried out at a rate of 15 °C/min and cooling at a rate of 17 °C/min, under highly purified argon atmosphere. The results were processed using the NETZSCH Proteus software.

Experimental processing and discussion of research results. Studies were conducted on the overburden rocks from the Kempirsai chromite deposits. The samples of overburden rocks were represented by stone-like material of different sizes.

Pieces of rocks have different colors (gray, grayish-marsh, dark-marsh, light with yellow coating, etc.). Despite the difference in color, they all represent an ultramafic rock - serpentinite, containing various impurity minerals.

The main mineral of the raw material is serpentine, a transparent anisotropic phase (Nm = 1.56) with low birefringence and wavy extinction. The shape of the grains is fibrous (chrysotile) and lamellar (antigorite) (figure 1). Less common are formations of the ophite in the form of a colorless isotropic mass with a lowered refractive index (Nm = 1.54). Also there are various impurity minerals. Identified impurity minerals in the raw materials are shown in fFigure 1.

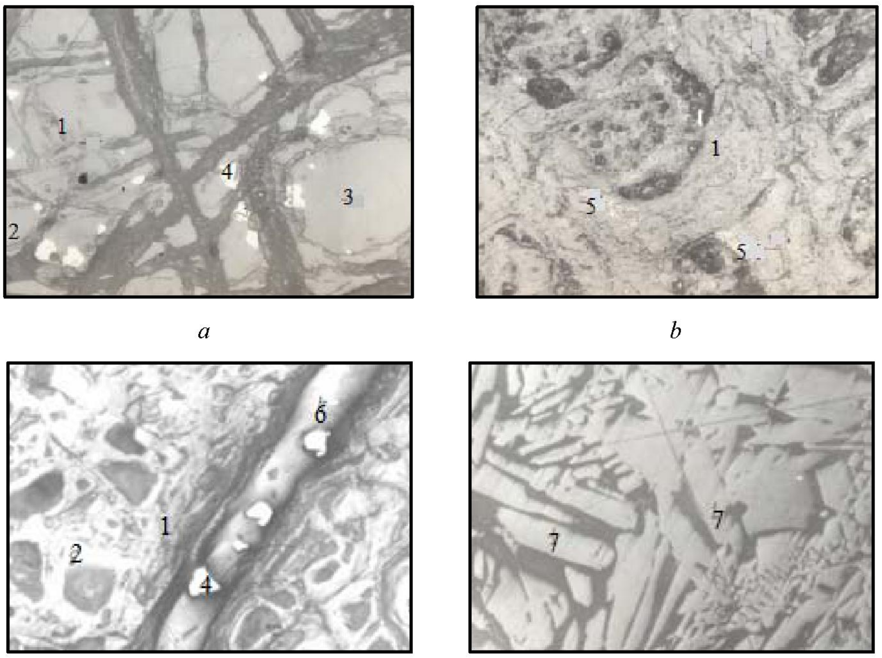
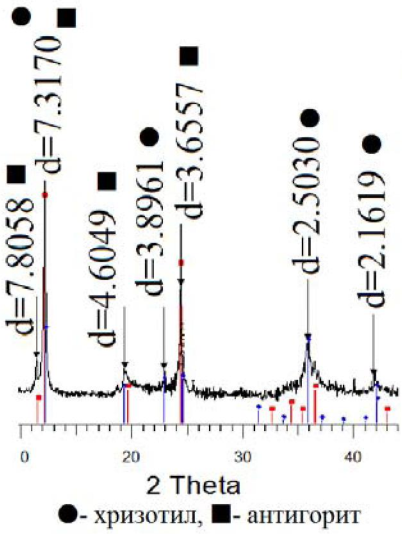
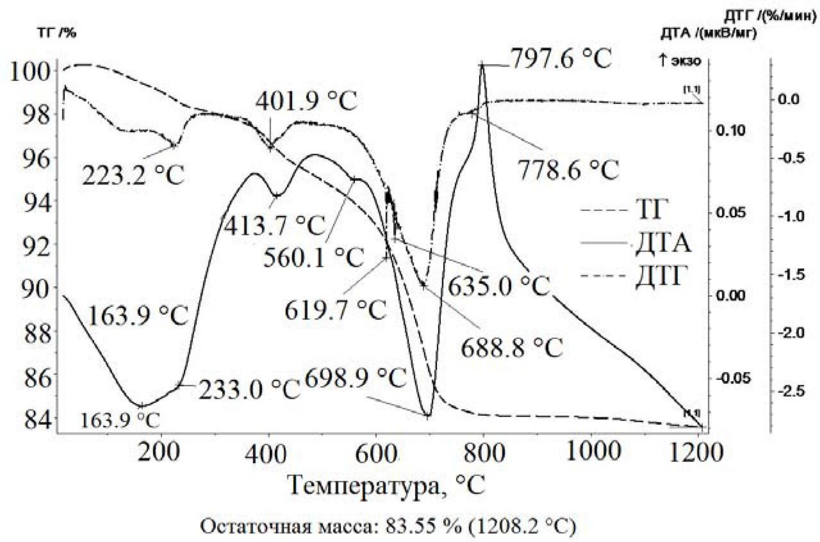


Figure 1 – Mineralogical composition of overburden rocks: 1 – serpentine, 2 – olivine, 3 – dolomite, 4 – iron oxides, 5 – hydroxides of iron, 6 – quartz, 7 – hydromagnesite. Reflected light, 100 magnification

The chemical composition of the averaged raw materials, mass.%: MgO – 37,6; SiO_2 – 34,61; Fe_2O_3 – 6,59; Al_2O_3 – 0,82; CaO – 0,67; Cr_2O_3 – 1,46; ignition loss – 15,26.

The mineralogical composition of the averaged sample is shown in figure 2.





a *b*

Figure 2 – Diffractogram - *a* and derivatogram - *b* of the averaged overburden rocks

The DTA curve shows a combination of an endothermic effect with a maximum at 695.9 °C and an exothermic effect with a peak at 797.6 °C, which is characteristic of serpentine.

In the area of the endothermic effect, the structure of the mineral breaks down with the simultaneous removal of the -OH group. From the decay products "x-ray amorphous" forsterite and enstatite are formed. In the temperature range of the exothermic effect, the newly formed mineral phases crystallize.

The endothermic effect with a peak at 695.9 °C reflects the dehydration of a small amount of brucite. The endothermic effect with a maximum at 413.7 °C presumably shows the dehydration of goethite.

At the same time, the combination of the endothermic effect with the maximum at 233 °C, and the endothermic effect with the maximum at 413.7 °C can be interpreted as the presence of a complex carbonate-pyroaurite plate – $Mg_6Fe_2[CO_3](OH)_{16}4H_2O$.

Overburden rocks are a poly mineral raw material and during of heat treatment physical-chemical processes occur related to structure and composition changes of the initial minerals. Depending on the direction of these processes, certain phases will be formed that determine the properties of the future ceramics. Knowledge of these processes’ regularities and various ways of influencing them will make it possible to create ceramics with a given set of properties. An important technological factor in proppant technology is the temperature of the sintering firing, during which the main properties of the final product are formed.

We studied the sintering processes and structural-phase transformations that occur during heat treatment of overburden rocks in the interval 600-1400 °C.

The temperature of the sintering firing of the samples was determined as follows. Pieces of overburden rocks were crushed on the jaw and roller crushers. Fine grinding of the raw materials was carried out by dry method in a ball mill. After that samples were prepared with a diameter of 26 mm by the method of semi-dry pressing at a pressure of 15 MPa. CMC 2% solution was used as a temporary binder. After drying samples are fired in the temperature range 600-1400 °C. The properties of the ceramic samples after firing are shown in table 1.

The experiments showed that heating of the ceramic samples up to 1000 °C leads to intensive loosening of the material structure, as a result of which the open porosity (P_o) reached 36.2% (at 1000 °C). The apparent density decreased to 1.76 g/cm^3, while the sample volume was certain increased. The loosening of the structure is caused by the dehydration processes of serpentine, impurity hydrosilicates of iron, brucite and decomposition of carbonates.

Oxidation-reduction reactions also take place in the temperature range of 1000-1200 °C. These reactions are associated with the decomposition of iron oxides and hydroxides, which are isomorphically present in serpentine and olivine. As a result, the samples change color from yellow to dark brown. In the

Table 1 – Properties of magnesium silicate ceramic samples fired at in the range of 600-1400 °C

Firing temp, °C	Open porosity, %	Water absorption, %	Apparent density, g/cm^3	Total shrinkage, %	Compressive streght, N/mm^2
600	28,1	15,8	1,78	3,8	–
800	35,3	18,5	1,72	1,98	–
1000	36,2	19,1	1,76	2,12	11
1100	33,07	15,06	2,20	9,64	20
1200	25,09	10,13	2,48	15,66	30
1300	14,36	5,01	2,76	19,3	55
1400	8,1	3,4	2,67	16,8	54

samples fired at temperatures over 1000 °C, hematite and magnetite were detected. Hematite is identified by its anisotropy and reddish-brown color in transmitted light.

Further increase of the firing temperature leads to appearance of a liquid phase, that formed due to the presence of low-melting magnesium metasilicate, calcium and aluminum oxides. This promotes the sintering of the mass and recrystallization growth of forsterite grains.

At a roasting temperature of 1400 °C, swelling of the samples takes place due to a decrease of the viscosity of the melt formed. Closed pores are formed in the structure of ceramic samples, as a result of which the parameters of open porosity and water absorption have decreased (table 1). The maximum strength is obtained by samples fired at 1300 °C.

In the samples burned at 1300 ° C, the following phases are present, mass%: forsterite – 50-55; magnesium metasilicate – 20-25; other phases formed by impurities of raw materials – 11-15, glass phase – 8-10%. The fired samples are dense, dark-colored and sintered materials.

Usually, in the technology of refractory and ceramic materials, serpentinite containing raw material is subjected to a preliminary heat treatment (thermal activation) for the dehydration of minerals. Thermal activation of the raw material helps to reduce the shrinkage of the mass during the sintering firing process, which is necessary to control the size of the ceramic samples and to prevent rejection.

Literature review has showed necessity of serpentine containing raw materials preliminary heat treatment in the interval 1100-1200 °C [11, 12, 15].

The influence of the temperature of preliminary heat treatment of overburden rocks on the properties magnesium-silicate ceramic was studied. Considering the results of X-ray and thermal analyzes, the crushed raw material was heat treated at various temperatures. The samples were prepared as described above from thermal activated raw materials at various temperatures. The molded samples were fired at a temperature of 1300 °C. The properties of the ceramic samples are given in table 2.

Table 2 – Properties of magnesian-silicate ceramic from thermal activated raw materials

Thermal activation temp, °C	Open porosity, %	Water absorption, %	Apparent density, g/cm^3	Total shrinkage, %	Compressive strength, N/mm^2
non	14,36	5,01	2,87	15,66	55
600	20,30	8,00	2,54	12,5	41
700	18,90	7,31	2,59	12,5	50
800	18,12	6,98	2,60	10,6	50
1000	16,79	6,39	2,63	9,4	74

The results showed that the samples obtained from the thermal activated raw material at 1000 °C have the maximum compressive strength. Therefore, further experiments were carried out using thermal activated raw material at 1000 °C.

Proppants were obtained from powders of overburden rocks thermally activated at 1000 °C (fractions less than 0.063 mm). Granulation was carried out in a granulator Eirich EL1.

a *b*

Figure 3 – Magnesian-silicate proppant obtained from overburden rocks, fractions: *a* – 16/20, *b* – 20/40

CMC 2% solution was used as binder. After drying in natural conditions, the granules fired in an electric furnace at 1300 °C, then subjected to fractionation and determination of properties.

Samples of proppants obtained from overburden rocks of Kempirsai chromite ores are shown in figure 3.

Obtained proppants properties: crush resistance for 20/40 – 14 %, for 16/20 – 22 %; apparent density – 1.6 g/cm^3; sphericity – 0,8; roundness – 0,8, chemical resistance to hydrochloric acid – 98%; static strength of granules – 72-118 N/granule.

Conclusion. Possibility of the use of overburden rocks of Kempirsai chromite ore deposits in Kazakhstan as a raw material for obtaining magnesian-silicate proppants was evaluated.

1. The chemical-mineralogical composition of overburden rocks of chromite deposits was studied.

It was established that the main mineral of overburden is serpentine, present in the form of fibrous chrysotile and lamellar antigorite; oxides and hydroxides of iron, carbonates, quartz, hydromagnesite and talc are present as impurities.

2. It was established that during heat treatment of raw materials structural-phase changes of the initial minerals occur with the formation of forsterite and enstatite.

The optimum temperature of sintering firing of ceramics based on overburden rocks is 1300 °C.

3. Proppants from thermal activated raw materials at 1000 °C were obtained: with an apparent density of 1.6 g/cm^3; crush resistance, for 20/40 – 14 %, for 16/20 – 22 %; sphericity – 0,8.

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А. А. Бирюкова[1,2], Т. Д. Джиенальев[1], А. В. Боронина[1]

[1]АО «Институт металлургии и обогащения», Алматы, Казахстан,
[2]НАО «Казахский национальный исследовательский технический университет им. К. И. Сатпаева», Алматы, Казахстан

ВСКРЫШНЫЕ ПОРОДЫ КЕМПИРСАЙСКИХ МЕСТОРОЖДЕНИЙ ХРОМИТОВЫХ РУД – СЫРЬЕ ДЛЯ ПРОИЗВОДСТВА КЕРАМИЧЕСКИХ ПРОППАНТОВ

Аннотация. Цель работы – оценка вскрышных пород, образующихся при разработке кемпирсайских хромитовых руд, в качестве сырья для производства керамических проппантов. Изучен химико-минералогический состав вскрышных пород разрабатываемых месторождений Кемпирсайских хромитовых руд методами химического, микроскопического и рентгеноструктурного анализов. Установлено, что основным минералом вскрышных пород является серпентин, присутствующий в форме волокнистого хризотила и пластинчатого антигорита. В примесях находятся оксиды и гидроксиды железа, карбонаты, кварц. Проведена технологическая оценка вскрышных пород в качестве сырья для получения керамических проппантов. Определен интервал спекания вскрышных пород, равный 1280-1300 °С. Оптимальная температура спекающего обжига керамики на основе указанного вида сырья - 1300 °С. Изучено влияние предварительной термообработки сырья на свойства керамических проппантов магнезиальносиликатного состава. Установлено положительное влияние термообработки сырья при температуре 1000 °С на формирование структуры и упрочнение образцов магнезиальносиликатного состава. Получены гранулы проппантов магнезиальносиликатного состава из вскрышных пород со свойствами: насыпная плотность – 1,6 г/см^3, доля разрушенных гранул при нагрузке 52 МПа – 14%, сферичность и округлость – 0,8; химическая стойкость к воздействию соляной кислоты – 98%, статическая прочность гранул фракции 16/20 составила 72-118 Н/гранулу. Область применения – нефтегазодобывающая отрасль, металлургические и керамические предприятия.

Ключевые слова: керамический магнезиальносиликатный проппант, вскрышные породы, минералы, фазы, серпентин, хризотил, антигорит, пористость, водопоглощение, прочность, структура, насыпная плотность.

А. А. Бирюкова[1, 2], Т. Д. Джиенальев[1], А. В. Боронина[1]

[1]«Металлургия және кен байыту институты» АҚ, Алматы, Казақстан,
[2]«Қ. И. Сәтбаев атындағы Қазақ ұлттық техникалық зерттеу университеті», Алматы, Казақстан

КЕМПІРСАЙ ХРОМИТТІ КЕН ОРНЫНЫҢ АРШЫМА ТАУ ЖЫНЫСТАРЫ – КЕРАМИАЛЫҚ ПРОППАНТ ӨНДІРІСІНІҢ ШИКІЗАТЫ

Аннотоция. Жұмыс мақсаты – Кемпірсай хромитті кен орындарын өңдеу барысында түзілетін аршыма тау жыныстарын керамикалық проппант өндірісіне шикізат ретінде қолдану мүмкіншілігін бағалау. Кемпірсай хромитті кен орнының аршыма тау жыныстарының химико-минералогиялық құрамы химиялық, микроскопиялық және рентгендік әдістермен анықталды. Аршыма тау жыныстарының басты минералы болып серпентин табылатыны анықталды. Серпентин талшық тәрізді хризотил түрінде және пластина тәрізді антигорит түрінде кездеседі. Сонымен қатар, темір оксидтері мен гидроксидтері, карбонаттар және кварц түрінде қоспалар бар екені анықталды.

Түйін сөздер: керамикалық магнезиалды-силикатты проппант, аршыма тау жыныстары, минералдар, фазалар, серпентин, хризотил, антигорит, кеуектілік, су сіңіру, беріктік, құрылым, үйінділік тығыздық.

Information of the authors:

Biryukova A. A. – JSC «Institute of metallurgy and ore benefication», Almaty, Kazakhstan; NJSC «The Kazakh National Research Technical University after K. I. Satpaev», Almaty, Kazakhstan; biryuk.silikat@mail.ru; https://orcid.org/0000-0001-6797-7471

Dzhienalyev T.D. – JSC «Institute of metallurgy and ore benefication», Almaty, Kazakhstan; https://orcid.org/0000-0001-9984-4649

Boronina A.V. – JSC «Institute of metallurgy and ore benefication», Almaty, Kazakhstan; https://orcid.org/0000-0003-0543-0387