Ceramic proppants for hydraulic fracturing

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Abstract. The purpose of the work is the development of ceramic proppants from serpentinites and red mud. The chemical and mineralogical composition of the raw material was studied. It has been established that the main mineral of serpentinites is serpentine, which is present in the form of fibrous chrysotile and lamellar antigorite. Red mud is represented by sodium aluminosilicates of various hydrated forms, silicon oxide and hematite. Structural-phase transformations of compositions based on serpentinite and red mud were studied in the heat treatment process. The proppant phase composition is represented by forsterite, clinoenstatite, spinel compounds and complex sodium aluminosilicates. Proppants of magnesia-silicate composition based on serpentinite and red mud have been obtained with the following properties: bulk density 1.59-1.61 g/cm³, fraction of crushed granules with a compressive load of 69 MPa no more than 22%, sphericity and roundness - 0.8, chemical resistance - 98%.

1. Introduction
The hydraulic fracturing is widely used to increase hydrocarbon production in the oil and gas industry in hard-to-develop fields. Hydraulic fracturing is an oil and gas production process that involves injecting water, propping agent and fracturing fluid under high pressure into a rock formation via the well. Propping agents or proppants, fixe cracks in the open state after depressurization [1-4]. Various chemicals are used as a fracturing fluid.

The main functional properties of proppants are crush resistance, chemical resistance and also permeability of proppant pack [2, 3]. Depending on the characteristics of the field, the structure and structure of the oil reservoir, various proppants are required. Proppants vary in composition and properties. The most widely used in hydraulic fracturing were aluminosilicate [4-11] and magnesia-silicate [12-17] proppants. For the production of proppants, both natural raw materials and waste from various industries are used [18-20].

The growth in the extraction and processing of minerals in the world leads to the depletion of natural resources and the accumulation of man-made waste. In this regard, there is an urgent need for the rational use of natural resources and the disposal of man-made waste.

The results of studies on the obtaining of magnesium-silicate ceramic proppants using natural serpentinite and waste from Pavlodar alumina production - red mud are presented. The research results will improve the proppant production efficiency through the use of cheap natural raw materials and alumina production wastes, as well as reducing the energy intensity of the process due to a decrease in the proppant firing temperature.
2. Materials and methods

Chemical analysis of raw materials was carried out in a specialized laboratory using certified methods. X-ray structural analysis of the feedstock and synthesized compositions was carried out on a D8 Advance diffractometer (BRUKER).

Serpentinite and red mud were used as raw materials. The chemical composition of the raw materials is shown in Table 1.

| Sample/Oxide | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | CaO | Na₂O | TiO₂ | LOI |
|--------------|------|-------|-------|-----|-----|------|------|-----|
| Serpentinite  | 34.8 | 0.9   | 7.3   | 39.0| 0.8 | -    | -    | 17.2|
| Red mud      | 17.8 | 20.0  | 25.9  | 0.6 | 12.2| 2.9  | 19.6 |

A sample of serpentinite was represented by stone material. Pieces of various colors were present - gray, grayish-mousse, dark-mousse, light with a yellow coating, etc. Despite the difference in color, all varieties of pieces were serpentinite rock containing the main mineral - serpentine (Figure 1).

![Figure 1. XRD patterns of serpentinite rock.](image)

Red mud is a waste from alumina production containing both alumina and silicon, as well as iron oxides. The phase composition of the red mud sample is shown in Figure 2. The main phases of red mud are hematite, quartz, aluminum silicates Na₆(AlSiO₄)₆, AlNa(SiO₄). Na₇.₆(Al₆Si₆O₂₄)(CO₃)₀.₉₃(H₂O)₂.₉₃.

![Figure 2. XRD patterns of red mud.](image)
Two-component mixtures were investigated. Serpentinites were used as the main magnesium and silica-containing component of the charge, and red mud was used as a component with an increased content of iron impurities. Table 2 shows compositions of the studied mixtures.

| Mixture | Serpentinite (%) | Red mud (%) | Chemical composition (wt%) |
|---------|-----------------|-------------|---------------------------|
|         |                 | SiO₂        | Al₂O₃ | Fe₂O₃ | MgO | Others |
| 1       | 100             | 42.0        | 1.08  | 8.85  | 47.1 | 0.97   |
| 2       | 90              | 40.04       | 3.43  | 11.25 | 42.5 | 2.78   |
| 3       | 80              | 38.06       | 5.76  | 14.1  | 37.38| 4.66   |
| 4       | 70              | 36.12       | 8.25  | 15.93 | 32.93| 6.77   |
| 5       | 60              | 34.16       | 10.65 | 18.31 | 28.26| 13.28  |

Presumably, silicon oxides should contribute to the formation of magnesium metasilicate during the firing of the ceramic composition, aluminum and iron oxides to the formation of spinel phases, which can increase the strength properties of proppants. The assimilation of sodium-containing compounds will contribute to the formation of low-temperature eutectics, which should reduce the temperature of sintering proppant firing. With a decrease in the amount of serpentinite in the mixture, the content of silicon and magnesium oxides decreases, while the content of aluminum, iron and sodium oxides increases. Depending on the composition of the charge during the firing process, certain phases will be formed, and their ratio will change.

3. Experimental part and results

Earlier, in [21], the efficiency of preliminary thermal activation at 1000 °C of Kazakhstan serpentinite raw materials for the production of ceramic materials was established. The materials were preliminarily subjected to heat treatment at 900-1000 °C in order to remove chemically bound water. In order to assess the strength properties and phase composition of the compositions based on a mixture of serpentinite and red mud, cylinder samples with a diameter of 16 mm were made by pressing. The prepared samples were fired in the range of 1200-1350 °C in an electric furnace with subsequent determination of properties (Table 3). Samples of serpentinite used as a standard of comparison.

| Sample | Firing temp. (°C) | Water absorption (%) | Apparent density (g/cm³) | Compressive strength (MPa) |
|--------|-------------------|----------------------|--------------------------|---------------------------|
| 1      | 1350              | 7.5                  | 2.72                     | 65                        |
| 2      | 1300              | 4.5                  | 2.70                     | 71                        |
| 3      | 1240              | 2.8                  | 2.67                     | 75                        |
| 4      | 1230              | 2.1                  | 2.68                     | 78                        |
| 5      | 1200              | 0.9                  | 2.68                     | 69                        |

The test results showed that samples of composition 1 (standard) have the minimum strength. X-ray phase analysis (Table 4) of the products of firing of composition 1 revealed the presence of the main phase of forsterite, which has anisotropic properties, poorly sintering, which prevents the compaction and hardening of the ceramic structure.

The introduction of red mud in the mixture leads to an increase in the content of iron, aluminum and sodium oxides. The presence of sodium oxides (Figure 3) in the composition contributes to the formation of low-temperature eutectics, activating the process of sintering of the mass due to the participation of the melt, which contributes to the compaction and hardening of the ceramic structure.
(compositions 2-5). The phase composition of the remaining samples containing red mud is similar to sample 3 with a difference in a phase ratios.

**Table 4. Phase composition of ceramics.**

| Samples | Phases                                                                 |
|---------|------------------------------------------------------------------------|
| 1       | Forsterite, ferror (Fe_{0.12}Mg_{0.88})(SiO_4), Magnesium Iron Silicate (Mg_{0.74}Fe_{0.26})(Si_2O_3), Magnesioferrite aluminian (MgAl_{0.74}Fe_{1.26})O_4, Forsterite (Mg_{1.8}Fe_{0.19})(SiO_3), Nepheline, Na_{6.65}Al_{6.24}Si_{9.76}O_{32}, Jadeite |
| 3       | NaAl(SiO_3)_2, Spinel Mg_{1.01}Fe_{1.77}Al_{0.22}O_4, Maghemite, syn (Fe_2O_3), Clinoenstatite ferroan (Mg_{0.54}Fe_{0.46})SiO_3. |

**Figure 3.** XRD patterns of the sample 3.

This has a positive effect on lowering the temperature of sintering proppant firing. An increase in the content of red mud (more than 40%) leads to a significant formation of low-temperature phases. An increase in the amount of melt during the firing process promotes wetting and sintering of solid particles. However, upon cooling of the samples, the melt crystallizes in the form of glass mass and the strength properties of the samples decrease.

Reducing the content of red mud in the composition of the charge of less than 20% does not provide a sufficient content of sodium oxides, necessary to reduce the firing temperature of proppants.

The presence of aluminum and iron oxides in the charge facilitates the formation of defective solid solutions of interstitial and (or) iron substitution in the lattice of metaserpentin and magnesium orthosilicate nuclei, as well as in the formation of sintering complex magnesia spinels that activate sintering. This effect from the presence of Fe2O3 in the composition of the charge is possible due to the proximity of ionic radius of Al3+ (0.057 nm) and of Fe3+ (0.067 nm). The presence of spinel phases in the structure of ceramics increases the strength of samples and chemical resistance to aggressive solutions.

The research results showed that all obtained ceramic samples by phase composition belong to magnesia-silicate. The main magnesia-silicate phases of all compositions are forsterite and clinoenstatite, the content of which depends on the composition of the charge. The formation of solid solutions of magnesia and iron silicates has also been established. Samples of magnesium-silicate ceramics obtained from a mixture containing from 10 to 30% red mud have maximum strength.
Proppants were obtained from compositions containing 10-30% red mud. Proppants were prepared as follows. The raw materials were subjected to grinding to a fraction of 0.063 mm, followed by heat treatment of the mixture at 900-1000 °C in order to: remove constitutional moisture; decomposition of the initial mineral serpentine with the formation of metastable metaserpentine and magnesium orthosilicates with a defective structure. This will activate the sintering process and densification of the ceramic structure in sintering firing.

Structural-phase transformations during heat treatment of serpentinite rock with the formation of forsterite through the metastable phase of metaserpentine in the range of 200–1000 °C were established earlier in [21].

Heat-treated fine-ground powders of raw materials (fraction less than 0.063 mm) were loaded into a granulator-mixer Eirich EL1 to obtain proppant granules. The mixing of the mass took place for 30 seconds, at a maximum speed of rotation of the swirler. Then introduced the binder component of a 1.5% solution of methylcellulose in an amount of 20% of the total mass of the charge. The mass was mixed for 30 seconds, then the rest of the ligament was gradually introduced. After supplying the entire volume of the binder component, the mass was mixed for another 1 minute to evenly moisten and compact the mass.

The swirler speed was reduced to 700 rpm at the time of the appearance of small granules (0.1-0.3 mm). At this time, crushed powder for dusting in an amount of 10-15% of the charge necessary to obtain granules of a given size was additionally uniformly introduced into the granulator. After 1-3 minutes after dusting, the raw granules were unloaded, dried under natural conditions during the day, then at a temperature of 105-115 °C for 40-60 minutes to a residual moisture content of 1-3 mass. %.

The proppants were roasted at a sintering temperature, depending on the composition of the charge, in the range of 1,200-1,250 °C for 1 hour.

After cooling, the calcined proppant granules were fractionated to isolate the 16/20 fraction, which was tested to determine the properties in accordance with GOST R 54571-2011 (KZ). Results of testing are shown in Table 5.

| Mixture | Firing temp. (°C) | Bulk density (g/cm³) | Crush loss under 69 MPa (%) |
|---------|-----------------|---------------------|----------------------------|
| 1       | 1350            | 1.59                | 23.9                       |
| 2       | 1300            | 1.61                | 19.4                       |
| 3       | 1240            | 1.60                | 21.8                       |
| 4       | 1230            | 1.59                | 21.5                       |
| 5       | 1200            | 1.59                | 22.1                       |

The test results showed that the obtained ceramic proppant granules are proppants of medium density with a bulk density of 1.59-1.61 g/cm³. The crush resistance of the 16/20 fraction at a pressure of 69 MPa is 19-23%. Proppant granules were also tested for corrosion resistance to a solution of 10% hydrochloric acid. The sphericity and roundness of the obtained proppants is 0.8, and the chemical resistance to hydrochloric acid is 98%. Tested proppant samples of all compositions according to their technical properties comply with the requirements of GOST R 54571-2011 (KZ) for magnesium-quartz proppants.

4. Conclusions

Studies on the development of ceramic proppant compositions based on serpentinites of the Kempirsai region and red mud of Pavlodar alumina production have been carried out.

1. The chemical and mineralogical composition of serpentinite and red mud has been studied. It has been established that the main mineral of overburden is serpentine, which is present in the form of...
fibrous chrysotile and plate antigorite, in the form of impurities there are iron oxides and hydroxides, carbonates, quartz, hydromagnesite, talc. The main components of red mud are oxides of aluminum, iron, silicon and sodium.

2. It was found that during the heat treatment of compositions based on serpentinite and red mud, structural-phase changes of the initial minerals occur with the formation on their basis of the main phases of magnesia-silicate ceramics: forsterite and clinoenstatite, the content of which depends on the composition of the charge. The formation of solid solutions of magnesia and iron silicates and impurity sodium aluminosilicates has also been established.

3. Obtained proppants with a bulk density of 1.6 g/cm³; with crush resistance for granules 16/20 no more than 25%; sphericity and roundness - 0.8; chemical resistance to hydrochloric acid - 98%.

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