

Alumosilicate ceramic proppants based on natural refractory raw materials

T V Vakalova¹, L P Devyashina¹, M A Burihina¹, A S Kisner¹ and N V Pashenko¹

¹Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk 634050, Russia,

E-mail: tvv@tpu.ru

Abstract. The sintering-strengthening effect of the additions of the highly ferrous bauxite (with Fe₂O₃ content of 20-25 % in the calcined state) in the compositions with refractory clays was established. It was found that in the temperature range 1350-1500°C the additions of bauxite in amounts of 10-40% have a fluxing effect due to the iron oxide introduced with bauxite in compositions with clay. An increasing the bauxite additive in the amount of 50-70% ensures its strengthening effect by increasing the total content of the mullite of the prismatic habit in the firing products of composites with clay. Preliminary clay and bauxite calcination at 900 °C and an increase in the content of bauxite additive up to 50-70% in compositions with clay allow to produce aluminosilicate proppants with a bulk density of 1.62-1.65 g/cm³ and compressive strength up to 52 MPa.

1. Introduction

Alumosilicate ceramics based on natural raw materials, combining high refractoriness, chemical resistance and increased strength, have not lost their relevance in the total volume of modern ceramic and refractory materials. The perspective of such ceramics is also the fact that the main raw materials for its production are available natural and technogenic raw materials, such as refractory clays and kaolins, bauxites, rocks containing hydrates and silicates of alumina, refractory and metallurgical waste.

The availability of a raw material base for the production of aluminosilica ceramic materials determines the further traditional use of such materials in ferrous and non-ferrous metallurgy, glass and cement industries, the construction industry and others [1-5]. Recently, alumina-silicate ceramics has been used in non-traditional applications in the oil and gas extraction industry as propping-up materials for extracting difficult-to-recover oil and gas by hydraulic fracturing [6-11]. This is a mechanical method of influencing the productive oil and gas bearing layer, in which the rock breaks along the lines of the line of strength due to the impact on the formation of the pressure created by injecting into the formation of fracturing fluid. After rupture under pressure, the created cracks increase, and their connection with the system of natural cracks arises. Granular material (proppant) in size from 2 to 0.2 mm is transported to the cracks formed by the fracturing fluids and fix the cracks in the opened state after removal of the excess pressure. The conditions of service of proppants determine their basic functional properties, according to which they must withstand high reservoir pressures and withstand the corrosive action of the corrosive medium (acid gases, saline solutions). The complex of required physico-mechanical and chemical properties of proppants largely determines the efficiency of

¹ Corresponding author: tvv@tpu.ru



hydraulic fracturing. Therefore, improving the quality of proppants is one of the most important reserves to improve the technical and economic indicators of oil and gas production, which entails the need to improve the technology for manufacturing these proppants.

After years of research, preference in the production of proppants is given to ceramic technology, because ceramic proppants combine high strength, relatively low bulk density, chemical resistance and high conductivity. Medium and high strength materials, preferably aluminous (in the case of heavy proppants) or aluminosilicate (in the case of lightweight proppants) composition can be used as ceramic proppants.

Further developments are under way to expand the raw material base of ceramic proppants based on wollastonite, forsterite, clinoenstatite and other minerals. However, strict requirements to the raw materials for high-quality ceramic proppants, combining high strength with reduced bulk density have not been established either in domestic or in foreign practice of obtaining ceramic proppants. Possible ways of solving the problem are to increase the proportion of crystalline phases in the ceramic matrix (preferably with a fibrous-needle structure [12-14]), to ensure the most dense packing of grains during granulation and the minimum porosity of the granular material after firing.

Of the total variety of natural aluminosilicate raw materials, the most common are basic kaolins, bauxites and refractory clays, as well as various additives of natural and technogenic genesis, enhancing the sintering process of the material and increasing raw material strength for the production of aluminosilicate proppants.

Previously, the authors established physicochemical parameters for assessing the suitability of refractory clay raw materials for the production of aluminosilicate proppants, which include mineralogical (the content of kaolinite is not less than 65% by weight, the content of free quartz is not more than 15% by weight), the chemical (Al_2O_3 content in the calcined state, not less than 35% by weight, preferably 40 - 45% by weight, and the content of alkaline oxides is not more than 1.2% by weight).

The purpose of this work was the development of compositions and technological parameters for the production of aluminosilicate ceramic proppants based on the refractory clay-containing raw materials - argillite refractory clay and high-iron bauxite.

2. Materials and methods

As raw materials, refractory clay and bauxite were used in the work. The study of the physicochemical features of clay was carried out with the aim of elucidating the prospects of its use as the main component of the ceramic masses, and bauxite as a natural reinforcing additive in compositions with clay. According to the chemical-mineralogical composition, clay is a highly basic raw material (the content of Al_2O_3 in the calcined state is 48.3 mass %), with an average content of coloring oxides ($\text{Fe}_2\text{O}_3 + \text{TiO}_2 - 5.5$ mass%), kaolinite composition with hydrargillite (gibbsite) admixture in clay part, hematite and quartz – in the non-plastic part.

Bauxite is a kind of hematite-gibbsite-kaolinite bauxite with a content of up to 62% Al_2O_3 with an a low silica content (up to 10 wt%) and a low content of alkali and alkaline-earth oxides (less than 2% by weight) in the chemical composition.

Both types of investigated raw materials are clay-containing starting materials of predominantly kaolinite composition (in the case of clay) or an admixture of kaolinite (clay bauxite). Therefore, one of the ways to increase the strength characteristics of ceramic materials based on them is the addition of clay-containing additives [15-19]. These additives neutralize the negative softening effect of cristobalite, which is formed during the polymorphic transformation of impurity quartz and the crystallization of amorphous silica released from the structure of kaolinite. This will increase the total content of the crystalline phase and reduce the amount of unstable vitreous phase in the structure of the calcined material, which, in the future, will favorably enhance the hardening of the calcined material.

To improve the mechanical strength of aluminosilicate proppants while reducing the temperature of their firing, the possibility of improving the functional properties of the ceramic materials of the

system (RO, RO₂, R₂O₃) - Al₂O₃-SiO₂ was examined by activating the processes of mullite synthesis and sintering of aluminosilicate ceramics on the basis of raw materials with mineral oxide additives.

As additives-mineralizers, the following oxides were chosen: 2% MnO₂ - in the form of manganese concentrate; 5% Fe₂O₃ - in the form of pyritic cinders; 2% MgO - in the form of caustic magnesite. Mineralizing additives in an amount of 2-5 % over 100% were introduced into the aluminosilicate raw materials (clay and bauxite) calcined at 900 °C and 980 °C.

Chemical analysis of the materials sample was carried out as per GOST 2642. The mineralogical composition of raw materials was determined by a set of physicochemical analysis techniques (X-ray and thermal methods). X-ray study was carried out on a diffractometer «Shimadzu XRD-7000S» with Cu K α -radiation at the tube voltage of 40 kV and the current of 25 mA, the goniometer rotation speed was 4°/min.

The thermal analysis of the samples was performed on combined SDT Q600 TGA/DSC/DTA analyzer under the following imaging conditions: the heating rate was 10 °C/min, the surrounding medium was air, crucibles were from corundum, and weighed amount was 20-40 mg.

The samples were molded from calcined clay rock by semi-dry pressing under the pressure of 10 MPa; the solution of 0.3% carboxymethylcellulose was involved as the binder. The sintering of the compacted samples was carried out in the temperature range of 1350–1450 °C with the step of 50 degrees with holding at the maximum temperature for 2 hours.

Structural and phase changes were evaluated by X-ray analysis. The microstructure of the starting and processed materials were investigated using JEOL 6000 scanning electron microscope.

3. Results and discussion

A comparative analysis of the effect of the oxide additives on the sintering process of refractory clay showed that the optimum reinforcing additive is the addition of 5% Fe₂O₃, which provides an increase in strength from 230 to 300 MPa (1.3 times) of molded clay samples heat-treated at 900°C and calcined at 1350 °C (Figure 1). In the case of high-iron bauxite, the obtained data (Figure 2) indicate that the optimal pre-calcination temperature of bauxite is 980 °C, the optimum sintering temperature of the samples is 1300 °C, since there is a danger of vitrification of the surface of the samples and the formation of cakes and fusions in the furnace at the burning temperature of 1350 °C.

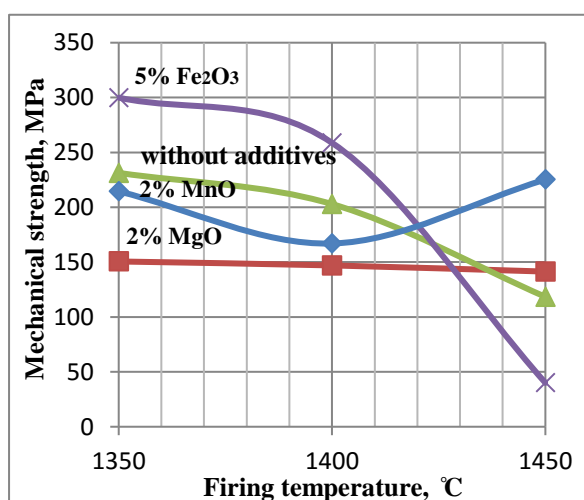


Figure 1. The influence of additives and of preliminary calcination temperature (900 °C) of the argillaceous clay on the its sinterability at 1350-1450 °C

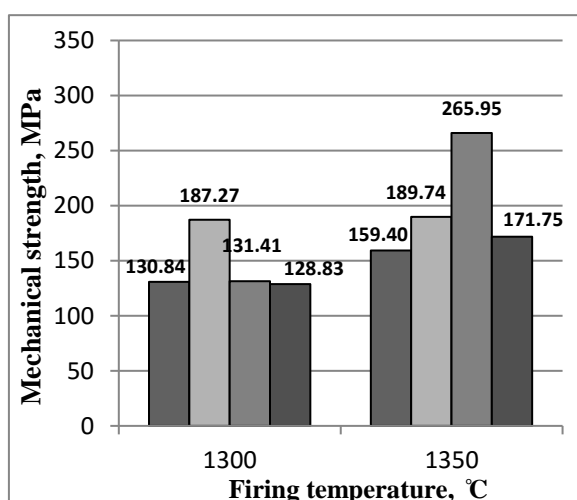


Figure 2. The influence of preliminary calcination temperature (980°C) on the high-iron bauxite sinterability at 1350-1450 °C

An evaluation of the effect of the oxide additives on the process of sintering of bauxite rock showed that the optimum reinforcing additive is the 2% MnO, which increases the strength from 130 to 187 MPa (by a factor of 1.5) from bauxite samples thermally treated at 980 °C and calcined at 1300 °C.

The strengthening effect of these additives is due to the formation of defective solid solutions for the introduction and / or replacement of iron in corundum in connection with the proximity of the ionic radius of Al³⁺ (0.057 nm) and the ionic radius of Mn⁴⁺ (0.052nm) and Fe³⁺(0.067 nm), which causes a significant activation of the Al₂O₃ lattice and, as a result, improvement of its sintering. Moreover, the possibility of the influence of Mn²⁺ and Fe²⁺ cations on the appearance of melts and on their properties, which promote sintering and recrystallization of corundum and mullite, is not excluded.

Thus, according to the degree of activation of the sintering process of the clay and the bauxite, ferruginous additives are of interest for using them in aluminosilicate proppants from this raw material.

The production of aluminosilicate proppants based on clay with additions of bauxite was carried out according to the traditional technological scheme, which includes heat treatment of raw materials at a temperature of 900 °C for the purpose of dehydration of clay and bauxite minerals, wet grinding of the heat-treated products to a particle size of less than 63 µm, drying the slurry, mixing and homogenizing the components, granulating to a bulk density of 0.9 to 1.0 g/cm³ (dry), drying and firing granules, sieving into commodity fractions of proppants. On the granules with a fraction of 20/40 (0.4-0.8 mm), compressive strength and bulk density were determined (Table 1).

Table 1. Properties of proppants fraction 20/40 from clay-based compositions with the addition of bauxite, fired at 1450 -1500°C (crush pressure – 52 MPa)

number	Clay / bauxite wt %	Temperature		Properties of proppants			Chemical composition proppants	
		heat treatment		Firing granules	Bulk density, g/cm ³	Crush resistance ² , %	Oxide content, wt.%	
		Clay	bauxite				Al ₂ O ₃	Fe ₂ O ₃
Clay without additives								
A	100/0	900	-	1450	1.50	25.6	48.1	2.3
				1500	1.54	23.5		
Bauxite additive								
AB50	50/50	900	900	1450	1.61	14.7	54.6	12.2
				1500	1.62	9.8		
AB70	30/70	900	900	1450	1.63	9.7	57.5	16.2
				1500	1.65	9.5		

4. Conclusion

It has been established that the addition of high-iron bauxite in an amount of 10 to 40% does not ensure the production of proppants based on argillic clay with a strength at a fracture pressure of 52 MPa. The increase in the content of bauxite additives from 50 to 70% by weight in compositions with refractory clay ensures the production of aluminosilica proppants at a firing temperature of 1450-1500 °C with a bulk density of 1.62-1.65 g/cm³ and strength, withstanding the destructive pressure of 52 MPa.

² According to the requirements of the API (American Petroleum Institute) - the fraction of broken granules at a pressure of 52 MPa fraction 20/40 - no more than 10%.

Acknowledgement

The research is carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant, Project Number TPU CEP_IHTP_73\2017.

References

- [1] Migal V P, Margishvili A P and Skurikhin V V Mullitic products for blast furnace blast furnaces 2010 *Ref. and Tech. Ceramics* **3** 39–46
- [2] Shvetsov R N, Tretyakova Yu Yu and Pilipchatin L D Development of a non-shrinkage mullite-corundum mass for lining the steel casting ladle 2008 *Ref. and Tech. Ceramics* **10** 30–6
- [3] Franken M and Van Berkel P Refractories for the aluminum industry. Melting furnaces and mixers 2009 *Ref. and Tech. Ceramics* **6** 35–42
- [4] Azarov S M, Azarova T A, Rat'ko N V and et al. Multilayer porous aluminosilicate ceramic 2009 *Steklo i Keramika* **3** 23-25
- [5] Maslennikova G N Some trends in the development of aluminosilicate ceramics 2001 *Glass and Ceramics* **2** 10–4
- [6] Liang F, Sayed M,-Muntasheri G and et.al A comprehensive review on proppant technologies 2016 *Petroleum* **2** 26-39
- [7] McDaniel G, Abbott J, Mueller F and et.al Changing the shape of fracturing: new proppant improves fracture conductivity 2010 *Proceedings–SPE Annual Technic. Conference and Exhibition* **6** 4764-4784
- [8] Edelman J, Maghrabia M, Semary A and et.al. Rod-shaped proppant provides superior proppant flowback control in the Egyptian Eastern Desert 2013 *Society of Petroleum Engineers–SPE Middle East Unconventional Gas Conference and Exhibition* 659-665
- [9] Liu Z, Zhao J, Li Y and et.al. Lowerature sintering of bauxite-based fracturing proppants containing CaO and MnO₂ additives 2016 *Materials Letters* **171** 300-303
- [10] Usova Z Yu and Pogrebenkov V M Ceramic proppant based on aluminum borate 2012 *Ref. and Tech. Ceramics* **1–2** 28–32
- [11] Biryukova A A, Tikhonova T A, Akchulakova S T and et al. Influence of fluorine-containing additives on synthesis and properties of mullite ceramics based on aluminosilicate raw materials of Kazakhstan 2016 *Complex use of min. raw mat.* **1** 80-87
- [12] Vakalova T V, Pogrebenkov V M and Chernousova O A Structure-phase transitions upon firing of new ceramic feedstock, topaz-containing rocks 2002 *Steklo i Keramika* **6** 24-27
- [13] Vakalova T V, Pogrebenkov V M, Chernousova O A and Khabas T A Special features of phase formation in fireclay in the presence of topaz 2001 *Steklo i Keramika* **4** 13-17
- [14] Pogrebenkova V V, Vakalova T V, Gorbatenko V V and Grekhova M V Features of phaseformation of mullite-corundum materials in mixtures of kaolin with a fluoriding component 2010 *Ref. and Indust. Ceramics* **51 (3)** 197–201
- [15] Temuujin J, MacKenzie K J D and Schmucker D M Phase evolution in mechanically treated mixtures of kaolinite and alumina hydrates (gibbsite and boehmite) 2000 *J. Eur. Ceram. Soc.* **20 (4)** 413-421
- [16] Oliveira M and Ferreira J M F Structural and mechanical characterisation of MgO-, CaO- and BaO- doped aluminosilicate ceramics 2003 *Materials Science and Engineering* **344 (1-2)** 35-44
- [17] Kawai S and Yoshida M Preparation of mullite from kaolin by dry grinding 1990 *J. Ceram. Soc. Japan* **98** 363-369
- [18] Allahverdi M, Allaire C and Afshar S Effect of BaSO₄, CaF₂, and AlF₃ as well as Na₂O on aluminosilicates having a mullite-like composition 1997 *Canadian Ceramics* **66 (3)** 223-230
- [19] Ma X, Yao X, Hua S and Chen Y Effects of MnO₂ and Fe₂O₃ on microstructure and crush resistance of alumina matrix fracturing proppant 2009 *Journal of the Chinese Ceramic Society* **37 (2)**, 280-284