Arch. Metall. Mater. **63** (2018), 2, 1065-1070

DOI: 10.24425/122444

K. KASPRZYK*[#], K. KOGUT*, B. ZBOROMIRSKA-WNUKIEWICZ*, A. DYJAKON**

PREPARATION OF A CERAMIC PROPPANTS FOR HYDRAULIC FRACTURING USING F – TYPE FLY ASH

In the paper, the technology of the production of the modified ceramic proppants used in the shale gas extracting process is described. The natural available materials and uncomplicated process to new ceramic proppants preparation were applied. The modification of the ceramic proppants based on the addition of the waste material as fly ash. The produced ceramic material in the form of granules characterized by high mechanical properties and low production costs. Moreover, the obtained good values of compressive strength and gas permeability for investigated proppants confirmed that this material has appropriate properties to be used in the hydraulic fracturing.

Keywords: proppants, ceramic materials, shale gas, hydraulic fracturing, fly ash

1. Introduction

Proppants, according to Polish Standard PN-93-G: 11010, are a composition of non-combustible solid grains, which are use to mechanical support in mining excavation. They are placed by some transporter medium, embed and densified [1].

Proppants could be prepared as a natural or synthetic chipping, in the form of regular spheres with diameter of 0.15-1.0 mm and high compressive strength. Proppants due to the expected application to filling (mechanical support) in gaps, during and after gas exploitation, should have a high mechanical compressive strength to stabilize lode at great depths and high pressures.

Regular shape of proppants and small diameter of the grains (balls) are required to provide minimum resistance during the injection of liquid material to lode and create the cavity effect on the borders between the balls. Synthetic materials have an advantage over the natural chipping (sands mainly) with sharp edges of grain. Natural chipping have a limited applicability, if they are not covered by different type of resins.

The research of the properties of natural raw materials to meet the required standards are still under development. For example, the sands from different World regions, like Malaysia, are tested [2].

Considering the scale of requirements, the proppants should be relatively cheap. Hence, the searching for different raw materials and their preparing in order to meet this requirement is still on-going [3].

Basic requirements for proppants used in the hydraulic fracturing are, as follow:

– diameter of the grains lower than 1 mm,
– appropriate compression strength,
– appropriate specific gravity,
– spherical shape,
– no reaction with hydraulic liquids (chemically neutral),
– high gas permeability.

2. Experiment

The main goal of the research was to examine the properties of the selected proppants in order to compare them with the required parameters for the ceramic materials, used in the hydraulic fracturing.

2.1. Materials

For proppants preparation, the general and easy available raw materials were used:

– quartz silica (SiO_2), particle size range of 0.1-1.0 mm
– aluminium oxide (Al_2O_3) – Martinswerk a company of Albemarle Corporation,
– calcined kaolin,
– clay from „JARO Company”,
– titanium oxide (TiO_2) – anatase, Kronos 1001,
– bentonite type „C” clair T,
– grey glaze for insulators,
– F – type fly ash,
– demineralised water.

* ELECTROTECHNICAL INSTITUTE, DIVISION OF ELECTROTECHNOLOGY AND MATERIALS SCIENCE (IEL), M. SKŁODOWSKIEJ-CURIE 55/61, 50-369 WROCŁAW, POLAND
** WROCŁAW UNIVERSITY OF ENVIRONMENTAL AND LIFE SCIENCES, INSTITUTE OF AGRICULTURAL ENGINEERING, 37 A CHEŁMOŃSKIEGO STR., 51-630 WROCŁAW, POLAND
# Corresponding author: k.kasprzyk@iel.wroc.pl

Calcined kaolin was received by sintering of kaolin at 700°C to remove the CO_2, water or other fly components [4].

The fly ashes used in the investigations were collected from the dedusting systems of the pulverized bituminous coal fired boiler OP-650 PC in power plant EL Dolna Odra (Table 1).

The PC boiler was operating without dry desulphurization systems. Therefore, the fly ash was characterized by a high rate of aluminosilicate and small amounts of CaO and SO_3. The fly ash used can be classified as the K (silicate) type according to the Polish standard (BN-79/6722-09). Due to the use of fly ash in the cement industry, these include the class F (low calcareous), where the total sum of three most important oxides: silica oxide (SiO_2), iron (III) oxide (Fe_2O_3) and aluminium oxide (Al_2O_3) is greater than 70% and amount of CaO is less than 5% [6,7]. Due to ash, they are very valuable building material and could be use as material increasing the parameters of the cement.

Chemical and phase composition of fly ash used as one of the ingredients in ceramic proppants is shown in Table 1 and Fig. 1. In the literature, not to much information about the use of this material in the proppants production have been found. The waste material used in filling materials preparation is very innovative element of technology having also ecological aspect of work.

TABLE 1

Chemical composition of fly ashes (Power Plant Dolna Odra)

Fly Ash	Content, wt %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	the rest
PC boiler	76.4	8.46	4.43	0.50	1.71	0.37	0.69	0.38	7.06

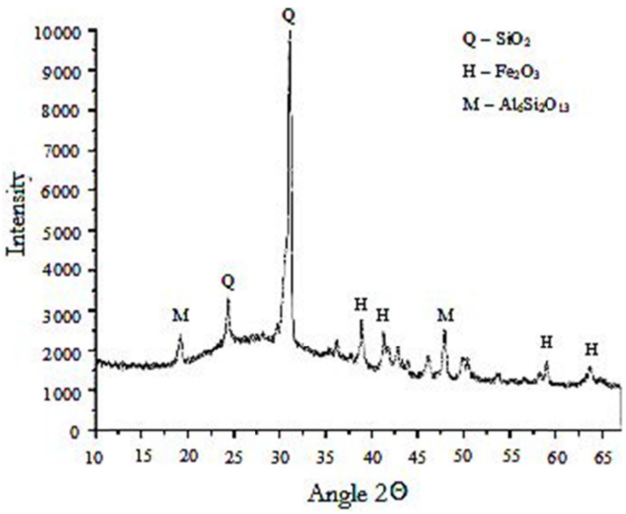

Fig. 1. Phase composition of fly ash from the combustion of coal

In the frame of this work many composition of materials to hydraulic fracturing were prepared. Based on the first mechanical strength tests three types of mass with the best properties were selected. For these materials more detailed research and tests were carried out.

2.2. Sample preparation

The sample of raw material was dried for two hours at the temperature of 105-110°C. Dry components were precisely mixed in the ball mill for 1.5 hour. Finally, the obtained sample was granulated.

The granulation process was performed in the 5 dm^3 and 150 mm in diameter glass container placed horizontally and driven by motor with the 85 r.p.m. speed. Water was used as the binder liquid. According to literature [5], the typical rotational speeds applied during the granulation process is higher. However, due to the specifications of mass and the wetting process, in this work the lower chamber speed was used [5]. The granulation was provided for 2 minutes. After this time, the granulates were formed. Wet product was dried in a curing chamber at room temperature for one day under cover to achieve the hydration of cementations components. Afterwards, the granules were dried at 50°C for 60 minutes, then the temperature was raise up to 70°C with 30 minutes hold and finally up to 100°C for 30 minutes. Then granules were sintered in a furnace at experimentally selected temperatures between 1100-1300°C. Three types of materials marked as Mass I, II and III were prepared (Table 2).

TABLE 2

Composition of three types of materials used in the tests

Raw materials	Mass I	Mass II	Mass III
Calcinated kaolin	55-65%	55-65%	55-65%
Al_2O_3	18-22%	18-22%	18-22%
SiO_2	—	13-18%	—
Clay from „JARO Company"	10-15%	—	10-15%
Bentonit type "C"	2-5%	2-5%	2-5%
Fly ash	5-10%	—	5-10%
TiO_2	—	1-2%	—
Grey glaze – for insulators	—	—	27.5 cm^3/250 g
Demineralised water	10-15%	10-15%	—

3. Research methodology, results and discussion

3.1. Macroscopic description of material

The analysis of the porosity, density and water absorption in accordance to Polish standard PN-89/E-06307 were carried out. The results are shown in Table 3.

TABLE 3

The average density, porosity and water absorption of the investigated proppants

Type	Density, [g/cm^3]	Water absorption, [%]	Porosity, [%]
Mass I	1.55	27.53	42.64
Mass III	1.45	33.57	48.63

Based on the results, it was found out that the above-mentioned parameters of materials meet the requirements for materials used in the fracturing process during gas extraction from shale.

Masłowski and Beckaman [8,9] informed that the best ceramic proppants should have the apparent density about 2.0 g/cm^3. The measured density of proppants obtained in this work, from Mass I and III had density about 1.55 g/cm^3 and 1.45 g/cm^3, respectively.

3.2. Microscopic structure the material

Microscopic analysis was examined by scanning microscope image method in magnification 100× (a), 1000× (b) and 5000× (c) using electron microscope TESCAN. The structure of proppants samples sintered at the temperature of 1300°C with particle sizes range 1.0-1.2 mm, were determined. Images of proppants samples are shown in figures 2-4.

The microscopic analysis revealed that the spherical shape as well as good mechanical stability have been obtained for proppants made of Mass I and III. It is correlated also with high mechanical strength test. These proppants are characterized by good compressive strength.

In the case of the proppants made of Mass II, the lowest mechanical strength was identified. It might be explained by significant fragmentation of granulates. Additionally, the highly porous structure of surface of these proppants was observed.

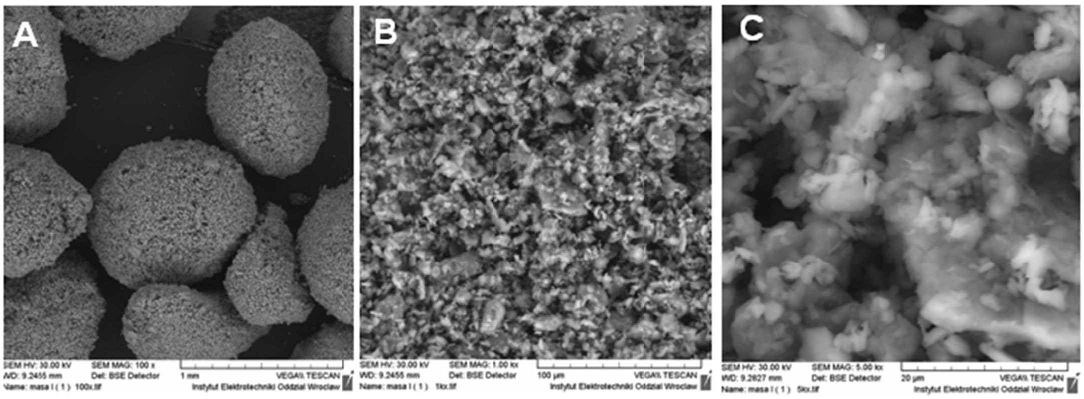

Fig. 2. The proppants obtained from Mass I, sintered at the temperature of 1300°C (particle size in the range of 1.0-1.2 mm)

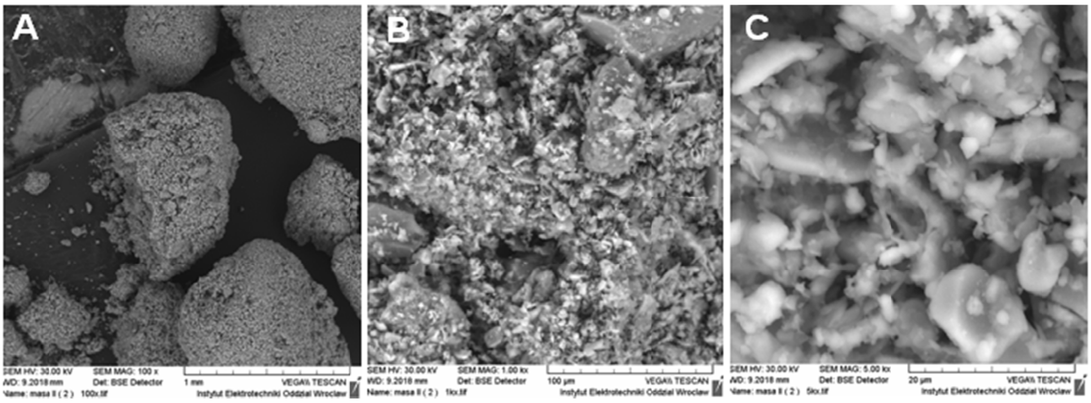

Fig. 3. The proppants obtained from Mass II, sintered at the temperature of 1300°C (particle size in the range of 1.0-1.2 mm)

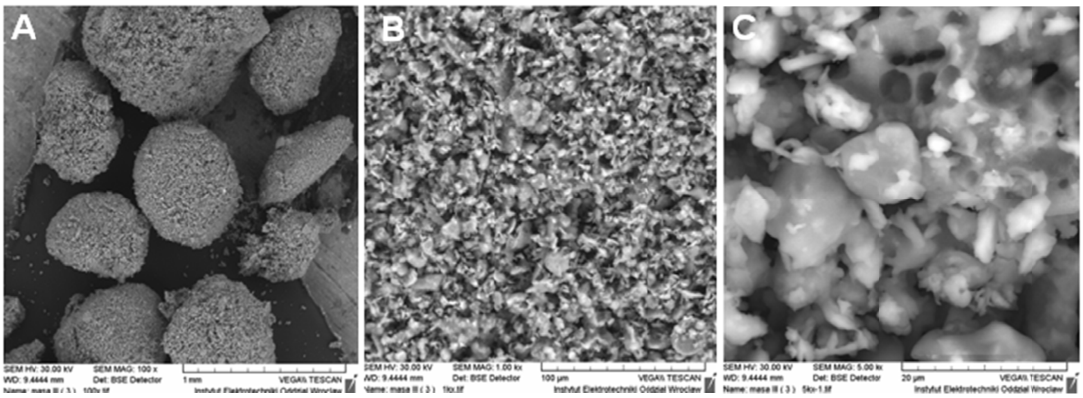

Fig. 4. The proppants obtained from Mass III, sintered at the temperature of 1300°C (particle size in the range of 1.0-1.2 mm)

3.3. Chemical and phase composition of material

Spectra/phase composition of the selected proppants was determined by X–ray diffraction method using powder diffractometer DRON – 2 with filtered Fe Co radiation. The results of the X-ray diffractions analysis for proppants are shown in figure 5.

Based on the results of the analysis, it was found out that the main phases of the proppants are aluminium oxide, oxide silica and mullite. Mullite phase was obtained by the initial sintering of kaolin at the temperature of 700°C.

3.4. Properties of obtained material

3.4.1. Mechanical compressive strength test

Mechanical, compressive strength tests of the three types of proppants were carried out. The measurements were conducted in WPM Rauenstein strength testing machine with operation range 0-5000 N. The granulates with different size were weighed and placed next to the cylinder. For the tests three different pressure values: 10, 20 and 30 MPa were used. After the tests, the granulates were sieved to obtain a size fraction below 0.088 mm. For mechanical strength evaluation, the ratio of the proppants weight with a size below 0.088 mm to proppants weight with original grain size expressed in percentage, was applied.

The results of the compressive strength test obtained for sintered proppants at the temperature of 1300°C, prepared from Mass I, II and III for a grain size of 0.5-1.0 mm and 1.0-1.2 mm are shown in figures 6-7.

For Mass I with particle size range of 0.5-1.0 mm, 1.0-1.2 mm and Mass III with particle size range of 1.0-1.2 mm at 10 MPa pressure, the fragmentation were about 25% and 16%, respectively. It was shown that two types of proppants with that particle size are characterized by highest mechanical compression strength.

The research of the gas permeability were carried out by permeability controller with flow meter function MW – Instruments MFC:D-6231.

The measurements of permeability for three dry types of selected proppants were carried out. Granules with different particle size were located in metal tube 50 mm long and 8 mm in diameter. The material was initial compressed under the pressure 10 MPa. The ends of the tubes were secured by net with very small spots. For prepared sample the air with demanded flow was inserted. Air flow at the end part of tube was measured. The gas permeability has been determined by measure its reduction during the air flow through the proppants with different size fraction and initial compression. The results are shown in figure 8.

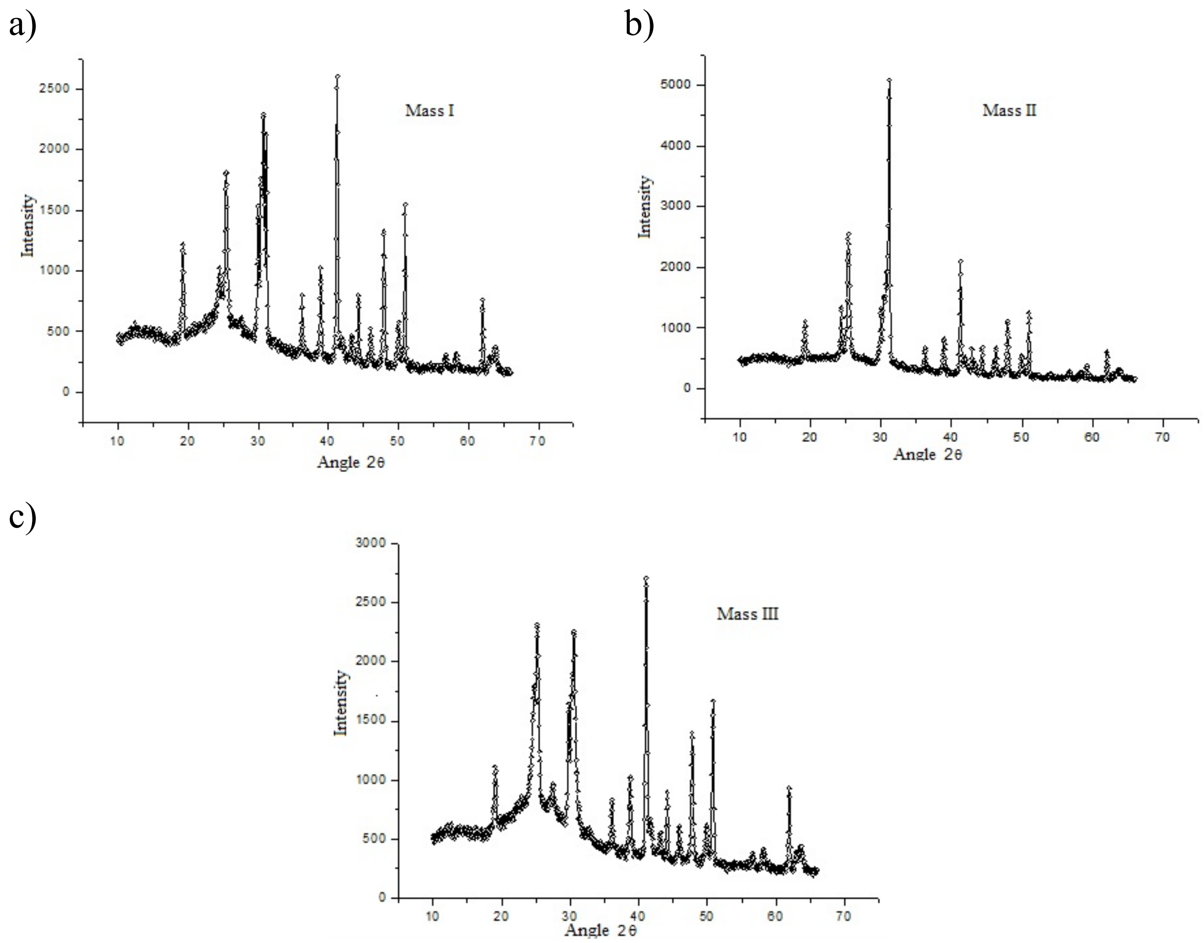

Fig. 5. XRD spectra/phase composition for investigated proppants: a) Mass I, b) Mass II, c) Mass III

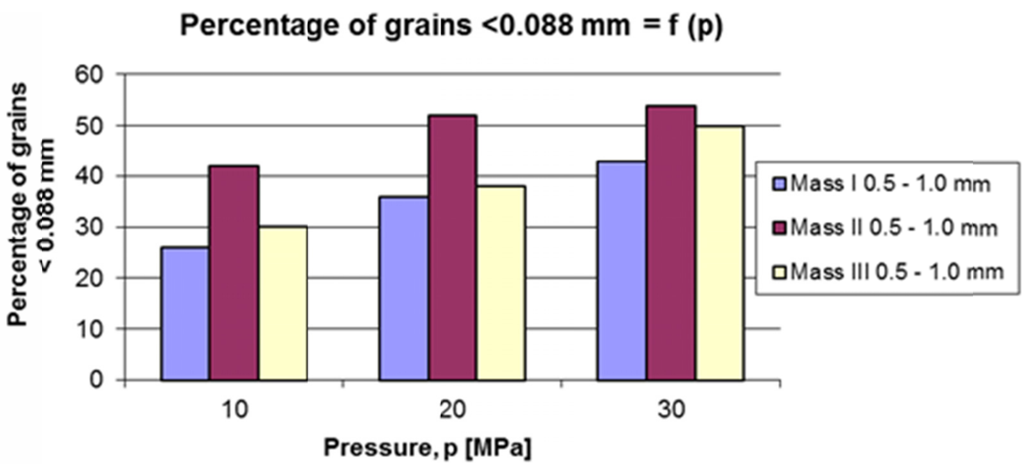

Fig. 6. The compressive strength tests of the sintered proppants at the temperature of 1300°C (particle size range of 0.5-1.0 mm)

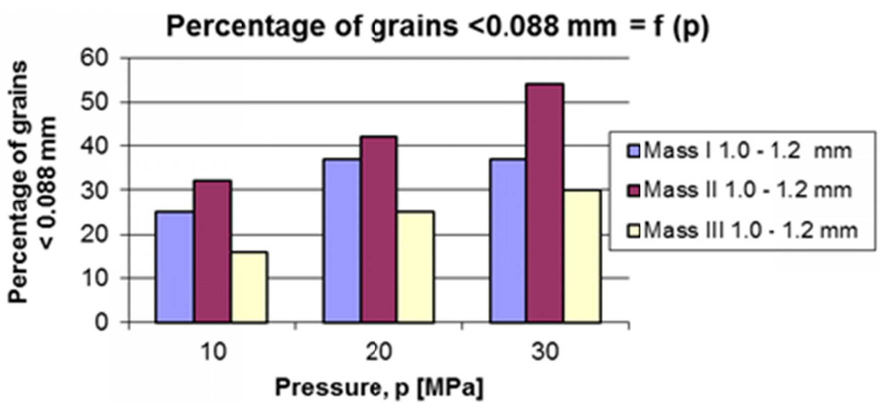

Fig. 7. The compressive strength tests of sintered proppants at the temperature of 1300°C (particle size range of 1.0-1.2 mm)

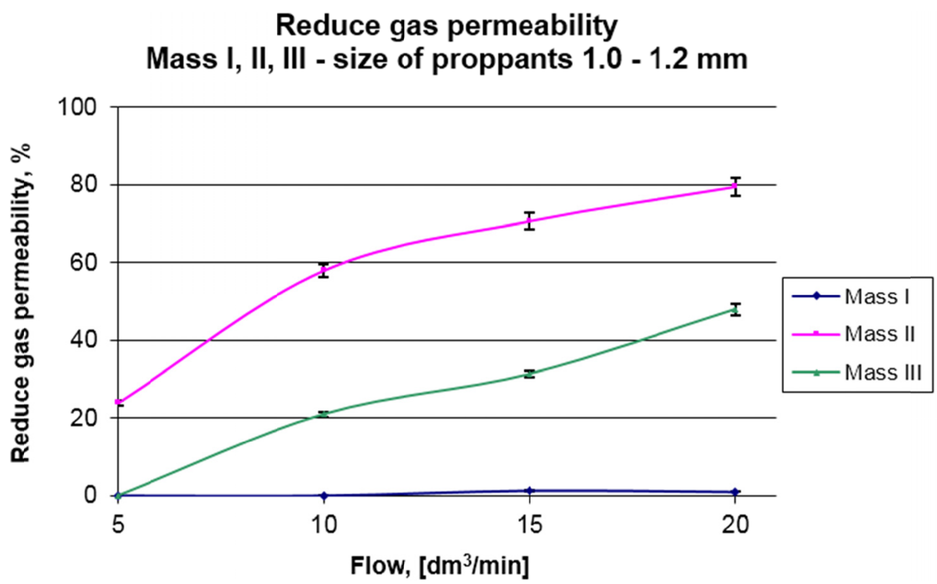

Fig. 8. Gas permeability for investigated proppants

The performed measurements indicated that the best properties in respect of the gas permeability was obtained for the Mass I. For particle size in range of 1.0-1.2 mm gas permeability was 99%, with initial compression 10 MPa.

It should be marked, that additional data could be gained from the comparison of the results for "dry" experimental conditions and "wet" environment of real shale gas exploitation, which are planned to carry out in the next tests.

4. Conclusion

- The available natural waste materials (fly ash) and uncomplicated process might be used to prepare low cost ceramic proppants.
- Ceramic material in the form of granules with high mechanical properties, was obtained.
- The density of the proppants obtained from Mass I and III were 1.55 g/cm^3 and 1.45 g/cm^3 respectively.
- The best properties - the compressive strength and gas permeability - was obtained for proppants made of Mass I.
- For particle size in range of the 1.0-1.2 mm, the gas permeability was 99%, with initial compression ca. 10 MPa.
- Compressive strength was determined by measuring the amount of crushed grains below 0.088 mm. For Mass I with particle size range of 0.5-1.0 mm, 1.0-1.2 mm and Mass III with particle size range of 1.0-1.2 mm at 10 MPa pressure, the fragmentation were about 25% and 16%, respectively.
- The results indicated that the obtained material has appropriate properties for its application in the hydraulic fracturing.

REFERENCES

[1] Polish Standard PN-93-G: 11010 "Stabilized backfill materials and filling of caving areas. Requirements and tests".
[2] D. Kamat, I.M. Saaid, S. Muhammad, National Postgraduate Conference (NPC), Kuala Lumpur, 1-6 (2011).
[3] C. Dziubak, K. Szamałek, P. Bylina, Szkło i Ceramika **63**, 2 (2012).
[4] M.A. Soleimani, R. Naghizadeh, A.R. Mirhabibi, F. Golestanifard, Iranian Journal of Materials Science & Engineering **9** (4), 43-51 (2012).
[5] S. Serkowski, H. Guenter, Ceramic Materials **63** (2), 266-272 (2011).
[6] D.N. Singh, P.K. Kolay, Prog. Energy Combust. Sci. **28**, 267-299 (2002).
[7] K. Kasprzyk, K. Kogut, B. Zboromirska-Wnukiewicz, A. Dyjakon, Z. Kasprzyk, Archives of Metallurgy and Materials **54** (4), 1021-1027 (2009).
[8] M. Masłowski, Nafta-Gaz **2**, 75-86 (2014).
[9] G. Beckmann, Measuring the Size and Shape of Frac Sand and other Proppants. Webinar Presentation, (2012).