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Optimizing the Lightweight Ceramic Proppants Properties

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The paper presents results of sintering proppants parameters and its influence on light ceramic proppants obtained by the mechanical granulation method. The proppants were prepared basing on a ceramic composition consisting of three raw materials such as kaolin, clay and bauxite mixed with poly(vinyl alcohol) binder with a molecular weight 26000 g/mol and hydrolysis degree of 88%, added in amount of 5 wt% with respect to the powder. Sintering temperature range oscillated between 1200 and 1225 °C, kiln rotations were 1–2 rpm. Sintered proppants were characterized in compliance with PN-EN ISO 13503-2 norm and bulk density, sphericity coefficient, turbidity, solubility in acids and scanning electron microscopy observations have been estimated. The results demonstrated that sintering temperature and kiln rotation have an essential effect of the proppants parameters.

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1. Introduction

The light ceramic proppants characterized by a spherical shape are classified as a natural or synthetic propping agent with a chemical neutrality and a bulk density value below 2 g/cm^3 having a fundamental impact on a hydraulic fracturing process [1–4]. With decreasing density of proppant — approximate to density of a fracturing fluid, pumping proppants into the borehole proceeds easier [5, 6]. Moreover, the ceramic proppants should be characterized by regular shape (high value of sphericity coefficient) and high mechanical strength to stabilize deposits at high depths and pressure underground. Present shale gas exploitation applies 4 kinds of proppants: sand, resin-coated sand, sintered bauxites and ceramic proppants differing in content and density [6, 7]. Increased unconventional gas exploration leads to demand for fine quality and low price propping agents. The ceramic proppants fulfill these requirements and constitute an interesting alternative for other granules [8].

Aim of this research was to determine sintering parameters impact on properties of proppants and consequently obtaining granules in accordance with PN-EN ISO 13503-2 norm to open up opportunities to their commercialization and further usage in shale gas output [9].

2. Materials and methods

2.1. Ceramic proppants technology

The following research concerns relation between sintering temperature, rotary kiln speed and properties of light ceramic proppants. Presented results of four proppants series (A, B, C, and D — Table I) obtained in the one granulation process comprise comparable quantitative and qualitative content. The granules have been obtained basing on a slurry prepared from 3 raw materials: kaolin, clay, and bauxite where poly(vinyl alcohol) with a molecular weight equal to 26000 g/mol and hydrolysis of 88% acted as a binder (Mowiol, Germany) added in amount of 5 wt% with respect to the powder. The proppants were prepared in a mechanical granulator R08 (EIRICH, Germany) within 6 min. Furthermore, the samples have been sintered in the kiln in the range of temperatures 1200–1225 °C/20 min. In Table I proppants sintering parameters were presented.

TABLE I

Sintering parameters of the lightweight ceramic proppants.

Proppants series	Sintering temperature [°C]	Kiln rotations [rpm]
A	1200	1.00
B	1210	1.25
C	1200	1.50
D	1225	2.00

Studies of bulk density, turbidity and solubility in acids have been carried out in accordance with PN-EN ISO 13503-2 norm.

2.2. Morphology of proppants

Morphology of the light ceramic proppants has been analyzed with the use of stereoscopic microscope Nikon DS-FI 2 (Japan) and scanning electron microscope Hitachi SU-8000 (Japan) at voltage equal to 5 kV.

2.3. Bulk density

Bulk density determination was enabled with normalized device equipped with a funnel and bushing (volume 150 ml). The density was estimated as ratio of amount of loosely poured off granules to its volume.

2.4. Turbidity

That study was based on estimation of solid state particles suspended in a water solution and executed with

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the use of turbidimeter *TurbiDirect_4a* (Lovibond, Germany) where beam of incident light is directed perpendicularly to the detector circuit. Results were given in NTU (nefelometric turbidity unit). In compliance with PN-EN ISO 13503-2 norm a peak admissible turbidity value amounts to 250 NTU.

2.5. Solubility in acids

Measurement of proppants solubility in acids has been carried out in order to determine propping agents solubility in acid environment that is characteristic for exploitation conditions. The experiment was proceeded basing on an acid mixture consisting of HCl:HF in weight ratio 12:3. Proppants solubility in acids indicates soluble materials content (such as carbonates, mica, Fe_xO_x, loams, etc.) typical for the examined propping material. PN-EN ISO 13503-2 norm regulates the maximum permissible value of the solubility in HCl:HF solution to 7 wt%.

2.6. Sphericity coefficient

Sphericity coefficient has been evaluated with the use of MicroMeter 1.04 tool with respect to images obtained from stereoscopic microscope Nikon DS-FI 2. Estimation of granules shape was determined by MicroMeter 1.04 tool basing on granules diameter and their area, thus their sphericity coefficient was an average from several dozen of proppant samples.

3. Results and discussion

Figure 1 shows ceramic proppants images obtained with the use of stereoscopic microscope, whereas Fig. 2 illustrates morphology of ceramic proppants obtained by SEM.

Presented ceramic proppants are characterized by similar morphology and typical shape for materials obtained on the way of mechanical granulation. Results of ceramic proppants properties have been presented in Table II.

TABLE II

Properties of lightweight ceramic proppants.

Proppants series	Bulk density [g/cm^3]	Turbidity [NTU]	Solubility in acids [%]	Sphericity coefficient
A	1.31	70.30	4.00	0.86
B	1.35	37.25	7.39	0.90
C	1.34	65.00	4.60	0.83
D	1.40	28.66	3.40	0.85

Sphericity coefficient of studied granules results in a narrow range 0.83–0.90. Further increase of kiln rotations and sintering temperature caused decrease of sphericity coefficient. Sintering temperature increase by 10 °C and kiln rotations from 1 to 1.25 rpm (A and B granules) caused change of the parameter from 0.86 to 0.90 and almost double decrease of turbidity that is profitable phenomenon. Furthermore, in the case of proppants from B

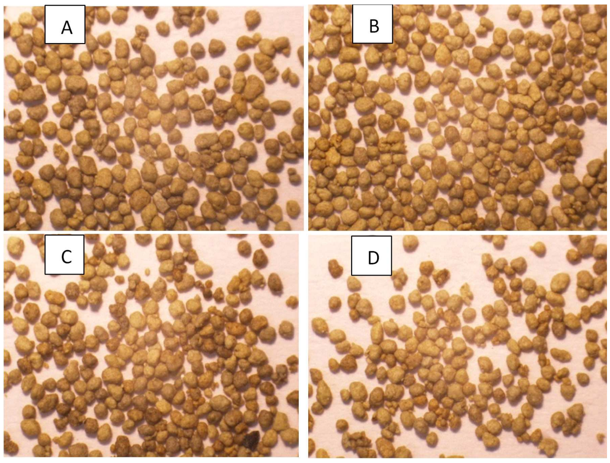

Fig. 1. Images of ceramic proppants (stereoscopic microscope) series A, B, C, D, where: (A) series A — sintered at 1200 °C/1.0 rpm, (B) series B — sintered at 1210 °C/1.25 rpm, (C) series C — sintered at 1200 °C/1.5 rpm, (D) series D — sintered at 1225 °C/2.00 rpm.

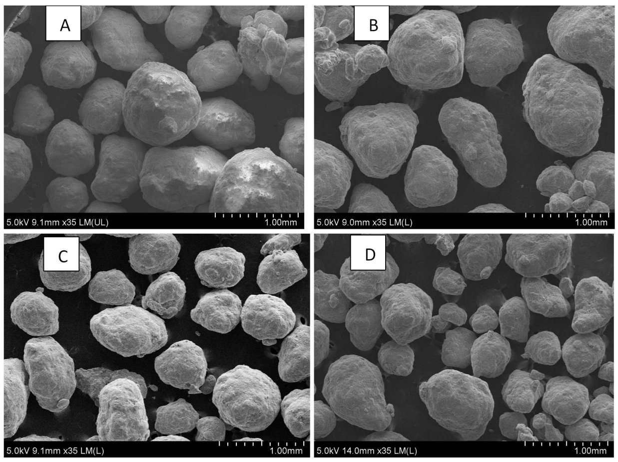

Fig. 2. SEM images of ceramic proppants series A, B, C, D, where: (A) series A — sintered at 1200 °C/1.0 rpm; (B) series B — sintered at 1210 °C/1.25 rpm, (C) series C — sintered at 1200 °C/1.5 rpm, (D) series D — sintered at 1225 °C/2.00 rpm.

series the highest solubility in acids occurs — exceeding 0.39 wt% in comparison to the permissible value constituted in the norm (7%). As the result, it disqualifies commercial use of this material. What is more, increase of kiln rotations from 1 to 1.5 rpm has been conducted with no change of sintering temperature (A and C proppants series). Analysis of obtained outcomes for A and C granules indicates decrease of turbidity value by 5 [NTU] with increase of bulk density. However, solubility in acids increased slightly and sphericity coefficient decreased. The final optimization step was preparation and examination of ceramic proppants sintered at temperature of 1225 °C/20 min at rotations speed equal to 2.0 rpm (D proppants series). The sintering temperature increase and kiln rotations had an impact on obtaining proppants with the highest density (1.40 g/cm^3) whereas solubility in acids reached the lowest level. It also resulted in the lowest turbidity. Sphericity coefficient reached a satisfying value.

4. Conclusions

The results obtained in this study have revealed that the light ceramic proppants properties are correlated with the slight sintering temperature and kiln rotations speed change as well. Regulation of both parameters in some extent might contribute to better design of light ceramic proppants. Sintering temperature up to 1200 °C should be noted as low that might reflect the highest turbidity values. Increase of the sintering temperature from 1200 to 1225 °C and double augmentation of kiln rotations have an impact on established critical parameters as the lowest turbidity (28.66 NTU), solubility in acids (3.4%), proper density and sphericity coefficient. The range of sintering temperature for the proppants with a proposed content are relevant for a more effective industrial process of their production. The measurements proved correlation between the light ceramic proppants sintering and high sphericity coefficient and bulk density below 2 g/cm^3. Lower density of propping agents is relevant for financial expenditures during shale gas production. This parameter is also crucial for fracturing fluids price that also takes effect in a profitable output process. The results reported here give a new insight into unconventional gas exploration at severe geological conditions, particularly in Europe.

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