Studies of the properties of green ceramic proppants obtained by spray drying method

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ABSTRACT

Purpose: The aim of this work was to elaborate composition and preparation method of ceramic granulates. In this paper results of properties studies of obtained proppants are presented.

Design/methodology/approach: The properties: bulk density, roundness coefficient, grain size and also structure and morphology of proppants were investigated by Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). The results indicate that composition of raw materials and type of binder have an essential effect on proppants properties in green state.

Findings: The influence of polymeric binder was examined. Two types of green proppants obtained in spray dryer without binder and with poly(vinyl alcohol) in amount of 5 wt. % with respect to the powder were tested.

Research limitations/implications: The main limitations are: proppants compositions and complex process to produce of them in spray dryer. Due to processing requirements and conditions in formations, proppants should be characterized by suitable physico-mechanical properties.

Practical implications: Proppants are ceramic materials applied in hydraulic fracturing during extraction of shale gas. Granulates pumped with liquid into the deposit cause destruction of the rock structure. The role of proppants is to avoid closing of formed pores and as result enable gas migration from the deposit. Ceramic proppants have been produced by the spray drying method with the use of naturally occurring raw materials i.e. clay, bauxite and kaolin

Originality/value: This is one of first research to preparing ceramic proppants in spray dryer using developed slurries contains Polish raw materials. The presented method for the preparation of ceramic proppants is an alternative technique in relation to the mechanical granulation.

Keywords: Ceramic proppants; Kaolin; Shale gas; Poly(vinyl alcohol); Slurry; Spray drying

Reference to this paper should be given in the following way:

PROPERTIES
1. Introduction

Shale gas definition derives from kind of rocks accumulating this hydrocarbon reserves. In comparison to conventional gas, coal bed methane or petroleum, shale gas is trapped at largest depths [1-3]. Shale formations belong to the fine-grained sedimentary rocks of thin laminated structure of silt and clay that were deposited at the bottom 460-420 mln years ago. Shale definition originates from a natural tendency of the rock to fracturing along its parallel areas [4-6]. However, shale rocks are characterized by very low permeability with nanoDarcy scale [7-8]. That is why, shale gas exploitation is realized by hydraulic fracturing technique based on rocks fracturing with use of ceramic proppants transported deep into the fracture with frac fluid to create a mechanical prop [9]. Such operation allows to free gas migration in the cracks (with a diameter equal to 1-2mm) to surface. Proppants (also called ‘propping agents’) act as a solid nonflammable material with a regular spherical shape that has to fulfil restrictions such as mechanical strenght and large roundness coefficient [10].

2. Experimental methodology

This research was based on study of pol(vinyl alcohol) influence on light ceramic proppants properties obtained in the laboratory spray dryer B-290 (BUCHI Labortechnik AG, Switzerland). The drying process was carried out at a temperature the inlet of the drying air of 150°C. The flow rate of the ceramic slurry was set at 5 ml/min. The ceramic proppants were obtained from the mix of Lubsko clay, KOC kaolin (Polish raw materials) and bauxite from Sardinia applied with a ratio: 45:45:10 wt.%. Subject of this comparison were granulates prepared without the binder (proppants A) and with the binder (proppants B). The proppants were composed of three raw materials with addition of poly(vinyl alcohol) with the molecular weight 26000 g/mole and hydrolysis degree 88% (Mowiol Germany) added in mount 5% in respect to the solid phase. The mean size of the mixed powder was 13.60µm estimated by laser diffraction method in the analyzer LA-950 (Horiba, Japan). The bulk density was obtained according to PN-EN ISO 13503-2 norm with the use of normalized device equipped with a funnel and bush with volume 150 ml. The bulk density has been calculated as a ratio of amount of loosely spilled granulates to its volume [11]. Morphology of the light ceramic proppants and the analysis at microareas EDS were concuted with use of scanning electron microscope SU-3500 (Hitachi, Japan) at voltage 5kV.

Granulates shape estimation proceeded in a programme MicroMeter 1.04 basing on stereoscopic images prepared with Nikon DS-FI 2 (Japan). In this procedure diameter and area of proppants were calculated and subsequently roundness coefficient was obtained as the average value from several dozen of the examined particles.

3. Test Results

Figures 1-2 illustrates SEM images of the ceramic proppants, whereas on Figure 3 example of result from EDS analysis at microareas has been shown.

The ceramic proppants are characterized by shape typical for materials obtained from the spray dryer. Moreover, A and B proppants morphology is similar. Proppants contamination is a consequence of the spray drying process. Both kind of granulates were prepared at analogous conditions and presented similar size. However, B proppants appear as stronger in relation to the mechanical strenght as it has been predicted. A lot of cracks, slivers and contamination have been also noticed in the case of the A proppants distinguished by more porous and irregular surface. Hence, the above results prove that addition of poly(vinyl alcohol) enhances the mechanical strenghts.

EDS analysis indicated typical part of components and contaminations present in loamy raw materials. Al and Si content dominate in aluminosilicates that were a building material for the ceramic proppants. Presence of alkali such as K, Mg, Na is a result of feldspars, while Fe comes from clays and kaolins where it occurs in a form of Fe₂O₃ and FeS₂ (pyrite). Figure 4 illustrates an exemplary estimation of granulates shape in programme MicroMeter 1.04, whereas in table 1 there are results of the bulk density and calculated roundness.

The roundness coefficient of the granulates is in the analogous range of 0.77 - 0.80. The obtained values are acceptable in hydraulic fracturing technology. Sintering of the granulates in a rotary kiln results with roundness coefficient increase. In this step there was observed no influence of the polymer on the bulk density. The raw propping agent was characterized by relatively small bulk density that is favorable result with respect to the similarity to water density used as a liquid medium in fracturing process.

However, the final verification of A and B proppants utility is possible after sintering and studies of roundness coefficient, crush test, solubility in acids, turbidity, porosity and pore size distribution and also density.

Table 1.
Properties of the light ceramic proppants in green state

<table>
<thead>
<tr>
<th>Proppant</th>
<th>Bulk density [g/cm³]</th>
<th>Roundness coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.02</td>
<td>0.77</td>
</tr>
<tr>
<td>B</td>
<td>1.03</td>
<td>0.80</td>
</tr>
</tbody>
</table>
Fig. 1. SEM images of the ceramic proppants A, imagination: a) 35x, b) 80x, c) 400x

Fig. 2. SEM images of the ceramic proppants B, imagination: a) 35x, b) 80x, c) 400x
4. Conclusions

The realized research confirms the possibility to obtain the light ceramic proppants basing on prepared raw materials with a large roundness coefficient and bulk density in the spray drying chamber. Reduced density of the material lowers price of the whole process of shale gas extraction through application of cheaper fracturing fluids and lower expenditures at pumping process. To obtain the ceramic proppants revealing a proper mechanical strenght, the use of polymer binder is essential. It ensures wetting and particles binding at green state and thus production of the proppants with required parameters after sintering proces.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME’2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS’2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

References