 XV Portuguese Conference on Fracture, PCF 2016, 10-12 February 2016, Paço de Arcos, Portugal

Selecting key parameters of the green pellets and lightweight ceramic proppants for enhanced shale gas exploitation

J. Szymanska*, P. Wisniewski, P. Wawulska-Marek, M. Malek, J. Mizera

*Warsaw University of Technology, Faculty of Materials Science and Engineering, Woloska 141 Street, 02-507, Warsaw, Poland

Abstract

Ceramic proppants are classified as propping agents commonly used for the shale gas industry. Fractures created in shale deposits due to high fluid pressure (hydraulic fracturing) have to be propped allowing unconventional gas migration to a borehole. Ceramic granules located in the newly created fissures act as a prop so that the shale gas can flow up the well. It occurs if the proppants can resist the huge forces of the closing fractures at high temperature. Due to these strict geological conditions and processing requirements the proppants have to be characterized by proper physico- mechanical properties. The aim of this research was to study, compare and select the ceramic proppants characterized by the most appropriate parameters. The investigation relates to the industrial granules obtained by the mechanical granulation method and afterwards sintered which were confronted and analyzed. Utility of the proppants was estimated basing on bulk density and roundness coefficient. Structure, morphology and chemical composition of the samples were determined by the Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS). The sintered proppants were also characterized with X-Ray Tomography, turbidity and solubility in acid additionally. The crucial parameter as mechanical strength was established during the propping samples subjection to the crush tests. The obtained outcomes prove that chemical composition, pores distribution, grain size and mechanical strength influence the integrity of created fractures and therefore the extraction of the unconventional gas out of the well.

© 2016, PROSTR (Procedia Structural Integrity) Hosting by Elsevier Ltd. All rights reserved.
Peer-review under responsibility of the Scientific Committee of PCF 2016.

Keywords: ceramic proppants; granulation; raw materials; shale gas; hydraulic fracturing

Corresponding author. Tel.: +48-791-191-329.
E-mail address: joanna.szymanska.pl@gmail.com
1. Introduction

In the last 20 years global electricity consumption per capita has risen 40% (150% in China, 90% in India, 20% in the United States and 7% in the European Union). Predictions of the International Energy Agency (IEA) state that in 2035 the world demand for electric energy will exceed 35% in comparison to 2010. Natural gas is the third (after oil and coal) main carrier of energy with growing consumption even 1.6% annually, as predicted by Polish Geological Survey (2013). This source of energy was initially regarded as component creating problems in exploitation. However, a huge breakthrough in geological knowledge and the possibility of extracting energy from unconventional resources as shale gas has initiated a revolution of the global mining industry in the last decade. Standard permeability of conventional gas deposits equals to $10^{-3}$ D (Darcy), while shale gas is permeable only at of $10^{-9}$ D (Wozniak et al. (2013)). In spite of limited access to this resource, the world unconventional reservoirs prevail nearly twice over conventional ones. Hence, according to predictions in BP Energy Outlook 2035, the global shale gas exploitation will increase from 13% in 2009 up to 23% in 2035 what is equal to 1.6 bln m$^3$.

The shale gas revolution took place in the USA in the second half of 20th century. Directional drillings and new advanced methods used to release unconventional gas determine the present world gas market, especially in the North America where occurred a significant drop in price of this raw material. Actually, the USA predominates over shale gas extraction for over ten years, bringing a lot of valuable experience. However, the American reservoirs demonstrate more favorable geological conditions in comparison to the European deposits (ranges, thicknesses, thermal maturity, organic matter and clay mineral contents, reservoir pressure and depth). This is why, there is a need to modify the exploration of unconventional hydrocarbon resources and maximize the yielding at severe conditions (Woznicka (2013)).

Shale gas is trapped under high pressure in pores and open fractures of the shale rock (free gas). Moreover, it can be dissolved in brine or adsorbed at the surfaces of organic and mineral matter as associated gas (Polish Geological Survey (2013)). Hydraulic fracturing is the key method exercised across Europe for more than six decades and even longer in the USA (Wozniak (2013)). This technique involves injections of highly pressurized water to vertical or horizontal boreholes to break the rock with reservoirs. The liquid or another medium (e.g. carbon dioxide, nitrogen), containing chemicals with suspended proppants, propagates in the broken rock. Obtained fractures enable gas migration as pressure increases beyond the minimum stress tangential to the wellbore wall. The induced fracture always spreads in a direction approximately to the horizontal stress axis, at fracture pressure being higher than the minimum contemporary stress. A significant role act proppants injected into the network of opened cracks which prevent fracture closure when pressure drops rapidly after completion of the procedure (Polish Geological Survey (2013)).

Taking into consideration presence of any geomechanical barriers, that prevent fracture propagation beyond shale formations, it is important to optimize fracturing technique by choosing the best kind of proppants with proper chemical and mechanical parameters. Commonly applied propping agents consist of quartz sand and resin-coated sand that are used for the American shales fracturing since the early 50s of the 20th century. Whereas, bauxites and ceramic granules are granular materials proper for deeply deposited unconventional gas extraction at hard geomechanical conditions (i.e. in Europe) to increase output of gas even by 30-50% (Wozniak et al. (2013)). To create a permeable channel for hydrocarbons flow, these proppants must be characterized by uniform round shape, thermal stability and much higher strength than sand (Wozniak et al. (2013)). In comparison to other propping materials, ceramic granules predominate also with smoother surface and low solubility in acids (Wozniak et al. (2013)). Such parameters can be available through a proper proppants production based on higher amount of Al$_2$O$_3$ than SiO$_2$. The crucial proppant characteristics can be also modified by polymer addition to the initial raw materials mixture that undergo a mechanical granulation and further sintering. Ciechowska et al. (2012) demonstrated that uniformity of the proppants determines facilitated gas migration to the well bore. Fines exceeding 1% of proppants reduce fracture conductivity. Moreover, high roundness coefficient ensures a stable prop for the fracture. At high stresses, over 4000psi, increase of the proppant sphericity results in improved permeability. However, at lower stresses, the proper gas flow is an effect of more angular shape of the proppant. The crucial factor is also size of granules varying between 8-140 Mesh (where sphere diameters is 106 µm – 2.36 mm). A minimum 90% of the proppants must be within the specified screen size. Diameter of the single granule regulates the material permeability which rises maximum with lowering size. Moreover, larger proppants settle closer to the wellbore...
where they also bridge. While smaller granules can cover a further distance (Bankong Arop (2011)). Additionally, lower specific weight (~ 2 g/cm³) favours economical aspect of the whole fracturing process and it also determines proppants settling in the fractures. The proppants have to reveal reduced solubility in acids as HCl and HF applied in fracturing treatment. Turbidity determines the amount of suspended particles in water environment typical for fracturing treatment. A high concentration of proppant fines relates to incorrect proppant manufacturing, transportation, or handling practices which may affect fracturing fluid chemistry (Ottestad (2013)).

The most impact feature, when selecting propping agents, is resistance to mechanical compression. It enables to determine the maximum stress level that proppant crushing reduces gas production. The pressure in the fracture increases with distance from the wellbore. According to predictions by Schlumberger (2014), at extremely hard conditions propping agents have to resist closure stress from 15 000 even to 20 000 psi (at temperature up to 260°C). Insufficient crush resistance results in material fracture into fines carrying a risk of blocking the permeability. Barely 5% of splinters cause gas flow reduction by 60% (Don (2011)). In case of stress increase, there occurs limitation of proppant. The strength is also strictly determined by effective porosity of ceramic materials. Pores geometry, distance between them and surface induce the mechanical properties of granule (Richerson (2006)). As Kullman et al. said that fracture width can strictly affect the crush what increases significantly in narrow fissures. Interior granules are loaded evenly on 6 sides. However, exterior grains are exposed to fewer load points, thus their mechanical strength decreases significantly with drop of proppant loading. The contact angle between granules being a function of Young’s modulus, Poisson ratio and loading force, regulates the stress distribution in a sphere. A large contact angle reduces tensile stress concentration and thus protect the proppant. That is why, decrease of Young’s modulus/ increase of Poisson ratio may reduce proppant crushing (Reinicken et al. (2010)).

There was also proved that for all proppant types, larger grains resulted with greater individual strength. However, the reason of crush increase in case of larger proppants is limited number of settled grains in a narrow fissure. That is why, smaller mesh sizes distribute the load across more particles in comparison to larger mesh size. It is evident that different proppant types crush otherwise. Quartz crystals that withstand closure pressure result in a greater number of fine shards in comparison to resin coated sand. RSC presents improved distribution of stress. Particle encapsulation prevents from fines loss and thus they will not be measured as “crush”. On the other hand, ceramic proppants tend to cleave or part into relatively few, larger pieces. As seen in fig.1, the rock type also determines the proppant behavior under high pressure. In case of soft more loamy and thus plastic formations (present in Europe), the stress propagation in the fissure will be different. The high contrast that occurs between rock and proppant may cause substantial proppant embedment and a rapid fracture closure during reservoir depletion (Reinicken et al. (2010)).

![Fig. 1. Proppant settlement in the shale rocks (Proppants, 2010)](image)

All these conditions determine permeability of proppants loaded in the fracture. With increasing closure stress (from 1000 to 16000 psi), the gas flow decreases to a larger extent in case of sand. More gas migrates through resin coated...
sand and the highest permeability value occurs to ceramic proppants. Moreover, the packing arrangement for similarly Meshed granules will be different depending on kind of proppants, even at comparable stresses. Weaver et al. (2005) proved that sands and coated proppants with similar grain sizes fracture into significantly smaller “craters” in the rock in comparison to ceramic proppants, thus proppant embedment is reduced. Sand is characterized by a smaller Young’s modulus than ceramic granule. That is why, there is a larger contact areas and reduced stresses in case of the rock–proppant interface (Reinicken et al. (2010)). There was also indicated that the proppants tend to be more damaged by continued stress cycling. Kullman et al. confronted results of three cycles from 6000 to 1000 psi with 50 hours stress duration what proved this assumption.

The following research of light ceramic proppants obtained by mechanical granulation method will be contribution to improvement their properties and taking the lead on the global shale market.

2. Materials

Experimental samples of 4 kinds of sintered proppants (P1-P4) have been produced from raw materials based on clays and bauxite mixed with water and chemical additives in oscillatory and turret mills. P4 samples consist from ash particles additionally. Afterwards, the slurries were subjected to granulation process in a turret granulator and sintering in a rotary kiln at high temperature (1550°C). The sintering exposition period has averaged to 15 minutes at speed of the kiln heating to the maximum temperature amounted to 0.5 RPM. The final sintered proppants were sieved with proper mesh sizes.

3. Methodology

The ceramic proppant specimens were investigated in relation to fracture surface, size and shape in SEM analysis with HITACHI SU 8000 (Hitachi, Japan). The microstructure identification was conducted using SE detector at voltage 5 kV, working distance 9-9.4 mm and magnification from 30 to 1000 times.

In order to estimate chemical composition by located particular elements Energy Dispersive Spectroscopy (EDS) was applied with use of Thermo Noran detector combined with Scanning Electron Microscope Hitachi SU 8000. Roentgen microanalysis enabled detection of surface topography by back scattered electrons.

Roentgen tomography was carried out with use of Roentgen Microtomograph SkySkan 1742. The samples were scanned with 2000 px x 1000 px resolution in range rotation 0 - 180° (results registration every 0.4° with use Al-Cu filter). The scanning data the results were subjected to reconstruction and thus obtaining the cross-section.

Aim of bulk density study was estimation of proppants weight required to unit volume filling. This parameter is dependent on the material handling and allows to proppants mass preparation during hydraulic fracturing and further storage of the propping material. The experiment was based on sleeve calibration (volume 150 ml) with a defined mass (mf+g) and then water pouring to its upper rim (mass determination mf+g+l). The sleeve volume Vt was computed according to the equation (1):

\[ Vt = \frac{m_w}{0.9971} \text{ [cm}^3\text{]} \]  
where: \( m_w \) – water mass (netto) from mf+g+l - mf+g [g]; 0.9971 [g/cm\(^3\)] – water density at 21°C.

Further step was dry and empty sleeve weighting (m_p) and the same procedure in case of beaker completely filled with proppants (volume150 ml, mass m_{f+g+P}). Hence the bulk density \( \rho_{bulk} \) was obtained from equation (2):

\[ \rho_{bulk} = \frac{m_p}{Vt} \text{ [g/cm}^3\text{]} \]  
where: \( m_p \) – mass of proppants from m_{f+g+P} – m_f [g]; Vt – sleeve volume [cm\(^3\)].

The degree of roundness was determined with use of MicroMeter 1.04 programme where proppants stereoscopic images (Nikon DS – F12) were analyzed. The granule diameter and their areas were used to roundness coefficient
calculated according to equation (3):

\[ W_k = \frac{4 \pi \times A}{L^2} \]  

(3)

where: \( A \) – surface area of proppant; \( L \) – perimeter of proppant.

Turbidity measurement proceeded according to PN – EN ISO 13503 – 2 norm with use of TurbiDirect_4a Turbidimeter where a beam was directed perpendicularly to the detector track. Increased turbidity level corresponds to large content of suspended solid particles in a suspension.

Solubility in acids was also determined according to PN – EN ISO 13503 – 2 norm. In the experiment 5 g of proppants were immersed in 100 ml of 12:3 HCl:HF solution (12 wt.% HCl, 3 wt.% HF) in a bath at 66°C temperature for 30 minutes. The solubility in such acid solution correlates to soluble compounds content (carbonates, micas, ferrous oxides, loams) present in the investigated material. The solubility \( S \) was obtained basing on formula (4).

\[ S = \frac{(m_S + m_F - m_{FS})}{m_S} \times 100 \% \]  

(4)

where: \( m_S \) – mass of the sample [g]; \( m_F \) – mass of the filter [g]; \( m_{FS} \) – mass of the dry filter with sample [g].

According to PN – EN ISO 13503 – 2 norm assumption, crush test was conducted of hydraulic press adjusted to exert pressure up to 15 000 psi. Mass of the proppant sample poured into a cylinder was obtained according to equation (5):

\[ m_p = 24.7 \times \rho_{bulk} \]  

(5)

where: \( \rho_{bulk} \) – a bulk density [g/cm³].

The material should fill the cylinder to specific height so as exerted pressure on a piston’s surface averaged 1.95 g/cm². The examined sample gave a flat surface of material inside the cylinder. The piston was inserted into the cylinder in centric position with reference to the hydraulic press. Force exerted on the piston to obtain required stress values was determined according to equation (6):

\[ F_c = \frac{\pi \times O \times \sigma \times d^2}{4} \]  

(6)

where: \( F_c \) – force exerted on the piston [N]; \( \sigma \) – stress exerted on the sample [MPa]; \( d \) – inner diameter of the cylinder [mm].

The force was increasing with a constant speed of increasing piston loading corresponding to growth of the stress (13.8 MPa/min ~ 2000 psi/min) up to the final stress value maintained for 2 minutes.

4. Results and discussion

Analysis of the proppant samples microstructure and their shape were conducted with scanning electron microscopy. SEM images (shown in figure 2) indicate a size similarity of most of proppants. P4 demonstrate the smallest diameter whereas P2 samples exceed their dimension few times (~ 1 mm). The coarse surface is characteristic to all of samples. However, P1 proppants present the most round shape. The most non-uniform particle size distribution is attributed to P2 grains that may affect their proper settlement in the fissure, permeability
and strength. P3–P4 proppant morphology indicate a huge porosity which may lower their specific weight and increase gas migration. From the other hand, there is a risk of insufficient resistivity to closure stress.

EDS analysis at microareas indicated chemical purity among all the studies granule series. Dominating element is Al that creates with oxygen Al$_2$O$_3$. Si is also one of the main components, while Mg, Ca, K and Ti occur in minimal amounts. All of these elements are typical for proppants obtained from on mineral raw materials.

Basing on tomography results with structure images as the intersection of the x, y, z planes (fig. 3), P1 samples demonstrate the highest roundness coefficient and proper effective porosity. Pores arrangement in the form of elongated cracks is typical for P2 proppants, while P3–P4 samples contain widely arranged macropores inside the material. Propping agents cannot contain more than 20–30% conjoined to pores to assure a proper gas flow at high mechanical strength.

In table 1 roundness coefficient, bulk density, solubility in acids and turbidity of the granules have been compared. All the kind of proppants demonstrate required round shape value that enhances shale gas conductivity.
According to US 2011/0160104 A1 patent required bulk density of sintered proppants ranges between 1 – 3 g/cm³. All of the samples fulfil this condition. However, proppants with ash addition (P4) present the lowest value. Three kinds of proppants demonstrate low susceptibility to acids. Acceptable solubility limit is 7%. This permission was slightly exceeded by P3 samples. Whereas, the acceptable turbidity level is typical only for two kinds of proppants. The Polish water quality norms permit turbidity of drinking water to 1 [NTU]. In case of proppants it grows up to 58 [NTU]. So taking into analysis P3 and P4 proppants, there is a risk of hydraulic fluid contamination due to material disintegration and further fracture clogging.

Table 1. Proppant parameters

<table>
<thead>
<tr>
<th>Proppant</th>
<th>Roundness coefficient</th>
<th>Bulk density g/cm³</th>
<th>Solubility in acids [%]</th>
<th>Turbidity [NTU]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.82</td>
<td>1.59</td>
<td>4.95</td>
<td>47.24</td>
</tr>
<tr>
<td>P2</td>
<td>0.80</td>
<td>1.57</td>
<td>2.79</td>
<td>34.96</td>
</tr>
<tr>
<td>P3</td>
<td>0.83</td>
<td>1.67</td>
<td>7.72</td>
<td>109.20</td>
</tr>
<tr>
<td>P4</td>
<td>0.82</td>
<td>1.39</td>
<td>3.76</td>
<td>73.94</td>
</tr>
</tbody>
</table>

Conducted crush tests indicate that all the proppant series were able to resist even in the highest stress of 210 kN (103 MPa ~15000 psi). P1 samples characterized by round shape and even porous arrangement were less susceptible to the stress in comparison to P2 and P3 granules (fig.4). Proppants with the largest size (P2) demonstrated lower resistivity even to the lowest exerted pressure after 4 min (51.71 MPa ~105,5 kN~7500 psi). While P4 proppants distinguished by ash content and high effective porosity indicated the highest mechanical strength.

![Fig.4. Crush test results of sintered proppants at 3 increasing stresses; a) P1 proppants; b) P2 proppants; c) P3 proppants; d) P4 proppants.](image-url)
5. Conclusions

The outcomes of proceeded studies indicate that all the examined proppants are characterized by proper roundness coefficient and slightly coarse surface. Regular pores arrangement is characteristic for P1 sintered samples what results in their high mechanical strength. There is a risk the largest granules (P2) can be insufficient resistive to high stress values in fracturing environment thus they can flatten and pack together under high closure stresses blocking shale gas extraction. The sintered proppants are stable in strong acidic environment. However, two kinds of proppants are prone to disintegration in fracturing medium based on water. Thus, a fracture may be clogged decreasing its yield. All samples are characterized by low thus bulk density that results in their facilitated transport in liquid medium. Addition of ash particles to the one of proppant series results in their reduced mass and increased mechanical strength.

To sum up, the investigated light ceramic proppants perform properties which enable their application for hydraulic fracturing in strict geological conditions determined by extremely high pressure, temperature and low permeability of shale formations. The granules fulfil the norms thus state a prospective material on a global proppants market.

Acknowledgements

Financial support of BLUE GAS financed from The National Centre for Research and Development- Project “Optimizing the lightweight high strength and low specific gravity ceramic proppants production technology maximally using naturally occurring Polish raw materials and fly ash”, No. BG1/BALTICPROPP/13 is gratefully acknowledged.

References

Ottestad, E., 2013. Proppants, properties and requirements, NTNU.
Wozniak, P., 2013. The need for a debate on the shale gas in Europe, European National Geological Surveys have their role to play, Przeglad Geologiczny, 61, 11/1.