Applied Clay Science 166 (2018) 327–338

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research Paper

Determination of loamy resources impact on granulation of ceramic proppants and their properties

Joanna Szymanska*, Pawel Wisniewski, Paulina Wawulska-Marek, Jaroslaw Mizera

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

ARTICLE INFO

Keywords:
Ceramic proppants
Raw clays
Bauxite
Kaolin
Granulation
Shale gas

ABSTRACT

Currently, the global oil & gas sector is focused on enhanced natural gas exploration from unconventional rock formations. The potential deposits are located within large-scale basins of impermeable shales (hydrocarbons accumulated in closed pores) with plastic zones at great depths with high reservoir pressure. These severe geological conditions determine the application of granulated propping agents, named "proppants". They are pumped with hydraulic fluid during hydraulic fracturing and subsequently locate tightly inside created rock fractures. Proppants function as a prop to facilitate gas flow up the wellbore. Quartz sands are applied mainly for low pressure basins. However, only ceramic proppants, granules produced from raw clays in a mechanical granulation and sintering process, are proper for deeper shales due to their homogeneity, higher sphericity, and mechanical and chemical stability.

Aim of this research was verification of the impact of natural loamy resources (aluminosilicates in powder form) mixed with binder on ceramic proppants quality. Utility of the clays was estimated by their particle size distribution (PSD by laser diffraction method) and thermal stability (thermogravimetry - TGA). The unique platy morphology was determined by scanning electron microscopy (SEM), while energy dispersive spectroscopy (EDS), X-ray fluorescence (XRF) and X-ray diffraction (XRD) revealed chemical-phase composition. Moreover, aluminosilicates were subjected to analysis of specific surface area (BET method) – very crucial for powder consolidation into granules in mechanical granulation.

Quality of the granulated, and consequently sintered, bodies was evaluated by calculations of roundness and sphericity coefficient, specific gravity and bulk density, combined with microtomography (μCT) - a key investigation of porosity and proppant settlement in fracture. SEM studies also revealed phase transitions due to high temperature exposition of the green proppants and the correlation with proppant strength, evaluated in crush tests. Moreover, measurements of turbidity and solubility in acids revealed risk of the granules' decay in the shale gas wells.

The obtained outcomes show dependence of the proppant's structure on the binder and the loamy materials ratio, proving the utility of the applied natural resources in the granules production. In consequence, these proppants can be used for hydraulic fracturing in severe mining conditions in accordance to the strict international ISO standards.

1. Introduction

In the last decade, a huge breakthrough in unconventional rock drilling, initiated in the USA, allowed for enhanced natural gas extraction on a global scale. Unconventional formations relate mainly to impermeable shales which comprise of potential gas reservoirs in the form of hydrocarbons, trapped under high pressure, in closed pores, or adsorbed at the surfaces of organic/mineral matter (Wozniak and Janus, 2013; Maslowski, 2014, 2015).

The most widely practiced technique of enhanced shale well stimulation is hydraulic fracturing (Mandar et al., 2017). The injected proppants have a significant role as a prop for the induced/re-opened natural cracks over distances of several hundreds of meters in the rock, preventing fracture closure and thus allowing the natural gas flow up to the well (Liang et al., 2016; Liu et al., 2016).

Taking into consideration enhanced shale gas output, proper filling material selection is a very crucial step. Fused zirconium dioxide, quartz sand and resin-coated sand dominate among currently applied proppants (Montgomery and Smith, 2010). Nevertheless, sintered bauxites and ceramic granules can intensify gas extraction by 30–50%

---

* Corresponding author.
E-mail address: joanna.szymanska.dokt@pw.edu.pl (J. Szymanska).

https://doi.org/10.1016/j.clay.2018.09.032
Received 29 May 2018; Received in revised form 28 September 2018; Accepted 30 September 2018

in more extreme geomechanical conditions (i.e. in Europe, China) resulting from their particular attributes (Wozniak and Janus, 2013). Of huge importance for hydraulic fracturing treatment is the size of the granules varying between 8 and 140 Mesh (with sphere diameters of 105 μm – 2.38 mm) (Montgomery and Smith, 2010). Furthermore, 90% of proppants need to fall within a range to prevent a fracture clogging (O'Driscoll, 2013).

Furthermore, extreme geological conditions, determine the demand of proppant injection with spherical or near-spherical shape comparable to 0.7 or greater roundness and sphericity coefficient. Such parameters ensure the economic transport of granules and stabilize a fracture width to maximize streamline fluid flow (O'Driscoll, 2013; Szymanska et al., 2016a). Ceramic proppants are also differentiated by their density resulting from alumina content. Lightweight ceramic proppants (LWC) contain between 45 and 50% of Al_2O_3, have a specific gravity of 2.55–2.71 g/cm^3 and bulk density of 1.57 g/cm^3, intermediate density ceramics (IDC) consist of 70–75% of alumina, demonstrate a specific gravity close to 3.27 g/cm^3 and bulk density of 1.88 g/cm^3, while HSP (high strength ceramics) contain 80 to 85% of Al_2O_3, density reaching almost 3.5 g/cm^3 and volume filling of 2.00 g/cm^3 (Liang et al., 2016). Although, higher bulk density enhances the proppant's package in a fracture, increase in the apparent density leads to a faster pellet settling rate in the carrier fluid that results from the application of higher viscosity liquids and additional expenditures. On the other hand, there is a strict correlation between alumina content and mechanical strength of the granules. Higher amounts of Al_2O_3 allow proppants to resist closure stress which surpasses even up to 20,000 psi (138 MPa) (at 260 °C) (Montgomery and Smith, 2010), while sand and resin-coated sand maintain stability only to 5000 psi (34 MPa) (Montgomery and Smith, 2010; Ciechanowska et al., 2012; O'Driscoll, 2013). This most crucial issue determines the amount of the material crushed into fines, which may block open channels in a fissure. The minimal amount of the splinters (up to 5%) can occupy the pores in the granular pack and lower conductivity by up to 60% (Don, 2011; Mandar et al., 2017). Deposit compressive and tensile pressure, displayed as differential pressure along a fracture length, tend to dislodge and crush the proppants. Their mechanical restrictions have a crucial impact on further hydrocarbon exploitation (Mandar et al., 2012). The strength is definitely related to porosity of the granules. Such phenomenon - a correlation between proppants embedment and their behaviour under high pressure in different geological scenarios (hard shales, soft shales) was precisely discussed in the previous work (Szymanska et al., 2016b).

Ceramic propping agents also take a lead in the shale industry due to minimal solubility in acids injected with hydraulic fluid. Moreover, the granules cannot be prone to disintegration in water. Such proppants' behaviour minimizes the risk of creating new pieces of the broken grains (O'Driscoll, 2013; Ottestad, 2013).

Except bauxites, matrix of ceramic pellets can be also based on silicate, kaolin, iron –titanium oxide and zirconium dioxide (O'Driscoll, 2013; Hellmann et al., 2014; Szymanska, 2014; Wisniewski et al., 2015; Liang et al., 2016; Liu et al., 2016; Wisniewski et al., 2016; Mocciaro et al., 2018). Kaolin minerals characterized by specific layer structure are particularly applied due to their high degree of order and chemical purity being greater than other clay minerals (Balan et al., 2014). Especially calcinated kaolin (75–90%) enhances the proppant's crush resistance after firing operations. Due to lower apparent density compared to bauxite, kaolin is a main component for LWC (O'Driscoll, 2013). However, the presence of any additional impurities needs to be taken into consideration. In particular, iron or titanium oxides should fall maximally within 5% and 6% respectively. Increased Fe_2O_3 concentration is conductive to low-temperature melting ferrites. Furthermore, alkalis in a powder may form an undesirable glassy state at low melting temperatures (Bolewski et al., 1991). Apart from aluminosilicates and other mineral applications, many binders, such as polymers, can be applied in small amounts to the raw material mixture at the initial step of the proppant's production. Such operation ensures effective powder particle consolidation and thus improves the mechanical characteristics and their spherical shape during mechanical granulation process (Szymanska et al., 2016a). Addition of any other supportive materials, such as fly ashes or coke, is aimed to control proper closed porosity, microstructure and real density, affecting proppant crush resistance (Maa et al., 2010; O'Driscoll, 2013).

The main purpose of the present research was to investigate the influence of raw natural materials, in powder form and polymer, on pore distribution, shape and its correlation with ceramic proppant sphericity and mechanical properties (crush resistance). Quality of the raw loamy materials was also analysed and discussed in order to determine stability and highlighted key values of the granules. The following research will be a contribution to further proppant~~s~~ production by mechanical granulation, consequently solving a main problem of effective hydraulic fracturing under extreme conditions.

2. Experimental procedure

2.1. Materials and production

For this study, blends of raw bauxite, kaolin and clay (in amounts of 60 wt%, 20 wt% and 20 wt% respectively) were used as starting materials to prepare a proppant's matrix. Such proportions were conditioned by the highest mechanical strength of bauxite which is correlated to the highest content of alumina. The addition of kaolin and clay was in order to decrease proppant's shrinkage during the sintering process, thus preventing undesired stress propagation inside the material. Implementation of kaolin enhances powder dispersibility, essential in various clays' processing (Pruett, 2016). Moreover, the clays served as plasticizers in propping agent formation. The granules were produced in a mechanical granulator (*EIRICH Intensive Mixer Type EL01*) with 30° inclination of the rotating pan. Vinyl acrylic was doped as a binder (in concentrations of 1, 2 and 3% of the solid phase) and dry homogenized with the powders in the mixing pan for 2 min (rotation rate of 1800 rpm) to obtain finely dispersed medium for three different kinds of proppant, named P1, P2 and P3 (in relation to the increasing binder content). The polymer was added mainly to reinforce liquid bridge between particles of the powders during the moistening process with use of a pre-determined amount of water, as seen in Fig. 1.

Through homogenous liquid distribution to the powder surface, with the use of a hydraulically operated spray nozzle, a desirable particle nucleation, consolidation and controlled growth proceeded, facilitating the formation of spherical pellets. Spray droplet size was also essential to avoid agglomeration of the granules and fine particle separation resulting from the dry powder particles' immersion in larger water droplets. Vinyl acrylic was applied to increase porosity of the granules. High speeds and alternating direction of the mixing tool of the mixing pan (the counter-current mode) were applied to prevent local inhomogeneity of the binder and the powder, and unfavourable material adhesion to the wall of the mixing pan, too. Moreover, determination of the tool speed during the granulation and duration of particular phases (homogenization, liquid addition and granulation) had a key impact on the granules size distribution, shape and density modification. Afterwards, the obtained granules were subjected to firing at 1400 °C in a chamber kiln (*Nabertherm*) with determined rate of sintering and cooling and also sintering time. The sintered ceramic granules were finally sieved (20/40 mesh), with a *Retsch Sieve Shaker AS 300 control,* to ensure homogeneity of the material - essential to the further studies. The produced proppants were also compared with one commercial kind of proppant (*Wanli Ceramic Proppant* 20/40 mesh, derived mainly from calcined bauxite, kaolin, blends of bauxite and kaolin, > 50% Al_2O_3, and magnesium silicate).