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Research paper

Effect of raw material milling on ceramic proppants properties

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ABSTRACT

Low density and high breakage resistance ceramic proppants were developed from kaolin, bauxite and monoaluminum phosphate (MAP). The effect of the particle size on the raw materials over the density, the open porosity and the breakage resistance of the proppants was evaluated. The phase composition and the structure of the proppants due to the milling process were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and pore size distribution by mercury intrusion. The proppants obtained with raw materials of smaller size improved its breakage resistance and developed a smaller open pore size, achieving an apparent density of 2.4 g/cm3 with a breakage ratio of 9.61% under 64 MPa. Some properties of the AG3 proppants with sand, low density ceramic proppants of the literature and commercial low density ceramics proppants were compared.

1. Introduction

Proppants are agents used in the hydraulic fracture process for the extraction of non-conventional gas and oil. This process involves the injection of a fracture liquid with solid spherical proppants at high pressure to break the rock and release the hydrocarbons. The purpose of the proppants is to help in the fracture, keeping the fracture walls open resisting the forces that tend to close it. Thus, proppants prevent the collapse of the fracture, forming the channels that increase the gas and oil conductivity (Kulkarni and Ochoa, 2012; Snegirev and Slobodin, 1998). There are different types of proppants: polymeric, quartz sands and ceramic materials (Liang et al., 2016; Yin and Dai, 2005; Zhao et al., 2015). The advantage of the first one is its low density; however, they do not have a great breakage resistance such as ceramic materials.

A low bulk density of the proppants allows them to be dragged by the fracture liquid with efficiency and prevent their accumulation in the first part of the fracture, which negatively influence in the whole conductivity. This indicates a need to develop a low density ceramic proppants with and acceptable breakage resistance (Bestaoui-Spurr and Hudson, 2017; Cutler et al., 1985; Gaurav et al., 2012; Gu et al., 2015).

Low density ceramic proppants are those with similar apparent density values as sand (2.60–2.65 g/cm^3) (Cannan and Palamara, 2006; Lunghofer, 1992).

Mullite ($3Al_2O_3{\cdot}2SiO_2$) is one of the main components of the ceramic proppants available in the market, due to its properties such as high mechanical strength, low thermal expansion coefficient and high resistance to acid corrosion (Aksay et al., 1991; Schneider et al., 2008).

These properties makes the mullite a suitable material for preparing proppants because of the closure stress and corrosive conditions that are subjected in the hydraulic fracture.

One of the synthesis methods to obtained mullite is by sintering kaolin with an alumina source (Al_2O_3), the solid phase reaction is: $3Al_2O_3 + 2SiO_2 \rightarrow 3Al_2O_3{\cdot}2SiO_2$ (Brindley and Nakahira, 1959; Burst, 1991; Chen et al., 2000).

Some researchers reported the milling of the raw materials but the final size of the particles is not specified (Liu et al., 2016; Wu et al., 2017; Zhao et al., 2015). Also some patents recommended an average particle size less than about 15 μm, preferably less than about 10 μm and most preferably, less than about 5 μm (Fitzgibbon and Lafayettw, 1984; Khaund, 1987).

In this work, mullite ceramic proppants were developed, studying how the particle size of the raw materials affects the bulk density, the breakage resistance and the structural properties. Also the low density ceramic proppants obtained were compared with sand, low ceramic proppants of the literature, and a commercial low ceramic proppant.

2. Materials and methods

2.1. Raw materials

A kaolin Tincar Super (Santa Cruz, Argentina) and bauxite (Brasil) were used as solid raw materials (Burst, 1991). Monoaluminum phosphate (MAP or $Al(H_2PO_4)_3$) solution was used as a phosphoric binder when it is exposed at temperature (Giskow et al., 2004; Kingery, 1950; Morris et al., 1977).

In this work, MAP was synthesized in the laboratory from a

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stoichiometric mixture of pseudobohemite ($Al_2O_3 \cdot xH_2O$) and phosphoric acid (H_3PO_4). The MAP obtained from the reaction was brought to a mass concentration of 40% and heated at 80 °C for 40 min to obtain a sol-gel system as the commercial solutions (Giskow et al., 2004).

The kaolin and bauxite powders were subjected to X-ray diffraction (XRD) analysis to determine their mineralogical composition using Cu kα radiation and a Ni filter at constant voltage 40 kV, and 35 mA using Philips PW-3710 Diffractometer.

Chemical analyses for the major oxides (mass %) of the kaolin and bauxite were performed using X-ray fluorescence spectrometry (XRF). Thermo gravimetric analysis (TG) and differential thermal analysis (DTA) of the raw materials was done up to 1300 °C by Rigaku Evo plus II TG-DTA Instrument. Both thermal analyses were carried out simultaneously at a 10 °C/min heating rate in air atmosphere (TG-DTA Rigaku Evo plus II, Japan).

The percentage of both bauxite and MAP used was 10%, based on the mass of clay. The roll of bauxite is to increase the amount of mullite in the proppants after thermal treatment.

2.2. Experimental procedures

Initially the solids were wet milled in porcelain ball mill for 48 h, 72 h, and 48 h with the addition of a dispersant (sodium polyacrylate). These mixtures were referred as AG1, AG2 and AG3 respectively. The particle size distribution obtained in each milling was determined using a laser diffraction based size analyzer using a Mastersizer 2000 Malvern Instrument.

The dispersions obtained by milling were dried at 110 °C and the agglomerates were broken using a hammer mill with a powder outlet of < 70 μm.

With a high energy mixer (R20E, Erich Industrial Ltd., Brazil), the green bodies proppants were formed from the mixtures of solids with the three milling parameters mentioned above (48 h, 72 h and 48 h with the addition of dispersant) and with the addition of MAP and water. The spherical green proppants were calcined in an electric furnace at air atmosphere with a heating rate of 5 °C/min until 1450 °C with a residence time of 1 h.

After calcination, the proppants were sieved through the 20/50 meshes (one of the sizes required for hydraulic fracture), and bulk density, apparent density, sphericity, roundness and breakage ratio at 64 MPa, were tested by API 19C standards (API 19C, 2008). Complementary tests, pore size distribution, X-ray diffraction and scanning electron microscopy analysis, were performed in order to understand the results.

2.2.1. Bulk and apparent density test

Bulk density, describes the mass of proppants that fills a unit volume and includes both the proppants and the spaces generated between them. In contrast, the apparent density is measured by picnometry and the mass of the material is evaluated per unit of volume of the proppants including the internal porosity.

2.2.2. Sphericity and roundness test

Sphericity is a measure of how much the proppants approaches to the sphere shape, and the roundness is a relative measure of the curvature and not the sharpness of the edges of the proppants. The standard API 19C says that ceramic proppants must have an average sphericity and an average roundness equal to or > 0.7.

2.2.3. Breakage ratio test

The breakage ratio is a measure of the mechanical strength of the proppants, and the equipment used is strictly following the API 19C standards. It is to determine the amount of proppants crushed at a given stress, the breakage ratio is calculated by the formula: $\eta = Wc / Wo \times 100\%$, where Wc is the weight of crushed specimens after testing and Wo is the weight of proppants before testing. The standard API 19C requires a $\eta \leq 10\%$ to be used for the hydraulic fracture.

Table 1
Chemical composition of kaolin and bauxite.

	Kaolin (%mass)	Bauxite (%mass)
SiO_2	61.82	13.38
Al_2O_3	27.55	53.91
Fe_2O_3	0.79	6.2
MgO	0.66	0.48
K_2O	0.76	0.22
TiO_2	0.39	0.72
Others	3.20	0.77
LOI (1000 °C)	7.63	24.33

2.2.4. Porosimetry test

The pore size distribution was analyzed by mercury intrusion porosimetry (Pascal-Thermo Fisher 440 and 140). It allows to know the *meso* and macro open porosity in the proppants as a relationship with the final density. Pores in the material can be determined by the volume of mercury, which is a non-wetting liquid.

2.2.5. X-ray diffraction (XRD) and scanning electron microscopy (SEM)

The crystalline phases and the structural changes due to the milling process present in the proppants were identified by X-ray diffraction. The morphology and microstructural characterization of the proppants were carried out by scanning electron microscopy (JEOL CM-600 Neo Scope). In order to reveal mullite grains, chemical etching was done with 5% hydrofluoric acid (HF) for 5 min (Elssner et al., 1999).

3. Results and discussion

The chemical composition of the raw materials was determined and showed the composition (mass %) of the samples in Table 1. The main components of the clay as oxides were alumina (Al_2O_3) and silica (Si_2O). The main components of the bauxite as oxides were Al_2O_3, Si_2O, Fe_2O_3 and Ti_2O indicating that was a low-grade bauxite (Liu et al., 2016; Ma et al., 2016).

The X-ray diffraction spectra of the kaolin (Fig. 1a) and the bauxite (Fig. 1b) showed the predominant crystalline phases. The kaolin sample revealed the presence of kaolinite and quartz (Moore and Reynolds, 1997; Zbik et al., 2010). In the bauxite sample X-ray diffraction spectra reflections associated with gibbsite ($Al(OH)_3$) and boehmite (AlO(OH)) were identified as the main sources of alumina; also, kaolinite, anatase (Ti_2O) and goethite (FeO(OH)) were observed.

The DTA curve of kaolin (Fig. 2a) showed two endothermic peaks at 74.8 °C and 512.8 °C and an exothermic peak at 983.9 °C. The first endothermic peak was relative to the dehydration of the clay and correlating with this in the TG curve at 21–200 °C there was a mass loss of 2%. The second endothermic peak on the DTA curve and a mass loss of 7% on the TG curve in the range of 200–800 °C was induced by the dehydroxylation of kaolinite. The exothermic peak, at 938.9 °C corresponded to the metakaolin-mullite transformation (Lee et al., 1999; Saikia et al., 2003).

Two endothermic peaks were observed on the bauxite DTA curve (Fig. 2b). The first peak at 298.9 °C was induced by the dehydration of $Al(OH)_3$ into AlO(OH) and corresponding to this peak a mass loss (− 22%) was observed from 200 to 380 °C in the TG curve. The second peak at 480 °C was induced by the dehydration of AlO(OH) into amorphous Al_2O_3 and related with this dehydration a mass loss (− 5%) was observed in the TG curve at the range of 400–650 °C (Laskou et al., 2006; Zhu et al., 2010).

The particle size distribution of the mixes with different millings process was determined (Fig. 3) and the maximum diameters in μm of 10%, 50% and 90% ($d_{0.1}$, $d_{0.5}$ and $d_{0.9}$ respectively) of each sample