Hydraulic fracturing proppants

(Propantes para fraturamento hidráulico)

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Abstract

Hydrocarbon reservoirs can be classified as unconventional or conventional depending on the oil and gas extraction difficulty, such as the need for high-cost technology and techniques. The hydrocarbon extraction from bituminous shale, commonly known as shale gas/oil, is performed by using the hydraulic fracturing technique in unconventional reservoirs where 95% water, 0.5% of additives and 4.5% of proppants are used. Environmental problems related to hydraulic fracturing technique and better performance/development of proppants are the current challenge faced by companies, researchers, regulatory agencies, environmentalists, governments and society. Shale gas is expected to increase USA fuel production, which triggers the development of new proppants and technologies of exploration. This paper presents a review of the definition of proppants, their types, characteristics and situation in the world market and information about manufacturers. The production of nanoscale materials such as anticorrosive and intelligent proppants besides proppants with carbon nanotubes is already carried out on a scale of tonnes per year in Belgium, Germany and Asia countries.

Keywords: ceramic synthetic proppant, hydraulic fracturing, nanotechnology, proppant materials.

Os reservatórios de hidrocarbonetos podem ser classificados como não convencionais ou convencionais de acordo com a dificuldade de extração de óleo e gás, como a necessidade de tecnologia e técnicas de alto custo. Atualmente a extração de hidrocarbonetos do xisto betuminoso, conhecido popularmente como gás/sólido de xisto (“shale gas/oil”), é realizada por meio da técnica de fraturamento hidráulico em reservatórios não convencionais onde se utilizam 95% de água, 0.5% de aditivos e 4,5% de propantes. Problemas ambientais relacionados à técnica de fraturamento hidráulico e ao desenvolvimento de novos tipos de propantes são os desafios atuais enfrentados pelas empresas, pesquisadores, agências regulatórias, ambientalistas, governo e sociedade. É previsto um aumento na produção de combustível nos EUA por meio do “shale” que traz consigo o desenvolvimento de novos propantes e tecnologias de exploração. Esse artigo apresenta uma revisão sobre propantes: suas definições, usos, classificações além de informações sobre o mercado mundial, principais produtores e suas características técnicas. A produção de produtos em nanomais como propantes anticorrosivos, propantes inteligentes e contendo nanotubos de carbono já é realizada em países como Bélgica e Alemanha, além de vários países asiáticos.

Palavras-chave: propante cerâmico sintético, fraturamento hidráulico, nanotecnologia, propantes.

INTRODUCTION

Hydrocarbon sources are classified as unconventional or conventional. The differentiation is determined by chemical characteristics, the location of the reservoir and the technology required for its extraction. The main characteristics of the conventional reservoirs are the smaller amount of resource, smaller depth, lower cost of extraction and the use of fluid displacement technique. The difficulty in exploring hydrocarbon reservoirs (gas and oil) due to the entrapment of hydrocarbons in the low permeability rock, high viscosity oils, special technology needs for extraction and/or high amounts of hydrocarbons is characteristic of non-conventional reservoirs. Some examples of these reservoirs are: low permeability layered oil, compact sand gas, coalbed methane, petroleum shale, heavy oil, reservoirs located at extreme depths (below 5 km depth), shale gas, among others [1, 2]. The term shale refers to olefin shale, bituminous or pyrobituminous materials. The shale formation comes from the sedimentation of organic matter over time that generates rocks of low permeability. The increase on temperature and pressure produce the shale gas, usually with a composition of 75 to 95% of methane containing nitrogen and traces of ethane, propane, oxygen and carbon monoxide. At the present time, the use of hydraulic fracturing in assistance of the extraction of hydrocarbon from shale formation has significantly increased [3, 4].

The idea of hydraulic fracturing arose in a study by Floyd...
Farris (1947) for Stanolind company (Standard Oil Indiana - AMOCO) on well pressure, more specifically the formation breakdown during the acidification fracture (acidizing), water injection and cement filling in order to determine the relation between the performance observed in the well and treatment pressures [5]. Thus, an experimental treatment for well stimulation using the recent technical discovery called HydraFrac was performed the same year at Hugoton Field in Grant County, Kansas-USA. Approximately 3,785 L of Napalm were used in a well approximately 731 m deep [5].

Commercial hydraulic fracturing operations were registered on March 17, 1949 conducted by Halliburton (HOWCO - Halliburton Oil Well Cementing Co.) in Stephens County, Oklahoma and in Archer County, Texas [6]. The fracture fluid of the method used, HydraFrac material, was composed of 25/75 gasoline and crude blend, Napalm (6%), sand (Ottawa sand - 45-68 kg) and S-60 breaker gel [5].

The most common drilling techniques are the directional and horizontal. These techniques are popular because they have greater contact in the area with the reservoir, causing more hydrocarbons to be extracted [7]. The proppant, usually sand or support agent, is used in the hydraulic fracturing process (fracking) in the production of hydrocarbons in non-conventional reservoirs. The technique is performed with the injection of fracture fluid, a high-pressure fluid containing water in approximately 95%, additives (0.5%) and proppant (4.5%). When the fracture fluid is injected, the fractures that had been generated and propagated by implosion into the reservoir expand as the proppants fill and maintain them open when the pressure is finally relieved [8]. The objective of this review is to share essential details about proppant materials involving the most recent researches and their main properties and characteristics. This paper discusses market prospect associated with world production and proppant producers.

**PROPPANT TYPES AND PROPERTIES**

Proppants materials can be grouped into three main categories (Fig. 1): rounded silica sand, gravel and resin coated sands, sintered and/or fused synthetic ceramic materials [9]. The most commonly used materials are sand, ceramic, sand-lined resin and sintered bauxite [10, 11]. Over the past six decades, materials such as walnut shell, Brandy and Ottawa sand, glass, kaolin and molten zirconia have been used as proppants [12]. Walnut shell, steel shot, aluminosilicates, molten zirconia, plastic pellets, glass beads, aluminum pellets and ash are also used and tested [13]. There are several types of proppants with different characteristics according to standard classification. These characteristics must be appropriate to the type of well and reservoir in order to be hydraulically fractured. Proppants act correctly in the support of opened cracks from fracking operation. Fig. 2 shows some types of proppants fixed in different types of rocks with and without applied stress. Fig. 3 presents a scheme of the choice of proppant material according to the tension of fracture closure [15].

Several properties must be evaluated adequately for the selection of proppant materials. Table I shows important factors for this selection [13], resistance being one of the main properties to be considered since it defines the lifetime and the limit of closure stress. The proppant’s resistance is also related to the porosity, which is therefore connected to its density. The method of production determines the quality of the format (sphericity and roundness) and the size of the final product. Worldwide technical standards have been used for proppant classification. The most important ones are API RP 56, 60 and 61 [17-19], ISO 13503-2 [20, 21], and ASTM E11 [22]: size designation by sieves: ASTM E11; format (sphericity and rounding): ISO 13503-2 §7; density: ISO 13503-2 §10; acid solubility: ISO 13503-2 §8; turbidity: ISO 13503-2 §9; crush test: ISO 13503-2 §11/13503-5; conductivity test: API RP 61/19D. The proppants’ main particle sizes are between USA mesh 30 equivalent to 0.589 mm and USA mesh 50 equivalent to 0.297 mm. For selection, 90% of the material passing through the upper sieve and only 1% passing through the lower sieve are considered [17-23]. A water-based polymer (e.g., water-based guar gum) is normally used for transporting the proppants and especially for the opening and propagation of fractures [24].

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**Figure 1:** Pyramid of proppants’ flow, adapted from [14].

**Figure 2:** Relationship between some types of proppants and some types of rocks, where sand grains are the sand proppants without covering, soft proppant is the synthetic proppant of low mechanical strength, and hard proppant is the high-strength synthetic proppant. Adapted from Saint-Gobain Innovation Center [15].
studies on the use of sea water as part of the composition of the fracture fluid [25] and the use of proppants in geothermal reservoirs [26] requiring chemical stability and resistance in saline/acid media. The proppants’ typical specific bulk density (SBD) is between 2.65 and 3.56 g/cm³ and the bulk density (BD) is between 1.60 and 2.00 g/cm³. Table II shows a few types and their respective typical densities.

Table II - Variation of typical density of different types of proppants [27].

<table>
<thead>
<tr>
<th>Proppant type</th>
<th>SBD (g/cm³)</th>
<th>BD (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure sand</td>
<td>2.65</td>
<td>1.60</td>
</tr>
<tr>
<td>Resin-coated sand (RCS)</td>
<td>2.55</td>
<td>1.60</td>
</tr>
<tr>
<td>Intermediate resistance ceramic (IRC)</td>
<td>2.7-3.3</td>
<td>1.84</td>
</tr>
<tr>
<td>High resistance ceramic (HRC)</td>
<td>3.4</td>
<td>2.00</td>
</tr>
<tr>
<td>Bauxite</td>
<td>2.00</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Figure 3: Scheme of choice of proppant type according to the fracture closure stress in the reservoir [15, 16].

[Figura 3: Esquema de escolha do tipo de propante em função da pressão de fechamento da fratura do reservatório [15, 16].]

The main difference between SBD and BD is the accuracy in approaching the material actual density in reference to the volume occupied in liquid and outdoor media. The characteristics of each type of proppant in hydraulic fracturing efficiency are presented below.

Silica sand: commonly known as Canadian sand, Ottawa sand, Jordan, Hickory, Badger, Brady, Colorado silica, Arizona, white, brown and Ottawa white, silica sand proppants are the cheapest proppant of low crushing strength. However, there is a difference between white sand and brown sand proppants. White sand is monocrystalline and...
Figure 5: Examples of: (a) standard RCS; (b, c) premium RCS proppants; and (d) resin-coated proppants failure test ceramography (courtesy from Stim-Lab) [14].

Ceramic synthetics/bauxite: synthetic ceramic proppants are mainly made by burning, melting or sintering bauxite (Fig. 6) and/or kaolinite clays $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$. The final mineralogical composition, after material processing, is composed of the mixture of mullite ($\text{Al}_2\text{Si}_3\text{O}_9$) and corundum ($\text{X-Al}_2\text{O}_3$, where $\text{X} = \text{Ti}$ or $\text{Fe}$). Proppants can also be prepared by mixing other ceramic materials such as silicon carbide ($\text{SiC}$), mixed yttrium or stabilized ceria and cubic zirconia, zircon ($\text{ZrSiO}_4$) [9], kaolin, magnesium silicate (serpentinite derivatives, olivine and dunite), andalusite, metabasalt, ash (cenospheres [28]), alumina rich clay, nanostructured ceramics/glass, metallurgical slag and mineral tailings. The bauxite-based proppant is the most used. It is also important to note that increasing alumina content increases strength and cost [14]. Some additives such as diatomite, titanium dioxide, chromite, boron, magnetite, magnesite, manganese oxide and rare earth oxides are used, for example, to decrease the matrix sintering temperature [13]. With higher resistance to crushing, sintered ceramic materials can be used in environments up to 140 MPa (~20,305 psi) besides being chemically inert. However, due to their high density, the use of viscous loading fluids in the fracture becomes necessary, leading to higher pumping rates and increased energy during pumping (braking power). The cost of these proppants is relatively high [9]. Table III presents the characteristics of medium, medium to high and high-density ceramic proppants of a given supplier (values may vary among manufacturers). The density of the proppants influences their performance such as crush strength and reach along the fracture channel [29], varying
between 1.5-3.7 g/cm³ [29-31].

**Synthetic proppants processing**: there are several processing routes for granulation employed in the ceramics industry through the production of synthetic proppants. Some material granulation processes are highlighted [9]: granulation by agitation: fluidization; granulation by pressure: pelletizing/granulation; granulation by spray: atomization. Strong proppants are obtained by sintering, which can be performed after obtaining the spherical material or simultaneously in the rounding step (flame method). The proppants are usually made by the sintering of high-grade bauxite and kaolin. High-grade bauxite is used because it achieves high mechanical strength, a requirement for proppants at great depths where the closure stress in the hydrocarbon region can exceed 8,000 to 10,000 psi (~55.2 to 68.9 MPa) [12]. As mentioned in [12], the underutilized industrial waste and minerals from other industrial processes are a potential resource as feedstock for the proppants. Therefore, the common process is carried out by means of the granulation technique in which the processed raw material (a fine powder material between 45-80 μm of different compositions which can normally contain silica, alumina and iron) is mixed in an intensive mixer and the moisture is controlled in order to obtain granulated material. After this step, the material can be classified and sintered. Finally, the material is again classified and the proppant is obtained in the chosen range that is influenced by the steps of granulation and granulometric classification. During this process, some beads may become imperfect, be collected in the granulometric grading step and be used as abrasives.

**Table IV - Examples of the use of proppants in different wells in the USA; adapted from: Company filings, Morgan Stanley Equity Research, OilPRO estimates.**

<table>
<thead>
<tr>
<th>Shale well</th>
<th>Depth (feet)</th>
<th>Stress (MPa)</th>
<th>Stress (kpsi or K)</th>
<th>Commercial grade proppants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bakken</td>
<td>10,000</td>
<td>41-69</td>
<td>6-10</td>
<td>Ceramic, RCS, sand; 20/40 mesh (0.84/0.4 mm)</td>
</tr>
<tr>
<td>Barnett</td>
<td>7,500</td>
<td>21-27</td>
<td>3-4</td>
<td>RCS, white sand; 40/70 &amp; 100+ mesh (0.4/0.21 &amp; 0.14+ mm)</td>
</tr>
<tr>
<td>Eagle Ford</td>
<td>11,000</td>
<td>48+</td>
<td>7+</td>
<td>Ceramic, RCS, sand; 20/40; 30/50, 40/70 mesh (0.84/0.4; 0.59/0.29; 0.4/0.21 mm)</td>
</tr>
<tr>
<td>Fayetteville</td>
<td>8,000</td>
<td>14-27</td>
<td>2-4</td>
<td>RCS, sand; 40/70 mesh (0.4/0.21 mm)</td>
</tr>
<tr>
<td>Haynesville</td>
<td>10,500</td>
<td>62+</td>
<td>9+</td>
<td>Ceramic, premium RCS; 30/50; 30/60; 40/70 mesh (0.59/0.29; 0.59/0.25; 0.4/0.21 mm)</td>
</tr>
<tr>
<td>Marcellus</td>
<td>7,000</td>
<td>34-48</td>
<td>5-7</td>
<td>Sand, limited RCS &amp; ceramic; 40/70; 30/50; 100+ mesh (0.4/0.21; 0.59/0.29; 0.14+ mm)</td>
</tr>
</tbody>
</table>

**Notes**: plus signs (+) refer to values that can be equal or higher than the number before the signs; RCS - resin coated sand.
**Synthetic proppants based on recycled materials:** New proppants are developed aiming at the best performance in their application such as lifetime, acid/saline resistance and crushing, flow and environmental impact. In this class, there are proppants of high control of sphericity, uniform size and high resistance to crushing of approximately 135 MPa (~19,626 psi) [32]. Some studies are presented below.

**Special and other proppants:** A comparative study among ground ceramic tile, granular porcelain tile, cast beads, solid beads and glass microspheres was carried out in order to compare the performance of these materials, using API, ISO and ABNT proppants standards [33]. The summary of conclusions of the analyzed work is: 1) approved materials for making proppants: ceramic floor - ecological alternative; spheroidized porcelain - application to shallow wells, need for coating; resin glass microspheres - with properties similar to commercial proppants'; massive beads - need coating; 2) reprobate materials for making proppants: beaded beads - brittle, unstable in acidic environment. Another special development was the tagged ceramic proppant made of a chemical marker to determine the source of proppant reflux. However, non-radioactive traced ceramic proppants are used to determine their location [11, 14].

**Mineral waste based synthetic proppants:** the Russian patent RU 2476478 (and sequences) [34] provides details of the production of magnesium silicate based proppants containing flux agent such as titanium oxide, zirconia silicate and clay and emphasizes the magnetic characteristic of the material. Details of the tests are given in the patent. The development of acid-resistant red mud based proppants was performed in [35]. In this study, an evaluation was performed with 3 test methods using red mud, barium carbonate and plasticizer. It was verified that the acid solubility of the samples was lower than 4.5%, which meets the Chinese petroleum standard, SY/T 5108-2006, and that by adding barium carbonate the acid solubility is effectively reduced due to the formation of celsian-BaAl$_2$Si$_2$O$_8$ monoclinic in the sintering process, which protects and prevents erosion in the sample by the acid use. Some works on the recycling of glass trimmings, ashes, metallurgical slag and mineral tailings were carried out at the Pennsylvania State University [36-39]. Examples of the mixture granulation using residues from the asphalt industry, andesite, rhyolite and basalt fines were pre-cast and aggregated forming high sphericity and rounding material by means of a melting tower (via flame) of laboratorial scale (Fig. 7a). The obtained material reaches the scale 0.9 (KS) for both sphericity and rounding parameters, resulting in a smooth and vitreous sphere (Fig. 7b) [39].

A study on the residue rich in magnesium silicate as feedstock and fluxes was carried out by evaluating the mechanical strength, time and temperature of sintering in cylindrical samples of 11.0 x 11.0 mm. The initial tests showed that the use of these residues as synthetic ceramic proppant is possible, directing the study to a new phase of confection of granulated and classified material [40].

A study of the addition of barium carbonate (BaCO$_3$) and reduction of silicon oxide (SiO$_2$) in the composition of the proppant was conducted in order to increase the acid resistance (the acid environment being proppant fracturing fluid and the reservoir itself) [41]. It was also found out that the use of red mud from the Bayer process of alumina extraction via bauxite ore can be used to make acid resistant proppants [42]. Another study using residues from different media was performed aiming at the preparation of synthetic ceramic proppants with acid resistance. The group used red mud from the Bayer process, refractory residue (containing alumina), Weilu (a region of Guangxi province, China) mud containing kaolin and acting as plasticizer (additive), calcium fluoride (for increase in ceramic conversion degree) and barium carbonate (additive). The study concludes that the resistance in acid medium has not been improved with the increase of either alumina content or calcium fluoride, but was satisfactory with the addition of barium carbonate. Finally, it was also concluded that it is possible to make fracture proppants with good resistance by using red mud as raw material [42]. The effect of chromite addition on bauxite-based proppants was studied, leading to the conclusion that it forms a solid solution of chromium ore and phases of mullite-shaped rod that may contribute to fortify the proppant and lower the melting temperature [43]. To reduce the migration of fines, the commercialization of nanocrystals to fix them through the treatment of proppant packs is a possible solution [44]. The format memory effect is a property that can be scanned in nanoscale. The changes in shape can be activated by changes in temperature, humidity or pH. This effect can be obtained with the presence of nanoparticles based on specific steels or polymeric composites that maximize the efficiency of shape memory phenomenon [45].
NANOTECHNOLOGY APPLIED TO HYDRAULIC FRACTURING

Nanoparticles have been successfully used in fluid drilling for the past 50 years and recently all other key areas of the oil industry (such as exploration, primary and assisted production, monitoring, refinement and distribution) have employed nanotechnology to solve critical problems such as exploration in ultra-deep waters, high pressure and high temperature formations, especially in non-conventional reservoirs [46-48]. The following are some types of nanotechnology applied to the recovery of oil and gas that can act along with the proppants.

Nanosensors: nanotechnology such as the use of single-walled carbon nanotubes (SWNTs) treated with gold plus electric current and 4-amino-TEMPO molecules formed a reusable sensor that in the presence of H2S break and interrupt the signal, enabling the study of properties, chemical composition and reservoir conditions [49]. The use of contrasting nanoparticles is also studied [50] by using nuclear magnetic resonance (NMR) or other measurement techniques to locate them indicating if the initial hydraulic fracturing was adequate and if re-fracking with higher pressure is needed [49]. These particles can be transported in the proppants into the reservoir. Contrasts and sensors obtained from nanomaterials or nanostructures such as nanorobots (still considered a goal in the medical and oil sectors) are also alternatives for reservoir mapping [48] and can be added in the fracturing fluid or transported in the proppants’ pores [51]. Intelligent and/or multifunction polymer special coatings are also studied and combine network formation with the functions of sensors or actuators and physical, chemical or mechanical stimuli by means of readable signals [52].

Coatings and membranes: the use of nanometric thin films for corrosion protection in probes, drilling systems, tanks and pipelines can also be extended to proppants [48]. The nanotechnology-based application will bring savings in the cited segments and is attractive for several factors such as relatively low risk, high efficiency and low complexity [48]. Carbon nanotubes have been used as coating materials and will be on the market in the near future [53] perhaps acting as conductors and heating the surface evenly with the possibility of being used in pipelines to reduce the formation of gaseous hydrate or to melt ice on wind turbine blades [53]. They may also be used to heat the oil into the reservoir by decreasing its viscosity and increasing its flow among the proppants. Polysilicon nanoparticles may alter the surface pore wettability of reservoir rocks and thus affect the flow of water and oil by improving water injection and oil recovery [54]. Such application might be extended to the proppants.

Special fluids: fracture fluid tests containing proppants made with nanosilica were performed to investigate the effects of the electrical resistivity of the fracture fluid (increased with the addition of nanosilica, decreased with increasing temperature) and the yield strength of the fluid (increased with the addition of nanosilica - 1% nanosilica increased 10% yield strength at room temperature) [47]. Also, by adding 1% of nanosilica and reducing 4% of the sand content (proppant), the loss of fluid was reduced by 16% at room temperature and 18% at 85 °C. Other studies of nanotechnology fracturing fluid are also investigated, such as the use of super fine powders and nanometric particles mixed with an advanced fluid that generates a significant increase in the drilling speed and can eliminate the damage formed near the well zone [55]. In addition, intelligent fluids that improve drilling due to benefits such as wettability, advanced drag reduction and proppant consolidation have also been studied [56]. Some examples of the development of super-resistant materials include the use of nanostructured dispersed-hardened materials [57], or physical-mechanical properties of polycrystalline diamond nanocomposites [57], boron nitride nanocomposites [58], and nanocomposites of WC-Co-diamond [59].

Companies and nanotechnology: the production of nanoscale products such as anticorrosive proppants, intelligent proppants and nanotubes is already carried out on a scale of tonnes per year in Belgium, Germany and Asia [50]. Several proppant production industries are located in China, highlighting DC Global Oil & Gas Service Co., which makes proppants reinforced with nanomaterials fixed with thermoset polymer by a special process available on the market. The company guarantees to have the lightest, perfectly spherical and smooth proppants that will not crush, chip and break or generate fines like other proppants on the market. Oxane® Materials, another company that uses nanotechnology, founded by specialists from Rice University in the city of Houston, Texas, USA, now seeks to use nanotechnology to enhance the produced proppants using resistant and lightweight nanostructured ceramic. Halliburton and other major hydrocarbon explorers planned to embed nanotechnology in their products by the end of 2015. The company does not show the kind of nanotechnology used, but highlights that nanosensors (patented by NASA, without reference details) can monitor qualities such as humidity, temperature, pressure and detect the presence or lack of specific molecules [48].

Other nanotechnologies: to increase the reach of the proppants within the fracture, researchers [50, 60] have studied the development of alumina (α-Al2O3) with empty core proppants in order to ensure high sphericity versus low-density ratio. Controlled electrolytic materials (CEM) composed of magnesium, nickel, aluminum and other metals are ultrafine powders studied for possible uses as proppants [61]. Once the beads are formed, they will be lighter than aluminum and more resistant than steel. These CEM proppants may be programmed to become powder again and be removed from within the reservoir. Another example is the cryogenic treatment of proppants that may promote improvements in shape (sphericity) and a smooth texture on the surface, reduce the friction between proppants or other particles of different materials that may have treated the proppant before, reduce prominent projections when compared to other untreated proppants, inhibit the anchoring
of undesirable materials on the surface or reduce the production of fines [62]. The same treatment can also be extended in the cryogenic treatment of nanomaterials (such as carbon nanotubes - CNT) that can be used to coat the surface of the proppant and, besides promoting the same characteristics previously mentioned, also aims at increasing the resistance, improving thermal and electrical properties, reducing electrical resistance and improving the electrical conductivity of conductive nanomaterials [62]. Studies on synthesis and characterization of alkaline activated metakaolin based ceramic proppants incorporating different types of nanocarbon materials (carbon nanotubes, carbon black and graphene) were performed at the Polytechnic School of the University of São Paulo. A resistance on 4K (1K-value equals 1,000 psi) in the crush test was achieved on pure metakaolin samples, enabling their application in reservoirs with crushing pressure up to 4,000 psi. The nanocarbon dispersion achieved in the matrix was homogeneous [63, 64].

**PROPPANT MARKET AND MAIN PRODUCERS**

The consumption of proppants in the USA for well stimulation is expected to grow from 23 bn ton to 38 bn ton in only 4 years. The consumption of 43 million tpy (tonnes per year) was expected to reach 55 million tpy in 2016. Fig. 8 shows the estimation of USA proppant consumption by each type. An increase in the consumption of resin-coated proppants (RCP) can be observed [65]. In the first experiments in the 1940’s, about 228 kg of sand were used. Currently, this value has grown to 228 thousand tonnes per well (Fig. 9) [67]. Some examples of commercial proppants are presented in the Table V and classified by size, name, origin, compressive strength within the reservoir and price per ton [68].

Brazil is among the primary producers of ceramic proppants, reaching 4% of the world’s production capacity, behind China with 66%, USA with 23% and Russia with 7% [65]. Fig. 10 shows the ratio of the primary proppant producers, reporting the total values of the world’s ceramic proppant production capacity in the year of 2012 with 5.2 million metric ton (mt), 2013 with 6.8 million mt and an estimate for 2017 of a total of 10.9 million mt. With the fall in the price of oil in 2015, the adjacent sectors also suffered with the drop-in drilling activities, which consequently caused the drop-in demand for proppants. In the USA, proppant producers are over capacity and as a result Oxnade Materials announced the closure of the Van Buren, AR plant on January 23, 2015, Saint-Gobain announced plant inactivation in Fort Smith.

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**Table V - Variety of traded proppants (adapted from Downholetrader) [68].**

<table>
<thead>
<tr>
<th>Size (mesh)</th>
<th>Name</th>
<th>Source</th>
<th>Crush resistance (MPa/kpsi or K)</th>
<th>Price (US$/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/40</td>
<td>Seed sand</td>
<td>Millet, TX</td>
<td>41 / 6</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>Packers Frac. sand</td>
<td>Wisconsin</td>
<td>48 / 7</td>
<td>77.50</td>
</tr>
<tr>
<td></td>
<td>Sailing sand</td>
<td>East Texas</td>
<td>55 / 8</td>
<td>95-100</td>
</tr>
<tr>
<td>40/70</td>
<td>Winter white sand</td>
<td>Port, Texas</td>
<td>76 / 11</td>
<td>137.50</td>
</tr>
<tr>
<td></td>
<td>Garnett sand</td>
<td>South</td>
<td>48 / 7</td>
<td>70</td>
</tr>
<tr>
<td>100</td>
<td>Baker sand</td>
<td>Wisconsin</td>
<td>76-90 / 11-13</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Seine River sand</td>
<td>Texas</td>
<td>62-90 / 9-13</td>
<td>117</td>
</tr>
</tbody>
</table>

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**Figure 9: History of the use of proppants since their first use in the 1940s (source PropTesters, 2011) [66].**

**Figure 8: Cylinder chart of USA proppant consumption forecast by type (adapted from PacWest Consulting) (a), and pie chart of the expected average use of proppants (adapted from PropTesters, 2011) (b) [65, 66].**

**Figure 8: Gráfico em barras da previsão de consumo de propantes por tipo nos EUA (adaptado de PacWest Consulting Partners) (a) e gráfico de pizza da média prevista do uso de propantes (adaptado de PropTesters, 2011) (b) [65, 66].**
On January 21, 2015, Imerys company deactivated the Gemini plant in Andersonville, GA and reduced the production of the Wrens plant, GA and Carbo Ceramics postponed indefinitely the activities of the McIntyre plant March 10, 2015, as exemplified in Table VI [69]. Some proppant manufacturers from different parts of the globe are: Carbo Ceramics (USA); Oxane Materials (USA); Saint-Gobain Proppants (France); Mineração Curimbaba (Brazil); Hexion (USA); JSC Borovichi Refractories Plant (Russia); Yixing Orient Petroleum Proppant Co. (China); China Gengsheng Minerals Inc. (China); Fracsand (USA); Super Silica Sand (USA); Baltic Ceramics (Poland); Fairmount Minerals (USA).

### FINAL COMMENTS

With the increase of shale gas extraction, the use of proppants is essential to maintain the productivity of the extraction plant and its technological development becomes an attraction for the R&D sector. The drop in the price of the barrel of oil directly influences the demand for proppants. However, it is estimated that the market will stabilize in 2017 with an expected increase between 2018-2019. In order to supply the demand and present new materials, the development of ceramic proppants with specific properties for different applications has a strong impact on the technological evolution of the sector. The

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**Table VI - List of plants developing activities involving gas/shale oil and/or use/manufacture of proppants (adapted from IMFORMED 2015) [69].**

<table>
<thead>
<tr>
<th></th>
<th>Plant</th>
<th>Estimated share production capacity (%)</th>
<th>Company</th>
<th>Capacity (thou. ton/year)</th>
<th>Feedstock</th>
<th>Status/remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eufaula, AL</td>
<td>125</td>
<td>Carbo Ceramics Inc.</td>
<td>Kaolin</td>
<td>Active</td>
<td></td>
<td></td>
</tr>
<tr>
<td>McIntyre, GA</td>
<td>125</td>
<td></td>
<td>Kaolin and bauxite</td>
<td>Idled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toomsboro, GA</td>
<td>454</td>
<td>Saint-Gobain Proppants</td>
<td>Kaolin</td>
<td>Active</td>
<td></td>
<td></td>
</tr>
<tr>
<td>New Iberia, LA</td>
<td>9</td>
<td>Imerys Oilfield Solutions</td>
<td>Alumina, kaolin</td>
<td>Kryptosphere hd; +250, ld. retrofit at another factory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Millen, GA</td>
<td>113</td>
<td></td>
<td>Kaolin and bauxite</td>
<td>Active, +250, end 2015/2016</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbo USA total</td>
<td>65</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Andersonville, GA</td>
<td>100</td>
<td>Imerys Oilfield Solutions</td>
<td>Kaolin</td>
<td>Idled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wrens, GA</td>
<td>227</td>
<td></td>
<td>Kaolin</td>
<td>Active (reduced output)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imerys USA total</td>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fort Smith, AR</td>
<td>91 (estimated)</td>
<td>Saint-Gobain Proppants</td>
<td>Bauxite</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bryant, Saline, AR</td>
<td>150</td>
<td></td>
<td>Bauxite</td>
<td>Idled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saint-Gobain USA total</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>USA total</td>
<td>1,393</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
importance of this development in the domestic market also becomes an attraction as shale gas reservoirs are discovered. Nanomaterials can be studied in conjunction with the development of advanced synthetic ceramic proppant enabling the addition of additives, load of materials, trace of paths and possible changes in their physical properties.

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REFERENCES

[39] D.G. Hartwich, “Development of proppants from ion exchanged recycled glass and metabasalt glass ceramics”,...