Hydraulic fracturing proppants

(Propantes para fraturamento hidráulico)

V. P. P. de Campos[1]*, E. C. Sansone[2], G. F. B. L. e Silva[1]
[1]*Universidade de São Paulo, Escola Politécnica, Departamento de Engenharia Metalúrgica e de Materiais, 05508-010, São Paulo, SP, Brazil*
[2]*Universidade de São Paulo, Escola Politécnica, Departamento de Engenharia de Minas e Petróleo, São Paulo, SP, Brazil*

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.

Resumo

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/óleo 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 a 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 nanoescala 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 pyrobetuminous 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

*vitorppc@usp.br

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].

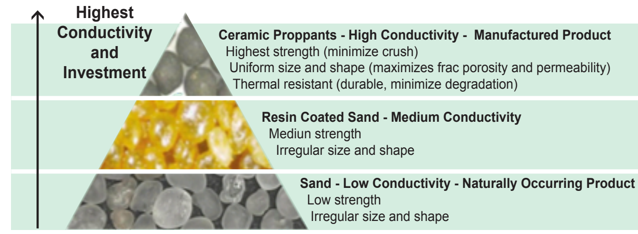

Figure 1: Pyramid of proppants' flow, adapted from [14].
[Figura 1: Pirâmide de fluxo dos propantes, adaptado de [14].]

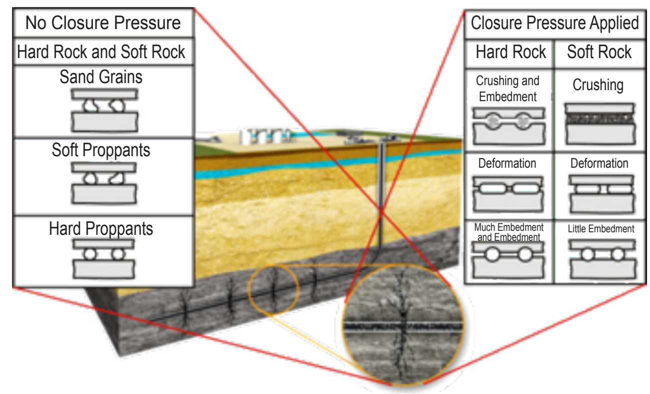

Figure 2: Relationship between some types of proppants and some types of rocks, where sand grains are the sand proppants without covering, soft proppant is the synthetic proppant of low mechanical strength, and hard proppant is the high-strength synthetic proppant. Adapted from Saint-Gobain Innovation Center [15].
[Figura 2: Relação entre alguns tipos de propantes com alguns tipos de rochas, onde grãos de areia são os propantes de areia sem recobrimento, propantes leves são os propantes sintéticos de baixa resistência mecânica e propantes rígidos são os propantes sintéticos de alta resistência. Adaptado de Saint-Gobain Innovation Center [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]. There are

Proppant type	Density (g/cm³)	Resistance (psi)
Pure sand	2.65	< 6,000 (~41 MPa)
Resin-coated sand (RCS)	2.55	< 8,000 (~55 MPa)
Intermediate resistance ceramic (IRC)	2.7-3.3	5,000-10,000 (34-69 MPa)
High resistance ceramic (HRC)	3.4	> 10,000 (69 MPa)
Bauxite	2.00	> 7,000 (48 MPa)

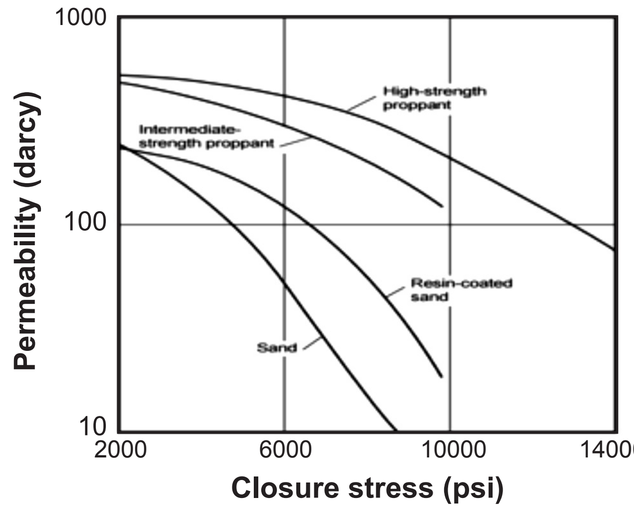

Figure 3: Scheme of choice of proppant type according to the fracture closure stress in the reservoir [15, 16].
[Figura 3: Esquema de escolha do tipo de propante em função da pressão de fechamento da fratura do reservatório [15, 16].]

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 I - Proppants selection factors.
[Tabela I - Fatores de seleção dos propantes.]

Property	Availability	Fracture treatment	Flow requirement
Resistance	Source of supply	Fluid system required	Desired flow
Format	Quality	Impact of proppant size	Cost x benefit (set, cost of proppant for recovery of hydrocarbons)
Size		Relation between fluids such as slickwater and cross-linked	
Durability	Cost		

Table II - Variation of typical density of different types of proppants [27].
[Tabela II - Variação da densidade típica de diferentes tipos de propantes [27].]

Proppant type	SBD (g/cm³)	BD (g/cm³)
Sand/resin-coated sand (RCS)	2.65	1.60
Light ceramics	2.72	1.62
Intermediate density ceramics	3.27	1.84
High density ceramics	3.56	2.00

Notes: SBD - specific bulk density; BD - bulk density.

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

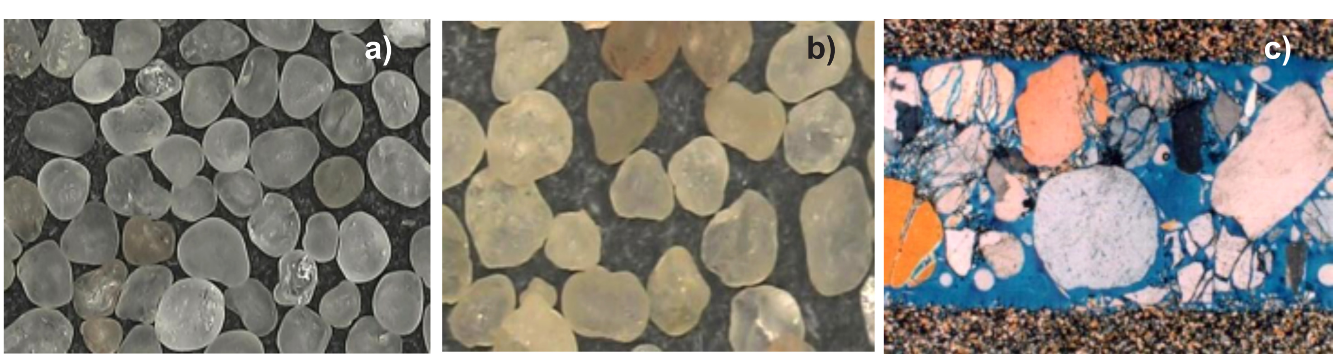

Figure 4: Images of: (a) white sand; (b) brown sand; and (c) proppant failure test ceramography (courtesy from Stim-Lab) [14].
[Figura 4: Imagem de: (a) areia branca; (b) areia marrom; e (c) ceramografia do teste de falha do propante de areia (cortesia de Stim-Lab) [14].]

stronger than the polycrystalline brown sand (Fig. 4) [14]. A common problem of this type of proppant is the formation of fines from grain fractures caused by stress. To avoid this, resin can be used as coating on the proppant. Fig. 4c presents a failure test ceramography performed with Hickory/Brady sand proppants' fraction of 12/20 at 6,000 psi (408.3 atm or 41.4 MPa) [14]. It is possible to observe the fragmentation of the material generating fines that prevent the passage of oil and gas, thus reducing the flow of the system.

Resin coated sand/proppants: proppants coated with partially cured phenolic resins are also used during the extraction process when the coated proppants (Figs. 5a, 5b and 5c) must undergo *in-situ* polymerization inside the reservoir forming a filter at the bottom. There are various types and degrees of resin. Any substrate can be coated with resin (sand, ceramic/bauxite, walnut hull, etc.) [14]. The previously brittle material becomes resistant to crushing and to the acid environment through the use of resin coating, thereby reducing the reflux of material from the well. However, the uses of these materials are limited to pressures in the range of 35 to 69 MPa (~5,000 to 10,000 psi) [9]. Fig. 5d shows a failure test section on resin-coated proppants with 8,000 psi (544.4 atm or 55.2 MPa) stress [14]. It is possible to observe that there is no fragmentation of the material generating the fines that would otherwise decrease the flow. The performance of resin-coated proppants consists of injecting the fracture fluid containing the proppants, curing the resin and joining the adjacent proppants. After being crushed due to stress, the resin acts as a film that prevents fine movement, inhibiting the clogging of the flow channel. Two types of resins can be used: the curable resins that consolidate the package reduce the proppants' flowback and encapsulate the fines of the proppants (as mentioned above) and the pre-cured resins, which encapsulate the fines and promote the distribution of stress [14].

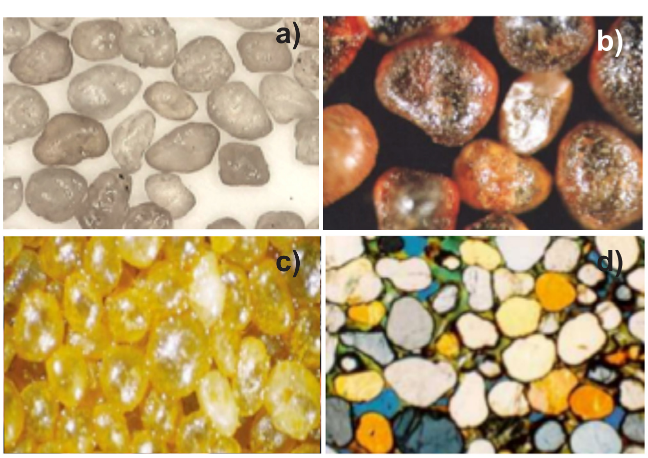

Figure 5: Examples of: (a) standard RCS; (b, c) premium RCS proppants; and (d) resin-coated proppants failure test ceramography (courtesy from Stim-Lab) [14].
[Figura 5: Exemplos de: (a) propante de areia padrão recoberto com resina; (b, c) propante de areia prêmio recoberto com resina; e (d) ceramografia do teste de falha do propante revestido com resina (cortesia de Stim-Lab) [14].]

Ceramic synthetics/bauxite: synthetic ceramic proppants are mainly made by burning, melting or sintering bauxite (Fig. 6) and/or kaolinite clays [$Al_4Si_4O_{10}(OH)_8$]. The final mineralogical composition, after material processing, is composed of the mixture of mullite ($Al_6Si_2O_{13}$) and corundum [X-Al_2O_3, where X= Ti or Fe]. Proppants can also be prepared by mixing other ceramic materials such as silicon carbide (SiC), mixed yttrium or stabilized ceria and cubic zirconia, zircon ($ZrSiO_4$) [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

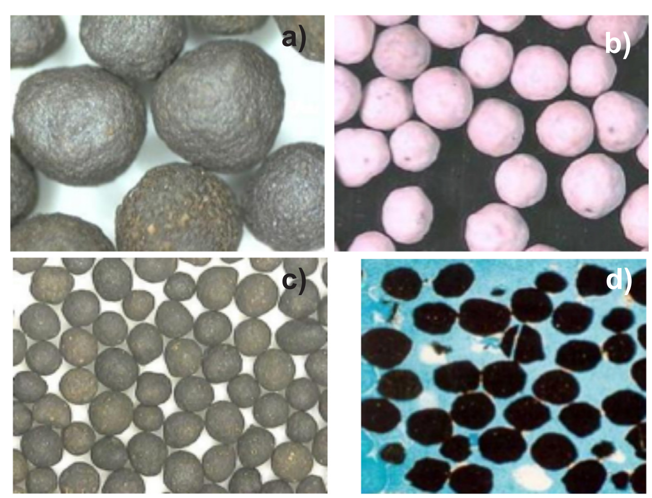

Figure 6: Images of: (a) high density bauxite ceramic proppants (SBD 3.56 g/cm³); (b) low-density ceramic proppants (SBD ~2.72 g/cm³); (c) intermediate density proppants (SBD ~3.27 g/cm³); and (d) cross-section of failure test of intermediate density ceramic proppants (courtesy from Stim-Lab) [14].
[Figura 6: Imagens de: (a) propante cerâmico de alta densidade de bauxita (DEM, densidade específica em massa, 3,56 g/cm³); (b) propante de baixa densidade de bauxita (DEM média de 2,72 g/cm³); (c) propante de densidade intermediária (DEM média de 3,27 g/cm³); e (d) sessão de corte de um teste de falha de um propante cerâmico de densidade intermediária (cortesia do Stim-Lab) [14].]

Table III - Characteristics of ceramic proppants, adapted from [29].
[Tabela III - Características do propante cerâmico, adaptado de [29].]

Density	Proppant (size specification)	Bulk density (g/cm³)	Observant density (g/cm³)	Acid solubility (%)	Crushing limit at 69 MPa (%)	Crushing limit at 86 MPa (%)
mid	16/30 1.18-0.60 mm	1.7-1.9	3.10-3.30	<7	<10	<20
mid/high		1.8-2.0	> 3.35	<7	<8	<15
high		1.9-2.1	> 3.45	<6.5	<10	<15
mid	20/40 0.85-0.425 mm	1.7-1.9	3.10-3.30	<7	<6	<10
mid/high		1.8-2.0	> 3.35	<7	<5	<8
high		1.9-2.1	> 3.45	<6.5	<6	<10
mid	30/50 0.80-0.30 mm	1.7-1.9	3.10-3.30	<7	<5	<9
mid/high		1.8-2.0	> 3.35	<7	<4	<7
high		1.9-2.1	> 3.45	<6.5	≤5	<8

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 shows the ratio of wells in the USA, the consumption of proppants used in these wells and the types used in each of them. To minimize environmental impacts, such as the extraction of raw material that generates different types of tailings, their recycling at mineral and steel industry (containing high amount of Al_2O_3, up to 40% w/w, and SiO_2, at least 60% w/w) are examples of some of the alternatives sought.

Table IV - Examples of the use of proppants in different wells in the USA; adapted from: Company filings, Morgan Stanley Equity Research, OilPRO estimates.
[Tabela IV - Exemplos do uso de propantes em diferentes reservatórios nos EUA; adaptado de: Company filings, Morgan Stanley Equity Research, OilPRO estimates.]

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

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/T5108-2006, and that by adding barium carbonate the acid solubility is effectively reduced due to the formation of celsian-$BaAl_2Si_2O_8$ 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].

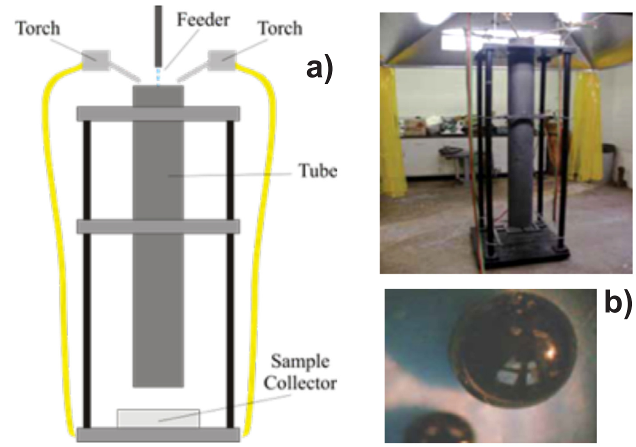

Figure 7: Study equipment (via flame) for the preparation of the vitreous proppant based on andesite, rhyolite and basalt (a), and material obtained using the apparatus via flame (b); adapted from [39].

[Figura 7: Equipamento de estudo (via chama) para preparação de propante vítreo baseado em andesita, riolita e basalto (a); e material obtido utilizando o aparato via chama (b); adaptado de [39].]

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), Weiluo (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 H_2S 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-Al_2O_3) 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

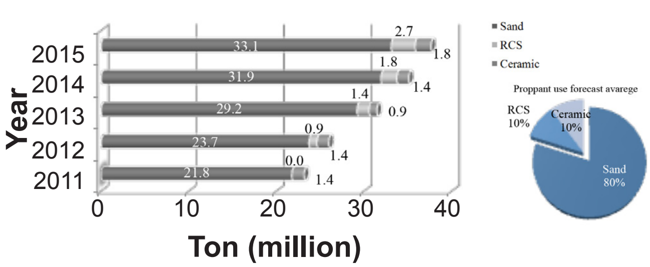

Figure 8: Cylinder chart of USA proppant consumption forecast by type (adapted from PacWest Consulting) (a), and pie chart of the expected average use of proppants (adapted from PropTesters, 2011) (b) [65, 66].

[Figura 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].

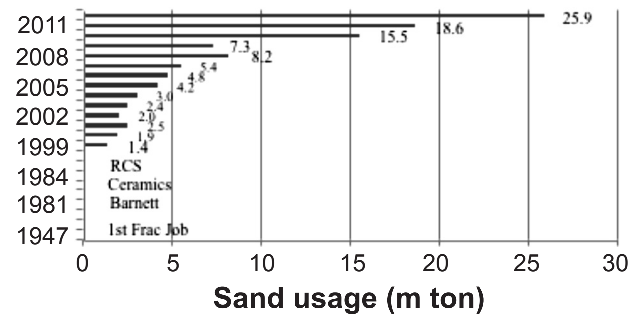

Figure 9: History of the use of proppants since their first use in the 1940s (source PropTesters, 2011) [66].

[Figura 9: Histórico do uso de propantes desde seu primeiro uso nos anos 1940 (fonte PropTesters, 2011) [66].].

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 Oxane Materials announced the closure of the Van Buren, AR plant on January 23, 2015, Saint-Gobain announced plant inactivation in Fort Smith,

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

[Tabela V - Variedades de propantes comercializados (adaptado de Downholetrader) [68].]

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

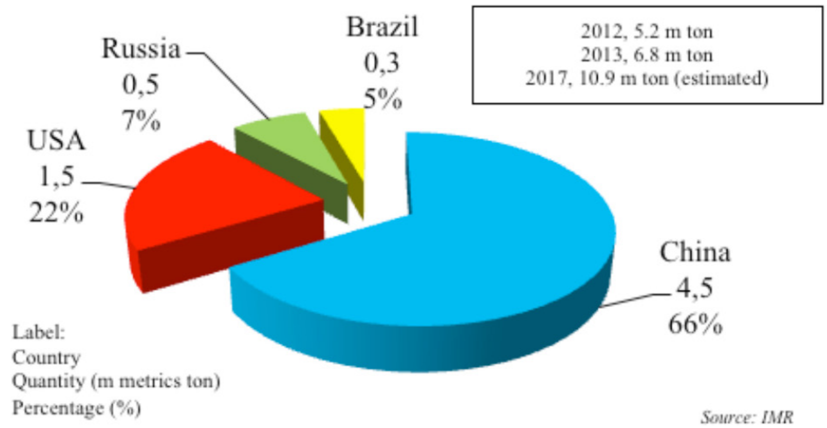

Figure 10: Production capacity of ceramic proppants in the world, primary producers in 2013; adapted from [65].
[Figura 10: Capacidade de produção de propantes cerâmicos no mundo, produtores primários em 2013; adaptado de [65].]

Table VI - List of plants developing activities involving gas/shale oil and/or use/manufacture of proppants (adapted from IMFORMED 2015) [69].
[Tabela VI - Lista de plantas que desenvolvem atividades envolvendo gás/óleo de xisto e/ou uso/produção de propantes (adaptado de IMFORMED 2015) [69].]

Plant	Estimated share production capacity (%)	Company	Capacity (thou. ton/year)	Feedstock	Status/remarks
Eufaula, AL		Carbo Ceramics Inc.	125	Kaolin	Active
McIntery, GA			125	Kaolin and bauxite	Idled
Toomsboro, GA			454	Kaolin	Active
New Iberia, LA			9	Alumina, kaolin	Kryptosphere hd; +250, ld. retrofit at another factory
Millen, GA			113	Kaolin and bauxite	Active, +250, end 2015/2016
Carbo USA total	65		825		
Andersonville, GA		Imerys Oilfield Solutions	100	Kaolin	Idled
Wrens, GA			227	Kaolin	Active (reduced output)
Imerys USA total	21		327		
Fort Smith, AR		Saint-Gobain Proppants	91 (estimated)	Bauxite	
Bryant, Saline, AR			150	Bauxite	Idled
Saint-Gobain USA total	14		240		Active
USA total			1,393		

AR 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-Gobin Proppants (France); Mineração Curimbaba (Brazil); Hexion (USA); JSC Borovichi Refractories Plant (Russia); Yixing Orient Petroleum Proppant Co. (China); China Gengssheng 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 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.

ACKNOWLEDGMENTS

Authors would like to thank Capes, CNPq, ANP, EPUSP, Clariant and Metacaulim company-Brazil.

REFERENCES

[1] C.C.G. Tassinari, "Shale gas: uma alternativa energética possível no Brasil", Inst. Eletrot. Energia, Un. S. Paulo, S. Paulo (2012).

[2] A. Bale, K. Owren, M.B. Smith, Soc. Petrol. Eng. **9**, 1 (1994) 19.

[3] O. Colela, *in* XI Sem. Int. Britcham Energ. Não Convenc., ANP (2013).

[4] CTMA/PROMINP, "Aproveitamento de hidrocarbonetos em reservatórios não convencionais no Brasil", Proj. MA 09 (2016).

[5] M.B. Smith, C.T. Montgomery, *Hydraulic fracturing*, CRC Press, Boca Raton, FL (2015).

[6] C.T. Montgomery, M.B. Smith, J. Petrol. Technol. **12**, 62 (2010) 26.

[7] URS Australia Pty Ltd, "Hydraulic fracturing ('fraccing') techniques, including reporting requirements and governance arrangements", Background review, Dept. Envir., Commonwealth Australia, Australia (2014).

[8] K. Armstrong, R. Card, R. Navarrete, E. Nelson, K. Nimerick, M. Samuelson, J. Collins, G. Dumont, M. Priaro, N. Wasylycia, G. Slusher, Oilfield Rev. **3**, 7 (1995) 34.

[9] D. Droppert, P. Fiore, Y. Dessureault, F. Cardarelli, "High strength, heat- and corrosion-resistant ceramic granules for proppants", Canadian Patent CA 2 329 834 (2002).

[10] K. McLin, D. Brinton, P. Mandalaparty, C. Jones, J. Moore, Trans. Geotherm. Resour. Counc. **1**, 34 (2010) 365.

[11] F. Liang, M. Sayeda, G.A. Al-Muntasheria, F.F. Chang, L. Lia, Petroleum **2**, 1 (2016) 26.

[12] J.R. Hellmann, B.E. Scheetz, W.G. Luscher, D.G. Hartwich, R.P. Koseski, Am. Ceram. Soc. Bull. **93**, 1 (2014) 29.

[13] M. O'Driscoll, I. Clarke, *in* Proc. SME Ann. Conf. Expo - CMA 117th Nat. West. Min. Conf., Colorado, USA (2015).

[14] J. Kullman, "The complicated world of proppant selection", South Dakkota Sch. Mines Techn., Dakota (2011).

[15] G.F.B.L. Silva, *in* Proc. 55º Congr. Brasil. Cerâm., Porto de Galinhas, PE, Brasil (2011).

[16] J. Gulbis, R.M. Hodge, *in* Reservoir stimulation, Eds.: M.J. Economides, K.G. Nolte, Wiley, Chichester (2000) 7-1.

[17] Am. Petrol. Inst., "Recommended practices for testing sand used in hydraulic fracturing operations", RP 56, API, Washington (1995).

[18] Am. Petrol. Inst., "Recommended practices for testing high-strength proppants used in hydraulic fracturing operations", 2ª Ed., RP 60, API, Washington (1995).

[19] Am. Petrol. Inst., "Recommended practices for evaluating short term proppant pack conductivity", RP 61, API, Washington (1989).

[20] Int. Org. Stand., "Petroleum and natural gas industries, completion fluids and materials, part 2: measurement of properties of proppants used in hydraulic fracturing and gravel-packing operations", ISO (2006).

[21] W.C. Krumbein, L.L. Sloss, Geol. J. **1**, 1 (1951) viii.

[22] ASTM E11 "Standard specification for woven wire test sieve cloth and test sieves", v.14.02, ASTM, West Conshohocken (2013).

[23] J. Getty, *in* Frac Sand Insider 2013 Conf. Exh., Pittsburgh, PA (2013).

[24] R. Barati, J.-T. Liang, J. Appl. Polym. Sci. **131** (2014) 40735.

[25] L.K. Vo, B. Sparks, C. Parton, J. Cortez, T. Greenet, *in* Proc. AADE Fluids Techn. Conf. Exh., Am. Ass. Drilling Eng., Houston, USA (2014).

[26] F. Deon, S. Regenspurg, G. Zimmermann, Geothermics **47** (2013) 53.

[27] J. Kullman, T.T. Palisch, M. Chapman, R. Duenckel, S. Woolfolk, M.C. Vincent, *in* Proc. SPE Hydr. Fract. Techn. Conf., Soc. Petrol. Eng. Int., Woodlands, USA (2009).

[28] Plomp Mineral Services, PMS (2015), <http://www.pms.nl/pt/cenospheres-white/>, ac. March 8, 2016.

[29] KT Refractories, ktrefractories (2013), <http://www.ktrefractories.com/Ceramic-Proppant.cfm>, ac. July 17, 2015.

[30] Superior Silica Sands, sssands (2015), <http://sssand.com/frac-sand-grades/>, ac. July 17, 2015.

[31] Mineração Curimbaba, MC (2014), <http://www.curimbaba.com.br/sinterball.html>, ac. July 17, 2015.

[32] Carbo Ceramics (2013), <http://www.carboceramics.com/kryptosphere/>, ac. Dez. 7, 2013.

[33] M.N. Barreto, "Caracterização de materiais para garantir a condutividade de fraturas hidraulicamente induzidas em poços de petróleo e gás", PhD Thesis, Pont. Un. Catól. Rio Janeiro, Rio de Janeiro, Brazil (2010).

[34] П. В. Георгиевич, V.G. Pejchev, "Manufacturing method of magnesium-silicate proppant, and proppant itself", Russian Patent: RU 2476477 (2013).

[35] X. Tian, B. Wu, J. Li, J. Hazard. Mater. **160** (2008) 589.

[36] J.R. Hellmann, B.E. Scheetz, W.G. Luscher, D.G. Hartwich, R.P. Koseski, Am. Ceram. Soc. Bull. **93**, 1 (2014) 29.

[37] J.R. Hellmann, W.G. Luscher, R.P. Koseski, D.G. Hartwich, P.J. McClure, *in* Proc. 46th Efficiency, Am. Ceram. Soc. Westerville, Ohio (2010) 66.

[38] R.P. Koseski, "Manipulation of microstructure, phase evolution, and mechanical properties by devitrification of andersite for use as proppant", PhD Thesis, Pennsylv. State Un., Un. Park, PA (2008).

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

M.Sc. Thesis, Pennsylv. State Un., Pennsylvania (2011).
[40] V.P.P. Campos, S.M. Toffoli, D. Gouvea, G.F.B.L. Silva, Mater. Sci. Forum **798-799** (2014) 503.
[41] T. Wu, B. Wu, Corros. Sci. **63** (2012) 399.
[42] X. Tian, B. Wu, J. Li, J. Hazard. Mater. **160** (2008) 589.
[43] F. Gao, Y.-P. Wu, J. Liu, H.-W. He, L.-T. Kang, W. Liang, J. Inorg. Mater. **28**, 9 (2013) 1019.
[44] T.T Huang, J.B. Crews, J.R. Willingham, *in* Proc. SPE Ann. Techn. Conf. Exh., Colorado, USA (2008) 21.
[45] J. Hu, *Shape memory polymers and textiles*, Woodhead Publ. (2007).
[46] R. Krishnamoorti, J. Petrol. Technol. **58** (2006) 24.
[47] C. Vipulanandan, A. Mohammed, Q. Qu, *in* Proc. AADE Fluids Techn. Conf. Exh., Am. Assoc. Drill. Eng., Houston, Texas (2014) 39.
[48] C. Matteo, P. Candido, R. Vera, V. Francesca, Am. J. Appl. Sci. **6**, 9 (2012) 784.
[49] A.R. Barron, J.M. Tour, A.A. Busnaina, Y.J. Jung, S. Somu, M.Y. Kanj, D. Potter, D. Resasco, J. Ullo, Oilfield Rev. **22**, 3 (2010) 38.
[50] K. Johnson, "Nanoscale technologies leap from science fiction into real-world engineering", Am. Oil Gas Report. (2010).
[51] S. Ryoo, A.R. Rahmani, K.Y. Yoon, M. Prodanović, C. Kotsmar, T.E. Milner, K.P. Johnston, S.L. Bryant, C. Huh, *in* Proc. SPE Ann. Techn. Conf. Exh., Florence, Italy (2010) 19.
[52] S.H. Boura, M. Samadzadeh, M. Peikari, A. Ashrafi, *in* Proc. SPE Int. Conf. Oilfield Corros., Aberdeen, United Kingdom (2010) 24.
[53] S. Rassenfoss, J. Petrol. Technol. **63** (2011) 32.
[54] B. Ju, T. Fa, Powder Technol. **192** (2009) 195.
[55] A. Esmaeili, *in* Proc. 2nd Int. Conf. Methods Models Sci. Techn., Jaipur, India (2009) 19.
[56] M.K. Chaaudhury, Nature **423** (2003) 131.
[57] M.L. Terranova, S. Piccirillo, V. Sessa, M. Rossi, S. Botti, J. Phys. **IV**, 9 (1999) 365.
[58] N. Dubrovinskaia, V.L. Solozhenko, N. Miyajima, V. Dmitriev, O.O. Kurakevych, L. Dubrovinsky, Appl. Phys. Lett. **90** (2007) 101912.
[59] M. Jain, Scripta Mater. **44** (2001) 8.
[60] A.R. Barron, *in* RSC Conf. (2011).
[61] D.N. Meehan, *in* Economist's Corner, SPE (2011).
[62] L. Guy, I. McClung. "Cryogenic treatments & systems, materials made with them & methods for using them", Patent WO 2014204517 A2 (2013).
[63] V.P.P. Campos, G.A.A. Labat, E.C. Sansone, D. Gouvea, G.F.B.L. Silva, J. Mater. Res. (submitted).
[64] V.P.P. Campos, G.A.A. Labat, E.C. Sansone, D. Gouvea, G.F.B.L. Silva, J. Mater. Res. (submitted).
[65] V. Nicoletopoulos, *in* Oilfield Min. Outlook 2015, Houston, USA (2015).
[66] M. Yang, J.M. Economides, *in* Proc. SPE East. Reg. Meet., Soc. Petrol. Eng. Int., Lexington, USA (2012).
[67] E. Roach, "Proppant: the greatest oilfield innovation of the 21st century" (2014), <http://info.drillinginfo.com/proppant-the-greatest-oilfield-innovation/>, ac. Jan. 21, 2016.
[68] Down Hole Trader, "Trading board offerings", <http://downholetrader.com/#2040>, ac. Jan. 21 (2016).
[69] M. O'Driscoll, C. Rehn, "US ceramic proppants review", Energy Global, Oilfield Techn. (2015), <http://www.energyglobal.com/upstream/drilling-and-production/01042015/US-ceramic-proppants-review/>, ac. Jan. 21, 2016.

(Rec. 23/03/2017, Rev. 10/08/2017, 06/09/2017, 15/09/2017, Ac. 12/10/2017)