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Novel highly dispersible, thermally stable core/shell proppants for geothermal applications

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ABSTRACT

The use of proppants, especially larger and more dense proppants, during reservoir stimulation in tight oil and gas plays requires the introduction of highly viscous fluids to transport the proppants (mm–mm) with the fracturing fluid. The highly viscous fluids required result in increased pump loads and energy costs. Furthermore, although proppant deployment with fracturing fluids is a standard practice for unconventional oil and gas stimulation operations, there are only a few examples in the US of the applying proppant technology to geothermal energy production. This is due to proppant dissolution, proppant flowback, and loss of permeability that, although also occurs during unconventional oil/gas stimulation (hydraulic fracturing) operations, it is amplified under the extreme temperatures found in enhanced geothermal systems (EGS). This work demonstrates proof-of-concept of a novel, CO_2-responsive, lightweight sintered-bauxite/polymer core/shell proppant. The polymer shell has two main roles; (1) increase the stability of the proppant dispersion in water without the addition of rheology modifiers, and (2) once at the fracture network react with CO_2 to promote particle aggregation and prop fractures open. In this work, both roles are demonstrated together with the thermal and chemical stability of the materials showing the potential of these CO_2-responsive proppants as an alternative proppant technology for geothermal and unconventional oil/gas applications.

1. Introduction

Geothermal energy has the potential to develop into a major energy source within the United States and worldwide (Duffield and Sass, 2003; Blackwell et al., 2006). To date, geothermal production has been limited to natural, high-permeability reservoirs. This limitation is due to the difficulty of developing high fluid-flow rates from reservoirs where the natural permeability is insufficient. Stimulation (also known as fracturing) may be used to increase the permeability of the reservoir in enhanced geothermal systems (EGS) (Duffield and Sass, 2003; Pruess, 2006). Hydraulic fracturing is the most commonly used reservoir-stimulation method (Reinicke et al., 2010). Recently, there have been numerous advances in hydraulic fracturing techniques that have increased unconventional oil and gas production (Kargbo et al., 2010; Kerr, 2010; Scotchman, 2015) and could also increase the feasibility of EGS (Jung et al., 2015; Shao et al., 2015).

Reservoir-fracture creation and propagation by hydraulic fracturing in enhanced geothermal systems (EGS) may be vastly improved through the use of proppants to maintain fracture conductivity (Shiozawa and McClure, 2014). Proppants are solid materials injected in suspension with hydraulic-fracturing fluids that remain in newly opened fractures holding them open after hydraulic-fracturing pressures subside (Mader, 1989). The introduction of proppants with the hydraulic-fracturing fluid is a common procedure in the oil and gas industries, but its use has been restricted in the geothermal industry due to technical limitations (Shiozawa and McClure, 2014; McLin et al., 2011; Jones et al., 2014). Jones et al. lists only 5 reservoirs in the world that have used proppants in geothermal systems (Jones et al., 2014).

In EGS, like in the case of unconventional oil and gas recovery, proppants need to withstand high pressures (up to 700 atm), acidified fluids, acid treatments, and cleanouts while maintaining the porosity and permeability of the fracture (Shiozawa and McClure, 2014; McLin et al., 2011; Jones et al., 2014; Regenspurg et al., 2015; Brinton et al., 2014). However, the extreme temperatures (up to 400 °C) found in EGS play a critical role in proppant instability. During geothermal stimulation and geothermal plant operations mineral dissolution and

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precipitation may be exacerbated due to the high temperatures, abrupt temperature variations, and fluid salinity present in geothermal systems (Regenspurg et al., 2015). While some laboratory studies note only minor dissolution of proppant under wellbore representative conditions (McLin et al., 2011; Jones et al., 2014; Brinton et al., 2014), others report major proppant dissolution and salt precipitation (Deon et al., 2013). Dissolution issues can be addressed by pre-coating the proppants with a polymer shell as described next.

A variety of proppants are available, with the most commonly used consisting of silica sand, ceramic, resin coated sands, and bauxite (McLin et al., 2011). Moore et al. have demonstrated that sintered bauxite is an excellent candidate for application in EGS due to its high thermal and chemical resistance and mechanical strength (Jones et al., 2014). There have been recent advances in increasing the strength of proppants (Palisch et al., 2015), which may be critical for EGS. Typically, ceramic proppants have been developed with density optimization such as alumina content modification. However, proppant strength and density increases tend to decrease proppant transportability (Gu et al., 2015).

Injection and transport of proppant into the subsurface can be challenging. Proppants account for a significant fraction of the volume injected (typically 2–5 lb/gal of injected fluid). There is a large density difference between the proppant 2.6 g/cm^3) and the water (1–1.05 g/cm^3). As a result, highly viscous fluids or gels are often employed to transport the proppants, which introduces high loads on injection pumps and increases pumping energy requirements and costs (Reinicke et al., 2010; Jung et al., 2015; Shao et al., 2015; Barati and Liang, 2014). To increase proppant delivery, researchers have been examining lighter proppants with decreased viscosity requirements (Gu et al., 2015; Gaurav et al., 2012; Han et al., 2014; Chen et al., 2015). Using resin or hydrogel coatings or increasing the porosity of strong solid materials have successfully decreased proppant density of otherwise high-density solids (Gu et al., 2015; Gaurav et al., 2012; Chen et al., 2015; Kincaid et al., 2013). Coating of proppant with a thin layer of polymer can improve the stimulation process efficiency by preserving the particle under high operating temperatures and pressures in the subsurface (Mahoney et al., 2013). This improvement is obtained through fracture conductivity enhancement (Nguyen et al., 2000), minimizing formation fine production and proppant dissolution, (Gidley et al., 1995)and increase and maintenance of long term fracture permeability, (Montgomery and Steanson, 1985; Blauch et al., 2007). Two different types of polymer coating known as precured and curable proppants have been reported. Curable proppants are generally used in deeper wells where the temperatures are high enough to introduce in-situ curing while in shallow wells a precured polymer coating is recommended. Nevertheless, the market for curable proppants has grown dramatically and they are also used for shallow (low temperature) wells. The most common types of organic polymers for proppant coating are different types of resins, furan, polyesters and vinyl esters, and polyurethane. Readers are referred to a recent review on the use of polymers for proppant coating (Zoveidavianpoor and Gharibi, 2015). Proppant emplacement and flow-back reduction are also key considerations for effective and economic reservoir stimulation (Brinton et al., 2014; Vreeburg et al., 1994; McLennan et al., 2015). Vreeburg et al. found that large amounts of proppant may be back-produced after hydraulic fracturing. They note that proppant may be remobilized during fracture cleanup and over long-term production due to flow interruption stress cycling. Resin-coated proppants can have lower backproduction relative to uncoated proppants (Vreeburg et al., 1994). Still, there is an urgent need for the development, transport and efficient emplacement of thermally, mechanically, and chemically stable proppants in geothermal reservoirs and to understand their performance over long periods of time before they can successfully be applied in EGS reservoirs.

A number of reports exist where nanosized metal oxide particles, such as aluminum oxide and iron oxide nanoparticles, are functionalized and stabilized in aqueous solutions or organic solvents with polyamines and polyacrylates (Alexander et al., 1998; Gupta and Gupta, 2005; Studart et al., 2007). Our idea extends this concept to micrometer sized (10–100 mm) sintered bauxite proppants (largely comprised of aluminum oxides) by functionalizing their surface with inexpensive, non-toxic, water-soluble CO_2-reactive polymers, namely poly(acrylamide/sodium acrylate) (PAC) and poly(allylamine) (PAA). The polymers bind to the surface of sintered bauxite particles, decreasing the effective density of the proppants. By using high molecular weight polymers (up to 5 MDa), the proppant density could be, in principle, significantly reduced relative to unmodified bauxite proppants. In addition, the solvation of the polymer shell by water would also have an effect on the stability of the core/shell suspensions. This near-neutral buoyancy will eliminate the need for highly viscous fracturing fluids to stabilize the particle suspensions and should ensure substantial propped surface area. This work is a proof-of-concept demonstration of a stimuli-responsive lightweight proppant technology that represents a potential solution to proppant transport and emplacement problems. The main advantages introduced by this proppant concept are: (1) proppant thermal stability under representative EGS temperatures; (2) the small proppant size (200/400 mesh, 36–74 mm), lower proppant density introduced by the polymer coating, and the low viscosity of the carrier fluid will enhance transport and penetration of the proppant into low-aperture primary fractures, running in the direction of the maximum principal stress, as well as orthogonal or oblique secondary fractures; (3) when the proppant is at the fracture network after injection, the polymer shell will be crosslinked *in-situ* by activation with CO_2 bringing particles together and generating large aggregates to bridge fracture openings. The crosslinking reaction takes place in seconds, as reported previously (Jung et al., 2015; Shao et al., 2015). Therefore, provided CO2 is present, CO2-triggered crosslinking and particles aggregation will take place almost immediately before fluid pumping stops. These large aggregates are responsible for propping the fractures open maintaining reservoir permeability after stimulation operations. Herein, we report the performance of the lightweight core/shell proppants including thermal and chemical stability, dispersion stability studies as well as confirmation of CO_2-induced proppant aggregation demonstrating the potential of these CO_2-responsive proppants as an alternative proppant technology for geothermal and unconventional oil/gas applications.

2. Materials and methods

This section is divided in four subsections that include the preparation of core/shell proppants by assessing different reaction conditions (Subsection 2.1), characterization of the interactions between the surface of the proppant core with the polymer shell (Subsection 2.2), the evaluation of the core/shell proppant chemical and thermal stability (Subsection 2.3), and assessment of the dispersion stability of core/shell proppants in low viscosity waters as compared to similar size proppants with no polymer shell. Finally, experimental work to demonstrate the CO_2-induced particle agglomeration is described in Subsection 2.4.

Table 1 summarizes the methodologies employed to evaluate the different aspects/properties of the core/shell proppants presented in this work.

2.1. Preparation of core/shell proppants

Sintered bauxite particles were obtained from C-E Minerals and sieved to a particle range of 36–74 mm. The nominal composition of the bauxite according to the manufacturer's certificate of analysis is Al_2O_3 88.7 wt%, SiO_2 5.29 wt%, Fe_2O_3 1.46 wt%. TiO_2 3.62 wt%, K_2O + Na_2O 0.19 wt% and CaO + MgO 0.29 wt%. A number of aqueous solutions of polymers including poly(allylamine), poly(acrylamides), partially hydrolyzed poly(acrylamide), poly(acrylic acid), and poly