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Improvement of Hydraulic Fracture Conductivity Using Nanoparticles

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Additional information is available at the end of the chapter

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Abstract

Hydraulic fracturing is a commonly used practice in the oil industry for well stimulation and production enhancement. With the general theme of the oil and gas industry moving toward systems with nano-sized pores, nanoparticles have gained a significant amount of attention especially in the field of hydraulic fracturing. Several groups have developed different nanoparticle systems that improve hydraulic fracture conductivity. This paper is a review of the highlighted work published in the area of application of nanoparticles to improve fracture conductivity. Nanotechnology can be used to improve the efficiency of hydraulic fracturing process. Four major production challenges faced by the oil and gas industry including incomplete filter cake cleanup, proppant pack damage, formation damage, and having micro-fractures that are not packed with proppants and will close under closure stress are introduced in this work. Solutions have also been reported using the advances in nanotechnology to address some of these challenges.

Keywords: nanotechnology, oil & gas, hydraulic fracturing, shale, natural gas

1. Introduction

1.1. Nanotechnology

Nanotechnology is the application of nanomaterials with at least one dimension in the 1–100 nm range. Taking advantage of high surface/volume ratio and high specific surface functionalization, nanotechnology helps in the generation of materials which have properties very different from the original materials. Nanotechnology is an active research area with applications in almost all engineering domains, and petroleum engineering is no exception. Many

upstream researchers are trying their best to bring around an industrial revolution by making use of nanotechnology to find solutions to the existing technological challenges in the industry. Since the conception of this technology, nanomaterials have been used widely in different fields including drilling, completion, workover, stimulation, and wastewater treatment. Some recently discovered applications of nanotechnology in well stimulation treatments will be discussed in this work.

1.2. Hydraulic fracturing process

Hydraulic fracturing is a very common practice for stimulating oil and gas wells. It has contributed significantly toward making previously unrecoverable reserves exploitable and enhancing production rates from existing fields. The first hydraulic fracture treatment was carried out in Hugoton gas field in Grand county, KS, in 1947 [1–3].

The process consists of pumping a fracturing fluid into the pay zone at an injection pressure and rates high enough to generate and propagate fractures into the formation. The fracturing fluid used in the process is a blend of different additives like viscosifiers which aid in the creation of fractures which would then act as a conduit for the flow of hydrocarbons into the wellbore. First, fluid without additives called 'pad' is pumped to initiate the fracture and adjust the temperature and salinity of the near fracture area to compatible values with the injected fluid. This is followed by injection of a 'slurry,' which is a mixture of different additives and proppants, which would then continue to extend the fracture further into the formation and distribute the proppants along the length and height of the fracture. Once the injection pressure is removed and the well is 'shut-in,' the fractures tend to close because of the closure stress applied by the rocks. The proppants having been already injected into the fracture prevent the fractures from closing, ensuring a conductive path for the hydrocarbons to flow once the well is put into production. Before the production phase starts, the viscous fracturing fluid present in the fracture has to break down and flow back to the surface, to prevent it from causing hindrance to the flow of hydrocarbons during production. For this purpose, the 'slurry' of the cross-linked fluids contains chemicals termed 'breakers' which would break down the highly viscous fracturing fluids into less viscous fluid which can flow back to the surface during the 'flow back' period after the shut-in process. This process is termed 'cleanup.' After the flow back period, the well is put into production and the hydrocarbons flow into the wellbore through the highly conductive hydraulic fracture network. The industry tends to believe that slickwater-type fracturing fluids generate a minute filter cake, if any. Therefore, more and more operators are currently showing a tendency to exclude the breaker systems when they are using slickwater fluids [1].

The selection of a proper fracturing fluid involves several considerations. It starts with choosing the pad volume where one must consider what and how much pad is required to create the desired fracture geometry. This is followed by estimating the viscosity the fluid should possess, to generate sufficient fracture width (to ensure proppant entry into the fracture), to ensure proppant suspendability (to transport proppant from the wellbore to the fracture tip)

and to limit fluid loss. Fracturing fluid viscosity is the main mechanism for fluid loss control where a gel filter cake cannot form [1].

In short, an ideal fracturing fluid would be one that 'has an easily measured controllable viscosity, controllable fluid loss characteristics, would not damage the fracture or interact with the formation fluid, would be completely harmless and inert and cost less than \$4.00 US/gallon' [1, 4]. Excessive viscosity increases costs, raises treating pressure which may cause undesired height growth, and can reduce fracture conductivity as most chemicals that are used to increase viscosity leave residue which damages the proppant pack permeability. Insufficient viscosity causes improper proppant distribution, increased fluid loss, inferior fracture dimensions, and inadequate fracture conductivity [1, 4].

Oil-based fracturing fluids were the first to be used, but environmental and safety concerns raised by their applications have prompted the industry to move toward developing an alternative. Today, more than 90% of fracturing fluids are water based [2]. Aqueous fluids are not only economical, but the additives developed over the years to be used with them have helped in controlling the fracture parameters that would be generated [3].

The additives used in the fracturing fluids are:

- Gelling agents
- Cross-linkers
- Breakers
- Fluid loss additives
- Bactericides
- Surfactants and non-emulsifying agents
- Clay control additives

Guar-based fluids are commonly used as fracturing fluids to form a filter cake, propagate the fracture, and transport proppants during a typical hydraulic fracturing job. They are used in their cross-linked forms in conventional reservoirs and in their linear or cross-linked forms in unconventional reservoirs. They are relatively cheap, and they have been found to perform well under shear and temperature conditions encountered in the wellbore and formation. The viscosity of the polymer solutions decreases with increasing temperature.

It is very important that the fracturing fluids retain their viscosity so that they can apply adequate hydrostatic pressure on the rocks to crack them open. Hence, cross-linkers, such as borate and zirconate, are added to enhance the viscosity of the gel [1, 9]. Addition of cross-linkers to hydroxypropyl guar (HPG) solution increases the viscosity of the linear gel from less than 50 cP into the 100's or 1000's of cP range. The higher viscosity aids in generating wider fractures which can accept higher concentrations of proppant. Cross-linking also helps in reducing the fluid loss to improve fluid efficiency. Moreover, cross-linking increases the elasticity and proppant transport capability of the fluid while simultaneously reducing the friction pressure [1, 7].

1.3. Problems related to hydraulic fracturing in conventional formations

1.3.1. Incomplete fracture cleanup

Fracturing fluids cause reduction in proppant pack permeability because of their following disadvantages.

1.3.2. Filter cake buildup

During the fracturing operation, the high-pressure fracturing fluid leaks off into the formation. A polymer and fluid loss additive filter cake is formed. During fracture closure, the proppants are embedded into the filter cake, making it difficult to remove the filter cake during production. A typical filter cake thickness of 0.5 mm (0.13 in.) on each fracture wall is enough to completely block a thin fracture propped with two layers of 20/40-mesh proppants [8].

Filter cake is usually attacked by the injected breakers reducing its thickness during the cleanup period, but in most cases a thin layer of filter cake still remains during the production phase due to the inefficiency of the cleanup operation. The ratio of the filter cake to the fracture width determines the extent of resistance offered by the fluid, against the applied pressure difference across the proppant pack [9, 10]. A thick filter cake reduces the width of the fracture available for the flow of hydrocarbon [1]. A schematic picture of one side of a hydraulic fracture is shown in Figure 1.

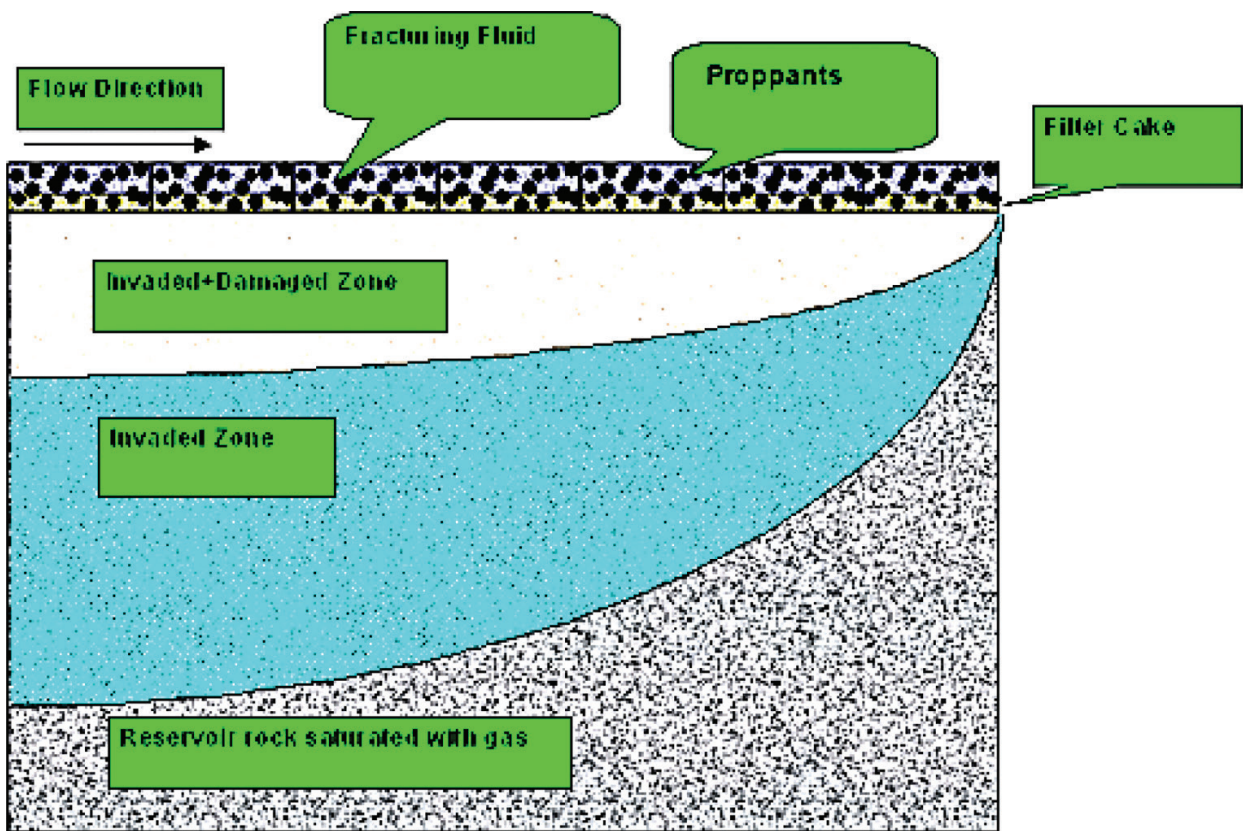


Figure 1. Schematic picture of one side of fracture after closure [5].

1.3.3. Gel residue

Despite the usage of copious amounts of breakers, the usage of cross-linked fluids usually leaves a proppant pack containing a lot of fibrous material between the grains, which are then 'glued' together [8]. Palisch et al. reported that gel damage is a significant factor which reduces proppant pack conductivity by different mechanisms [6]. The porosity and permeability of the proppant pack get significantly reduced by the gel residue (**Figure 2**) left in the proppant pack due to incomplete fracture cleanup. Moreover, the unbroken fluids found mostly near the tip of the fractures cause loss in effective fracture length. The gel saturation is usually higher near the tip of the fracture as the drawdown pressure is weaker toward the tip. This causes the effective fracture length available for production to be much less than the propagated fracture length as the yield stress required for the flow to start is harder to overcome near the fracture tip [2, 13].

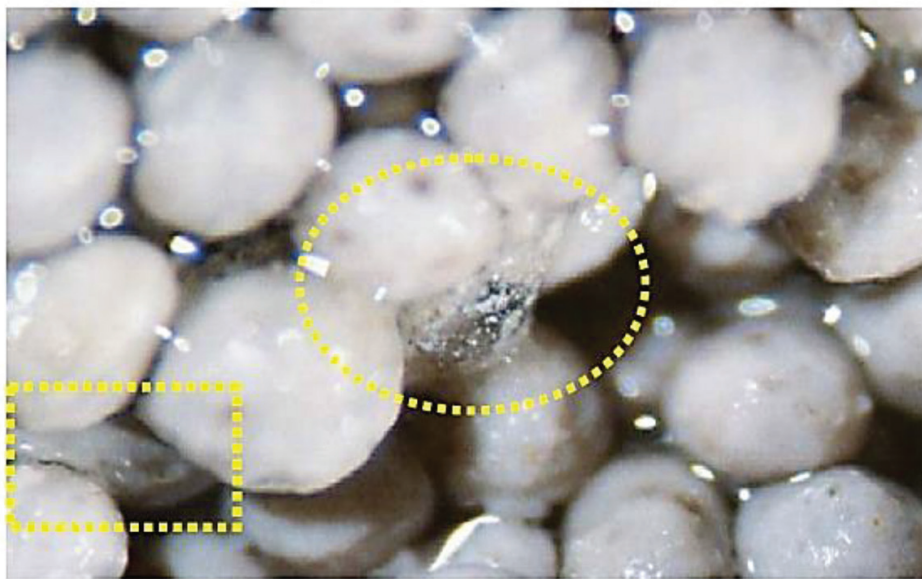


Figure 2. Gel residue in the proppant pack [6].

1.3.4. Non-degraded fracturing fluid

If you consider the scenario just after the fracturing job, the propped fracture will be almost completely saturated with fluids with viscosity much greater than that of the injected fluid because of the fluid leak off into the formation. The fluid which leaked off reduces the oil/gas saturation in the invaded zone to values closer to their irreducible saturation. The deliverability of the well will continue to remain impaired until this fluid is at least partially removed from the formation and the fracture. Further reduction in productivity can occur due to the increased bottom hole pressure as a result of the dense liquid which is held up in the wellbore [1, 31].

Incomplete cleanup of fractures leaves partially broken fracturing fluids and residues even after the breakers have degraded the filter cake. The significant damage caused by partially broken fracturing fluids and filter cake to the fracture conductivity, and thereby to the cumulative oil production, has been shown by many researchers [1].

1.3.5. Formation damage due to fluid loss

The fluid which 'leaks off' into the reservoir causes hydraulic and physical damage to the reservoir. In the area invaded by the leaked off fluid, hydraulic damage is caused by the shifts in capillary pressure and relative permeability curves. Physical damage is caused by processes like clay swelling, invasion of fracturing fluid into the formation, etc. [10]. These effects will be more prominent in shales because of their significant clay content; this is especially the case with shale rocks that contain smectite and montmorillonite clays [5]. The volume of the fluid lost into the formation has a direct relation with the permeability of the formation and also increases with decreasing viscosity of the fluid injected. Fluid loss also depends on the difference between fracture injection pressure and reservoir pressure, initial water saturation of the formation, etc. The more the fluid is lost into the formation, the less is the pressure applied on the formation rocks, thereby reducing the length and the width of the fractures propagated [1].

Damages due to the invasion of filtrate volumes are more significant in tight and ultra-tight formations, even though the fluid loss volumes are smaller for these very low permeability rocks because of the inverse square root relation between capillary pressure and permeability. To further compound this problem, the system of naturally induced micro-fractures, from which the tight and ultra-tight unconventional hydrocarbon reservoirs typically produce, can cause significant fluid loss volumes [30]. Reducing fluid loss to the formation would help in creating longer fractures with more fracture contact area which would help in increasing production [1].

1.4. Hydraulic fracture propagation in unconventional reservoirs

The main purpose of hydraulic fracturing in shale reservoirs is to increase hydrocarbon production by connecting the already existing fissures and fractures and creating a network of fractures and micro-fractures. It is also believed to dilate the already existing systems of small fissures and fractures which are initially filled with calcite, quartz, or other minerals [11, 16]. Reopening of natural fractures occurs when the induced stresses inside the rock overcome formation in situ stresses. Although the size of the induced cracks and reopened parts of the preexisting natural fractures are very small in comparison with the main hydraulic fracture, they can still tremendously increase the well-formation contact area if they are kept open during production using appropriate propping agents [1, 17].

Ultra-low permeability shale reservoirs are dependent on a large fracture and micro-fracture network to maximize well performance. Micro-seismic fracture mapping has shown that large fracture networks can be generated in many shale reservoirs [11]. Preexisting healed or open natural fractures and favorable stress-field conditions enhance the chances for creating large fracture networks (**Figure 3**). Such complex fracture networks are desirable in ultra-tight shale reservoirs because they maximize the fracture-surface contact area with the shale [1].

Conventional reservoirs are mostly reliant on single-plane-fracture half-length and conductivity for improving well performance. However, the concepts of single-fracture half-length and conductivity are inadequate to completely describe stimulation performance in shale reservoirs with complex network structures in multiple planes [11]. Hence, a concept called stimulated reservoir volume (SRV) was developed to be used as a correlation parameter against well

performance [11]. The size of the created fracture network was approximated as the 3D volume (SRV) of the micro-seismic event cloud [11]. It has been observed that the volume of SRV increases with the fracture network size and complexity. Mayerhofer et al. have shown earlier that the cumulative production from the reservoir is directly proportional to the SRV [1, 11].

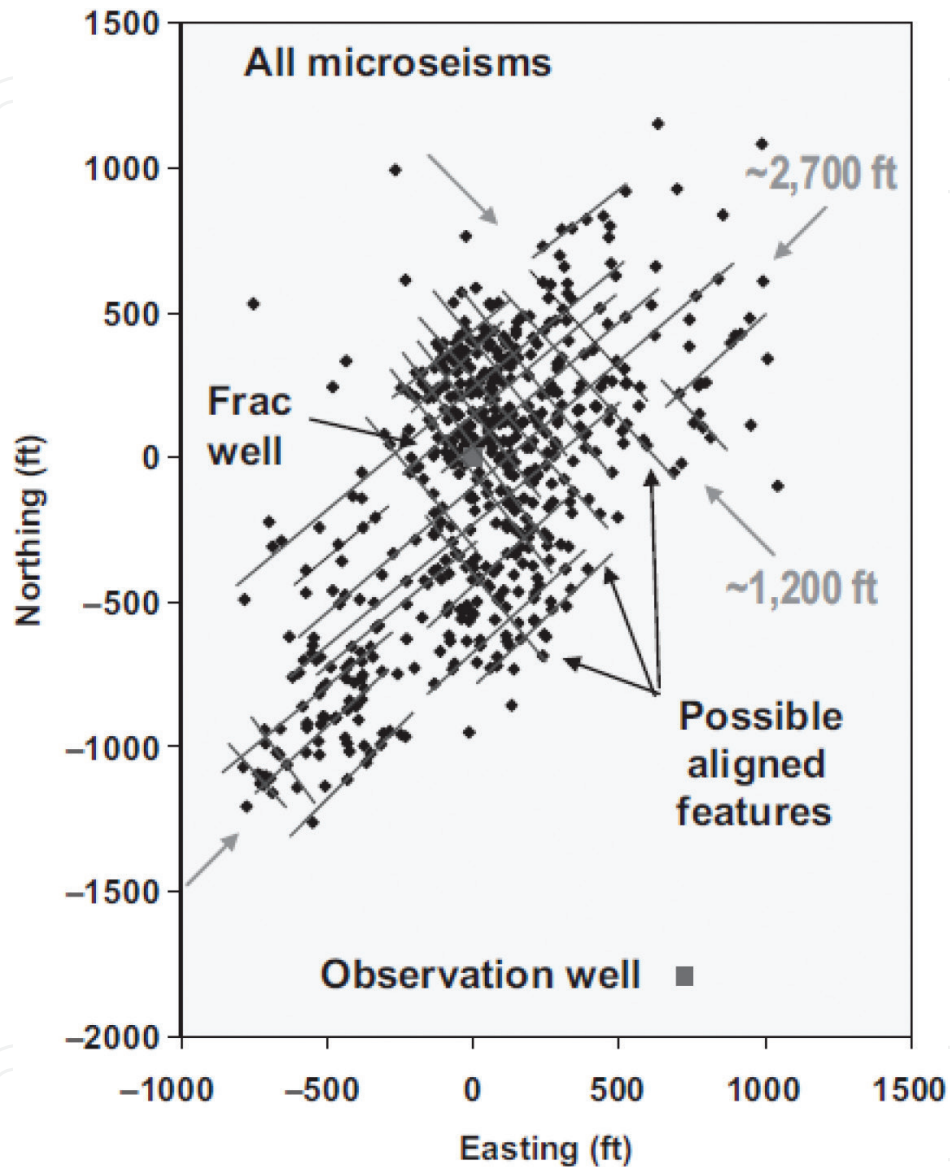


Figure 3. Micro-seismic fracture mapping shows complex network growth in shales [18].

1.5. Problems related to hydraulic fracturing in unconventional reservoirs

1.5.1. Proppants for unconventional reservoirs

Hydraulic fracturing process in unconventional formations face certain problems such as the lack of small, enough proppants that are capable of filling the micro-fractures. Proppants with different mesh sizes of 20/40, 30/50, 40/70, 70/140, and 80/200 with grain diameters ranging from 0.033 in. (0.8382 mm) to 0.0041 in. (104.14 μm) are conventionally used during hydraulic

fracturing of tight shale formations [12]. These proppants can create conductivity in the larger generated or existing fractures, but they are not small enough to penetrate into the existing or generated micro-fractures. This will reduce the length and conductivity of the complex fracture network caused by the closure of micro-fractures at the end of a fracturing job [12]. During fluid injection into the reservoir during hydraulic fracturing, the opening of the natural fractures and the pressure applied inside them decrease as the distance increases from the point of injection [1].

2. Nanotechnology as a solution to improve fracture conductivity during well stimulation

2.1. Nanoparticle-associated surfactant micellar fluids as an alternative to cross-linked polymer systems

Several researchers have been trying to develop surfactant-based fluids as a low damage alternative to cross-linked fluid systems. Surfactant-based systems, however, were still far from perfect when it comes to gel residue after hydraulic fracturing treatment. Crews et al. in 2012 came up with an improved fluid system which makes use of nanoparticles, internal breakers and low molecular weight surfactants to match the stimulation performance of cross-linked system while leaving almost negligible gel residues [32].

Surfactant-based fluids rely on the development of long, thin, threadlike micelles that overlap and entangle with one another for the generation of viscosity required to exert pressure on the formation. Nettesheim et al. investigated the influence of nanoparticles in micellar solutions and observed that low concentrations of 30 nm silica nanoparticles can increase the low shear rate viscosity, relaxation time and elastic storage modulus of surfactant-based fluids. They postulated that the surface of the nanoparticles might be interacting with the endcaps of threadlike micelles acting as junctions to network the micelles [14]. This helps in achieving targeted viscosity using reduced concentration of surfactants. The internal breakers, when used with this fluid system, not only reduced the viscosity significantly but also broke the pseudo-filter cake into brine and nanoparticles. These nanoparticles were small enough to easily pass through the pore throats of formation rocks during production, along with the production fluids. This eliminates the problem of production loss due to formation damage. **Figure 4** shows the effect of nanoparticles on fluid viscosity [15].

2.2. Nanoparticles to prevent migration of fines

Reservoirs which are prone to sand problems sometimes produce small particles which can make their way through proppant beds and sand screens to enter the wellbore. They are called fines, and they can erode and plug surface equipment and sand screens. They are also known to cause decline in production by plugging proppant pack and perforations.

Advent of nanotechnology has helped in finding cheaper ways to restrict migration of fines. Delaying the entry of fines into the wellbore helps in extending the production life of wells and in decreasing the frequency of required well interventions. It also helps in extending the life of fractures, fracturing equipment, and flow lines [33].

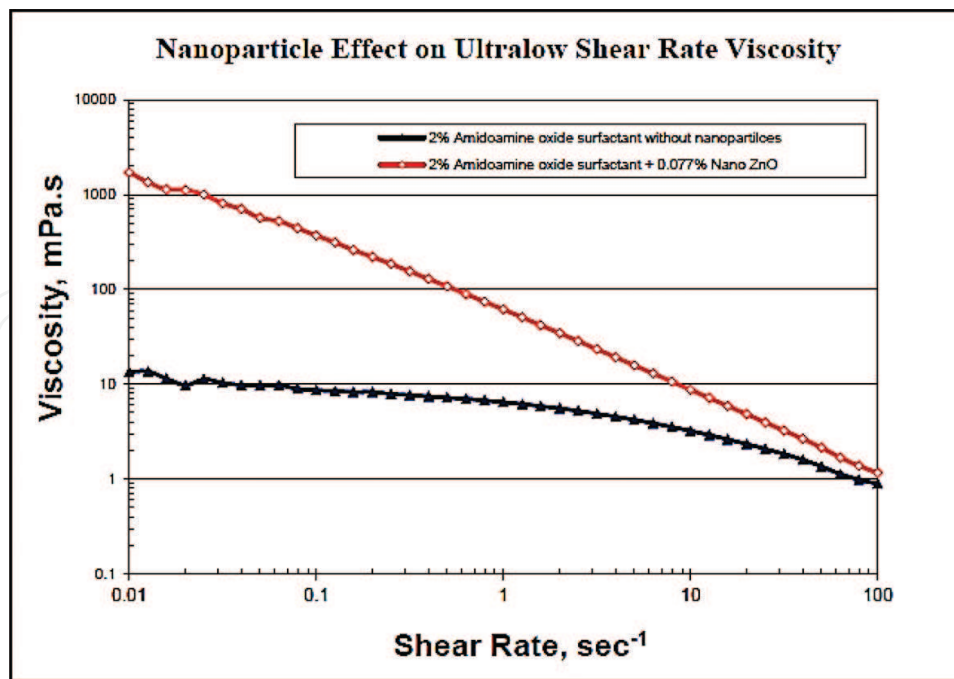


Figure 4. Low shear rate viscosity of threadlike micellar fluids with and without nanoparticles [15].

Huang et al. devised a new method of controlling fines migration by coating nanoparticles on proppants. Nanoparticles are injected in liquid slurry form into the blender tub during sand injection stages of the treatment [33]. These nanocrystals adhere to the surface of the proppants due to strong van der Waals and electrostatic forces of attraction. When the fines approach the proppant pack treated with nanocrystals, they get trapped by the same forces of attraction preventing them from moving into the wellbore. Once the fines are deposited in the proppant pack, attraction from the surrounding nanocrystals helps in preventing bridging and pore space plugging, thus maintaining the porosity of the proppant pack [33].

2.3. Delayed release of enzyme breakers using nanoparticles

In addition to denaturation of enzymes at higher temperature and pH conditions, operators face another problem while injecting enzymes along with the fracturing fluids. The enzymes, if used in high concentrations in the free state, cause premature degradation of polymer gels, thus decreasing the viscosity and proppant carrying properties of the fracturing fluid. This leads to the generation of comparatively inferior fracture parameters and proppant placement. However, the use of insufficient concentration of enzymes causes incomplete fracture cleanup and reduces the fracture conductivity.

Encapsulation of breakers gives the flexibility of using higher concentrations of breakers for better cleanup. A mixture of free and encapsulated breakers is usually used in the industry to achieve better results [9].

Industry badly required a delayed release agent to entrap the enzymes in order to make sure that they do not degrade the viscosity of the gel until the end of fracture propagation. This same entrapment agent should also be capable of releasing the enzymes after the fractures have been

created, in time for fracture cleanup. Such an encapsulating agent would ensure high fracture conductivity and minimum gel residue without compromising on generated fracture parameters.

Polymers carrying multiple ionic groups are called polyelectrolytes. They exhibit a dual character of highly charged electrolytes and macromolecular chain molecules simultaneously. Although they have the viscosity of a polymer and the electrical properties of an electrolyte, their ionic groups tend to dissociate in aqueous phase making the polymer charged [19].

A polyelectrolyte complex nanoparticle system with polyethylenimine (PEI) as the cation and dextran sulfate (DS) as the anion was developed by Tiyafoonchai and Middaugh [20]. It was a solid colloidal particle system with diameters ranging from 1 to 100 nm, designed to act as a delivery vehicle for pharmaceutical applications [21]. Cordova et al. modified this system to use in hydraulic fracturing operations (Table 1).

Polyelectrolyte complex nanoparticles	Mean size (nanometer)	Standard error size (nanometer)	pH	Mean zeta (mV)	Standard error zeta
	545.43	10.57	8.7	37.16	4.93

Table 1. Particle size and zeta potential measurement for polyelectrolyte complex nanoparticles with measurements done for three samples [22].

Reza Barati proved that these polyelectrolyte complex nanoparticles are capable of encapsulating enzymes and protecting them from temperature and pH conditions that are usually inhospitable to them when in free state [23]. Bose et al. proved that when the enzyme breakers are entrapped inside these nanoparticles, a highly conductive fracture is generated with the best fracture cleanup scenario. They have also proved that these nanoparticles are capable of preventing fluid loss into formations of 10 mD and tighter [1].

They conducted experiments using fracturing fluids of the following recipes:

- With only proppants (proppant baseline)
- With proppants and cross-linked HPG (gaur gel baseline)
- With proppants, cross-linked HPG, and enzyme (HPGE)
- With proppants, cross-linked HPG, and enzyme encapsulated inside the nanoparticle system (HPGEE)
- With proppants, cross-linked HPG, and the nanoparticle system (HPGNP)

Bose et al. reported the following results. Gaur gel (HPG) baseline, which used only the prop-pants and the cross-linked gaur, showed the least conductivity due to the high viscosity of the unbroken filter cake. HPGE fluid system showed higher values of conductivity, which was expected due to the degradation of cross-linked gaur by free enzyme. HPGEE (entrapped enzyme) showed a conductivity value higher than HPGE system. Thus, nanoparticles which entrapped the enzyme for a period of time during the injection gave significantly higher values of conductivity as reported by the free enzyme. This also implies that the enzyme is

being released after a period of time after which it acts like free enzyme. The higher value of conductivity obtained is due to the fact that the nanoparticles were able to distribute the enzyme more evenly in the filter cake and because of the fact that the enzymes were not lost to the formation since they were deposited in the filter cake [22].

Surprisingly, HPGNP gave a conductivity value comparable to that of HPGE. This may reduce the enzyme burden significantly. This shows that a relatively weaker filter cake, which can be easily cleaned up, was formed when nanoparticles were used with HPG solution. When nanoparticles were absent in the filter cake (HPG baseline case), a tight filter cake was formed by the polymer gel which resulted in very low fracture conductivity [22]. **Figure 5** summarizes the results of the experiments where each experiment was repeated three times and an error bar was reported for each bar chart.

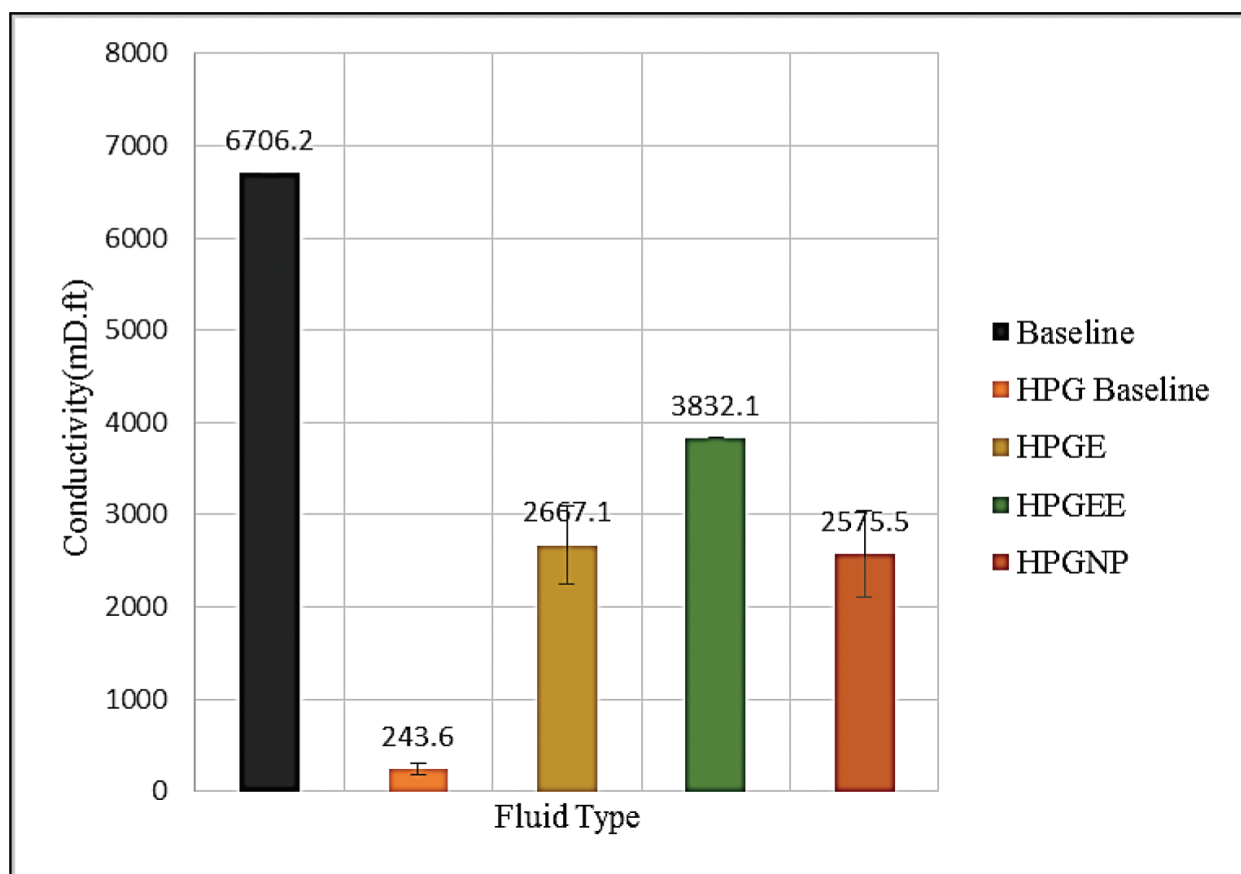


Figure 5. Conductivity values (in mD.ft) measured across the proppant pack for different experiments. Three experiments were conducted for each fluid, and standard error bars are provided in this figure [1].

2.4. Polyelectrolyte complex nanoparticles as fluid loss reducing agents

Fluid loss control additives are agents applied to reduce the volume of filtrate lost into the formation during the propagation of a hydraulic fracture. The reduction in filtrate volume helps in the propagation of longer networks of fractures. Fracture area has been found to increase when the fluid loss coefficient and volume decrease [22, 24].

Selecting a properly sized agent to plug the pores and direct the fluids into micro-fractures is very important. Fluid loss agents smaller than the currently used ones could theoretically plug the nano-sized pore throat diameters and micro-sized fractures in shale oil and gas reservoirs. Additives with diameters larger than one-third of the pore throat size cannot cause bridging by penetrating into the pores of the rock [24]. Using larger particles can cause the formation of external filter cakes, thereby reducing the filtrate volume. However, fluid loss additives having significantly larger sizes compared to the pore throat diameter will result in poor fluid loss prevention [22].

Pore throat sizes reported for different shale rocks are typically in the range of 10–1000 nm. Therefore, in order to plug the pore throats and reduce the filtrate volume, particles larger than 3 and 300 nm range must be used respectively, so as to cause only minimal damage to the rock [30]. Polyelectrolyte complex nanoparticles with particle sizes in the nanometer range were found to have the potential to act as fluid loss reduction agents. This potential acted as an impetus for Bose et al. to carry out static fluid loss tests using polyelectrolyte complex nanoparticles [22].

PEC nanoparticles performed as strong fluid loss control additives by reducing the fluid loss coefficient and the total fluid loss volume. HPG solution mixed with PEC nanoparticles showed significant reduction in fluid loss volume and fluid loss coefficient when compared with results obtained using the same volume of HPG solution without nanoparticles [22].

Fluid loss prevention capability of the nanoparticles will certainly help in the generation of longer fracture wings as well as in the extension of network of fractures. Reduction in the fluid loss volume caused by the nanoparticles will reduce the thickness of filter cake formed on the rock surface. This will result in cleaner highly conductive fractures capable of producing more hydrocarbons [22].

2.5. Fly ash nanoparticles as nano-proppants for tight unconventional reservoirs

Injecting nano-sized proppants after the injection of pad volume and prior to the placement of larger proppants is a good way to prevent the closure of micro-fractures and ensure their contribution in production [25]. These nano-proppants should be able to prop the micro-sized fractures, withstand the stress encountered in reservoir formations, and provide a conductive path for the flow of hydrocarbons during production. Injecting smaller proppants prior to the injection of larger ones may help in sequentially filling the widened natural fractures (widened during injection), allowing deeper percolation of proppants, and thus propping a longer fracture length [26]. Similarly, injecting nano-sized particles which can withstand the closure stress, followed by the conventionally used larger proppants, may help in propping more of the SRV, thereby increasing the seepage area and enhancing production [12, 25, 26].

Increasing the effective conductivity of the hydraulic fractures propagated in tight oil or gas plays by improving the type and placement of proppants will have the following results [12]:

- It will prevent the collapse of already existing micro- and nano-sized natural fractures which are opened up during injection.

- Using very small proppants before the injection of the larger proppants will prevent the collapse of the fissures that are generated during the injection, after the injection is stopped.
- It will improve the production of oil and/or gas from the formation by reducing fluid loss and improving the total fracture conductivity [12].

Figure 6 demonstrates how the injection of nano-proppants will keep the small fissures open and extend the network of small fissures, while commercial proppants with significantly larger size keep the main fracture open [12].

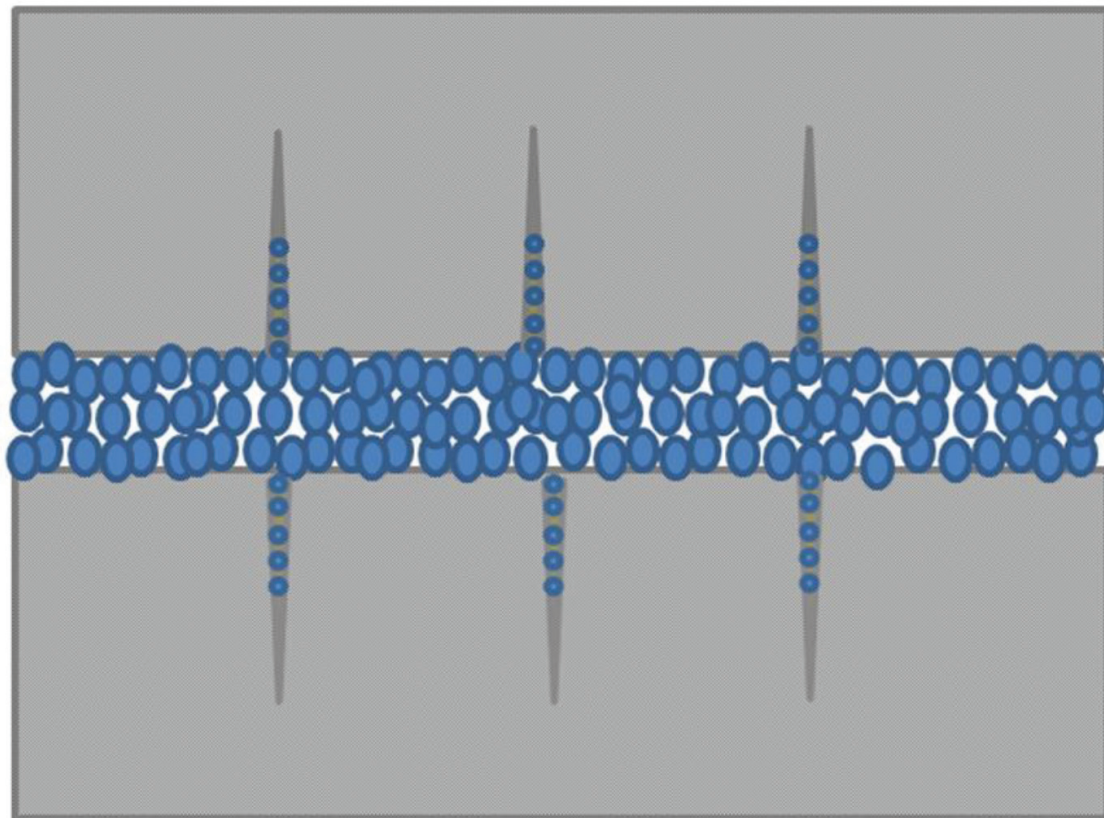


Figure 6. Schematic picture of proppants and nano-proppants distributed in fractures and micro-fractures [12].

Silica nanoparticles have been used successfully in drilling fluids to decrease water invasion into shale formations [27]. They showed good resistance against compressive stress. Fly ash nanoparticles obtained as a by-product in power plants is a cheap waste material comprising of nanoparticles of silica, calcium oxide, and aluminum oxide. These particles are removed and collected by electrostatic precipitators before the exhaust gases from the power plants are expelled into the atmosphere [28]. They are generally spherical in shape as the particles solidify rapidly while being suspended in the exhaust gas [1, 34]. There are mainly two types of fly ash particles namely class 'C' and class 'F.' Their composition varies slightly from each other as they are produced as a result of combustion of different types of coal.

Table 2 gives a list of constituents and their typical compositions in class F fly ash [12].

Constituent	Typical composition ranges
SiO ₂	40–60%
Al ₂ O ₃	18–31%
Fe ₂ O ₃	5–25%
CaO	1–6%
MgO	1–2%
TiO ₂	1–2%
Inorganic arsenic	16–210 ppm

Table 2. Constituents and their typical compositions in class F fly ash (Alliant energy, MSDS, 2005).

Bose et al. [12] used transmission electron microscope images to measure the size of fly ash nanoparticles. Round-shaped nanoparticles with diameters in the range of (100–800 nm) were observed in addition to some residue. The sphericity of the proppant particles plays a big role in determining the conductivity of the fracture propped by the respective proppants. The higher the sphericity, the better the conductivity of the fracture and vice versa. The finding that most of the sample particles are spherical in shape reaffirms their potential to create highly conductive flow paths for the flow of hydrocarbons when used as proppants for naturally existing micro-fractures [12]. TEM images of fly ash nanoparticles are shown in **Figure 7**.

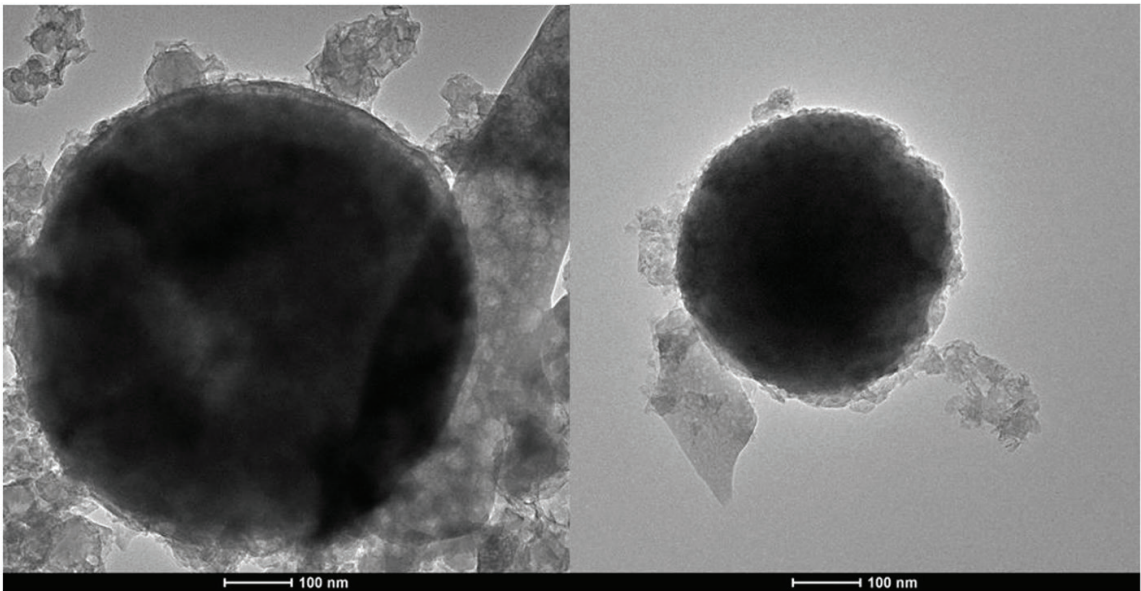


Figure 7. TEM images of fly ash nanoparticles collected from two different power plants. The left image presents a particle from the fly ash class C, and the right image shows the different size of the fly ash particle from the class F [12].

Nanoscale quasi-static indentation tests were conducted on fly ash particles to determine hardness and reduced elastic modulus. Force was applied to an indenter tip, and the displacement of the tip into the specimen was recorded. From the load-displacement curve, hardness and reduced

elastic modulus values were determined by applying the Oliver and Pharr method using a precalibrated indenter tip area function and a predetermined machine compliance value [12].

The conductivity of the fracture is adversely affected when the proppants get compressed after the injection pressure is removed. Measurement of the average value of reduced elastic modulus provides information about the extent of deformation that can happen to the proppants when subjected to stress. An average reduced elastic modulus of 33 GPa for class C and 20 GPa for class F shows the ability of the fly ash particles to withstand deformation [12].

Hardness of a material is a parameter which measures the resistance of the material against permanent deformation under the effect of compressive stress. In order to ensure good production rates, nano-proppants placed inside the fractures should be able to withstand the effective minimum stress usually encountered in the horizontal direction and the absolute vertical stress which is a function of their depth under the surface. Hardness value of 1.3 GPa for class C and 1.2 GPa for class F translates to 1.8×10^5 psi and 1.7×10^5 psi, respectively, which implies that these nano-proppants can withstand more than the maximum stress values encountered in a typical shale formation [12]. Barati [35] and Bose et al. [12] reported that fly ash nanoparticles acted as strong fluid loss control additives by reducing both fluid loss coefficient and total fluid loss volume when they were used with cores in 1–10 mD permeability range (**Figures 8 and 9**). There was an increase in the mass of external filter cake when the fly ash was used with HPG solution showing the significance of the role played by the contribution of fly ash particles to both external and internal filter cakes formed on the cores [12].

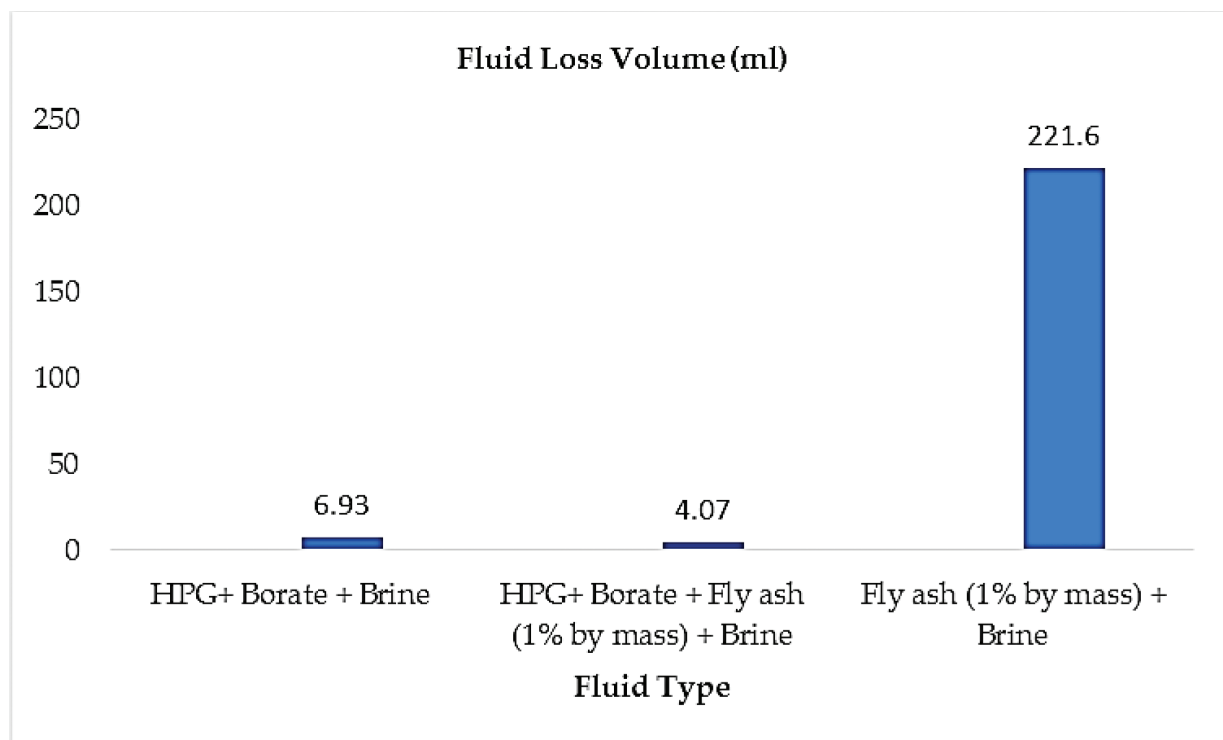


Figure 8. Fluid loss volumes obtained for different fluid [12].

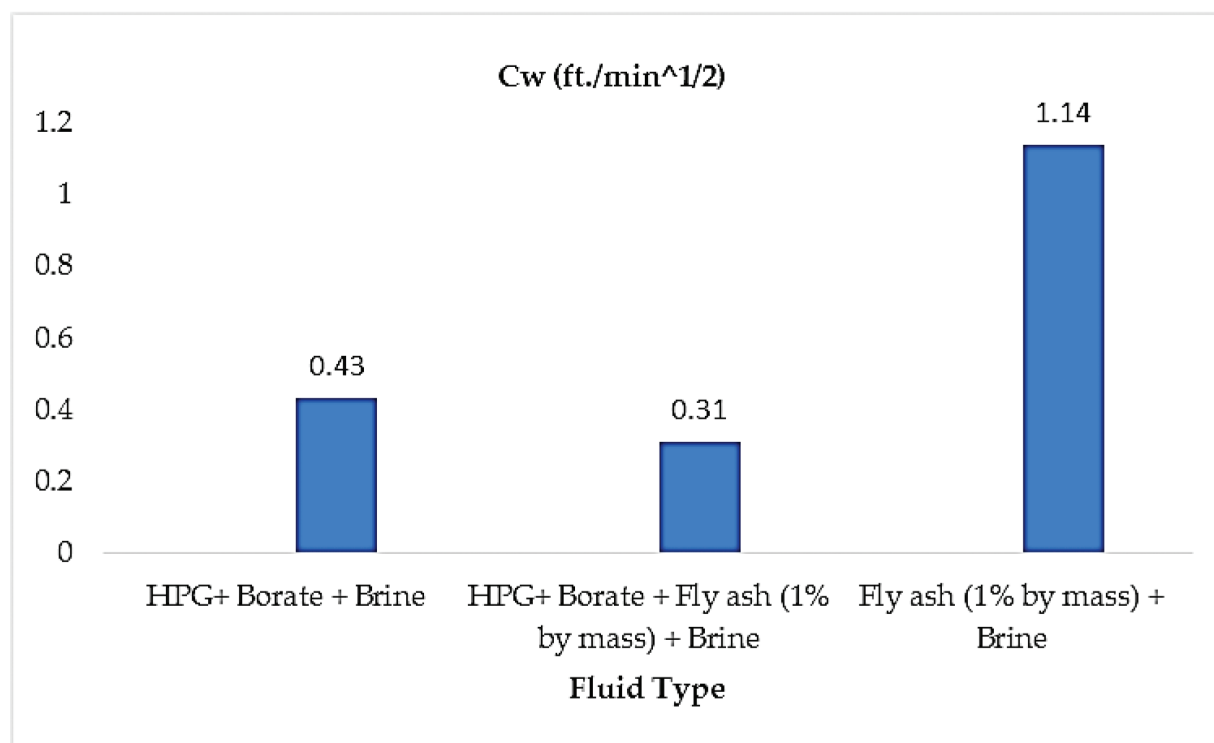


Figure 9. Fluid loss coefficients obtained for different tests [12].

Long-term fracture conductivity tests designed in accordance with the API recommendations were conducted using Scioto sandstone cores (permeability of approximately 0.01 mD). Fly ash samples of class F (which showed more uniform size distribution) were used as proppants between two core wafers placed under stress, and fracture conductivity of this proppant pack was measured. When a fly ash loading that generated similar width to 3 lbm/ft² proppant pack was used, conductivity of 0.779 mD.ft was obtained for class F fly ash sample, which translates to a dimensionless fracture conductivity value of approximately 10 [12].

Dimensionless fracture conductivity (F_{cd}) of a bi-wing vertical fracture is given by:

$$F_{cd} = \frac{K_f * W_f}{K * X_f} \quad (1)$$

where K_f is the fracture conductivity, W_f is the fracture width, K is the matrix permeability, X_f is the effective fracture length.

According to Prats [29], increasing the dimensionless fracture conductivity beyond 10 or 20 would not increase the production significantly. This implies that the fly ash nanoparticles when used as nano-proppants would create a fracture length with good fracture conductivity [12].

Fly ash nanoparticles can potentially be used as both fluid loss additives and nano-proppants for hydraulic fracturing of tight and ultra-tight formations. These particles can prevent the

fluid loss during the propagation of hydraulic fractures and then pack the system of micro-fractures which are opened up during the fracturing process. This would ensure the creation of a larger propped network of stimulated reservoir volume which would increase the production. The fluid loss prevention capability of such nanoparticles can also be applied to prevent mud loss during drilling of wells in tight and ultra-tight formations [12].

3. Summary

Despite the phenomenal amount of research carried out in the past few decades, hydraulic fracturing process is far from being perfect. Incomplete fracture cleanup causes the actual fracture conductivity to be much less than the desired fracture conductivity which would ultimately impact the cumulative production from the reservoir. Major problems include proppant pack damage, migration of fines, and formation damage. Similarly, hydraulic fracturing process in tight reservoirs can result in larger if the network of micro-fractures opened up during the injection phase is propped, enabling hydrocarbons to flow through them during the production phase.

Nanoparticle-associated surfactant micellar fluids when used as an alternative to cross-linked fluids ensure adequate viscosity for fracturing fluids by cutting down the polymer damage left after fracturing process. Huang et al. devised a nanoparticle system which when coated on proppants helps in controlling fines migration problem. Barati et al. and Bose et al. proved that polyelectrolyte complex nanoparticles can help in improving fracture cleanup by protecting and delaying the release of enzyme breakers. These nanoparticles also acted as fluid loss reducing agents, thereby improving the generated fracture parameters and minimizing the formation damage in the 'near fracture zone' usually invaded by the leak off fluid. Fly ash nanoparticles have been proven to act as nanopropants which can prop the micro-fractures in tight reservoirs and potentially improve the cumulative production.

Nomenclature

cP	Centipoise
Cw	Coefficient of fluid loss
mD	milli Darcy
PEC	Polyelectrolyte complex
PEIDS	Polyethylenimine dextran sulfate
SRV	Stimulated reservoir volume

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References

- [1] C. C. Bose, Application of Nanoparticles as Proppants and Breaker Encapsulating Agents, University of Kansas, Lawrence, 2016.
- [2] J. L. Gidley, S. A. Holditch, D. E. Nierode and R. W. Veatch Jr, Recent Advances in Hydraulic Fracturing, SPE, ISBN 978-1-55563-020-1 1990.
- [3] P. C. Harris, Fracturing-fluid additives, Journal of Petroleum Technology, SPE Distinguished Author Series, DOI:10.2118/17112-PA, October 1, 1988.
- [4] C. Montgomery, Fracturing fluids, Effective and Sustainable Hydraulic Fracturing, Dr. Rob Jeffrey (Ed.), InTech, DOI: 10.5772/56192, 2013. Available from: <http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/fracturing-fluids>.
- [5] R. Barati, R. Hutchins, T. Friedel, J. Ayoub, M. Dessinges and K. England, Fracture impact of yield stress and fracture-face damage on production with a three phase 2D Model, SPE Productions & Operations, 2009.
- [6] T. Palisch, R. Duenckel, L. Bazan, H. Heidt and G. Turk, Determining realistic fracture conductivity and understanding its impact on well performance—theory and field examples, In Hydraulic Fracturing Technology Conference, College Station, 2007.
- [7] C. Montgomery, Fracturing fluid components, Effective and Sustainable Hydraulic Fracturing, Dr. Rob Jeffrey (Ed.), InTech, DOI: 10.5772/56422, 2013. Available from: <http://www.intechopen.com/books/effective-and-sustainable-hydraulic-fracturing/fracturing-fluid-components>.
- [8] D. Davies and T. Kulper, Fracture conductivity in hydraulic fracture stimulation, Journal of Petroleum Technology, 1988.
- [9] M. Economides and K. Nolte, Reservoir Stimulation. 3 ed., John Wiley & Sons, Inc, 2000.
- [10] J. Ayoub, R. Hutchins, F. Van der bas, S. Cobianco, C. Emiliani, M. Glover, M. Kohler, S. Marino, G. Nitters, D. Norman and G. Turk, New findings in fracture cleanup change industry perceptions, In SPE International Symposium and Exhibition on Formation damage Control, Lafayette, LA, 15-17 February, 2006.
- [11] M. J. Mayerhofer, E. Lolon, N. Warpinski, C. Cipolla, D. Walser and C. M. F. A. Rightmire, What is stimulated reservoir volume? SPE Journal 119890-PA, 2010.

- [12] C. Bose, T. J. B. Fairchild, A. Gul and R. Ghahfarokhi, Application of nanopropants for fracture conductivity improvement by reducing fluid loss and packing of micro-fractures, *Journal of Natural Gas Science and Engineering*, 27, 2015, pp. 424-431.
- [13] J. Elbel and J. Ayoub, Evaluation of apparent fracture lengths indicated from transient tests, *Journal of Canadian Petroleum Technology*, 31(10), 1992.
- [14] F. Nettesheim, W. M. Liberatore, K. T. Hodgdon, J. N. Wagner, W. E. Kaler and M. Vethamuthu, Influence of nanoparticle addition on the properties of wormlike micellar solutions, In *Langmuir*, 2008, pp. 7718-7726.
- [15] T. Huang and J. Crews, Nanotechnology applications in viscoelastic surfactant stimulation fluids, *SPE Production & Operations Journal*, November, 2008.
- [16] O. Jaripatke, B. Grieser and K. Chong, A review of successful approach towards shale play stimulation in the last two decades – A Completions Road Map To Shale Play Development, in *SPE Deep Gas Conference and Exhibition*, Manama, Bahrain, 2010.
- [17] A. D. Taleghani, M. Ahmadi and J. Olson, Secondary fractures and their potential impacts on hydraulic fractures efficiency, in *International Conference for Effective and Sustainable Hydraulic Fracturing*, Brisbane, Australia, May, 2013.
- [18] N. Warpinski, M. Mayerhofer, M. Vincent, C. Cipolla and E. Lolon, Stimulating unconventional reservoirs: maximizing network growth while optimizing fracture conductivity. Paper SPE 114173, In *SPE Unconventional Reservoirs Conference*, Keystone, Colorado, 2008.
- [19] J. Koetz and S. Kosmella, *Polyelectrolytes and Nanoparticles*, Springer Laboratory, ISBN 978-3-540-46382-5 2007.
- [20] J. W. Waree Tiyaboonchai and C. R. Middaugh, Formulation and characterization of DNA-polyethylenimine-dextran sulfate nano-particles, *European Journal of Pharmaceutical Sciences*, 19, 2003, pp. 191-202.
- [21] W. Tiyaboonchai, Development of a New Nanoparticle Delivery Vehicle Based on an Aqueous Polymer System: Polyethylenimine and Dextran Sulfate, University of Kansas, Pharmaceutical Chemistry, 2002.
- [22] C. Bose, B. Alshatti, L. Swartz, A. Gupta and R. Barati, Dual application of polyelectrolyte complex nanoparticles as enzyme breaker carriers and fluid loss additives for fracturing fluids, In *SPE/CSUR Unconventional Resources Conference*, Calgary, Alberta, 2014.
- [23] R. Barati, Nano-particles as fluid loss additives for hydraulic fracturing of tight and ultra-tight formations manuscript accepted (peer-reviewed) to be published in proceedings of ASME 2014 I, in 33rd International Conference on Ocean, Offshore and Arctic Engineering, 2014.
- [24] J. D. Hawsey and C. L. Jacocks, The use of fluid-loss additives in hydraulic fracturing of oil and gas wells, In *SPE California Regional Meeting*, Bakersfield, California, 1961.

- [25] A. A. Khanna, Stimulation of the natural fracture system by graded proppant injection, *Journal of Petroleum Science and Engineering*, 2013.
- [26] A. Keshavarz, A. Badalyan, T. Carageorgos, R. Johnson and P. Bedrikovetsky, SPE 167757 Stimulation of unconventional naturally fractured reservoirs by graded proppant injection: experimental study and mathematical model, In SPE/EAGE European Unconventional Conference and Exhibition, Vienna, Austria, 25-27 February, 2014.
- [27] J. Cai, M. Chenevert, M. Sharma and J. Friedheim, Decreasing water invasion into atoka shale using nonmodified silica nanoparticles, *SPE Drilling and Completion*, March, 2012.
- [28] EPRI (Project Manager K. Ladwig), Comparison of Coal Combustion Products to Other Common Materials—Chemical Characteristics, Electric Power Research Institute, Palo Alto, CA, 2010.
- [29] M. Prats, Effect of vertical fractures on reservoir behavior—incompressible fluid case, *SPE Journal*, 1(2), 1961, pp. 105-118.
- [30] R. Barati, S. Johson, S. McCool, D. Green, G. Willhite and J.-T. Liang, Fracturing fluid cleanup by controlled release of enzymes from polyelectrolyte complex nanoparticles, *Journal of Applied Polymer Science*, 121(30), 2011, pp. 1292-1298.
- [31] J. Tannich, Liquid removal from hydraulically fractured gas wells, *Journal of Petroleum Technology*, 1975.
- [32] J. B. Crews and A. M. Goma, Nanoparticle associated surfactant micellar fluids: an alternative to crosslinked polymer systems, In SPE International Oilfield Nanotechnology Conference, Noorwijk, The Netherlands, 12-14 June, 2012.
- [33] B. Christopher, K. Seth, R. Hollier and B. Paternostro, Maximizing production life with the use of nanotechnology to prevent fines migration, In CPS/SPE International Oil & Gas Conference and Exhibition, Beijing, China, 8-10 June, 2010.
- [34] R. Snellings, M. G. and E. J., Supplementary cementitious materials. *Reviews in Mineralogy and Geochemistry* 74, 2012, pp. 211-278. DOI: 10.2138/rmg.2012.74.6.
- [35] R. B. Ghahfarokhi, Fracturing Fluid Cleanup by Controlled Release of Enzymes from Polyelectrolyte Complex Nanoparticles, PhD thesis, University of Kansas, Lawrence, 2010.