Silica gel as an economical and innovative alternative to bio-based polymers in aqueous hydraulic fracturing fluids

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Abstract

Bio-based polymers are the most widely used products for providing rheology to aqueous hydraulic fracturing fluids. The performance properties of these products are well known, as are their shortcomings. Ideally, any alternative viscosifier would be cost effective, readily available, and environmentally friendly with such performance attributes as: excellent proppant carrying capacity, resistance to high temperatures, good clean up and function in hard, high salinity water. Somewhat surprisingly, silica gel has been overlooked as a rheological agent with these performance characteristics.

This paper will provide an overview to inorganic silica gel chemistry and how it can be applied in the field to quickly yield viscosity. Similar to the biopolymers, silica gel comes in different shapes, sizes and with different performance properties. A next generation silica gel system has been developed that matches the performance requirements of a fracture fluid. Two focus areas of research have been on rheology and clean-up. The silica gel is formulated to have minimum affinity for adsorption on rock surfaces. Once placed, the silica gel is removed through syneresis, resulting in a propped fracture with enhanced conductivity as well as negligibly damaged reservoir permeability. Results obtained from experimental testing of fracture conductivity, retained permeability, and polymer residue from various proppant packs indicate that this new fluid system is easily removed from fractures.

The method of on-site production of the silica gel results in a product with similar health, safety and environmental characteristics as food grade silica. By formulating the silica gel to have low attraction for rock, it also has low affinity for metals and salts. This puts into play the use of produced water that further enhances the environmental credentials of the system.

Introduction

Over the last two decades, there has been a rapid commercial development of unconventional gas and oil reservoirs. The most often sited technical reasons for the development of these resources are horizontal drilling and sequenced, multi-stage hydraulic fracturing. This time period has also produced significant advancements in the area of fracturing fluids. Existing hydraulic fracturing fluid systems have evolved to be more efficient with better performance properties. At the same time, new fluid systems have been introduced to meet the needs of industry. For the purpose of this paper a quick review of hydraulic fracture fluid systems are presented to serve as a reference point to a silica gel-based fluid.

Regardless of the type of fracture fluid, it has to adequately perform the function of transmitting hydraulic pressure to fracture, propagating the fracture and transporting and suspending proppant until closure of the fracture. A selection and design criterion of fracturing fluid is based on multiple factors;

- fluid compatability with the formation
- reservoir temperature
- pore pressure
- friction pressure
- reservoir permeability
- gel breaking properties and conditions
- environmental considerations
- cost

Invariably, the selection of frac fluid will involve trade-offs. Fluid selection will be made from the classes of aqueous-based, oil-based or foam. Within aqueous-based systems the choices are narrowed to;

- Slickwater
- Linear polymer-viscosified fluids
- Crosslinked polymer gels
- Viscoelastic surfactant gels
- Unconventional /emerging fluid systems

As the name implies, unconventional or emerging fluids systems are new technologies being developed to meet or improve the needs of the industry. Examples include; synthetic polymer-based frac fluids, methanol-containing fluids, liquid CO_2-based fluids, associative polymers, liquifiedpropane as well as others. Into this category is placed

silica gel. While the technology is unconventional it is not new. Silica gel as hydraulic fracturing fluid viscosifier was introduced to the petroleum industry in the late 1970s[1]. Early research identified this form of silica as providing a highly viscous, thixotropic fluid that was capable of maintaining viscosity at very high temperatures. A need for these particular set of performance attributes arose in geothermal wells being fracture stimulated in Hokkaido, Japan[2,3] in the early 1980s. Literature reports these early applications of silica gel viscosified frac fluids were a technical and economic success. There was a significant increase in steam volume and the cost of silica-based system was described as being comparable to that of the modified guar. After Hokkaido, a few other geothermal wells were successfully fractured with a silica gel system but the technology did not make the transition to main stay systems. Likely the explanation resides in being a good product at the wrong time.

Silica Chemistry

Not helping with adoption of silica gel was the underlying chemistry was based off of silica vs. organic chemistry. This was further complicated by the feedstock to make the silica gel being sodium silicate (note: there are other forms of alkali silicate but for this paper discussions will be restricted to sodium silicate). As is very well known, sodium silicates are highly effective sealant and blocking agents and have been used since 1922 for conformance applications[4]. Therefore it is quite understandable there would be hard questions on potential reservoir damage. As will be presented the sodium silicate is a starting point and it is converted to a useful silica gel. Or to rephrase, sodium silicate is as different to silica gel as mannose is to guar.

Silica and silicate chemistry covers a complex and diverse family of natural and synthetic materials. This paper provides only a snapshot of the chemistry but serves as a foundation for understanding the performance properties and its HS&E characteristics.

Silica gel is produced by the polymerization of sodium silicate. As guar, xantham, locust bean. carrageenan, corn starch are some examples of polysaccharides there are likewise different and distinct forms of silica gel. Figure 1[5] shows the different pathways to making a silica and provides a summary of the shape and size of the silica particles. Figure 2 summarizes the surface chemistry of the silica. Outside of pH, other factors that impact silica gel chemsitry and final silica gel properties include; acid type, salinity, type of salt, and temperature.

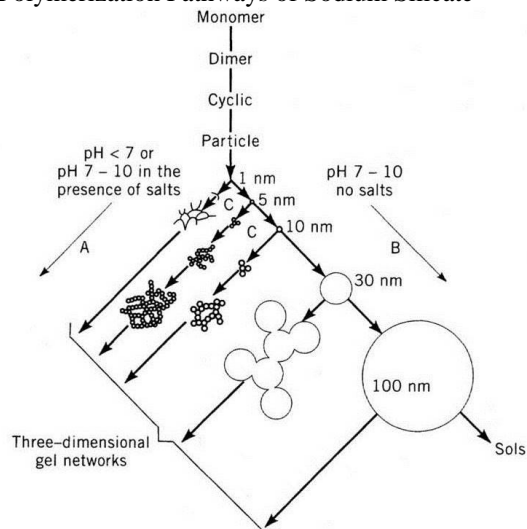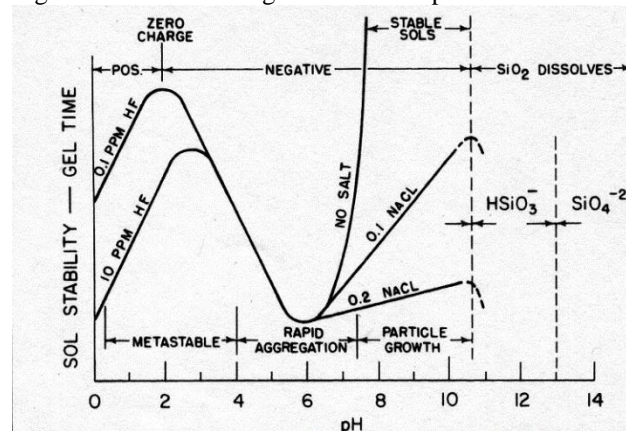Figure 1: Polymerization Pathways of Sodium Silicate

Figure 2: Surface Charge on Silica vs. pH

Per figure 1 there are several different pathways to making silica gel. The earlier silica gel technology followed the pathway on the right. Or in a sentence, acid was added to sodium silicate and the pH reduced to induce gelation. This paper describes a silica gel that is produced by taking the pathway at the left. In other words, sodium silicate is added to an acid solution and the pH raised to induce gelation.

"Breaking" via Syneresis

The outside-of-the-box nature of silica gel extends to the breaking and removal of the silica gel from the fracture. Outside the use of hydrofluoric acid, it is very difficult to break the silane (Si-O-Si) linkages. Clean up is achieved through a combination of factors. As will be described the silica gel has been formulated to maximize removal efficiency.

The primary method for removal is syneresis. To fully appreciate the syneresis (shrinking) effects in silica gel, one must be familiar with sol-gel synthesis in silica gel systems. Silica gel is typically synthesized by acid reaction with soluble silicates. A long-time production method for silica gel is the

reaction of aqueous sodium silicate with sulfuric acid. Sodium silicate is in the form of an aqueous solution, normally 30% dissolved SiO_2, 10% dissolved alkali (as Na_2O), and the balance water.   The SiO_2 is present in solution as a multiplicity of anionic species derived from silicic acid ($Si(OH)_4$), examples of which are shown in Figure 3[6]. In these structures, charge balance is provided by sodium cations from the alkali and the resulting set of species are a stable collection of molecules, the relative abundance of which are driven by the SiO_2 concentration, the Na concentration (or OH^- concentration) and by temperature[7].

Figure 3: Low Molecular Weight Sodium Silicate Species
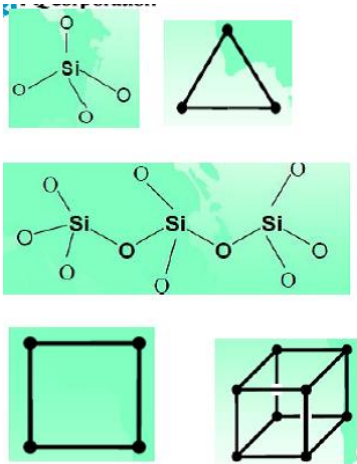
When this collection of silicate molecules is contacted by acid, the stabilizing alkali is neutralized and the silicate anions react to form polymeric silica; that is two silicate anions react to form a siloxane bond (Si-O-Si) with expulsion of one molecule of water.   This reaction is controlled by concentration of SiO_2 and by concentration of acid; also by order of addition,   quality of mixing, and temperature[8]. Progression of gelation is by formation of a silica sol; namely colloidal silica particles in solution and subsequent conversion of the sol to the silica gel. Primary particles are the colloidal silica particles and these particles aggregate to become the silica gel or silica precipitate, see Figure 4.

Figure 4: Aggregation of Primary Silica Particles
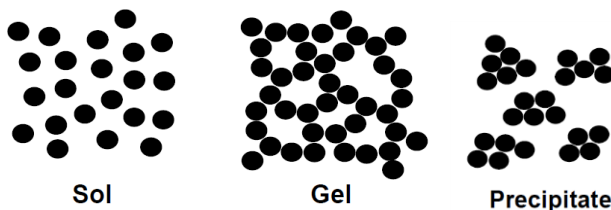

Primary   particle   size   and   pH   set   the   porosity characteristics of the synthesized silica gel. For example, low pH promotes smaller primary particle size, which in turn promotes high surface area, e.g. 700 m^2/g and high pore

volume, e.g. 3 mL/g in the silica gel. These properties are greatly influenced by ionic strength, post-processing pH, and drying conditions.

Once the gel has set up (converted from liquid phase to a semi-solid phase), there is a period of time where secondary reactions occur and the gel consolidates or shrinks with the expulsion of water and salts. This shrinkage effect is known as syneresis and can continue for hours depending on the size of the silica gel monolith. Graph 1 shows gel shrinkage as decreasing bed height vs. time/temperature.

Graph 1:   Syneresis as bed height vs. time at different temperatures (K. Berg, PQ)
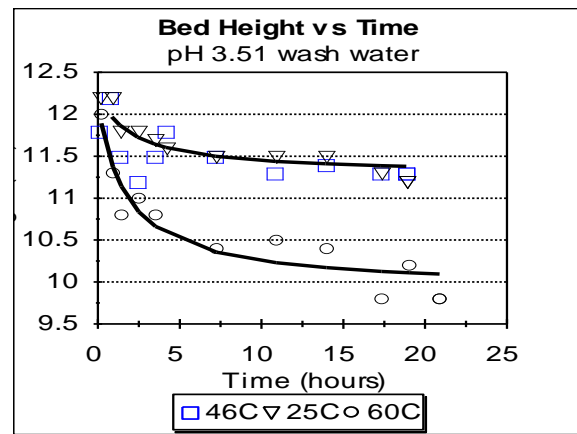
It is important to understand that silica gel is amorphous with significant porosity, that is water will remain in the pores unless displaced or dehydrated. Dehydration can lead to gel collapse and further shrinkage. Gel will shrink away from fracture faces and can be removed from the fracture via flow-back of water.   Breaking for silica gel systems is a combination of gel consolidation (syneresis) and shrinkage due to water loss.

Silica gel surface chemistry is one of surface hydroxyl type and concentration. Under the conditions of the above gelation, the surface is fully hydroxylated and in the presence of water is relatively inert.

Syneresis is aided in the post-fracturing process.   The fracture closure pressure induces a pressure difference between the silica gel and the hydraulic fracture fluid. The entrained water/brine is forced out at an increasingly accelerated rate.

The lack of charge results in the silica gel having a low affinity for formation rock and, therefore, has a low liftoff pressure from the fracture face, making it readily removable.

Retained permeability as well as retained conductivity tests confirming low liftoff pressure were obtained, using a silica gel-based frac fluid formulated to pH 5.4 and SiO_2 concentration of 2% by weight. As seen in Tables 1 and 2, the silica gel fluid shows as non-damaging with good clean-up. In the case of retained permeability, the clean-up can be partially attributed to the silica gel not forming a filter cake (Figure 5). The resulting high fluid loss would not be an issue for use in negligibly permeable shales but would require the use of dissolvable fluid lost additives for some other applications.

Table 1: Summary of Retained Permeability (160°F)

Test	Fluid	Total Fluid Loss (ml)	Core Permeability (md)		% retained
			Initial	Final	
Bandera Gray	2% SiO_2, pH 5.4	35.2	0.91	0.75	82

Table 2: Summary of Retained Conductivity (160°F)

Test	Conductivity (md-ft.)		% Retained Conductivity (based on blank)
	after 10 ml/min Flow Stage	after 40 ml/min Flow Stage	
Blank	2966	2726	-
2% SiO_2, pH 5.4	1587	2069	76

Figure 5: Bandera Core after 30 min fluid loss at 100 psi

Rheology

A key performance property of silica gel is the type of viscosity it can impart to a frac fluid. The silica gels exhibit very high viscosity under low shear conditions. Application of shear significantly drops the viscosity. This allows for the suspension and transport of proppant without the comparable viscosity requirements of conventional fluids. Also, it allows for very high proppant loading or the carrying of high density proppant. Silica gel builds viscosity via the smaller silica gel fragments that mechanically entangle and interlock to form a much larger three dimensional structure. Gel strength is further enhanced as hydrogen bonds form between silica gels. The final viscosity build is dependent on several factors with silica concentration being the most dominant. The method developed by PQ lowers the required concentration of silica gel to achieve desirable proppant suspension and transport. This is achieved by increasing the pore volume and surface area of the silica gel. A usual load level of silica gel in a frac fluid would be ~2 to 2.5% SiO_2 by weight to water.

The viscosity of the silica gel can be tailored to suit field equipment, reservoir environments and fluid design. Silica gel viscosity is further controlled by pH, shear, time, acid selection, presence of polymers, salts and formation temperature. Silica gel has the noteworthy characteristic of having shear enhanced viscosity. This is in contrast to fluids crosslinked with borates, titanates or zirconates that are adversely affected by shear rate and shear history.

The rheology of a silica gel-based frac fluid was modeled using a variety of different rheological methods including; flow loop testing, different types of rheometers and settling rates of suspended material. Presented is data generated at Oklahoma University. The data collected in the flow test included: flow rate, differential pressure across various sections of straight and coiled tubing, fluid density, fluid temperature and system pressure.

The silica gel was prepared in a 55 gallon tank. The silica gel was circulated through a ½ in. diameter straight and coiled tubing. Silica gel was circulated using a progressive cavity pump along with a centrifugal pump. The use of two pumps in sequence allowed for higher levels of shear applied in series with the cavity pump. Frac fluid samples were tested at roughly 15 minute intervals. Testing was conducted at ambient temperatures with temperatures rising from 64°F in sample 1 to 105°F in sample 6 . (Table 3)

Graph 2: Viscosity vs. Shear Time
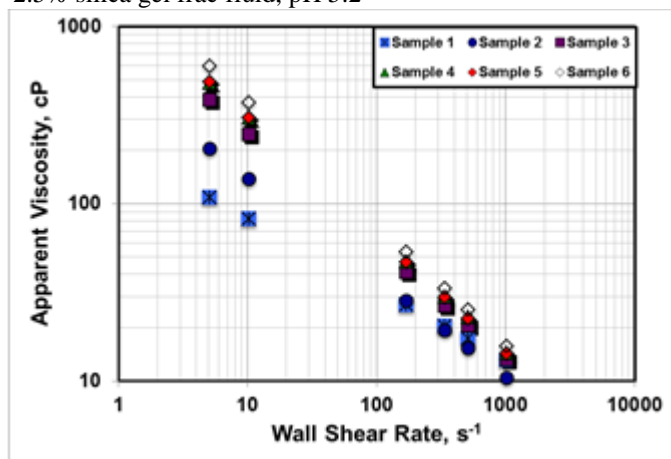2.5% silica gel frac fluid, pH 5.2

Table 3: Viscosity Readings for sample 6, 40°C

RPM	Shear Rate s^{-1}	Shear Stress lb./ft^2	Log SR	Log SS	Visc cP
3	5.11	0.064	0.71	-1.19	598.2
6	10.22	0.075	1.01	-1.13	371.4
100	170.3	0.22	2.23	-0.65	53.63
200	340.6	0.25	2.53	-0.61	33.30
300	510.9	0.26	2.71	-0.59	25.19
600	1021.8	0.31	3.01	-0.51	15.64

n = 0.312
K = 0.038

Safe & Green

Once again a comparison is made to guar and other polysaccharides, silica is a commonly used food additive. Existing regulatory approvals underlie the safe nature of silica. Depending on the jurisdiction, the use of silica as a food additive can be as high as 5% by weight, and in the U.S. has an upper limit of 2% for most food applications[9]. Beyond the benign nature of silica, there are several desirable environmental characteristics that flow though the use of silica gel as an aqueous fluid viscosifer.

Silica is also not a food source for bacteria. This reduces the risk for the development of H$_2$S in the reservoir. The introduction of bacteria is minimal from the starting materials of sodium silicate and hydrochloric acid. This further reduces the risk of generating H$_2$S and the need for bactericides. It should also be noted that silica gel does not undergo oxidative degradation, eliminating the need for using oxygen scavengers.

Water -Brine

It is anticipated that one of the most attractive features of a silica gel system is it can be formulated using water of extreme salinity and hardness. This allows the bulk of the silica gel to be formulated with untreated/minimally treated produced water. Fresh water or water with minor salinity is required in the first step of forming the silica sol concentrated. The silica sol is formulated to the isoelectric point or to a slightly cationic charge. As such, it is not attracted to cationic material such as sodium, calcium or magnesium. The gelation step can occur using water sources of high salinity and hardness such as produced water.

The tolerance to salts and hardness led to the natural extension of evaluating silica gel as a viscosifier for brine solutions. The tolerance for salts and hardness extended into various chloride, bromide and formate brines. Table 4 shows the viscosity characteristics of a calcium chloride brine that has been formulated with silica gel. This allows for the option to formulate high density brine frac fluids (or completions fluids). In the case of frac fluids, the ability to viscosify brines allows for significant reduction in pumping pressure requirements. Typically the need for a high density brine frac fluid would be with a high-temperature or ultra-high temperature well. The prior use of silica gel as a geothermal frac fluid indicates a usage temperature of over 500°F.

Table 4: 8% SiO$_2$ diluted to 2.5% SiO$_2$ by volume with a saturated calcium chloride solution (25°C)

pH	Density SG	600	300	200	100	6	3	10 s	10 min
4.8	1.34	103	78	58	53	20	17	17	17

Production on-site

The early field trials as well more recent pilot testing show the silcia gel can be made at the well site using existing equipment. Outlined is a formulation using 200 bbl as the base volume. This volume was selected to match the size of a conventional hydration tank. The making of the silica gel does require good agitation which should be sufficient in a hydration tank. In case of insufficient agitation then a 10 bbl blender tub could be used ahead of the hydration tank.

Major steps for making the silica gel would be;

- make silica sol feed stock (~10% SiO$_2$, pH 2.0)
- dilute silica stock feed stock (~2.0 to 2.5% SiO$_2$)
- raise pH to induce gelation (~pH 4 to 6)
- introduce other fluid additives as desired
- shear
- add proppant and pump into the well

The first step involves making the silica sol feedstock. Once made, the feedstock is a low viscosity solution that has several hours stability before it begins to form a silica gel. As mentioned earlier in the paper, the sodium silicate is metered into the hydrochloric acid solution under agitation. Prior to the addition of sodium silicate to acid, the sodium silicate is diluted with water for ease of handling. It is important that pH be accurately measured as the sodium silicate will begin to

raise the pH of the HCl solution. The indicated volumes should result in a 10% SiO_2 solution with a pH of 2.0.

Presented are the raw material requirements using a 200 bbl hydration tank as the base unit. The first step is the material requirements for making the silica sol feedstock

- N® grade sodium silicate – 525 gallons
- Fresh water – 725 gallons
- HCl (12% solution) – 580 gallons (stored in 2 polyethylene totes)
- Fresh water

Once the silica sol has been produced it is possible to switch to using non-freshwater. The water is added to the sol and the pH raised using a small volume of KOH. Once again, the 200 bbl hydration tank is used form mixing

Fresh/non fresh water – 6900 gallon
KOH (20%) ~40 gallons

Cost
While this paper has shown some of the value propositions of a silica gel system invariably the question comes to what is the cost per gallon with a comparison made to a guar-based system vs. a viscoelastic surfactant system. As was noted above, silica gel can be made on-site using existing hydraulic fracturing equipment so there are no capital costs. The two feedstock chemicals to make the silcia gel are hydrochloric acid and sodium silicate. Both these materials are widely available, inorganic chemicals that are not subject to wide price swings. The formulated silica gel fracture fluid has fewer components which reduces costs. It is anticipated that even at today's low guar pricing, a silica gel system would be comparably priced on a per gallon basis.

Conclusions
Silica gel is emerging as a viscosifier for fracture fluids. Past field trials coupled with recent lab work has shown silica gel has the following performance properties;
- Successfully applied at temperatures over 500°F
- formulated with hard water with high salinity
- very high proppant carrying capacity
- removed via syneresis
- cost effective
- environmentally friendly

Industry has shown a high level of interest in the use of silica gel. However with current market conditions there has been a reluctance to be the first to use in the field.

Acknowledgments
The authors would like to acknowledge the pioneers of the first silica gel fluid system.

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