A SIMPLE, COST-EFFECTIVE ALTERNATIVE TO CROSS-LINKED GUAR SYSTEMS THAT ALLOWS FOR THE USE OF PRODUCED WATER

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ABSTRACT

Environmental concerns and increasing costs create a need for a polymer that will allow the use of high salt and high hardness-produced water to make a viscosified frac fluid. Any new polymer would also need to tick the boxes for cost, rheology, HS&E characteristics, and breaking in the reservoir.

Past development efforts have focused on improving organic-based polymers. A new approach was taken, and a shift was made to a silica-based polymer. This paper reviews silica chemistry and how this form of silica allows for high salinity, high hardness water. The paper's focus will be on West Texas field trials where silica gel made with produced water and used as an alternative to 20 lb/Mgal cross-linked guar fluid made with fresh water. Covered topics will include a review of produced water chemistry, making the silica gel on-location, pumping characteristics, cost, and impact on production.

INTRODUCTION

The performance and rheological properties of silica gel are such that it opens the door to several possible frac fluid designs not associated with guar-based technology. The focus of this paper will be on the initial field trials and the use of high salinity-produced water to make the bulk of the hydraulic fracturing fluid volume. The emphasis on using produced water reflects the technical challenges associated with viscosifying high salinity, high hardness water and takes into account the increasing cost and environmental pressures related to using freshwater. Sharma (2019) gives a sense of total water cost in the Permian Basin with the following breakdown:

Water sourcing: \$0.10 to \$1.00/bbl
Transportation pipeline: \$0.45 to \$2.10/bbl
Transportation truck: \$2.00 to \$4.00/bbl
Disposal via Injection: \$0.40 to \$1.50/bbl

These costs tend to be at the upper end of the range for smaller oil companies operating older, vertical wells with a high water cut.

The idea of using produced water for making frac fluid is not new; however, the chemistry of carbohydrate-based viscosifiers restricts easy adoption. Leiming et al. (2016) provide an overview of the tolerance of a wide range of cross-linked fluids formulated using produced water. The paper notes improvements made in chemistry, but there are still challenges and limitations. The use of silica gel represents an underexplored path that would allow the use of high salinity and high hardness-produced water for viscosified frac fluid systems. Experimental work (McDonald et al., 2016) demonstrated that silica gel could viscosify a range of different brines if the silica gel was made in a two-step process. The paper also provides data for the critical testing of retained permeability and conductivity. Results showed the silica gel was nondamaging with little affinity for the rock surface. Experimental data and potential cost savings were sufficiently compelling that silica gel moved to field trials.

This paper will describe the initial field trials and benchmark cost and performance against borate-crosslinked guar fracturing fluids.

SILICA CHEMISTRY

Silica and silicate chemistry covers a complex and diverse family of natural and synthetic materials. Specific amorphous, synthetic silicas have highly desirable rheology and suspension properties and are commonly used as thickeners in adhesives, coatings, and paints. Silicas offering these properties include fumed silica and certain types of silica gels. These forms of silica consisting of nanosized silica particles with silanol groups on the surface. These particles have a huge surface area with a strong affinity for water. The thickening /thixotropic properties of these silicas are due to the surface hydroxyl groups on adjacent silica agglomerates being able to hydrogen bond and form a loose silica network in solution. The silica network is fragile and easily disrupted with shear force that breaks the inter-aggregate hydrogen bonds. This mechanism produces a shear-thinning fluid; at low shear rates, the silica begins to re-associate and provides a high viscosity fluid that is resistant to particle sag.

Over the years, silica has been periodically explored as a viscosifier in different oilfield fluid systems. Fumed silica was investigated by Dodson et al. (2000) as a viscosifier for high-density brine fluids such as calcium and zinc bromide. Fumed silica was the primary viscosifier, with its rheology and fluid loss properties modified with biopolymers. A fumed silica as the primary viscosifier and successful run as a drill-in fluid in the Gulf of Mexico. The brine weight was 13.2 lb/gal with a bottomhole temperature of 185°F. The described fluid rheology is easily maintained, with excellent hole conditions without torque or drag problems. The research and case history proved several learnings that can apply to a hydraulic fracture fluid;

- Fumed silica has an exceptional ability to thicken brines and, by extension, produced water fluid with excellent suspension properties.
- Static aged samples tended to lose viscosity, sag, and allow solids to settle. While detrimental in drilling fluids, the loss of viscosity and the dropping of solids would be highly desirable in a frac fluid.
- Shale stabilization occurs via the high salinity of the brine.
- The system deposited a nominal filter cake and was non-damaging

The use of fumed silica appeared to be technically successful but did not move beyond the trial stage. Fumed silica is a high-cost form of silica and was likely the deciding factor in preventing commercial adoption. Fumed silica is a very light and fluffy powder, and although it was not reported, handling would be an operational challenge.

Silica gel saw limited use as a hydraulic fracture fluid viscosifier. Research by Elphingstone (U.S. patent 4,215,001) demonstrated silica gel that could provide a viscous, thixotropic fluid capable of maintaining viscosity at very high temperatures. A need for this particular set of performance attributes arose in geothermal wells being fracture stimulated in Hokkaido, Japan, in the early 1980s. Literature reports these first applications of silica gel viscosified frac fluids were a technical and economic success (Katagiri et al., 1980, 1983). Despite meeting the performance and cost requirements, silica gel was used only on a handful of other geothermal wells, with the last use of the fluid system likely being in 1992 also in Japan.

Several factors likely played a role in silica gel not making the jump to being a conventional fracture fluid system. One factor was the association with sodium silicate. Readers are likely familiar with using as a commonly used conformance chemical and the corresponding concern with damage to the reservoir. In this application, sodium silicate functions as a source of Si that can be converted on location to a silica gel using an acid. Once reacted, the current technology has no residual sodium silicate. In contrast, fumed silica uses silicon tetrachloride as the source of Si and is produced by combustion in an oxygen-hydrogen flame. (i.e., a much more expensive source of Si and not easily replicated at the well site)

The current pathway to make the silica gel allows using any type of water vs. the original technology used in geothermal wells. This gelation is achieved by making the silica gel in a two-step process vs. the original one-step method. Table 1 and Figure 1 highlight the production of the silica gel.

The two-step process can be summarized as follows;

Step 1: Sodium silicate is converted to a neutral/slightly cationic silica sol

A high ratio, aqueous sodium silicate (table 2) is metered into a diluted solution of hydrochloric acid under constant agitation. The sodium silicate reacts with the acid to form a distinct silica sphere (e.g., silica sol). At approximately ~pH=2, the silica sol reaches the isoelectric point, and there is no charge on the silica sol. At the isoelectric point, the silica sol is metastable. It will only exist for a limited amount of time as a clear, low viscosity solution before it starts to form a silica gel.

The stability of the silica sol is controlled primarily by the concentration of SiO_2 in the solution. For example, a 10% SiO_2 sol would have ~5 hours stability at room temperature, while at 7.5% SiO_2, the silica sol would have >24 hours stability.

Step 2: Converting silica sol into a silica gel

The second step is taking the silica sol and converting it to a silica gel by diluting it with water and raising the pH. The presence of salts accelerates gelation kinetics.

CASE HISTORY

Trial #1 -Henderson 11

Henderson 11 well was the selected candidate for the first trial of the silica gel frac fluid. The well, drilled in 1952 and is situated just outside the city of Odessa. The well was at the point that was no longer economical but there, remained one unproduced zone that was part of the pressure-depleted San Andres formation. Offset wells had demonstrated commercial quantities of oil, but given the potential production volume and the age of the well, any stimulation treatment needed to be at a marginal expense. The conventional low-cost stimulation method would have been a 20 lb/Mgal cross-linked guar fluid made with fresh water. For this well, a single-stage frac, a 500 bbl initial hydraulic fracturing treatment, was considered a sufficient volume to stimulate the well.

The location and small volume requirements for Henderson 11 made it an ideal candidate for the first silica gel fluid field trial. The focus of the trial was proof of concept by demonstrating;

- silica gel frac fluid can be on-location using existing frac equipment.
- make the silica gel-based frac fluid using untreated produced water
- Demonstrate suitable rheology to carry and place the proppant.
- Demonstrate the silica gel frac fluid viscosity will flow back (i.e., “breaks”).
- Demonstrate that silica gel is non-damaging to the formation.

Silica Sol

For the first trial, it was felt there were enough moving parts, and the decision was made to make the silica sol off-site and then transport it to the location. Requirements for making the silica precursor were minimal. They could be achieved with a suitable mix tank that allowed for the controlled addition of sodium silicate into diluted HCl solution. This step was provided by a leading manufacturer of oilfield chemicals in the Midland-Odessa area. Formulation work had focused on making the silica precursor to a concentration of 10% SiO_2 weight to volume. However, with only a ~5 hr shelf life, this was deemed too short to prepare off-site, load, transport, unload, and make it into a silica gel frac fluid. Therefore, the SiO_2 concentration was lowered to 7.5% SiO_2 to obtain a shelf life of at least 24 hours.

Silica Gel Frac Fluid

The produced water used in the trial came from a sister well next to Henderson 11. The water was sampled and tested just prior to the field trial. The water analysis (Table 3) was typical for the field with~118 000 mg/l total dissolved solids. The required volume of produced water was transferred to a 500 bbl frac tank a few days prior to the trial. The produced water was adjusted to pH ~ 10 using a small volume of 50% NaOH solution. The addition of caustic ensured sufficient alkalinity to raise the pH of the silica concentrate and induce rapid gelation. The salts present in the produced water would also act to accelerate the gelation rate.

The SiO_2 sol was trucked to the location the morning of the trial. The silica sol concentrate precursor was converted to a silica gel in a continuous process by off-loading the $SiO2$ concentrate into the frac tank using a blender. The blender pump rate was 10-20 bbl/minute and had sufficient mixing and shear to create a homogenous gel. The gelation time to make the viscous silica gel frac fluid was less than a minute. The trial was targeting a final pH of 7.0 + 0.5; however, there was a modest disconnect going from lab to field, and the final pH of the silica gel frac fluid came in at pH 8.15.

Pumping Schedule

Two 2,000 HHp frac pump trucks pumped the silica gel frac fluid. The treatment program called for 35,000 lb of 40-70 mesh sand. Sand loading began at ½ lb per gallon of frac fluid and was gradually increased to 4½ ppg sand at 15 bpm with ~5,200 psi surface pressure down ~4,200 ft of 2⅞ in. tubing. All indications showed that the silica gel readily carried the sand proppant at high concentrations into the created fracture. It was likely possible that much higher proppant loading was possible.

Oil production post frac

After hydraulic fracturing, the well was shut-in for ~24 hours and then allowed to flow back. Silica gel “breaks” via dilution and syneresis of the gel structure. Likely, flowback can commence soon after fracture closure occurs. The flow back of the silica gel was monitored by measuring the background level of silica. The produced water had 12 ppm Si. Flowback water was sampled at 24 hours and found to have 118 ppm of Si, and at 48 hrs, the Si levels were down to 58 ppm. The increased levels of Si provided evidenced that silica is leaving the proppant pack.

Higher than normal reservoir pressure existed in the depleted San Andres zone, and for the first four months, oil/gas produced from ~350 psi of reservoir pressure. Over this timeframe, the flowing production volume averaged at ~20 bpd with ~80 bpd of water. After, four months an insert pump was run into the well. The pump was run to TD before setting, indicating there was no sand flow back. Current fluids production on a pump is ~12 bpd oil and ~87 bpd of water.

TRIAL #2; GOLDSMITH

Based on the first trial, planning began for a more substantial second trial treatment. The candidate well was drilled in 1968 and is located northwest of Goldsmith, Texas. The well, originally produced flowing 97 bpd of oil from the San Andres formation and was now down to 3 bpd of oil. Hydraulic refracture was deemed the best option to improve productivity and remain economically viable. Volume requirements to refracture the second trial well were calculated at 2000 bbl. Typically, this job would be using a 20 lb/Mgal cross-linked guar fluid made with fresh water.

Trial Preparation

Produced water was sampled from the collection tanks. Water analysis (table 4) showed a higher total dissolved solids at 162 000 mg/l total dissolved solids and the presence of a small amount of oil, which was not present in the produced water from the first trial.

The goals of the second trial were similar to the first trial with additional objectives of;

- Produce silica-sol/precursor on-location using existing field frac equipment
- Develop further data on the performance properties of the silica gel.
- Production of the silica gel precursor

The SiO_2 concentration was set at 8% weight to weight to give a 24-hour window to convert the silica sol to a gel. The first step consisted of diluting 22° Beaumé hydrochloric acid into freshwater and, in a separate tank diluting sodium silicate into freshwater. Both the sodium silicate and hydrochloric acid easily dilute and mix into freshwater.

The next step was reacting the sodium silicate with hydrochloric acid to form the silica sol. A 15 bbl/minute centrifugal pump circulated and blended the diluted sodium silicate into HCl and recirculated back into the frac tank holding hydrochloric acid. The silica concentration in the HCl gradually increased, and pH carefully monitored to stay under the isoelectric point. For added security, a slight excess of HCl was calculated to the volume requirements to reach the isoelectric point. This margin helped ensure not overshooting the pH, and the system prematurely gelled.

The silica sol took approximately 90 minutes to produce and, once made, sat overnight. Upon returning the next day, the silica sol remained a clear, water-thin solution with no early signs of gelation. Stability was a good sign that adequate mixing was present in the making of the SiO2 concentrate. The relatively low temperatures (~10^{o}C) also helped with the overall stability of the gel.

Production of Silica Gel

Before adding the silica sol, the pH of the produced water was raised with by25% NaOH. The addition of caustic allows for the quicker conversion of sol to gel, with the final pH of the frac fluid being closer to neutral vs. acidic. The gelation times are sufficiently fast to allow the silica gel to be made in a continuous process. For the trial, the silica gel was produced in 4 separate batches (i.e., 1 per frac tank) in a fashion similar to Trial #1. The blender provided sufficient shear to create a thixotropic fluid (graph 1). A mass balance showed 1.8% wt/vol of SiO_2 in the frac fluid. The final pH of the frac fluid was 7.6.

Pump Schedule

The well had 4½ in. casing requiring the use of 2⅜ in. tubing. Pump rates would, therefore, be a relatively low 10-15 bpm. The silica gel was to be pumped to ~4500 feet and enters through 16 perforations. After pumping approximately 280 bbl of the silica frac fluid, it became evident that the frac fluid was only entering a minimal number of open perforations. Subsequently, pumping stopped, the tubing pulled out of the hole, and the San Andres was re-perforated and acidized with 10° Beaumé hydrochloric acid.

The pumping company had a very narrow window to run the trial, after which their equipment would be tied up for several weeks. This situation necessitated using a different pumping company to complete the trial and resulted in a lag time of nearly three weeks to complete the job. Over three weeks, there was some loss of silica gel viscosity, but it mainly was regained by shearing the fluid through the blender. Note that no biocide was used in making the gel as silica is not a food source for bacteria.

Summarizing the hydraulic fracturing program

- ~90 000 lbs sand pumped
    - ~40000 lb 100 mesh sand
    - ~40000 lb 20-40 sand
    - ~10000 lb 20-40 resin coated sand
- Proppant addition began at ½ lb/gallon and gradually increasing to 3 ½ lb/gallon
- Pump rate was a relatively slow 10 bbl/min
- Even at a low pump rate, the silica gel could carry sand
- Friction appears to significantly depend on pump rate
- Silica gel showed a slighter lower friction value vs. freshwater

Upon completion, there were no signs of screenout, but some sand covered the bottom perforations and required bailout.

Oil production

Oil production started strong at 30 bpd on day one and then went to 20 bpd on day 2 and then quickly went back to the initial production rate of ~3bpd but with slightly less water at ~8bpd. Explanations for the production rate include the refracture occurred in the already depleted zone of the reservoir. Another possibility was the frac fluid might have hit a geologic feature such as an existing fracture system. As the frac fluid did not contain a tracer, it was difficult to account for the lack of impact on initial oil production. This point would have been the end of the story had the operator not returned several months later and re-enter the well and clean out the previously isolated lower section. After cleaning, this unproductive zone began producing oil at a steady rate of ~7-8 bpd of oil and ~15 bpd of water. Without using a radioactive or chemical tracer, it is difficult to say for sure that the refrac hit the lower zone of the San Andres. However, this would explain the unexpected production of oil.

Trial #3 (Pending)

At the time of writing the paper, preparations were being made to run a third trial. The trial would once again be hydraulic refracture of an older well in a partially depleted zone in the San Andres. The operator has several promising candidates where the initial fracture treatments used small volume treatments of 500 bbl with 25 000 pounds of proppant. The refract volume will be 2x the size of the original frac and making the next frac treatment 1000 bbls.

In light of the carrying and transport capacity exhibited in the field and the lab, the next trial will use 16/30 (595 µm - 1190 µm) sand. The use of larger particle sand will provide higher fracture conductivity and help maximize near-wellbore conductivity. The larger proppant size will also help re-open and widen any existing near wellbore fractures that might have blockages. The shallow depth and low closure pressure and further allow the use of a larger size proppant. Doubling the fracture volume and adding perforations will extend the fracture and better target new areas of the reservoir.

Lessons learned from the earlier trials would be applied to making the silica precursor and then gel.

CONCLUSIONS

Compared to drilling a new well or the cost of refracturing a horizontal well, the economics are very favorable for refracturing older, vertical wells in the Permian Basin. Economics is further improved if the frac fluid will allow the use of produced water. Currently, the unoptimized silica gel frac fluid has a higher cost than a 20 lb/Mgal cross-linked guar system if made with only freshwater. Assuming a savings of $3.00/bbl for using untreated produced water than a silica gel-based system has a less overall cost. The recovery of hydrocarbons will also dictate the economics, which will be benchmarked against historical data and offset wells.

Initial field trials have successfully shown that a silica gel made in a two-step process using untreated, high salinity, high hardness water. The field trials have also demonstrated;

- Silica gel can be made using existing equipment
- System is robust
- Proppant can be transported and placed with no screen out
- Friction will restrict use to vertical wells
- Biocides were not required

The two field trials have just scratched the surface on the performance and possibilities of using a silica gel-based fracture fluid. Short term, the focus will be on optimizing, making the gel on location, and the use of larger diameter proppants and energizing with carbon dioxide.

ACKNOWLEDGEMENTS

The authors would like to acknowledge and thank Satanta Oil for being the pioneer in running this new fluid system. Thanks and recognition to Catalyst Oilfield Services for making the silica precursor used in the first trial and Premier Pressure Pumping for their role in making and pumping the material.

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APPENDIX

Table 1: Comparison of earlier silica frac fluid technology vs. current technology

	Silica gel (1980s)	Silica gel (2020s)
Summary of method	Hydrochloric acid is metered into a dilute solution of sodium silicate	Sodium silicate is metered into hydrochloric acid
Starting pH	11.3	~1
Final pH	~7.5 to 8.5	~3 to 8
# of steps	1	2
Allows the use of produced water	No	Yes
Polymerization	Rapid polymerization	Silica gel formed in controlled stages
Molecular structure	Much larger silica particles with aggregated silica having less surface area	Small silica particles, aggregated silica has greater surface area = better suspension

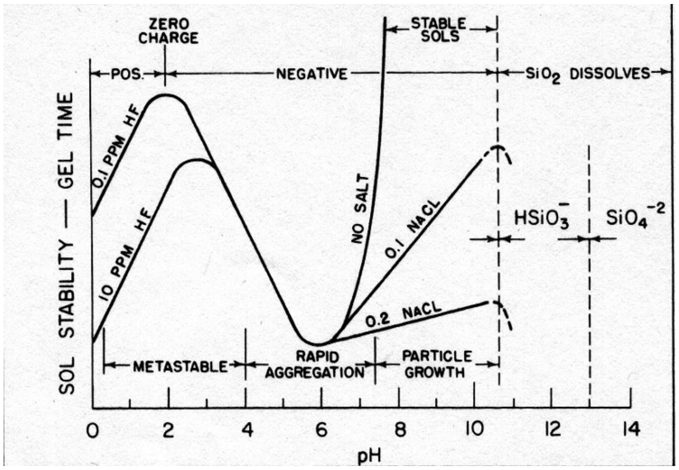

Figure 1: Effects of pH in the colloidal silica-water system (Iler, 1979). The current technology starts at the left of the graph vs. the right

Table 2: Grade of Sodium Silicate

Grade	Wt.% SiO_2	Wt % Na_2O	Ratio SiO_2:Na_2O	Solids	Density	pH
N®	28.3	8.9	3.22	37.2 %	1.38	11.2

Table 3: Produced Water Analysis for Henderson 11

Sodium	40110
Magnesium	1043
Calcium	3679
Potassium	450
Strontium	94
Barium	3.5
Manganese	1
Iron	0

Table 4: Goldsmith Produced Water Analysis

Sodium	59300
Magnesium	2780
Calcium	10500
Potassium	1530
Strontium	223
Barium	.15
Manganese	.5
Iron	0.9