SPI Conformance Gel Applications in Geothermal Zonal Isolation

Research Performance Progress Report (RPPR)
Phase II Final Report: 12/30/2015

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DOE Project Team:
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DOE Contracting Officer – Laura Merrick
DOE Project Monitor – Melisa Jacobi

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1.0 Project Status Summary

DOE's Energy Efficiency and Renewable Energy (EERE) objectives are to advance technologies to make it more cost effective to develop, produce, and monitor geothermal reservoirs and produce geothermal energy. More specifically this includes the Geothermal Technologies Program (GTP) goals for geothermal zonal isolation which include:

- Operating with differential pressures of 400 bar (6000 psi) in wellbore diameters of 6 5/8" to 10 5/8", retrievable hardware operation period of greater than 14 days, and

- Temporary sealing fracture openings from 2" to less than 1/16" wide, under up to 35 bar (500 psi) pressure differentials and up to 300^{0}C, for an operation period of up to 60 days.

This translates into this project's goal to determine up to three SPI gel products for High Temperature High Pressure (HTHP) operations that form hard, solid gels with some level of elasticity, as in other applications, withstanding up to 6,000 psi and tolerant/ stable at 300^{o}C. Such strong gels that are tolerant of high temperatures were demonstrated in this project to date.

Zonal isolation is critical to well drilling success and cost, as well as ensuring long term optimal reservoir performance. Traditional cementing of lost circulation or thief zones during drilling is often done to stem the drilling mud losses and allow drilling to progress. This is an expensive and generally unsuccessful technique losing the potential of ever producing from this particular zonal fracture system. Alternative mechanical methods are very expensive and the HTHP elastic seals used often fail at these Enhanced Geothermal System (EGS) conditions. Selective placement of strong SPI gels into only the offending fractures has the potential to allow continued drilling to the total depth desired as well as maintain and even improve operational efficiency of the resource and extend its economic life.

The official Phase I project start date was September 30, 2011. This project actually started in early March of 2012 and the Phase I objectives were met on and disclosed in the final report September 29, 2012 as a Go No-Go decision was made to proceed. Phase II was started in April 2013 using the remaining Phase I funding, but the actual Phase II funding contract was not signed until latter.

Phase II activities in second quarter 2013 were aimed at establishing a methodology for obtaining gel times at elevated temperatures and looking for new initiators that have longer, more reasonable delay times at higher temperatures. Other work involved industry standardization of the unconsolidated sand pack with resin coated ceramic proppant and possibly Berea sandstone.

From Phase I, some of the first formulations tested were extremely tolerant to the 177^{o}C temperatures encountered in the initial oven testing. These results were reproduced at 232 ^{o}C and again at 300 ^{o}C. Dynamic testing involving the injection of an queous fluid into the pack at the base produced a Δ P over 1,000 psi with the top of the sand pack open at a temperature of 92 ^{o}C. This was verified at 149 ^{o}C with various Δ P's at different pump rates. The SPI gel system may

need to become more of an inorganic gel system for tolerance in the 300^{o}C temperature range. We hope to verify and build on these results in Phase II.

1.1 Project Team And Acknowledgements

The following groups are responsible for the successes to date making progress into the Phase II. The Clean Tech Innovations LLC team in Bartlesville, Oklahoma was involved in the bench oven testing and the set up and running the dynamic testing system in sand pack samples. Ken Oglesby at Impact Technologies in Tulsa, OK is Clean Tech Innovation's customer. Clean Tech provides the R & D to the effort and Impact provides the field testing and commercialization efforts to the technology for a given application. Clean Tech and Impact have worked together using this relationship for SPI gel applications in casing leak repair, water and CO_2 flooding conformance applications, in the past. Impact is now the owner of the SPI gel patents through SPI Technologies, LLC. Ken is a technical expert in drilling and Enhanced Oil Recovery (EOR) in Oil and Gas operations as well as Geothermal Energy applications. Betty Felber, PhD, in Tulsa, Oklahoma is our consultant in the various projects, particularly the dynamic laboratory testing.

Lastly, we would like to thank the Department of Energy (DOE), particularly:

- William Vandermeer, Project Officer,
- Laura Merrick, DOE Contracting Officer, and
- Melisa Jacobi, DOE Project Monitor and others who may be involved at EERE-PMC,
- DOE Office of Science and NETL for the support of water and CO_2 flooding applications under Phase I and II SBIR efforts, and an additional Phase I and hopefully Phase II project in CO_2 sequestration effort in progress,
- The Stripper Well Consortium (partially funded by the DOE) and the Oklahoma Center for the Advancement of Science and Technology (OCAST) for its support in the early development of the SPI gels for casing leak repairs in the discover and field test stages leading toward commercialization.
- The Carbo Prop sand pack proppant product was received gratis from Daryl E. Johnson, Director Resin Coated Proppants at CARBO Ceramics Inc. in Houston, TX.

The SPI Gels have applications in casing leak repair, basement water deterrence, water flooding, CO_2 flooding, and we believe they can be modified to serve the geothermal industry for zonal isolation during drilling and conformance control when needed.

2.0 "Proof of Concept" Go-No-Go Decision

2.1 Task 4 – Management, Planning and Start-Up

Although there is officially not a Phase I and Phase II to this project, it is perhaps easy to make reference to the period before the Go-No-Go decision as the "Phase I" R&D period as it was the time when a milestone "Proof of Concept" discovery was made. The "Phase II" period would be the "innovative period" whereby R&D discoveries are made that further support and justify the "Proof of Concept" discovery preparing the technology for field testing and commercialization.

Phase I in this project had three tasks:

- **Task 1 – Management, Planning and Start-Up**
- **Task 2. Bench Scale "Proof of Concept"**
- **Task 3 - Dynamic Testing Design and Start Up**

These tasks were repeated in Phase II, Year 1 as:

- **Task 4 Management Planning, and Reporting**
- **Task 5. Bench Scale "Proof of Concept" Advancement & Compatibilities**
- **Task 6. Dynamic Testing of Potential Candidates**

and repeated again in Phase II, Year II:

- **Task 7 Management Planning, and Reporting**
- **Task 8. Bench Scale Advancement & Compatibilities**
- **Task 9. Dynamic Testing of Potential Candidates**

Mr. Burns and Mr. Oglesby attended the May 7 – May 10, 2012 Geothermal Technologies Program Peer Review Meeting in Westminster, CO where Mr. Burns presented the R&D plan at the meeting prior to the start of Phase I. Mr. Burns and Mr. Oglesby attended the April 22 – 25, 2013 Geothermal Technologies Peer Review Meeting in Denver, CO where Mr. Burns made a poster presentation on the Phase I success and "Proof of Concept" discovery for using SPI gels in geothermal zonal isolation. The team was awaiting the "Go Decision" for conducting the innovative Phase II R&D program. The Go Decision was received from EERE a few months later. We believed the SPI gel had potential to solve the geothermal zonal isolation problems since it could create a significant Δ P across flow rate zones in a sand pack at moderate temperatures. What we need to do was to slow down the gelling rate at the higher temperatures.

2.2 Task 5. Bench Scale "Proof of Concept" Advancement & Compatibilities

The bench scale experiments performed during Phase I were for the purpose of learning more about the variables inside the pressure chamber at elevated temperature that might be relevant to downhole conditions. As it turned out, the team had significant progress in Phase I with the bench testing at elevated temperatures. These SPI gel formulations selected for use in other applications were tested at higher temperatures. One formulation showed excellent stability at 177^{o}C and 305 ^{o}C, even though some discoloration was observed (Figures 1 and 2). Thus, it would follow that this formulation might have the desired stability at the higher geothermal temperature domain. This was a significant step in demonstrating the SPI technology had "Proof of Concept" capacity

Figure 1. 177^{o}C SPI Gel.

Figure 2. 305^{o}C SPI Gel.

for HTHP geothermal gels for zonal isolation.

The pre-gels solutions were prepared pressured to 100 psi with Ar (Ar) at room temperature (RT). They were heated to the desired temperature over a 4-5 hour period and held at that temperature for 1.0 hour. One of these hard gels had excellent stability and no syneresis or shrinkage. That particular gel formulation shown in Figure 1 contained a humectant additive to reduce syneresis potential. This particular gel formulation showed no syneresis in any of the three different temperature tests performed. A second gel formulation in this 177 ^{o}C test (not pictured) performed very similar to the gel sample in Figure 1. A third gel, also not shown, performed well in some of the 177 ^{o}C tests, but not all. The 177^{o}C test was repeated at 221^{o}C and the gel formulation in Figure 1 was unchanged in strength and appearance. A new sample of the gel composition in Figure 1 was heated to 305 ^{o}C as shown in Figure 2. The Ar pressure eventually stabilized at 1,230.1 psi at 305^{o}C. Gel integrity was not affected at the 305^{o}C with the first gel sample although there was some discoloration. This gel maintained its unique features as identified in previous work and allowed for a qualitative comparison of gels. These oven bench tests demonstrate that we can produce a gel that meets the standards desired for short time periods. They do not address gel time issues.

2.3 Task 9. Dynamic Testing and Candidate Verification

This select gel shown in Figures 1 and 2 was tested dynamically in a sand-pack core to determine if the gel could maintain a pressure differential in a standard sand-pack. To begin this evaluation, 100 mesh sand was washed and loaded in a 1.5” diameter by 11.5” length core. (Test method used for polymer mobility control lab tests for EOR flooding.) A temperature of 300^{o}F and a high enough pressure was maintained to minimize water vaporization. An overburden pressure differential of 500 psi was maintained throughout the testing sequence. Figure 3 shows the results of tap water from 0.4 to 40 ft/day across the pre-washed sand pack containing no SPI gel. The pressure increased slightly over the sand pack, but it never reached 1 psi.

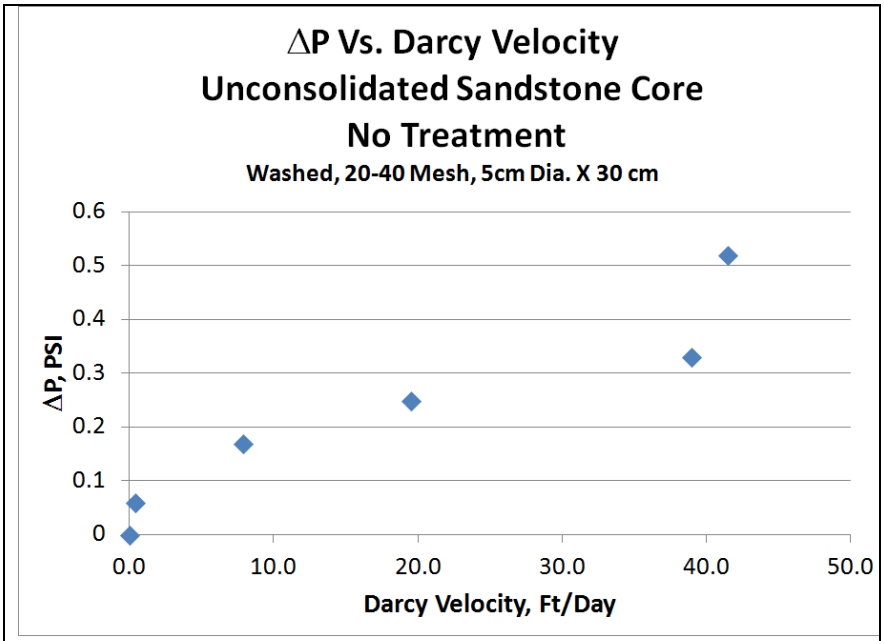

Figure 3. ΔP versus Velocity through the Sand Pack, No Gel.

Figure 4 shows the differential pressure across the sand-pack with a dilute gel initiated and injected into the core. The flow of injected water was increased incrementally from 0.4 to 20

ft/day. This "dilute" SPI gel system was tested in a standard sand-pack to determine if we could establish comparable performance of typical sand-pack tests with dilute SPI gels. These results provided a typical differential pressure, and thus permeability, and were a 100% improvement over previous tests with SPI gels in the same sand pack system. Conditions in the sand-pack were 149 ^{o}C and 820-1060 psig.

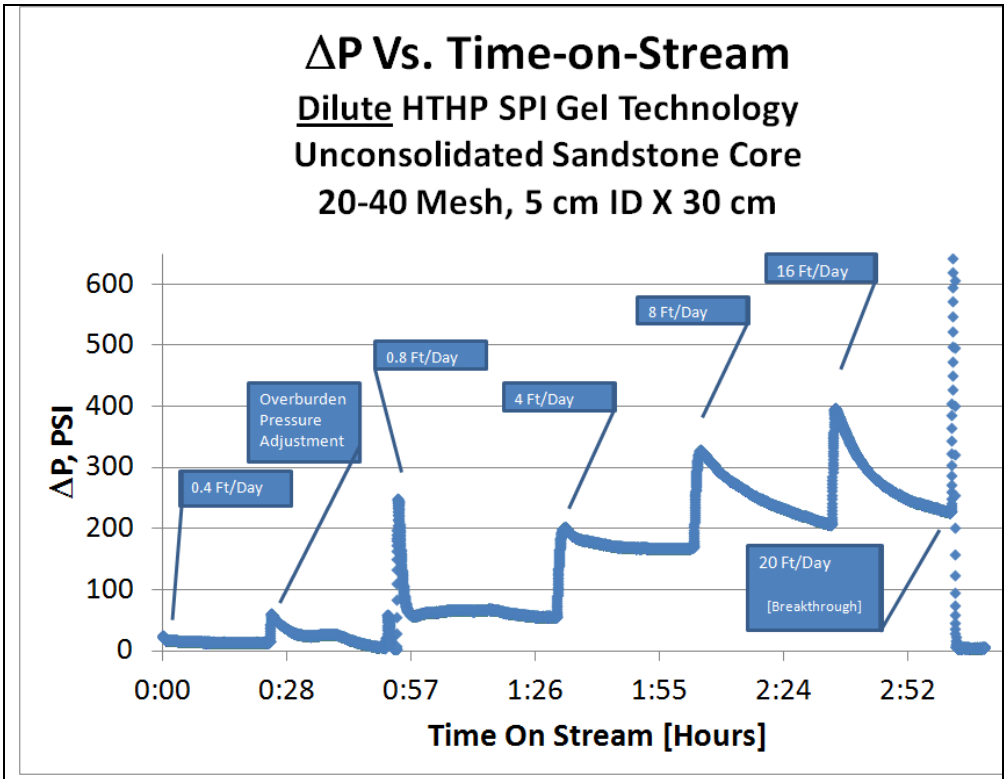

Figure 4. ΔP vs Velocity Across Sandpack with Dilute SPI Gel. (Increasing Space Velocity, 100 mesh Washed Sand)

Next, in Figure 5, the candidate SPI gel, optimized on the bench oven tests in Phase I (classified as the "strong" gel) was initiated *in situ* and injected into a 100 mesh sand-pack. A flow of 0.4 ft/day was charged across this pack. As Figure 5 indicates, the pressure continued to rise until it reached 1,000 psi. At that time the test was stopped because system pressure reached a maximum design pressure of the testing apparatus. Conditions in the sand-pack were 82 to 92^{o}C and 540-590 psig.

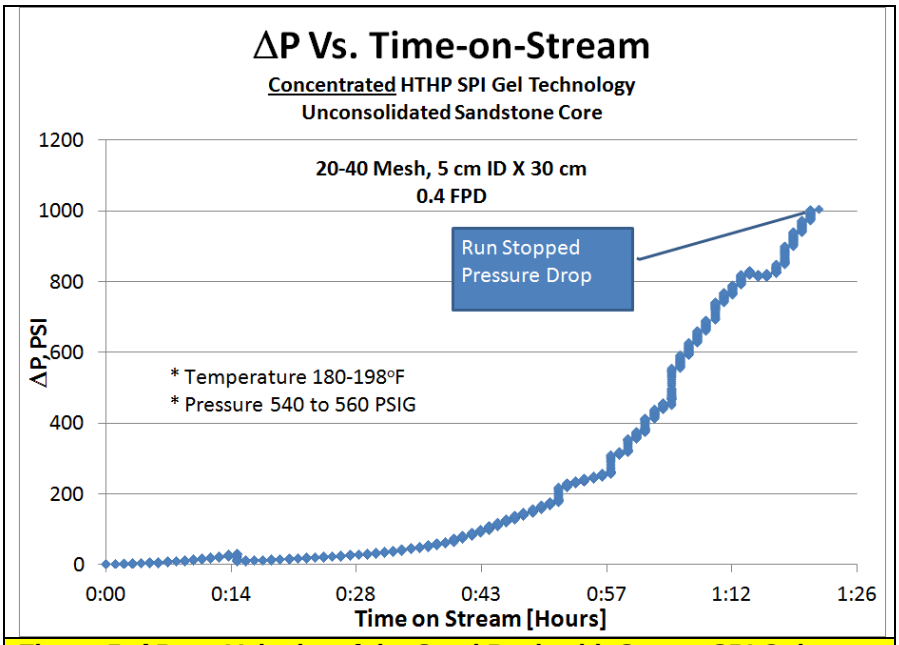

Figure 5. ΔP vs. Velocity of the Sand Pack with Strong SPI Gel at 0.4 Ft/Day Space Velocity.

The Residual Permeability Reduction Factor, F_{rr} was calculated since resistance

is related to mobility and viscosity determination of strong gels is difficult. Viscosity is not included in F_{rr}. Table 1 compares the F_{rr} of both the dilute gel and the strong gel, indicating a marked improvement in resistance using the strong gel at 0.4 ft/day.

The procedure for this experiment was to pump 2 pore volumes of water through the sand pack to reach equilibrium. Start the timer with an empty beaker on the balance and record pressures at each pressure tap. At 5 g of water, record weight, time and each pressure tap. Repeat measurements at 10 g of water and repeat again at 15 g of water. Repeat the permeability measurements as many times as necessary to get good agreement.

These were the successful laboratory bench results at 177 ^{o}C and 305 ^{o}C oven tests and the dynamic testing results at 94 and 149 ^{o}C. Ken Oglesby, project drilling consultant, reported that these results go a long way toward meeting the Geothermal Technologies Program (GTP) goal for geothermal zonal isolation of creating gels at up to 300^{0}C that can withstand up to 35 bar (500 psi) pressure differentials across fracture openings from 2" to less than 1/16" wide. Methods to create and destroy such gels have been identified by Clean Tech that will be demonstrated in Phase II. With further work in this project, methods to actually implement these gel systems in deep EGS and geothermal wells can be devised.

Table 1. Sand Pack Properties.

Parameter	Sandpack		
	Without Treatment	Dilute SPI Gel Treatment	Strong SPI Gel Treatment*
A, ft^2	1.23 E-02	1.23 E-02	1.23 E-02
ΔX, 1 ft	1	1	1
Q [cc/min]	0.09	0.09	0.09
Q [Bbl/Day]	8E-04	8E-04	8E-04
Δ P [psi]	0.06	43.6	1000
μ = visc of water [Cp]	1	1	1
K [md]	2212	1.35	.06
F_{krr}		1636	37527
K = (QμL)/((P1 – P2)A)			
K = permeability (darcies)			
F_{rr} = (perm to water before polymer)/(perm to water after polymer)			
*Final P recorded at 1,000 psi, but stopped because system reached device pressure limit.			
** Sheng, JJ., Modern Chemical EOR, Theory & Practice, 2011, Gulf Publishing, p 169.			

3.0 Phase II R & D

3.1 Task 4 – Management and Planning

Task 4 is the required management effort to evaluate the progress and manage the project during the 4 quarters of the first year of Phase II following DOE guidelines. Mr. Burns (PI), with the aid of his Impact staff, will be responsible for maintaining the project plan and budget and all reporting. Mr. Oglesby, Mr. Burns and Dr. Felber will meet in person, by email and phone to review the progress. The PI will take the lead in this effort. All lab work will be conducted at Clean Tech Innovations. Mr. Redcorn who had previously been a part of the dynamic testing accepted a full time position with the Osage Tribe. He was replaced by Dr. Felber in the area of dynamic testing.

3.1.1 Field Testing/Commercialization/Market Research Plan

As a consideration to DOE, we have agreed to create a market research or commercialization plan for use by the customer, Ken Oglesby of Impact Technologies. This plan will be not only for geothermal, but also include oil and gas applications. We are fortunate that Mr. Oglesby already has one market research report to use as a starting point for the gels in oil and applications. We also have Mr. Oglesby's and Dr. Felber's expertise in both areas as well as their broad network of people they are acquainted with in both industries. An initial effort has taken place on the market research commercialization plan. That information is found in Appendix I.

3.2.0 Task 5 - Bench Scale Proof of Concept Advancement & Compatibilities

Bench level screening efforts will continue during the next four quarters to identify SPI gel components that can be used to modify SPI gels and/or identify other components that will improve the current SPI technology to maintain gel integrity at HTHP for a period of time. These will include new initiators, polymer components or different co-additives. This will include additional testing at HT on the exiting gels that look extremely promising from this quarter's results. There are several aspects of work planned on the SPI gels during the next eight quarters as proposed below in the following discussions.

3.2.1.0 Initiator Improvement

First, it is necessary to present an introduction to the earlier work of the 1950's with silicate gels to differentiate the work we are doing from earlier work.

3.2.1.1 Historical Development of Silicate Gels (Precipitates) in EOR

Silicates are often described as silicic acid polymers in solution. The fundamental building block of silicate polymer is the SiO_4^{-4} silicic acid monomer – with the silicon atom at the center of an oxygen-cornered, four-sided tetrahedra. In sodium silicate, each oxygen atom is typically associated with a sodium or hydrogen atom, or it may be linked to another silicate tetrahedron. The silicate tetrahedra can link to form chains (Figure 6), cyclic and larger polymeric structures up to 100,000 in molecular weight.

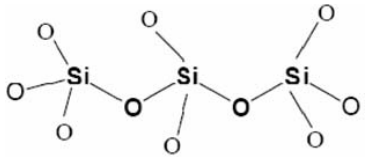

Figure 6. Silicate Trimer, SiO_4^{-2}

Until the discovery of the SPI gel, the original silicate gels were precipitous gels. Vail 1952, Patterson 1994, and Gronewald 2005[1–3] proved that the SiO_2:Na_2O ratio, concentration, and temperature play a major role in the different polymeric structures in silicate solutions. When the SiO_2:Na_2O ratio is below 0.05, the SiO_4^{-4} monomers dominate the distribution. Three-dimensional anions are most abundant at ratios of 2.5 and higher. When SiO_2:Na_2O ratio is about 3.2 at increased temperature, the larger cyclic anions are relatively stable and more abundant. Precipitation gels that result from the reaction of silicates with polyvalent metal ions are less soluble across a broader pH range than the metal hydroxide precipitates produced by other non-silicate processes. The ability to control the physicochemical properties of silicates by weight ratio of SiO_2 to Na_2O and other environmental and economical advantages of silicates make them

good alternatives to the various organic polymer technologies available for conformance control in the oil industry.

Injection of silicate solutions into reservoirs with the intention of EOR through a diverting effect was first proposed in a patent by Mills[4] in 1922. An extensive review of patents and numerous papers concerning silicate applications in EOR by Krumrine, and Boyce in 1985[5] and also by Falkowicz[6] provided conviction to the argument that permeability modification with silicate gel based systems is a viable alternative wherever the need arises. Krumrine and Boyce presented great variety of inorganic and organic compounds, and natural materials which cause gelation of water soluble silicates, and that the technology is adaptable to diverse reservoir conditions. They noted also that the silicates were inequitably neglected in practice in favor of crosslinked polymers, the leading technology at the time based on the toxic chromium VI ion in the form of chromates and dichromates.

Sodium silicate solution polymerization upon acidification with either sulfuric acid, hydrochloric acid, or the weaker acids, ammonium sulfate, ammonium bicarbonate were originally used with rapid silicate precipitation or "gelation." Alternating stages were used to delay the silicate precipitation. Later, it was found that for a given pH value, the polymerization rate decreases with higher SiO_2 concentration, ionic strength and accelerator concentration (Merril, Spencer 1950).[7] Moreover, it was observed that an increase in temperature promotes more rapid gelation and pH value corresponding to the minimum gel time increased from 5.5 hours for salt-free solutions to 7 hours and above with increasing brine concentration. Seventeen years later, a mixture of alkaline silicate and acid phosphate solution was proposed (Beecroft, Maier 1969).[8] Beecroft discovered that the addition of phosphates tend to reduce the influence of formation water salinity on the gelling time.

Bernard (1970) and Sarem (1974)[9, 10] used a common method for extending the gel time by sequentional injection of the fluid components. During the experiments alternate slugs of sodium silicate and calcium chloride solutions were injected to improve recovery factors in heterogeneous reservoirs. Solutions of the silicate (from about 0.5 up to 5.0 weight percent) and calcium chloride (about 2% by weight) were mixed and reacted to provide precipitates at some distance into the reservoir. Such treatments were designed to affect permeability throughout the bulk reservoir, but not completely shut off any zone.

For the most part, the early silicate gel initiators were alternating slugs of silicate and cheap acids. Later, an effort was under taken to use certain easily hydrolyzable esters that could in the process generate and acid proton. But at higher temperatures, there was still a need for better initiation systems for silicate gels.

The internally initiated gels used for lower temperature applications were not necessarily useful at higher temperature applications. Ideally, we would like a new type of internal initiator that is less sensitive to higher temperatures and hence more controllable for HTHP conditions. The lower temperature test protocol was to some extent qualitative. When checking on the gel performance, a qualitative description was assigned and then its hardness was quantitatively analyzed at room temperature or it was analyzed at a higher temperature in the range of 82^{o}C.

We have analyzed a multitude of different initiators over the last two quarters and are continuing with this part of the project which we think may produce some interesting concepts to be reported on later when finished. In the first quarter of 2014, we focused on the use of low cost acid mixtures largely because of the desirable economics for these acids. It appears that one initiator product of interest is a low pH acid mixture where we have lowered the hydrogen ion concentration. This aqueous product consists of two strong acids combined with two relatively weak acids such that the conjugate bases of the weaker acids serve as strong bases for controlling the hydrogen ion availability or production from the strong acids. By doing so, it appears the strongest acid characteristics are changed in a favorable way. When an initiator product such as this is used in the SPI gel, gelation is retarded by 12 to over 24 hours at 140F.

3.2.1.2 Innovation of a Significant Technical Discovery for SPI Gel Initiation

The plan is to innovate a significant new discovery made for initiating the SPI time delayed gel by establishing relationships between gel formation temperature, gel stability and the initiator components and their respective concentrations, Si/I ratio, pH and gel time. In order to establish these relationships, it is necessary to explore all the data over a complete temperature range including lower temperatures as well as the higher temperatures of interest in this project. The lower temperature data could be of value in certain other SPI gel applications. The high temperature data is of course of interest in this zonal isolation project, but it must be understood that to get the high temperature application developed, it may be easier if the lower temperature domain is first fully understood mechanistically. Mechanistic understanding provides the know-how to build successful chemical strategies with these gels. To fully innovate this discovery, it may be helpful to review some fundamental facts regarding acid - base chemistry.

3.2.1.3 Acid - Base Chemistry

Acid Dissociation Constant

According to Arrhenius's original definition, an acid is a substance that dissociates in aqueous solution, releasing the hydrogen ion H^+ as shown in Equation 1.[11]

$$HA \rightleftharpoons A^- + H^+ \quad \text{or} \quad HA \rightleftharpoons A^- + H_3O^+ \qquad \text{Equation 1}$$

An acid dissociation constant, K_a, quantitatively provides the strength of an acid in solution. It is the equilibrium constant for a dissociation reaction in the context of acid-base reactions. The larger the K_a value, the more dissociation of the molecules in solution and thus the stronger the acid. The equilibrium of acid dissociation is shown where HA is a generic acid that dissociates by splitting into the conjugate base (A^-) of the acid, and the hydrogen ion as shown in Equation 1. In aqueous solutions, H^+ exists as a hydronium ion, a solvated proton or an oxonium ion, H_3O^+. If HA represents acetic acid, then A^- represents the acetate ion or the conjugate base. The chemical species HA, A^- and H^+ are said to be in equilibrium when their concentrations do not change with time. The dissociation constant, K_a, is usually written as a quotient of the equilibrium concentrations (mol/L), denoted by [HA], [A^-] and [H^+] as shown in Equation 2.

$$K_a = [A^-][H^+]/[HA] \qquad \text{Equation 2}$$

Due to the many orders of magnitude spanned by K_a values, a logarithmic measure of the acid dissociation constant is more commonly used in practice. The logarithmic constant, pK_a, which is equal to $-\log_{10} K_a$, is an acid dissociation constant (Equation 3).

$$pK_a = -\log_{10} K_a \qquad \text{Equation 3}$$

The Henderson Hasselbalch[12-14] equation combines Equations 2 and 3 to derive the term, pH, for acids as shown in Equation 4.

$$\mathbf{pH = pK_a + \log ([A^-]/[HA])} \qquad \text{Equation 4}$$

The larger the pK_a value, the smaller the extent of dissociation at any given pH. A weak acid has a pK_a value in the approximate range −2 to 12 in water. Acids with a pK_a value of less than about −2 are considered strong acids. A strong acid is completely dissociated in aqueous solution. The concentration of the undissociated acid is undetectable.

The acid dissociation constant is a direct consequence of the underlying thermodynamics of the dissociation reaction. The pK_a is directly proportional to the Gibbs Free Energy change for the reaction. The pK_a value changes with temperature and can be understood qualitatively based on Le Chatelier's principle. If any change is imposed on a system in equilibrium, then the system adjusts to a new equilibrium counteracting the change. Thus, if a reaction is endothermic, the pK_a decreases with increasing temperature and for exothermic reactions, the opposite is true. The underlying structural factors that influence the magnitude of the acid dissociation constants also include Pauling's rules for acidity constants, inductive effects, mesomeric effects, and hydrogen bonding.

The quantitative behavior of acids and bases in solution is understood only if their pK_a values are known. In particular, the pH of a solution can be predicted when the analytical concentration and pK_a values of all acids and bases are known. Conversely, it is possible to calculate the equilibrium concentration of an acid and base in solution when the pH is known. A knowledge of pK_a values is necessary for the preparation of buffer solutions and is also a prerequisite for a quantitative understanding of the interaction between acids or bases and metal ions to form complexes. Experimentally, pK_a values can be determined by potentiometric (pH) titration, but for pK_a values less than 2 or more than about 11, spectrophotometric or nmr measurements may be required due to difficulties in measuring pH.

In the Brønsted-Lowry acid system,[15-17] an acid reacts by donating a proton to a base. In doing so, the acid becomes its conjugate base. The formula of the conjugate base is the formula of the acid less one hydrogen. The reacting base becomes its conjugate acid. The formula of the conjugate acid is the formula of the base plus one hydrogen ion. When hydrochloric acid is neutralized with sodium hydroxide as in Equation 5, the hydrochloric acid first hydrolyzes and then the proton reacts with hydroxide ion to form additional water, chloride ion and the sodium ion. In the equation for the reaction each acid-base pair has the same subscript. $Acid_1$ is HCl, its conjugate base is $base_1$; hydroxide ion is $base_2$, and its conjugate acid (water) is $acid_2$.

$$\underset{acid_1}{HCl} \rightarrow H_3O^+ + Cl^- + Na^+ + \underset{base_2}{OH^-} \rightarrow \underset{acid_2}{2H_2O} + Na^+ + \underset{base_1}{Cl^-} \qquad \text{Equation 5}$$

Chloride ion is the conjugate base of hydrochloric acid. Water is the conjugate acid of the hydroxide ion. In this equation the sodium ion is a spectator ion.

Monoprotic acids

From Equation 4, one has a form of the Henderson- Hasselbalch Equation, from which the following conclusions can be drawn as shown using Figure 7.

1. At half-neutralization $[A^-]/[HA] = 1$; since log(1) =0, the pH at half-neutralization is numerically equal to pK_a. Conversely, when $pH = pK_a$, the HA concentration is equal to A^- concentration.
2. The buffer region extends over the approximate range $pK_a \pm 2$, though buffering is weak outside the range $pK_a \pm 1$. At $pK_a \pm 1$, $[A^-]/[HA] = 10$ or 1/10.
3. If the pH is known, the ratio may be calculated. This ratio is independent of the analytical concentration of the acid.
4. At half-neutralization $[A^-]/[HA] = 1$; since log(1) =0, the pH at half-neutralization is numerically equal to pK_a. Conversely, when $pH = pK_a$, the HA concentration is equal to A^- concentration.
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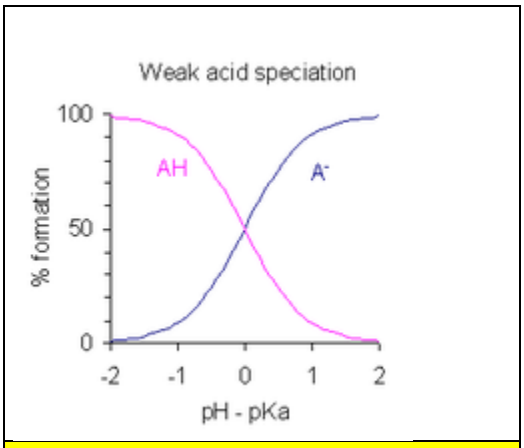


Figure 7. Variation of the Percent Formation of a Monoprotic Acid (AH) and its Conjugate Base (A^-) with the Difference Between pH and the Acid pK_a.

In water, measurable pK_a values range from about −2 for a strong acid to about 12 for a very weak acid (or strong base). All acids with a pK_a value of less than −2 are more than 99% dissociated at pH 0 (1 M acid). This is known as solvent leveling since all such acids are brought to the same level of being strong acids, regardless of their pK_a values. Likewise, all bases with a pK_a value larger than the upper limit are more than 99% protonated at all attainable pH values and are classified as strong bases.[14] An example of a strong acid is hydrochloric acid, HCl, which has a pK_a value, estimated from thermodynamic quantities, of -9.3 in water.[12] Hydrochloric acid is said to be "fully dissociated" in aqueous solution because the amount of undissociated acid is indiscernible.

A buffer solution of a desired pH can be prepared as a mixture of a weak acid and its conjugate base. In practice the mixture can be created by dissolving the acid in water, and adding the requisite amount of strong acid or base. The pK_a of the acid must be less than two units different from the target pH.

Polyprotic acids

Polyprotic acids are acids that can lose more than one proton. The constant for dissociation of the first proton may be

Table 2. The pK_a Values for Phosphoric Acid.

Equilibrium	pK_a value
$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	$pK_{a1} = 2.15$
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	$pK_{a2} = 7.20$
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	$pK_{a3} = 12.37$

denoted as K_{a1} and the constants for dissociation of successive protons as K_{a2}, K_{a3} etc. Phosphoric acid, H_3PO_4, is an example of a polyprotic acid as it can lose three protons. In general, it is true that successive p*K* values increase (Pauling's first rule)[19] such as with phosphoric acid. For example, for a triprotic acid, H_3A, the three equilibria are shown in Table 2.

When the difference between successive pK_a values (Table 2) is about four or more, as with phosphoric acid, each species may be considered as an acid in its own right.[20] It can be seen that the second proton is removed from a negatively charged species. Since the proton carries a positive charge and is removed from a negative ion, extra work is needed to remove it as the trend noted in Table 2. In fact, salts of $H_2PO_4^-$ may be crystallized from solution by adjustment of pH to about 5.5 and salts of HPO_4^{2-} may be crystallized from solution by adjustment of pH to about 10. The species distribution diagram in Figure 8 shows that the concentrations of the two ions, $H_2PO_4^-$ and HPO_4^{2-}, are maximum at pH 5.5 and 10. The pK_a's are found in Figure 8 at the intersecting 50% of formation levels.

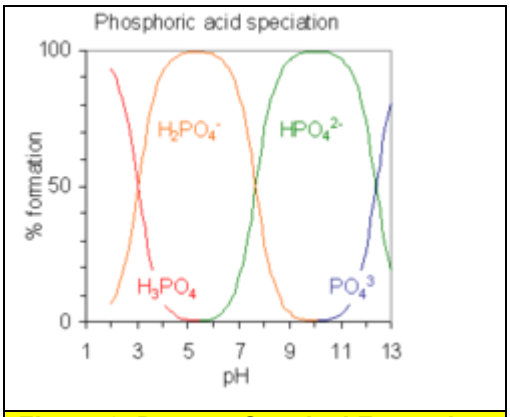


Figure 8. Percent Species' Formation as a Function of pH for Phosphoric Acid.

The pk_a values for Vanadic acid are shown in Table 3. Removing the second, third and fourth proton from vanadic acid, H_3VO_4, follow the same rule as phosphoric acid with each proton requiring more energy. But there is an exception to the rule with vanadic acid (Table 3) in removing the first proton. Vanadic acid causes a major structural change to occur when removing the first proton. In the case of VO_2^+(aq), the vanadium is octahedral, 6-coordinate, whereas vanadic acid is tetrahedral, 4-coordinate. This is why $pK_{a1} > pK_{a2} < pK_{a3} < pK_{a4}$ for vanadium (V) oxoacids.

Table 3. The pK_a Values for Vanadic Acid.

Equilibrium	p*K*$_a$ value
$[VO_2(H_2O)_4]^+ \rightleftharpoons H_3VO_4 + H^+ + 2H_2O$	pK_{a1} = 4.2
$H_3VO_4 \rightleftharpoons H_2VO_4^- + H^+$	pK_{a2} = 2.60
$H_2VO_4^- \rightleftharpoons HVO_4^{2-} + H^+$	pK_{a3} = 7.92
$HVO_4^{2-} \rightleftharpoons VO_4^{3-} + H^+$	pK_{a4} = 13.27

When the difference between successive pK values is less than four, there is overlap between the pH range of existence of the species in equilibrium. The smaller the difference, the more the overlap, as shown for the triprotic acid shown in Figure 9. Note, the pK_a's (pK_{a1} = 3.13, pK_{a2} = 4.76, pK_{a3} = 6.40) are found in Figure 9 at the intersecting 50% of formation levels. Solutions of these type of triprotic acids are different than phosphoric acid and they are buffered over the whole pH range from 2.5 to 7.5.

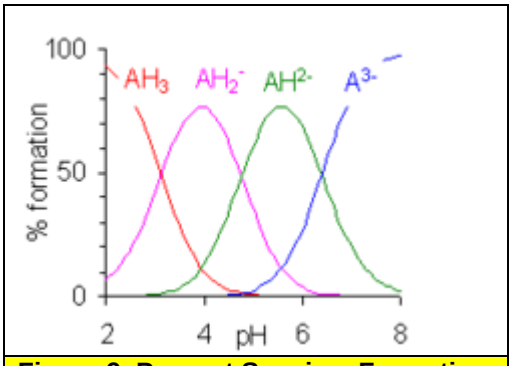


Figure 9. Percent Species: Formation as a Function of pH for a Triprotic Acid.

3.2.1.4 Reduction of Hydronium Ion Concentration in the Acid Mixtures

A product consisting of two strong acids and two weak acids was prepared in the lab. The goal was to produce an acid with reduced hydrogen ion availability. This would create a balancing

system between the conjugate of one of the strong acids and the conjugate of a relatively weaker acid. The remaining pair of acids would be expected to form a balancing system consisting of relatively strong and relatively weak acid conjugates. The exact acid components will remain confidential in this discussion for patent purposes.

Procedure:
Two series of titration experiments are presented, one at RT and the other at 82°C on two different sodium hydroxide compositions using different concentrations of a Reduced Activity Acid (RAA) as shown in Table 4. All solutions totaled 40.00 g. Two control diluted strong acid solutions (SHA) are presented in Table 4 along with the same primary strong acid with other acid counterparts to form a RAA mixture. The type and weight of the HA solutions are presented in Table 4. From that number, the maximum millimoles of total acid protons were calculated if all protons were released for consumption as well as the weight of NaOH and the millimoles of sodium hydroxide. The difference is noted as excess millimoles of OH^- in the last column. A negative number implies an acidic solution since all of the caustic has been neutralized. This calculated estimate assumes 100% dissociation and does not take into effect the pK_a for the various acids.

Table 4. Sodium Hydroxide Titration with a Reduced Activity Acid.

Acid Type	Number 117-46-	Total Soln. Wt., g	HA Soln. Wt., g	Tot Protons Mmole	NaOH Wt., g	HO^- Mmole	Excess OH^- Mmole
SHA, Dil.[1]	140	40.00	4.00	3.04	0.8	20.3	16.98
RAA[2]	141	40.00	4.00	16.01	0.8	20.3	4.01
RAA[2]	142	40.00	6.00	24.02	0.8	20.3	-4.00
RAA[2]	143	40.00	8.00	32.03	0.8	20.3	-12.00
RAA[2]	144	40.00	10.00	40.03	0.8	20.3	-20.01
SHA, Conc[1]	145	40.00	6.00	4.56	0.89	22.25	17.69
RAA[2]	146	40.00	6.00	24.02	0.89	22.25	-1.77
RAA[2]	147	40.00	8.00	32.03	0.89	22.25	-9.78
RAA[2]	148	40.00	10.00	40.03	0.89	22.25	-17.78
RAA[2]	149	40.00	12.00	48.04	0.89	22.25	-25.79

1. Strong Acid, Diluted, Control, d=1.07 g/ml
2. Reduced Activity Acid (RAA)

The data from these titrations are graphically shown in Figures 10-13 at 21°C and in Figures 14-17 at 82°C. Figure 10 shows the data at 0.8 g of NaOH corresponding to a high 9 percent sodium silicate level at 21°C. Figure 11 shows the same data for a 0.89 g of NaOH under the same conditions. Figures 12 and 13 show the addition of added polymer to the solution under those same conditions of NaOH weight. These experiments are repeated in Figures 14-17 at the higher temperature. In some of the plots such as Figure 13, it appears that some of the data plots are missing, but actually there are overlapping curves. In all of the data sets, there is a substantial delay in pH reduction resulting from acid volume added for neutralization using the RAA product vs using the strong acid (117-46-140). The strong acid had a typical strong acid-strong base titration curve, whereas the RAA had a delayed weak acid titration curve. The initial pH at 21°C was around 13.8 whereas the initial pH was reduced to approximately 11.8 at 82°C at 0 ml acid volume. This difference is believed to be due to a pH-temperature effect. The acid volumes are different correlating to a shorter length titration curves for those entries listed as sample numbers 141, 142, 146, and 147. This information is important because the SPI gels form on the

alkaline side of the pH rather than the acidic side. When SPI gels were made with the RAA, there were 12-36 hours gelation delay. What is believed to be very significant in Figures 10-13 is that a pH of 7 correlates to a RAA volume centered at about 4.75-5.25 ml for the 21^{o}C titrations. This graphical location (5 ml) did not change in the 82^{o}C plots. When polymer was added in the gel, the volume intersection increased to between 6.25-7.9 ml range at 21^{o}C. The higher level of NaOH at 7.9 seemed to be out of range. At 82^{o}C the polymer addition was in a tighter range acid volume requirement of 5.75-6.75.

Figure 10. NaOH (0.80g) Neutralized at 70F With Acid Mixture.

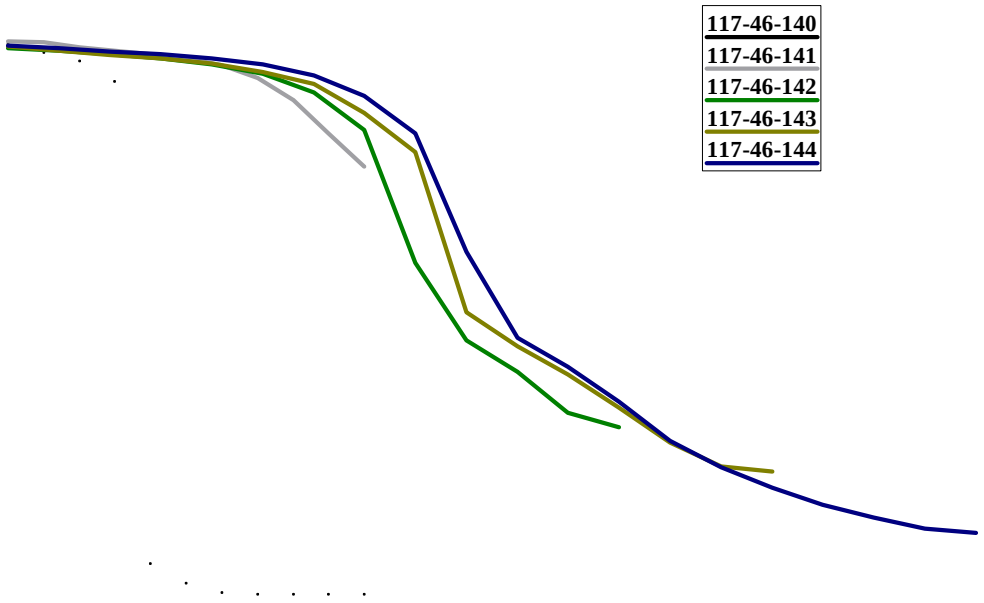


Figure 11. NaOH (0.89 g) Neutralized at 70F With Acid Mixture.

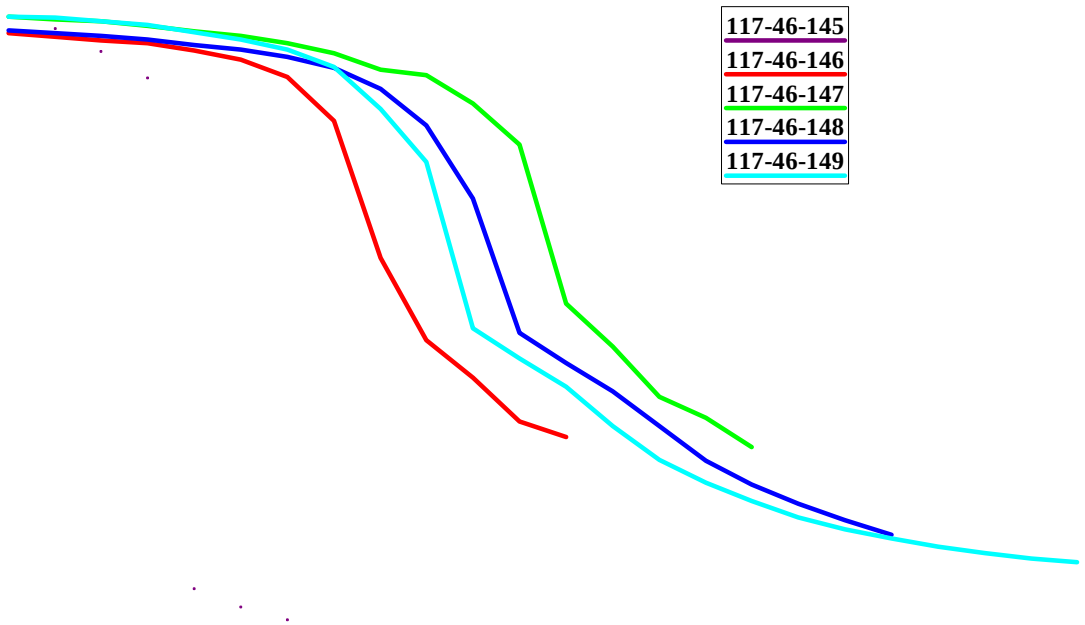


Figure 12. NaOH(0.80 g) - Polymer Neutralized at 70F With Acid Mixture.

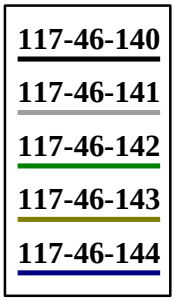


Figure 13. NaOH(0.89 g) - Polymer Neutralized at 70F With Acid Mixture.

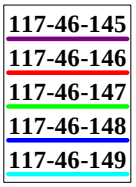


Figure 14. NaOH (0.80 g) - Neutralized at 180F With Acid Mixture.

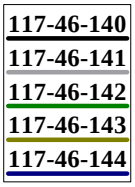


Figure 15. NaOH (0.89 g) - Neutralized at 180F With Acid Mixture.

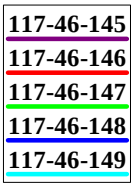


Figure 16. NaOH(0.80 g)/Polymer Neutralized at 180F With Acid Mixture.

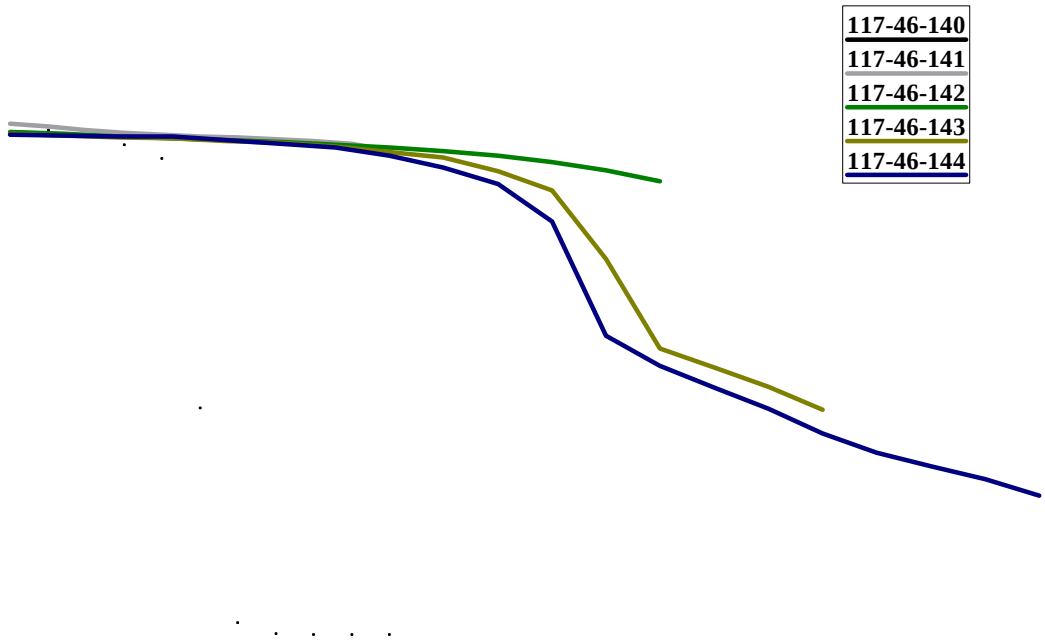
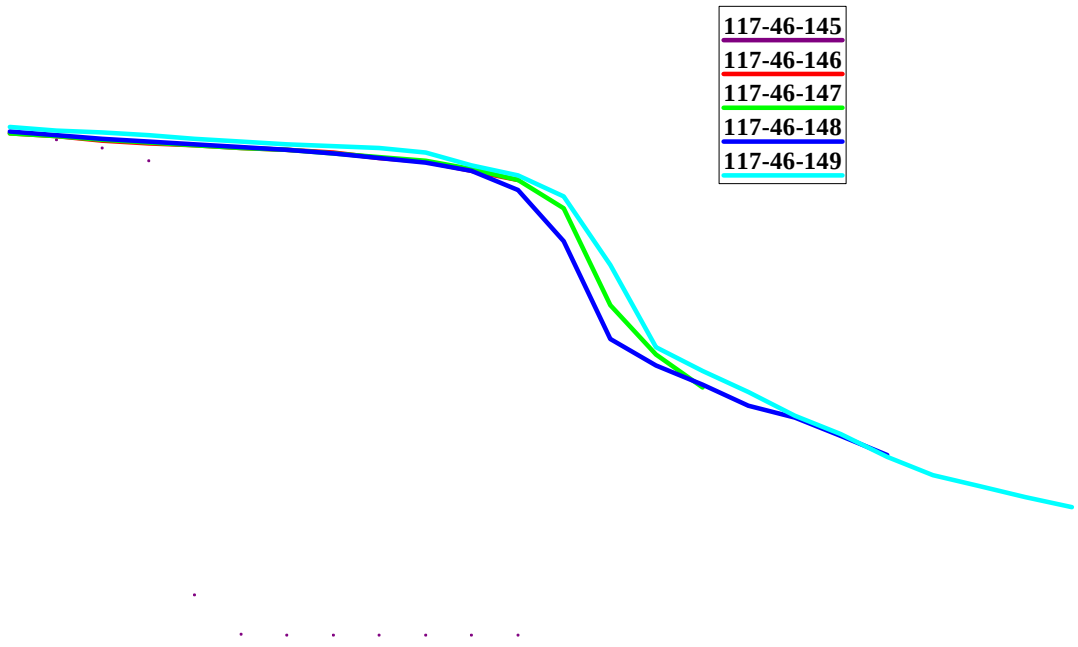


Figure 17. NaOH(0.80 g)/Polymer Neutralized at 180F With Acid Mixture.



3.2.1.5. Preliminary Analysis of RAA Multi-component Initiator System

In order to better understand the chemistry of the multi-component activator system, several acid combinations have been used as the titrant for various concentrations of sodium hydroxide. To analyze these results a Freeware program—CurTiPot[21] Version 4.1.1—was downloaded. The program was first available in 1991 with the most recent version being released in April 2014. There are seven different sections of this program. According to the developers, it has been used

in over 130 countries with countless applications. This program is for analyzing and simulating titration curves when up to seven components are involved. Our system varies from 1 to 6 components so the program is well suited for this application. The individual modules are discussed below.

One of the seven modules is the pH calculation. This module has seven sections. The output from it is the pH calculation and the related equilibrium data. There is also a titration module. The purpose of this sector is to show what might happen if one were to titrate solutions with numerous components. This can be utilized prior to doing actual laboratory work. There are 10 different parts to this module. A simulation module is also included. This six part module shows a virtual simulation of a titration curve. The program calculates the titration curve using either activities or concentrations. The seven part distribution diagram, buffer capacity and protonation curve module is also included. The output includes 12 plots. There are also five different titration curves that one can plot using the results of this module. The data entry for this section is very intensive.

The developer suggests that one start at the evaluation sector of this program. It is very robust which also complicates its use. For example, in the evaluation module alone there are eight sections to be familiar with in order to run it properly. The regression sector is the second module the developer suggests one use. There are 13 sections in this module. With this many options, data entry is tedious and one must be very careful to correctly enter it otherwise the regression will be flawed. Another module is the graphing section. Even though there are only 2 sectors in this module, there are 12 items to select in any order to plot on each graph. The final module is the database. It contains approximately 250 acid, base and indicator systems. Any user can add additional acids or bases after those already in the database. This data is utilized with the pH calculation, simulation and regression modules. One of the outputs from the evaluation module is the dissociation constants for the multi-component system.

The preliminary results were re-evaluated by looking carefully at the fitted pH results and the dpH/dV from the software. For example, the change in the measured pH with volume was subtracted from the previous measured data. This change was then subtracted to determine the change in the slope. The purpose of this work was to evaluate whether the computer program actually took into account the slope changes and if these were realistic. This further evaluation was conducted on the fitted data (generally less than 30) and the interpolated data (300 points) for each titration conducted at 70 and 180F.

Titration Module

Mixtures of acids are used to titrate the strong base in the Figures 10-16 and analyzed by CurTiPot Version 4.1.1 in Tables 5 and 6. Note that only the second dissociation constant of mixture 114-46-146 is the only one where the 9.73 equals any of the individual dissociation pH values. The explanation as to why these two numbers are equal is not thoroughly understood. Also note that the evaluation in Tables 5 and 6 are preliminary results. More data analyses are required to make certain that the values included in these Tables are the most accurate ones available.

Procedure

The various acid activator combinations were prepared and utilized to neutralize the sodium hydroxide solutions. The titrations were conducted at 70 and 180°F. The laboratory results were input into the evaluation module of CurTiPot. Only 70°F data are reported in Table 5.

Table 5. Results of Preliminary Analyses of 70 Degree F Multi-Component Titration Curves.

Sample 114-46-	Dissociation Constant 1	Dissociation Constant 2	Dissociation Constant 3	Dissociation Constant 4	Dissociation Constant 5	Final pH
140	6.78	–	–	–	–	-0.40
140P	6.91	–	–	–	–	0.00
140>OH	7.19	–	–	–	–	0.00
141	13.67	11.67	–	–	–	10.66
141P	13.03	11.27	–	–	–	10.59
141>OH	13.66	13.58	13.06	–	–	13.06
142	13.24	12.74	9.62	5.09	–	4.17
142P	13.40	13.10	8.49	5.29	–	4.33
142RR*	13.54	13.36	11.81	6.60		6.60
142PRR*	13.55	13.40	11.90	6.99		6.99
142>OH	13.80	13.50	12.65	–	–	12.65
143	13.11	12.39	9.03	5.57	4.33	3.06
143P	13.20	12.14	8.77	5.10	–	1.79
143>OH	Did not	conduct this	experiment	–	–	–
144	13.52	10.40	4.15	1.84	–	1.53
144P	13.22	9.42	4.68	1.42	–	1.16
144>OH	13.75	13.49	13.14	11.98	8.81/4.93**	3.68
145	6.69	–	–	–	–	0.00
145P	6.62	–	–	–	–	0.00
145>OH	6.90	–	–	–	–	0.00
146	13.51	13.26	12.74	9.73	5.20	4.25
146P	12.59	9.35	5.80	3.70	–	3.70
146>OH	13.72	13.52	12.69	–	–	12.69
147	13.72	13.02	9.20	5.87	4.02	4.01
147P	12.97	12.39	9.10	5.04	–	1.93
147>OH	13.72	13.51	7.02	–	–	6.95
148	13.58	13.40	8.48	4.33	–	1.98
148P	13.12	12.66	9.51	4.84	–	1.16
148>OH	13.63	13.46	13.24	11.86	8.72/5.98**	4.87
149	13.93	13.70	13.33	12.37	8.78/5.43**	1.43
149P	12.62	9.03	4.91	1.06	0.82	0.82
149>OH	13.81	11.99	8.94	6.066	4.32	3.24

*RR = Rerun lab test

**Dissociation constant 5/Dissociation constant 6

Some observations are that for the 70°F data the samples with the polymer—designated by a P following the number—the final pHs of the polymer samples are lower than the samples without the polymer. The exception is the 114-46-142 group—highlighted in yellow on the Table—where the sample containing polymer has a higher final pH than that without polymer.

In most cases when polymers are present, the first dissociation constants are also lower. What this may show is that some of the hydrogen ions are being absorbed by the polymer before reacting with the H_3O^+ availability control components of RAA and the sodium hydroxide. There are exceptions for example 114-46-148 where the polymer 1st dissociation constant pH is

actually higher that the sample without polymer. This also occurs in samples 114-46-143 and 114-46-142 series.

The ">OH" behind the sample number means that the hydroxide concentration has been increased compared to the other hydroxide concentrations utilized. Even though the hydroxide concentrations in these tests are higher, the 1st dissociation constant is not necessarily consistently higher than those recorded for the samples with and without polymer.

Six experiments have only one dissociation constant. Others may have as many as six dissociation constants. Some of these used a strong acid (HA) rather than a combination of acids. One dissociation constant is consistent with strong acids or bases (140 and 145).

The 180°F data has also been evaluated and summarized in Table 6. Three acid activators have only one dissociation constant. Conversely the 114-46-148P and 149 activator combinations have five dissociation constants. These results seem to be different from the 70 degree F titrations. In all cases, the final pH values in the titrations performed with polymer in the solution were all lower than those without the polymer, e.g. 149 final pH is 1.25 while the 149P final pH is 0.59.

Table 6. Results of Preliminary Analyses of 180 Degree F Multi-component Titration Curves.

Sample No. 114-46-	Dissociation Constant 1	Dissociation Constant 2	Dissociation Constant 3	Dissociation Constant 4	Dissociation Constant 5	Final pH
140	5.72	–	–	–	–	0.00
140P	5.45	0.02	–	–	–	0.00
141	11.50	11.10	–	–	–	10.68
141P	10.93	10.81	7.87	–	–	7.87
142	11.51	10.95	8.05	–	–	5.98
142P	11.05	8.79	4.69	–	–	2.74
143	10.93	8.50	5.44	3.87	–	3.08
143P	10.57	7.97	4.63	2.53	–	1.38
144	8.81	4.52	–	–	–	1.66
144P	8.24	4.35	–	–	–	0.80
145	5.40	–	–	–	–	0.00
145P	5.53	–	–	–	–	0.00
146	11.13	10.69	8.22	–	–	6.12
146P	11.39	10.99	8.40	5.10	–	4.28
147	11.49	8.00	4.75	2.69	–	4.14
147P	10.98	10.63	6.12	2.39	–	1.72
148	11.49	8.00	4.75	2.69	–	2.14
148P	11.10	8.72	5.40	1.54	1.28	1.05
149	11.36	11.12	8.50	4.41	1.38	1.25
149P	11.32	11.11	7.92	4.54	1.73	0.59

Three acid activators have only 1 dissociation constant. These results seem to be different from the 70 degree F titrations. The results are more random with respect to the dissociation constant pH values. However, in all cases the final pH values in the titrations performed with polymer in the solution.

Preliminary Conclusions Regarding the RAA Initiator System

- Temperature influences the chemical reactions occurring with the gel system.
- Polymer influences the chemical reactions occurring with the gel system.
- RAA mixtures do not react producing the same products as the individual acids produce. Note the differing pH values for the dissociation constants.
- The RAA initiator system is different from historical inorganic initiated silicate gels.
- The RAA initiator system is different from previous organic initiated silicate gels.
- The RAA base neutralizations differ in the end pH value (1 – 7) obtained as compared to the organically initiated gels (pH = 9-10.5).

3.2.1.6 Data Interpretation and Further Thought

The first system of strong/weak acid pairs is created by mixing the two acids in an aqueous environment. The strong acid dissociates according to Equation 6.

$$HA + H_2O \rightleftharpoons A^- + H_3O^+ \qquad \text{Equation 6}$$

Similarly, in a water environment, the first weak acid might be dissociated into two or perhaps three ionization states of decreasing strength as respectively characterized by Equations 7-9.

$$H_3A + H_2O \rightleftharpoons H_2A^{-1} + H_3O^+ \qquad \text{Equation 7}$$

$$H_2A^{-1} + H_2O \rightleftharpoons HA^{-2} + H_3O^+ \qquad \text{Equation 8}$$

$$HA^{-2} + H_2O \rightleftharpoons A^{-3} + H_3O^+ \qquad \text{Equation 9}$$

The main source of hydronium ions in the first mixture of HA and H_3A acids is provided by the dissociation of the HA. The anion, A^-, produced as a result of the dissociation expressed in Equations 6, provides a salt for the HA. *Given the strength of the HA, however, the anions as a practical matter cannot re-associate with hydronium ions at a rate fast enough to maintain a state of equilibrium during dissociation.* Thus, hydronium ion production in pure HA remains uncontrolled. In contrast, when an H_2A or an H_3A is added to the HA, the dissociation of H_3A will partially serve as a controller of the hydronium ion availability in the HA/H_3A acid mixture. Such control occurs because the first ionization state of H_3A, i.e H_2A^-, is present in relatively great concentration within the mixture of HA and H_3A acids. While considered a semi-weak base, the first ionization state of H_3A acid acts as a relatively strong base in the presence of the strong HA acid. Consequently, the first ionization constant of H_3A plays a primary role in capturing free hydronium ions present in the mixture of HA and H_3A acids.

Despite the modifying effect of H_3A on HA, the level of hydronium ion availability in a mixture of HA and H_3A acids is still too high to provide effective control over the mixture. A second pair of strong and weak acids, e.g., H_xA and H_yA acids, are needed in the mixture to provide additional control of the system. To this end, H_xA and H_yA acid are added to the HA and H_3A acid mixture to provide a second strong/weak acid pair. The dissociation reactions of H_xA and H_yA acids are in a water environment, respectively yielding the following equations:

$$H_xA + H_2O \rightleftharpoons H_{x-1}A^- + H_3O^+ \qquad \text{Equation 10}$$

$$H_yA + H_2O \rightleftharpoons H_{y-1}A^- + H_3O^+$$ Equation 11

Although the HA acid serves as the primary source of hydronium ions in the two strong/weak pairs of acids, the H_xA acid is a relatively strong acid in its own right and thus, constitutes a secondary source of hydronium ions when added to the mixture of HA and H_3A acids. The availability of the additional hydronium ions from the H_xA acid is quite important in as much as these additional hydronium ions may be responsible for the low pH of the full solution, i.e., the solution of HA, H_3A, H_xA and H_yA acids.

The action of the H_yA acid in the full solution is also important. Adding H_xA acid alone to the HA and H_3A acid mixture would produce an over abundance of hydronium ions destroying the sought after availability control of hydronium ion. The H_yA acid, however, is considered a weak acid, particularly in relation to the H_xA acid. As a result, the ionization state of the H_yA acid serves as a strong conjugate base for the H_xA acid. The strong conjugate base in turn provides a secondary mechanism for controlling the availability of the hydronium ions from both the primary and secondary hydronium ion sources, i.e,., from both the HA and H_xA acids, in the full solution.

A mechanism for achieving hydronium ion availability control in the mixture has been proposed. The first ionization state of H_3A acid created by combining the first strong/weak acid pair and the ionization state of H_yA acid created by combining the second strong/weak acid pair act in concert as relatively strong bases to regulate the production of free hydronium ions within the solution. The first ionization state of H_3A acid and the ionization state of H_yA acid are both decreased by respectively drawing off free hydronium ions, thereby causing an increase in the concentration of H_3A acid and H_yA acid in the solution. This latter condition favors the ionization state of the HA and H_xA acid, in the process providing a strong source of hydronium ions and allowing the dissociation reactions expressed in Equations (2) and (6) to reach a state of equilibrium. The ionization of the H_xA acid additionally produces A^- ions which act as a strong base relative to the HA acid, providing another means for capturing hydronium ions. As a net result, overall control of hydronium ion availability in the full solution is readily attainable in the very low pH solution.

It should be noted in connection with the dissociation reactions discussed above that water plays a key role in the actual ionizing and dissociation mechanisms of the various acids present. Equations (1), (2), (5) and (6) all demonstrate that water functions as a strong “base” during the dissociation reactions, furnishing a carrier for the hydrogen ions released by the acids of the present invention. In this manner, the various dissociations are greatly facilitated while the exchange of hydronium ions necessary to maintain equilibrium between the various dissociations and re-associations, and hence control over hydronium ion availability, is achieved.

What is also becoming apparent from the CurTiPot Version 4.1.1 software effort is that the presence of the polymer in the SPI gels is not as passive as it was thought to be with the earlier organic-type initiators. F the polymer is partially hydrolyzed, it could have two methods of interacting in the system. First, it could be simply a hydrogen ion acid soak in the hydrolyzed section replacing the ionic sodium ion with a proton to form an acrylic acid unit. Secondly, this

newly formed acrylic acid unit is now prepared to be further involved in the donation of that proton to the gelation mechanism creating an additional pk_a to the system. Third, acidic amide hydrolysis could occur resulting in an additional acrylic acid unit. Furthermore, one might argue that the silicic acid polymer might have its own pKa at high pH's and be involved in some fashion and under certain conditions as a base in the system. On the other hand the silicic acid is formed because of the systems relationship in a strong base which is being titrated. This makes for a very complicated mixture for a host of chemical reactions to occur.

3.2.1.7 Using the RAA Initiator Systems to Provide SPI Gels.

First we thought it useful to create a knowledge base of the gelation capacity of the individual RAA initiator components and all of the possible combinations. These combinations all had a constant sodium silicate and polymer concentrations in the gel formulation. All possible RAA initiated gel component combinations used to create the SPI gels are shown in Table 7a and 7b. The individual RAA initiator components are confidential and not released in this report. This technology is deemed patentable and it is very valuable to the SPI Gel initiation applications at low to moderate temperatures and hopefully it can be used in the higher temperature geothermal applications.

Table 7a contains the RT initiation with the RAA individual components and component mixtures. The abbreviations for the gel quality comments in Table 7a & 7b and all of the other Tables are provided in Table 8. For example, VHER stands for a Very Hard Elastic Ringing gel. When one picks up the gel and thumps the jar it is contained in, the sample will ring or vibrate in your hand. Sometimes when you lightly press 1-2 mm into the gel it will ring and if it is elastic it will return to its original shape.

In Table 7, Sample 1 contained only the strong acid component, HA, represented in Equation 6. It did not form a complete gel as indicated by the initial comment word "Broken" and then with time it became a very weak gel. This is supported by the fact that the final pH was 11 and thus the gel did not form completely before the protons from the strong acid were consumed by the alkalinity of the silicate formulation. The gel time is 180 minutes which is far longer than what one would normally anticipate for such a strong acid that normally reacts instantly in the form of a precipitation. But to create the precipitation gels of years ago required substantially more volume of strong acid than was used in this experiment. So it is obvious this formulation contains a low concentration of the strong acid. Samples 12, 13 and 14 with pH's in the 10 – 11 range also showed a broken gel or no gel at al. These formulations had only the weaker acids H_xA and H_yA and not the previously discussed strong acid. Now one might conclude that our RAA component concentrations were in the desired range for samples 2 – 11 which formed reasonably strong gels, but perhaps the concentrations were not optimum since the pH's were all over the place and the gel time at RT would not allow enough time for gel placement. The 20 minute gel time for sample 5 gave a very nice gel similar to sample 2, but with far too short of a gel time.

Sample 9 gave the longest gel time of 70 minutes and a fairly hard gel, but for these gels, the pH seems to still be too high. The organic ester gels previously used had gel pH's in the 9.5 – 11 range. Sample 9 gave the longest gel time of 70 minutes and a fairly hard gel, but for these gels,

the pH seems to still be too high. Sample 9 is a single RAA component, H_3A, which has more than one dissociation constant and acts like a weak acid in the RAA system. The first dissociation constant is far more acidic than the next two constants, therefore one might say this

Table 7a. RAA Initiator – Individual and Mixed Acid Component Contributions to SPI Gel at Room Temperature.

Entry No.	% HA Comp*	% H_3A Comp.	% H_xA Comp.	% H_yA Comp.	RT Gel Time, min	1 Day Gel Comment	1 Wk Gel Comment	1 Mo Gel Comment	pH 6 Day
1	W*				180	Broken	WNR	WSR	11
2	W	X*	Y*	Z*	12	VHER	VHER	HSR	4
3	W	X			4	VHSR	VHSR	HSR	6
4	W	X	Y		15	HNR	HNR	HSR	10
5	W	X		Z	20	VHNR	VHSR	VHSR	6
6	W		Y	Z	2	HER	HSR	HNR	7
7	W			Z	15	HSR	HSR	HNR	10
8		X	Y	Z	5	VHSR	VHR	HNR	6.5
9		X			70	HER	HER	HNR	11
10		X	Y		2	VHSR	VHR	VHR	9
11		X		Z	2	HNR	VHNR	HNR	9
12			Y	Z	No Gel	Broke Gel	Broke Gel	Broke Gel	10
13			Y		No Gel	No Gel	No Gel	No Gel	10
14				Z	No Gel	No Gel	No Gel	No Gel	11.5

- RAA component concentrations are W, X, Y, & Z. Comp. = Component.

could sort of be a RAA initiator in one acidic chemical. This explains the high pH, but still, 70 minutes is not sufficiently long enough for an SPI gel system especially at RT. So did we choose the right concentration range for these gels? The answer is no, probably not. Later we learned

Table 7b. Continued. RAA Initiator – Individual and Mixed Acid Component Contributions to SPI Gel at 180F.

Entry No.	% HA Comp*	% H_3A Comp.	% H_xA Comp.	% H_yA Comp.	180 F Gel Time, min	1 Day Gel Comment	1 Wk Gel Comment	1 Mo Gel Comment	pH 6 Day
1	W*				205	MNR	WNR	WNR	11
2	W	X*	Y*	Z*	98	HNR	HNR	HNR	3.5
3	W	X			5.5	HSR	HESR	HNR	7.5
4	W	X	Y		6	HSR	HESR	HNR	6
5	W	X		Z	5	HSR	HESR	HESR	6
6	W		Y	Z	3	HSR	HSR	HNR	7.5
7	W			Z	12	HSR	HNR	HNR	11
8		X	Y	Z	5or 300	HSR/WNR	HNR/WNR	MNR/WNR	7/11
9		X			30	HER	MER	MER	11
10		X	Y		5	HSR	HESR	HENR	10
11		X		Z	3	HSR	HENR	HENR	10
12			Y	Z	No Gel	No Gel	No Gel	No Gel	10
13			Y		No Gel	Broke Gel	Broke Gel	Broke Gel	11
14				Z	No Gel	Broke Gel	Broke Gel	Broke Gel	11

*RAA component concentrations are W, X, Y, & Z. Comp. = Component.

the Si/I ratio is very important relationship and it is scattered in Table 7a. It also seems that RT gel performance is often not always in line with the higher temperature performance.

In Table 7b at 82°C, gel sample 9 still has a pH of 11. The gel time is cut three-fold to 30 minutes and the sample has the same level of hardness, so it could be used in a few select lower temperature applications, but not for geothermal use. Perhaps the biggest surprise is gel Sample 1 which actually increased in gel time from 82 to 96°C to form a moderate to weak gel, but still at a pH of 11. There is no explanation for this response. Sample 5 has the same pH, gel time cut four-fold to 5 minutes and the gel is substantially weaker. Gel sample 2 has a low pH, lower gel hardness but the gel time has increased to 98 minutes which is good, but not good enough. The point is we may not have the most optimized RAA concentration in the SPI gel formulation for the selected RAA component concentration. We will later demonstrate the most optimum Si/I ratio for using RAA initiation. The SPI Si/I ratio values for Tables 7a and 7b are not given since this information is confidential and in these tables some of the components are a single initiator.

Table 8. Gel Comment Abbreviation Descriptions.

Abbreviation	Gel Description	Abbreviation	Gel Description
HER	Hard Elastic Ringing Gel	WNR	Weak Non Ringing Gel
HESR	Hard Elastic Slight Ring Gel	VHESR	Very Hard Elastic Slight Ringing Gel
HEVR	Hard Elastic Very Ringing Gel	VHNR	Very Hard Non Ringing Gel
HNR	Hard Non Ringing Gel	WSR	Weak Slight Ringing Gel
HR	Hard Ringing Gel	VHR	Very Hard Ringing Gel
HSR	Hard Slight Ring Gel	VHSR	Very Hard Slight Ringing Gel
HVR	Hard Very Ringing Gel	WNR	Weak Non Ringing Gel
HWR	Hard Weak Ringing Gel	VWER	Very Weak Elastic Ringing Gel
ME	Medium Elastic Gel	VVHR	Very, Very Hard Ringing Gel
MENR	Medium Elastic Non Ringing Gel	VVHWR	Very, Very Hard Weak Ringing Gel
MESR	Medium Elastic Slight Ringing Gel	VWNR	Very Weak Non Ringing Gel
MNR	Medium Non Ringing Gel	WESR	Weak Elastic Slight Ringing Gel
MR	Medium Ringing Gel	WENR	Weak Elastic Non Ringing Gel
MSR	Medium Slight Ringing Gel	WNR	Weak Non Ringing Gel
MVE	Medium Very Elastic Gel	VHER	Very Hard Elastic Ringing Gel

In May and June of 2014, numerous SPI gels were created for the purposes of expanding the development of the technology. The intent was to optimize the RAA by locating the sweet spots, and then determine the best RAA formulation areas. Table 9 contains more information regarding the various concentrations of the components to make an SPI gel using RAA. The RAA concentration is the weight percent of all of the acid components blended into a single product. The polymer weight percent is constant throughout all of the gels.

Over 250 gels were made at various silicate and RAA concentrations. The Si/I ratio is an important ratio for reactant stoichiometry purposes. Lower Si/I ratio's tend to provide better gels. Excess Neutralization Capacity, where a positive number indicates excess OH^- and a negative number indicates excess H^+ concentration is also an important concept to evaluate perhaps for higher temperature operation. This value is a calculated value based on complete utilization of all the acid potential in the RAA initiator. This likely does not occur, except maybe at ultra high temperatures for HT geothermal applications. As it turns out, there is a linear relationship between silicate and RAA concentrations. The curves have an excellent linear fit with 66% of the R^2 values ≥ 0.9778 and 00% ≥ 0.7531.

Table 9. The Best SPI Gels Made in Triplicate.									
Entry No.	Lab No. 117-46	Silicate Wt. %	RAA Wt.%	Si/I Ratio	180F Gel Time	180F Syneresis 1D/1W	Gel Description 1 day	Gel Description 1 Week	pH 6 Days
1.	-189	Hi	Hi	1.24	240	0.2/0	VHR	VHER	3
	-290	Hi	Hi	1.24	180	0/0	HENR	MNR	3
	-303	Hi	Hi	1.24	230	0.25/0	HER	HER	2
	233	Hi	Hi	1.24	165	0/0	HER	VHER	2
	294	Hi	Hi	1.24	200	0/0	HER	HER	2
	307	Hi	Hi	1.24	160	0/0	HNR	VHNR	2
Ave.					196	0.075/0	HER	VHER	2.3
2.	234	Hi	MH	1.13	215	0/0	HER	VHSER	2
	295	Hi	MH	1.13	270	0/0	VHER	VHWR	2
	308	Hi	MH	1.13	200	0/0	VHER	VHENR	2
Ave.					228	0/0	VHER	VHER	2
3.	232	Hi	ML	1.38	135	0/0	HR	VHER	4
	293	Hi	ML	1.38	130	0/0.25	HNER	VHER	3
	293a	Hi	ML	1.38	140	0/0	VHNR	VHNR	3
	306	Hi	ML	1.38	120	0/0	HER	VHNR	4
Ave.					131	0/0.08	HSR	VHER	3.5
4.	239	MH	Hi	1.02	270	0/0	HER	HER	1
	298	MH	Hi	1.02	300	0/0	HSR	HSR	2
	311	MH	Hi	1.02	340	0/0	HVER	HVER	1
Ave.					303	0/0	HER	HER	1.3
5.	238	MH	MH	1.12	210	0.2/0	VHER	VHER	1
	297	MH	MH	1.12	245	0/0	HVNR	HENR	2
	310	MH	MH	1.12	235	0/0	HVER	VHESR	2
Ave.					230	0/0.06	HVER	HER	1.7
6.	237	ML	ML	1.24	165	0/0	HESR	HER	2
	296	ML	ML	1.24	190	0/0	HNR	HNR	2
	309	ML	ML	1.24	185	0/0	Her	HER	2
Ave.					180	0/0	HESR	HER	2
7.	204	ML	MH	0.99	285	0/0	HER	HER	2
	292a	ML	MH	0.99	250	0/0	HER	-	3
Ave.					268	0/0	HER	HER	2.5
8.	203	ML	L	1.24	140	0/0	HR	HR	3
	291	ML	L	1.24	180	0/0	HENR	HENR	3
	304	ML	L	1.24	210	0.15/0	HER	HER	3
Ave.					177	0.05/0	HER	HER	3
9.	242	ML	ML	1.10	-	0/0	HER	HER	1.5
	300	Ml	ML	1.10	330	0.1/0	VHER	VHER	3
	313	ML	ML	1.10	305	0/0	HER	MENR	2
Ave.					318	0.0.3/0	HER	VHER	2.2
10.	241	ML	L	1.24	195	0/0	HER	HER	2
	299	ML	L	1.24	195	0/0	HESR	HENR	2
	312	Ml	L	1.24	190	0/0	HENR	HENR	3
Ave.					193	0/0	HESR	HENR	2.3
11.	244	L	Hi	0.9		0/0	HE	HESR	1
	301	L	Hi	0.9		0.3/0	MVER	HER	1
	314	L	Hi	0.9		0/0	HER	HESR	1
Ave.						0.1/0	HER	HESR	1
12.	246	L	L	1.09	180	0/0	HESR	HESR	2
	302	L	L	1.09	170	0/0	MVER	MVER	2

Ave.					175	0/0	HER	HER	2

1. GT = Gel Time
2. Syn = Syneresis
3. Silicate and RAA concentrations: Hi = high; MH = medium high; ML = medium low; an d L = low.

In July, August and September, the team was partially funded by another DOE SBIR project to develop initiation for lower temperature SPI gel applications for CO_2 sequestration. Thus, the effort for HT geothermal was reduced during those months in order to make time for the sequestration project. Our intent is to keep the specific R & D projects as separate as possible in terms of funding, but not miss technical innovation opportunities on either project. The data in this table is focused on lower temp RAA applications, but we kept an eye out for innovation potential that could relate to the geothermal project. It is only fair to the sequestration project that the data generated under that contract be reported to that group first which was in the February 2015 time frame under a Phase I project report. After presentation in that report, the results will be presented in this report as it might pertain to high temperature geothermal work. A useful time temperature relationship for geothermal system could be derived from the lower temperature work and new discoveries to date by "shorting" the RAA concentrations and using temperature to drive the H_3O^+ consumption reaction to the right.

Now that we have a better feel for creating RAA initiator formulations capable of making delayed gels (as per Tables 7 and 9) we will evaluate the effect of changing the component concentrations in Tables 10 and 11. The concentration of the RAA components will be decreased and increased by 20 percent in samples with and without the presence of polymer. The polymer is thought to possibly act as an acid soak at certain temperatures. Two control gels are shown in Table 10, numbers 1 - 4. Control 1 with high silicate concentration and Control 2 with a medium silicate concentration are shown both with and without polymer. The Si/I Ratios are 1.13 and 1.24 respectively for the two controls. The other Si/I values in Table 10 and 11 are dependent on the increase or decrease in the individual RAA components. The original control gels, both with and without polymer are almost identical. When the high silicate control has a 20% reduced amount of HA, the presence of polymer gave a 30 minute decrease in Gel Time (GT), and a slight decrease in gel hardness while the pH increased to 2. Reducing the silicate to medium concentration and decreasing the HA by 20% seemed to decrease the gel time further to 40 minutes with polymer while the gel stability comments suggest similarity to the controls. The pH has increased to 3 and the Si/I ratio also increased. These observations seem to be consistent with a reduced and/or controlled availability of H_3O^+ concentration whereby the polymer may also be a participant. Increasing the HA by 20% did significantly change Control 1's properties by shortening the GT by 60 minutes. The absence of polymer provided the same GT as Number 6 without polymer and a 20% increase in HA. Yet the control without polymer had a 220 GT. Therefore, one might conclude that with respect to the other components remaining at the same concentrations, there is no benefit.

Sample numbers 13 – 20 in Table 10 show the effect of reducing or increasing the H_3A acid by 20% in each Control with or without polymer. Decreasing H_3A concentration by 20% seemed to have more negative effects than positive effects especially when the silicate concentration in control 2 was reduced. But increasing the H_3A concentration seemed to have more of an overall positive effect. Number 20 had the highest GT of 300 minutes so far. Note the absence of polymer in both the controls with additional H_3A seems to suggest that the polymer and H_3A

may have something in common. The pH was back down to a pH of 1 and 2 for each gel. The gel hardness was not quite as good as the original controls. The same for Control 2 making the GT the longest in the series, but the pH was back up to 2. Usually in the past the increasing the initiator concentration decreased the GT.

Table 10. Effect of RAA Component Concentration Changes on SPI Gels at 180 °F.

No.	Formulation Description	Silicate Wt %	Si/I Ratio	Polymer Present	180F GT Min	Gel Comments 1Day/1Month	pH 6 Day
1	Control 1 , Poly	H	1.13	Yes	200	VHR/HSR	1
2	Control 1, No Poly	H	1.13	No	220	VHR/HSR	1
3	Control 2 , Poly	M	1.24	Y	200	MNR/MNR	2
4	Control 2, No Poly	M	1.24	N	180	VHER/VHSR	2
5	20% Less HA	H	1.17	Y	170	HNR/HNR	2
6	20% Less HA	H	1.17	N	170	VHSR/VHSR	2
7	20% Less HA	M	1.29	Y	160	MNR/MNR	3
8	20% Less HA	M	1.29	N	180	VHER/HSR	3
9	20% More HA	H	1.13	Y	140	HNR/HNR	3
10	20% More HA	H	1.13	N	170	VHSR/HNR	2
11	20% More HA	M	1.24	Y	190	HER/HNR	2
12	20% More HA	M	1.24	N	200	HER/HNR	2
13	20% Less H_3A	H	1.23	Y	195	HESR/HNR	2
14	20% Less H_3A	H	1.23	N	175	HENR/HNR	2
15	20% Less H_3A	M	1.35	Y	165	HNR/HNR	3
16	20% Less H_3A	M	1.35	N	165	HSR/HSR	3
17	20% More H_3A	H	1.04	Y	240	HESR/HNR	1
18	20% More H_3A	H	1.04	N	260	HENR/HNR	1
19	20% More H_3A	M	1.14	Y	250	HNR/HNR	2
20	20% More H_3A	M	1.14	N	300	HSR/HSR	2

Abbreviations used in this table: H, M, L = High, Medium and Low, RAA Components: HA, H_3A, H_xA, and H_yA, Si/I = Silicate/Initiator Wt Ratio, Silicate = Sodium Silicate, GT = Gel Time. 1D,/1W/1M = 1 Day/1 Week/1 Month.

Table 11 shows removal of 50% of H_xA component does not significantly change the Control 1 gel hardness with a slight reduction in GT leaving the pH at 2. Removal of 50% of H_xA component at lower silicate did have significant decrease in GT. The Gel Comments were similar to the controls. Removing 50% of H_xA from the RAA initiator system produced a surprising increase in GT by 60 - 80 minutes while retaining a pH of 2. Yet removing 50% of the H_xA component from the Control 2 gel had a significant reduction in GT to 110 and 120 from 200 and 180. Adding one of the acid components, particularly HA, the primary strong acid (since H_xA is the secondary strong acid) might improve the results and lower the Si/I ratio.

Adding 50% H_xA had a positive effect on Control 1 GT (Numbers 25 – 26), like the 20% H_3A increase in Numbers 19-20, in extending GT to 280 minutes each, the highest level in the H_xA series. This could be considered significant. The Si/I ratio is in a good range of 1.03 from 113, but the pH had increased to 2 each from the controls at pH = 1. The Control 2 gel showed similar improvements to the Control 1 gel, but again remember Control 2 started at a higher Si/I ratio, therefore this trend should be expected.

Table 11. Effect of RAA Component Concentration Changes on SPI Gels at 180 °F.							
No.	**Formulation Description**	**Silicate Wt %**	**Si/I Ratio**	**Polymer Con.**	**180F GT Min**	**Gel Comment 1Day/1Month**	**pH 6D**
21	50% Less H_xA	H	1.25	Y	180	HER/HER	2
22	50% Less H_xA	H	1.25	N	180	HER/VHSR	2
23	50% Less H_xA	M	1.38	Y	110	MNR/MNR	3
24	50% Less H_xA	M	1.38	N	120	HNR/VHNR	3
25	50% More H_xA	H	1.03	Y	280	HENR/HNR	2
26	50% More H_xA	H	1.03	N	280	HER/HNR	2
27	50% More H_xA	M	1.13	Y	220	HNR/MNR	2
28	50% More H_xA	M	1.13	N	260	HHER/NR	2
29	50% Less H_yA	H	1.25	Y	170	MNR/MNR	2
30	50% Less H_yA	H	1.25	N	170	HNR/HNR	2
31	50% Less H_yA	M	1.38	Y	150	MER/MSR	3
32	50% Less H_yA	M	1.38	N	150	HER/HER	3
33	50% More H_yA	H	1.03	Y	175	HNR/HNR	2
34	50% More H_yA	H	1.03	N	120	HER/HER	2
35	50% More H_yA	M	1.13	Y	120	MNR/MNR	3
36	50% More H_yA	M	1.13	N	120	HER/HNR	3
37	100% Less H_xA	H	1.41	Y	130	HNR/VHNR	3
38	100% Less H_xA	H	1.41	N	130	VHSR/VHNR	3
39	100% Less H_xA	M	1.55	Y	60	MNR/MNR	2
40	100% Less H_xA	M	1.55	N	60	MNR/HNR	4
41	100% Less H_yA	H	1.41	Y	180	MNR/MNR	2
42	100% Less H_yA	H	1.41	N	180	HENR/VHNR	2
43	100% Less H_yA	M	1.55	Y	150	MNR/MNR	4
44	100% Less H_yA	M	1.55	N	60	HER/VHNR	4
45	No H_xA & H_yA	H	1.82	Y	105	VHNR/HNR	2
46	No H_xA & H_yA	H	1.82	N	95	HNR/HSR	2
47	No H_xA & H_yA	M	2.00	Y	165	MNR/MNR	3
48	No H_xA & H_yA	M	2.00	N	180	MNR/HNR	3
Abbreviations used in this table: H, M, L = High, Medium and Low, RAA Components: HA, H_3A, H_xA, and H_yA, Si/I = Silicate/Initiator Wt Ratio, Silicate = Sodium Silicate, GT = Gel Time. 1D,/1W/1M = 1 Day/1 Week/1 Month. .							

Reducing the H_yA by 50% (Number 29 – 32) in Controls 1 and 2 resulted in a significant GT decreases in from 200 and 220 with polymer to 170 for high silicate and 150 for medium silicate and an increase in pH from 2 to 3 for both gels and a substantial decrease in gel hardness for both controls. Control 2, the same decrease in H_yA resulted in a very strong decrease in GT for both polymer and non-polymer gels (from 200 and 180 with polymer to 150 for each. The pH increased from 2 to 3 which also seems to follow an increase in the Si/I ratio to 1.38. Whereas increasing the H_yA concentration by 50% was even more detrimental to the GT (120 minutes), marginally detrimental to gel hardness and the pH increased from 1-2 to 2-3, yet these gels seem to be in a reasonable Si/I ratio regime (1.03 – 1.13). Therefore, one might not want to raise or lower the HyA concentration.

Sample Numbers 37-40 had all of the H_xA removed from the initiator formulation resulting in very short GT, but strong gels for the high silicate controls (1.41 Si/I ratio). The last four sample numbers 41–44 have 100% of the H_yA removed. The high silicate concentration gels (Numbers 41–42) had a reasonable GT and a pH=2, both similar to control 1. The sample without polymer was the hardest gel. Removing 100% of both H_xA and H_yA components was only similar to the controls in terms of GT for Control 2 without polymer. All other gel properties were poor.

The polymer does seem to play a role. It seems to contribute in cases where the weaker acids are removed and not contribute when there is an excess of weak acid. Since we do not have exact acid dissociation coefficients for the mixture, it is difficult to make a clearer statement about the polymer performance as a strong base or "acid soak" agent in the system.

Table 12 shows data on selected Si/I ratio SPI gels at high, medium and low sodium silicate concentrations, the GT in minutes (are significantly delayed at the lower temperatures), syneresis determined at 1 day/1 week/1 month, gel hardness comment at those same times and pH at six days after gel formation (obtained by pressing a pH paper on the gel surface) data are shown. These gels occurred at 70, 120, 150, and 180 ^oF. Data to note in Table 15 is that:

1. SPI gels formed with RAA initiation certainly have extensive time delays with lower temperatures to form moderate or high strength gels.
3. Syneresis is not a problem with the SPI gels made with RAA except for room temperature.
4. There is a difference with the gels made at 70^oF in that the RAA configuration may not be optimum like it is at higher temperatures.
5. The 70^oF gels also become stronger as one month time passes.

Table 12. SPI Gel Data at Temperatures between 70-180^oF.

Number	Silicate Wt %	Si/I Ratio	GT Min	Syn, ml, 1D/1W/1M	GC 1D	GC 1W	GC 1M	pH 6 D
		TEMPERATURE = 70 ^oF						
1	H	1.13	6980	0/2.4/4.5	MESR	MESR	VHESR	1
2	M	0.93	9060	0/0.3/2.5	VWNR	HESR	HESR	1
3	L	0.83	13080	0.5/0.3/3.6	WNR	MENR	MENR	1
		TEMPERATURE = 120 ^oF						
4	H	1.13	1320	0/0/0	WER	VHER	VHER	2
5	M	0.93	3150	0/0/0	MESR	MESR	MESR	1
6	L	0.83	3045	0/0/0	MESR	MSR	MNR	1
		TEMPERATURE = 150 ^oF						
7	H	1.13	240	0.2/0/0	HSR	HNR	VHNR	2
8	M	0.93	320	0/0/0	HER	HER	HNR	1
9	L	0.83	480	0/0/0	MNR	MNR	MNR	2
		TEMPERATURE = 180 ^oF						
10	H	1.13	140	0/0/0	HSR	HNR	VHNR	3
11	M	0.93	390	0/0/0	HNR	HNR	HNR	2
12	L	0.83	570	0/0/0.5	MENR	MENR	MENR	1

Abbreviations used in this table: Silicate = Sodium Silicate, Si/I = Silicate/Initiator Wt Ratio, H=High, M=Medium

and L = Low Sodium Silicate concentrations. GT = Gel Time. Syn. = Syneresis, 1D,/1W/1M = 1 Day/1 Week/1 Month, GC = Gel Comments, Gel Comment Abbreviations: E = Elastic, H=Hard, M = Moderate, N= No, R = Ringing, S= Slight, V= Very, W= Weak.

If the proton availability has changed in the RAA Initiator, could this mean that the system is not corrosive? Element Materials Technology tested a sample of the RAA for corrosion on 1522H carbon steel along with concentrated HA mineral acid and water. The steel samples were prepped for a simple room temperature atmospheric exposure two week corrosion test as shown in Table 13.

Table 13. Corrosion Testing on RAA.

Sample	Original Surface Area, cm^2	Solution pH, Initial	Solution pH, Final	Original Weight, g	Final Weight, g	Weight Loss, g	Corrosion Rate, g/m^2
RAA	39.60	0.41	-0.03	92.7660	92.7734	-0.0074	-1.87
Conc. HA	39.26	0.45	0.18	91.5366	90.4535	0.0831	21.16

The data in Table 13 actually suggests the carbon steel sample gained a slight amount of weight when compared to the mineral acid (HA) control. The photos that accompanied this data indicate the RAA sample had a slight amount of precipitation on the steel sample which may have contributed to the weight gain. Perhaps a film from one of the components deposited on the steel sample, but it appears there may not be a significant corrosion issue with RAA.

A question often asked when products are pumped downhole is "What is the effect of motion on the SPI gel components prior to or during gelation?" The concept is to see if the formulated SPI components will form a good gel after being pumped downhole and into the formation at or beyond the anticipated gel time. Will the gel plug in the tubing and the reservoir pathway or will it form and be destroyed by the shear and pressure? To create a motion that would resemble a pumping motion with a slight turbulence, we put the pre-gel in a jar with headspace and placed it in a device called an Environmental Rotator (Figure 18) that is specified in certain EPA tests to provide agitation through rotational motion to a jar containing an aqueous liquid that might extract metal ions or chemicals from soil samples. The Environmental Rotator makes 30 +/- 2 rpm while holding up to six quart sized jars. The particular unit Clean Tech owns was made by Lars Lande Manufacturing.

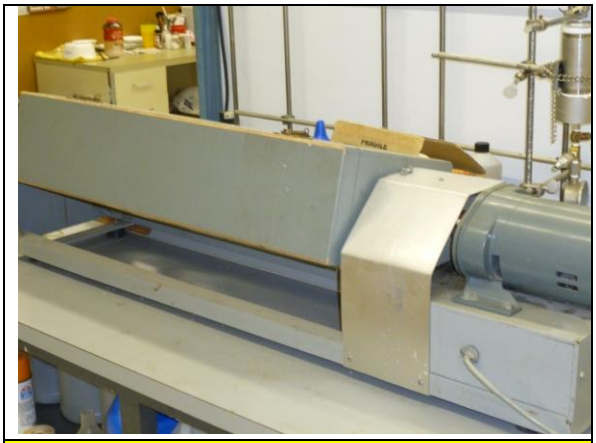


Figure 18. Rotational Device Used to Simulate Pumping on the Pre-Gel.

The SPI formulation has a known gel time obtained from prior testing. One sample is gelled in a stationary manner and the other sample is placed in the Environmental Rotator for one hour past the known gel time. The gel was allowed to set in a stationary position for an additional hour or until it gelled. A visual gel analysis was made and a penetrometer measurement was taken to represent gel hardness as shown in Table 14. Samples 1a – 1d were low silicate concentration gels initiated by an organic initiator. Samples 1a and 1d were controls formulated and gelled

while in a stationary jar at room temperature. The gels were an HER gel with a penetrometer depth of around 20 mm. It was a surprise to observe that the gels that were rotated in the Environmental Rotator for a period of time when they were expected to be undergoing gel formation turned out to be broken gels. The rotational energy was detrimental to the gel resulting in a broken gel with a penetrometer depth of 42 mm. The SPI gels created by the RAA initiator system (Samples 2a -2f) did not perform in the same manner. Samples 2a, 2d, and 2e were not exposed to rotation. Samples 2b, 2c, and 2d were rotated past the gel time. These gel components underwent a delay and gelled in the 1 – 2 hour period after the Environmental Rotator motion ceased and formed a strong gel that yielded the same penetrometry depth as the strong control gels that were not exposed to any motion.

Table 14. SPI Gel Exposure to Motion Before and During the Anticipated Gel Time.

No. 118-5-	Silicate conc	Initiator Type	Si/I Ratio	GT, min., RT	Gel Comments 1D/1W/1M	Agitated, Y or N	Penetrometer, Mm
1a	L	Organic1	1.34	220	HER	N	20.5
1b	L	Organic1	1.34		Broken Gel	Y	42.4
1c	L	Organic1	1.34		Broken Gel	Y	41.9
1d	L	Organic1	1.34	220	HER	N	19.5
2a	H	RAA	1.55	450	MER/HVER/VHNR	N	19.0
2b	H	RAA	1.55		MVER/HVER/HNR	Y	19.0
2c	H	RAA	1.55		MVER/HVER/HVENR	Y	20.4
2d	H	RAA	1.55	450	MVER/HVER/HVENR	N	17.8
2e	H	RAA	1.55	450	MER/HER/HNR	N	18.5
2f	H	RAA	1.55	510*	MER/HER/HNR	Y	19.5
3a	M	Organic2	1.50	100	VHER/VHER/VHER	N	15.0
3b	M	Organic2	1.50		Sludge/Sludge/Sludge	Y	38.5
3c	M	Organic2	1.50		Sludge/Sludge/Sludge	Y	39.0
3d	M	Organic2	1.50	100	HER/HER/VHER	N	18.7

*Rotated 8 hours and gelled 1.5 hours after rotating ceased.

Another organically initiated SPI gel is shown in Samples 3a – 3d with a moderate level of silicate. Again the organic initiated gels receiving motion during and through the period when the gel is gelling did not perform well, creating a sludge with high penetrometer ratings. All two of these gels had significant syneresis levels. Therefore, the gels organically initiated (Figure 19) showed deterioration and did not gel well when exposed to motion during the gel time period. The SPI gels that were RAA initiated (Figure 20) performed very well when exposed to motion during the gel time period. This is a significant and unexpected benefit of the RAA SPI gels and it will be explored further due to its significance.

Figure 19. Broken Gel Sample 1b Tilted at an Angle.

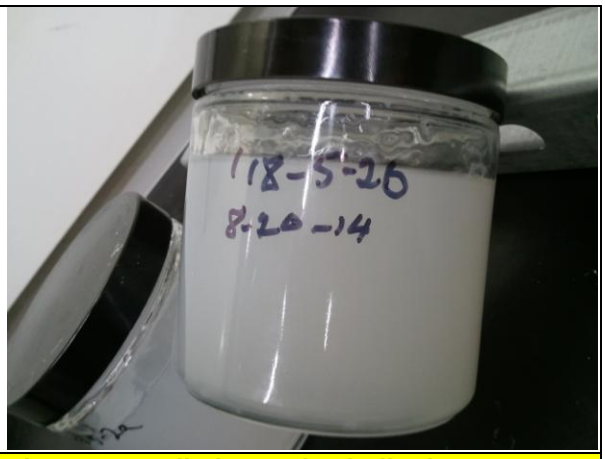


Figure 20. Gelled Sample 2b tilted at an Angle.

An extrusion test was performed on gel samples forcing the gel through a small opening. The desired intent is to have a gel that either plugs or takes a considerable time to flow through the hole. The device is pictured in Figure 21. The top is attached to an air compressor with a pressure gauge, a toggle valve that allows the pressure to be directed to a SS cylinder. The cylinder contains the gel in a plastic baby bottle drop-in which holds around 130 ml of gel (full to the top). The gel is formed in the baby bottle drop-in. The drop-in is installed from the bottom of the vessel and a cap secures the lip of the drop-in sealing it to the vessel. The air pressure only contacts the plastic baby bottle drop-in opposite the gel and not the gel on the topside. The vessel can rotate 180^{o} when filling it with gel versus operating. The gel is forced out of the drop-in by the air pressure in the top of the vessel through a small hole drilled in a fitting installed in the bottom cap. Nozzel 1 contains a 1.98 mm diameter hole that was used for the experiments. The air pressure forces the gel through the hole in the bottom of the cylinder without contacting the gel. The gel is captured in a vessel located on a balance so the time and gel weight variables can be recorded to establish a gel flow rate. The device in Figure 21 is operating as one can see and the competitive Maraseal chromium acetate colored gel is extruding from the bottom of the vessel.

Figure 21. Extrusion Device.

The data in Table 15 demonstrates that the RAA initiated SPI gels have the desired intent to create a gel that takes a considerable time to flow through the device opening. The worst of the SPI gels is equal to the best of the Cr (VI) or Cr (III) gels made at the chromium and polymer concentration limits from analyzing the data in Table 15.

Table 15. SPI and Competitive Gel Extrusion Data.

No. 117-46-	Silicate Concentration	Initiator Type	Si/I Ratio	GT, min, RT	Gel Comments 1D/1W/1M	Time, Ave. Sec.	Press, Psi	Sample Wt., g
455	H	RAA	1.24	100	VHNR/VHNR	35.40	25	50
457	H	RAA	1.38	90	VHNR/VHNR	43.83	25	50
470	H	RAA	1.02	210	VHNRG/VVHNRG	61.00	25	50
471	H	RAA	1.02	230	VHNRG/VVHNRG	8.67	25	50
113-90-	**Cr(VI), Wt % of $Na_2Cr_2O_7$**	**Na_2HSO_3 Wt %**	**SFHA110 Polymer Wt. %**					
2r	0.06	0.06	0.4			3.05	25	50
3r	0.09	0.09	0.6			4.93	25	50
5r	0.12	0.12	0.8			8.08	25	50
113-90-	**Cr(III)OAcOH Wt. %**		**SFN-300 Polymer**					
18	0.06		0.399			30.5	0	10
19	0.09		0.602			3.55	25	50
20	0.12		0.799			7.05	25	50
21	0.15		0.999			8.15	25	50

GT = Gel Time; 1D/1W/1M = 1 Day/1Week/1Month; Cr(VI) Wt% of $Na_2Cr_2O_7$= Chromium VI weight percent of sodium dichromate; Cr(III)OAcOH = Chromium III acetate hydroxide.

Conclusions From SPI Gels Initiated by RAA

There are several conclusions that can be made regarding the differences between the RAA initiated SPI gels and the original SPI gels and other technologies.

1. The titration curves in Figures 10 – 17 show the HCl titration behaves as a strong acid-strong base titration as expected, whereas the other curves with all or 1, 2 or 3 components appear to be a weak acid-strong (or weak conjugate) base titration curves.

2. The final pH of the earlier SPI gels was in the range of 9 – 10.5 for a very hard elastic gel. This was especially true if a high silicate was used and the Si/I wt ratio was between 1.0 – 1.5. The final pH of an RAA initiated SPI gel is usually lower and over a larger range. A pH of around 1 provides a better quality gel than a pH of 10 in this data with an RAA initiator. This is yet to be understood other than the mechanism of creating the gel is significantly different. The earlier SPI gels were formed by hydrolysis of a reactive carbonyl derivative to create a free proton from neutralization. With RAA, the proton is provided by one or more acids and the other acids provide a means for capturing and controlling the hydronium ions availability in the full solution by sodium exchange or re-association. The RAA acid mechanism is totally different than the decades old method of simply adding a concentrated acid or a weaker acid which both have the capacity to react immediately to form a precipitate gel. Thus, both the original SPI gel and the RAA initiated SPI gels have the capacity to form delayed gelation. The RAA initiated SPI gels are much better at delayed gelation than any other technology.

3. The Si/I ratio for the earlier SPI gels provided the best gels in the range of 1.0 to 1.5 over the complete range of silicate concentrations up to 10 % by weight sodium silicate. With the RAA acids, the better gels are probably in the 0.9 – 1.38 Si/I ratio. This difference

may not be significant. We have really not looked at the extremely high silicate concentrations (10%) with the RAA acids. The limit is around 6%.

4. With the RAA acid initiation, it appears that usually one must increase the acid concentration to lengthen the gel time. This is the opposite of the original SPI gels, but this may be due to a "lowering effect" on the Si/I ratio. Actually there is merit to lengthening the gel time by increasing the acid concentration as (shown in Table 19) and more specifically increasing the phosphoric acid and oxalic acid components when comparing Tables 13 and 14 with the controls Numbers 16 -20 & 25 through 28.

5. It seems apparent that a partially hydrolyzed polyacrylamide used in SPI gels might influence or interact in the chemical reactions occurring in the gel system by participating in the hydronium ion control or adsorption. This was not the case with the original SPI gels where the polymer only provided elasticity and stability to the SPI gel which is also the case with the RAA gels. Comment: Tables 7 & 8, the data is overpowered by acid component concentration change and the influence of the polymer is mute. I think there may be a role of the polymer in its affect on the gel time, but it is not significant.

6. RAA Initiation may provide gels with more stability than the original SPI gels. Syneresis appears to be lower and particularly at higher temps. This is significant, but it is not known what is causing it in RAA gels.

7. RAA Initiation of SPI gels increase the HTHP stability of SPI gels since they are more inorganic based.

8. We have seen some examples of gel mechanism change at certain temperatures possibly to invoke polymer participation in the gelation process.

9. Partial addition or removal of HA was detrimental to the gels. Partial removal of H_3A was detrimental but partial increase of H_3A improved the gel properties (Table 10)

10. Partial removal of either H_xA or H_yA was very detrimental to the gels. Partial increase of H_xA was very beneficial to gel quality, but increasing the H_yA concentration was detrimental to gel quality. (Table 11)

11. Complete removal of either H_xA or H_yA was very detrimental to the gels. Removal of both H_xA or H_yA is yet to be performed. Removal or addition of a small amount of HA did reduce, but not enhance gel quality. Yet, removal or addition of a small amount of H_3A did reduce and substantially enhance gel quality. Yes, see 4 above.

12. The presence of polymer increases gel stability as it did with the original SPI gel initiation systems. Without polymer, the gel is brittle making it sensitive to shattering. The polymer minimizes the damage. With RAA, the presence of polymer can affect gel time by making it 5 – 10 minutes longer, but at the higher gel times, it can be insignificant compared to the stability issue.

13. There seems to be a change in the data between the temperatures of 66 and 82 ^{o}C suggesting possibly a mechanistic change (Table 12). The 82 ^{o}C gel times are generally longer than the 66 ^{o}C gel times and there are some similar examples of such in the data from 49 ^{o}C to 66 ^{o}C.

14. The acid dissociation constant is a direct consequence of the underlying thermodynamics of the dissociation reaction. The pK_a is directly proportional to the Gibbs Free Energy change for the reaction. The pK_a value changes with temperature and can be understood qualitatively based on Le Chatelier's principle. If any change is imposed on a system in equilibrium, then the system adjusts to a new equilibrium counteracting the change. Thus, if a reaction is endothermic, the pK_a decreases with increasing temperature and for exothermic reactions, the opposite is true. The underlying structural factors that influence the magnitude of the acid dissociation constants also include Pauling's rules for acidity constants, inductive effects, mesomeric effects, and hydrogen bonding.

Further Initiator Work In Geothermal Zonal Isolation

15. It seems apparent that reformulation could be possible for the geothermal applications to possibly increase the H_3A and H_xA concentrations while reducing the HA and keeping the H_yA concentration constant.
16. It may be possible to perform other modifications to the RAA system such as reducing or eliminating the HA and maybe the H_3A.components at high temperature.
17. The polymer systems may have a larger role at high temperatures.

3.2.1.8 SPI Gel (RAA) Oven Testing

Using an oven and a high temp pressure cell to generate data on SPI gels has its limitations. "Proof of Concept" for this project was created during year 1 for proof that these gels had stability for high temperature high pressure applications. However, it is very difficult if not almost impossible to judge a gel time or determine other gel properties because the gel solvent, water, has superseded its boiling point. The procedure followed for this testing involved three days.

Three different gel formulations with triplicate sample sets were created including the RAA that is desired. These samples are then loaded on a tray and inserted into the cylindrical pressure

Figure 22. Oven Pressure Chamber with sample tray.

Chamber like that used in Phase I. The pressure chamber is then tightened and sealed with 35 lbs of torque per screw. The vessel was then placed in the oven and connected it to the Ar gas line, sealed and checked for leaks. If no leaks are found then oven door is closed and the sample is pressurized to 425 psi. If the chamber doesn't stabilize at 425 psi, then it is checked again for leaks and the sample is re-pressurized. Once pressurized shut off the gas line and close the valves on the gas cylinder. The oven is turned on and set to the desired temperature for the test. When it arrives at the desired temperature (usually requires 5 to 8 hrs), it stays at that temperature for a given time of 1 – 2 hours and the oven is turned off and the heat is slowly cooled over night.

On day 2, the oven is checked to see if it is equilibrated to room temperature, then the gas line is cracked to very slowly let the pressure inside of the vessel to slowly arrive at room pressure. The pressure release must be very slow so as not to disturb the samples inside of the vessel. This is usually at a rate of flow around 0.7 to 1 psi a minute. This usually takes all day long if not into the evening before the pressure is completely released and back to room temperature.

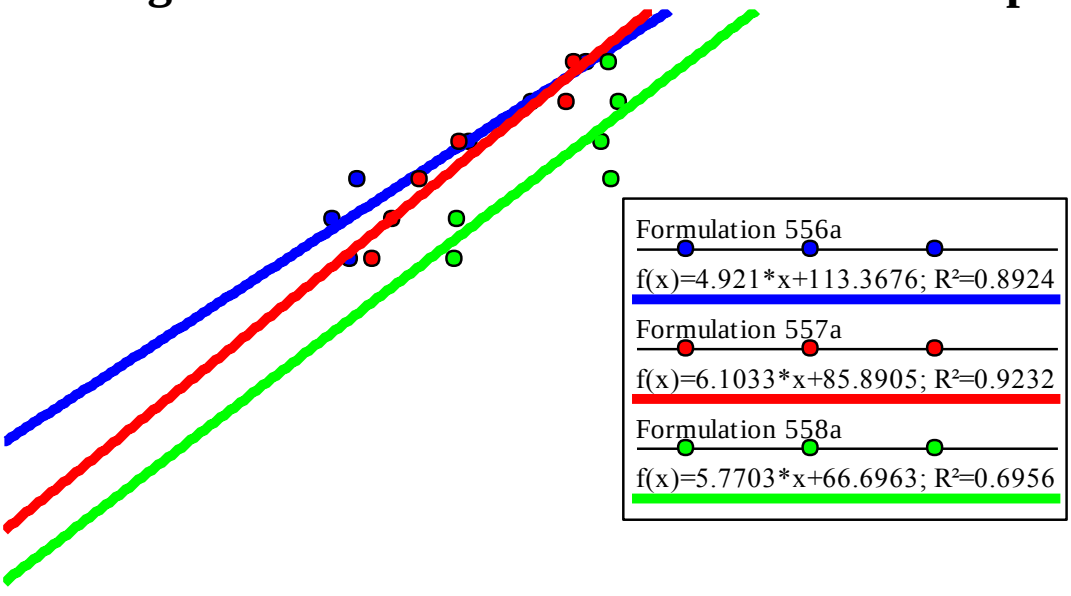
On day 3, the pressure is checked in the morning to see if it is at room pressure, then the vessel release is slowly closed off and the vessel is unhooked from the gas line. The lid is unbolted and the samples are removed from the trays. Water in the vessel is measured and recorded to see if a large portion of water escaped the samples. Usually the vessels each loose about 1.5 to 2.25 percent of the original water. Each sample is evaluated for strength, hardness, elasticity and resilience. The sample is placed on the penetrometer for penetration depth reading which is a measure of hardness as presented in Table 16 at different temperatures.

The first gel (117-46-556a) was made with the high silicate concentration of Table 9, Entry 2 with polymer. The second gel (117-46-557a) was made with the same high silicate concentration but absent the polymer. The third gel (117-46-558a) was made with a medium level of silicate similar to Table 9, Entry 6.

Table 16. SPI and Competitive Gel Extrusion Data.							
No. 117-46-	**Silicate Concentration**	**Initiator Type**	**Si/I Ratio**	**Polymer Present, Y/N**	**Gel Comments 3 days**	**Temp. °C**	**Penetrometer Penetration, Ave., mm**
556a	H	RAA	1.13	Y	VVHER Gel	163	13.00
					VVHER Gel	177	12.25
					VVHESR Gel	194	13.40
					VHER Gel	204	18.53
					VHER Gel	218	21.47
					HER Gel	232	23.93
557a	H	RAA	1.13	N	VVHER Gel	163	14.00
					VVHER Gel	177	15.03
					VVHESR Gel	194	16.23
					VHER Gel	204	18.03
					VHER Gel	218	23.03
					HER Gel	232	23.40
558a	M	RAA	1.13	Y	VVHER Gel	163	17.80
					VVHER Gel	177	17.97
					MHESR Gel	194	25.17
					VHER Gel	204	24.60
					VHER Gel	218	25.47
					HER Gel	232	25.00

The penetrometry data for each gel type are an average of three gels are plotted in Figure 23. It can be seen that the curve fitting is very good for the first two entries with higher silicate with but the third entry with lower silicate concentration had much weaker gels. It is also of interest that the high silicate concentration with polymer (117-46-556a) was slightly lower in hardness that the three higher temperature gels with polymer when compared with the high silicate gels without polymer (117-46-558a.

Figure 23. SPI Gel Hardness vs. Oven Temp.



3.2.2 Colloidal Silica

"Colloidal silica" refers to stable aqueous dispersions of discrete nonporous particles of amorphous silicon dioxide (SiO_2). Commercial colloidal silica contains 15 to 40 wt% SiO_2 as spherical particles with diameters ranging from 4 to 200 nm. Concentrated commercial colloidal silicas are stable at moderate pH (9.5 to 10.5) and at high silicon dioxide/alkali ratios (e.g., $SiO_2/Na_2O > 50$) because of silica particle repulsion resulting from surface ionization in alkaline solution.

Akzo Nobel is the major manufacturer of colloidal silica. According to Yi-GuanTsai, a silica scientist at Akzo Nobel, colloidal silica is about 4 – 5 times more expensive than aqueous sodium silicate largely because colloidal silicate is made from sodium silicate. Several commercially available colloidal silica samples have been acquired for testing as blends.

Table 17. Blends of Sodium Silicate and Colloidal Silica (Ludox SM).

No. 17-46	Description	Silicate Wt %	Si/I Ratio	Ludox SM, % Silicate	GT, Min.	Syn., ml 1D/1W/1M	Comments 1D/1W/1M	pH	Xs OH^- Neut Cap mmole
536	RAA Cont 66C P	H	1.03	0	310	0/0/	HER/HER/	1	-35.12
537	RAA Cont 82C P	H	1.03	0	245	0/0/	HNR/VHNR/	2	-35.12
538	RAA Cont 66C P	95% H	0.95	5%	310	0/0/	HER/HER/	1	-35.12
539	RAA Cont 82C P	95% H	0.95	5%	245	0/0/	HNR/HNR, Brit	2	-35.12
540	RAA Cont 66C P	91% H	0.93	9%	310	0/0/	HER/HER/	2	-35.68
541	RAA Cont 82C P	91% H	0.93	9%	245	0/0/	HNR/HNR, Brit	1	-35.68
542	RAA Cont 66C P	86% H	0.88	14%	300	0/0/	WESR/MESR/	2	-36.24
543	RAA Cont 82C P	86% H	0.88	14%	320	0./0/	WENR/MESR/	1	-36.24
544	RAA Cont 66C P	77% H	0.78	23%	440	0./0/	WESR/WENR/	1	-37.91
545	RAA Cont 82C P	77% H	0.78	23%	440	0./0/	WE/MSENR	1	-37.91
546	RAA Cont 66C P	53% H	0.52	47%	440	0./0/	Partial gel	1	-40.69
547	RAA Cont 82C P	53% H	0.52	47%	440	0./0/	WG/WSR	1	-40.69
548	RAA Cont 66C P	27% H	0.26	73%	NG	0./0/	No Gel	1	-43.47
549	RAA Cont 82C P	27% H	0.26	73%	370	0./0/	WG/WNR	1	-43.47
550	RAA Cont 66C P	6% H	0.05	94%	NG	0./0/	No Gel	0	-45.69
551	RAA Cont 82C P	6% H	0.05	94%	360	0./0/	W/VW	0	-45.69
552	RAA Cont 66C P	0% H	-	100%	NG	0./0/	No Gel	0	-46.25
553	RAA Cont 82C P	0% H	-	100%	560	0./0/	VW/VW	0	-46.25

RAA = Reduced Activity Acid Initiator, Cont = Control, C = Celsius P = Polymer, H = High Weight Percent, 95% H = 95% of High Weight Percent, Ludox SM = A very small particle size colloidal silica from W.R. Grace & Co., GT = Gel Time, Syn = Syneresis, 1D/1W/1M = 1Day/1Week/1Month, Comments – See Table 8 for Abreviations, Brit = Brittle, Xs MM OH- Neut Cap. = Excess millimole of base neutralization capacity, and NG = No Gel.

W. R. Grace is the manufacture of the Ludox® Colloidal Silicas. They are aqueous, opalescent dispersions of extremely small silica particles. These particles are grown by polymerization from silicic acid. They have chemically active surfaces that bond readily to other silica particles or other oxygen-containing surfaces. Ludox SM has a smaller particle size and higher surface area and is the most efficient binder in most applications.

The data in Table 17 were derived by taking two control SPI gels, 117-46-536 and -537 and replacing the reported sodium silicate with Ludox SM colloidal silica. The gel properties of Gel Time, Syneresis with Time, Gel Hardness Comments, pH and excess mmole of acid are a direct reflection of reducing the concentration of sodium silicate. This was a one series of experiments

and could be followed up with variations if time permitted. Researchers at Lawrence Livermore National Laboratory have published successful results using only colloidal silica gels.[23]

3.2.3 Gel Reversibility

The use of 2 N NaOH caustic to remove these gels was investigated and optimized in this task as well as compatibilities with all possible fluids that may be encountered in the zonal isolation. There were some experiments performed on this objective, but the results will be discussed later.

4.0 Task 6 - Dynamic Testing and Candidate Verification

4.1 Core and Unconsolidated Sedimentary Materials

For Oil and Gas work, the SPI gels were tested in sandstone and limestone/dolomite reservoir formations. Some of these were the cores from the sedimentary basins of the field test candidates. We would anticipate Phase II testing relative to this geothermal project to be in granite and limestone formations, since these are two predominate rock types in the geothermal/EGS environment. We also plan to perform most tests in standard Berea Sandstone.

For the past 30 years, Berea Sandstone™ core samples have been widely recognized by the petroleum industry as the best referenced core material for testing the efficiency of chemical products. This is really a question of choice for the customers to answer. We can use whatever formation rock that brings the most value to the R & D. Three 1.5 X 12 inch Berea Sandstone cores of 100-200 md and three 1.5 X 12 inch cores of 500 – 1,500 md were ordered from Cleveland Quarries along with the Residuum from each block. The Carbo Prop product was received gratis from Daryl E. Johnson, Director Resin Coated Proppants at CARBO Ceramics Inc. in Houston, TX.

We also intend to use proppants as a test matrix in some of the standardization tests because the bed is often homogeneous and many groups have data for us to use as reference for comparison. These materials will be used in unconsolidated sand packs and cores to establish how the fluids behave in a matrix-fracture structure. We retrieved a sample of Carbo Prop 70 – 140 mesh from Tulsa University, and later received a free five gallon sample of 50 mesh from the manufacturer, Carbo Ceramics. This Carbo Prop material was then sieved with 100 mesh making the resulting proppant 50-100 mesh. Carbo Prop is a ceramic proppant used in hydraulic fracturing operations to ensure quality fracturing in production zone workovers. Carbo Prop is very consistent ceramic material that is hard and does not expand or separate with extreme temperatures and pressures.

4.2 Task 6.0 Dynamic Evaluation

4.2.1 Gel Stability Testing – Reproduction of Phase I "Proof Of Concept"

The goal is to devise a dynamic test using a screen extrusion rheometer (Gel Strength Tester) to quantitatively compare strong bulk gels of the SPI compositions used for zonal isolation. Most of the work in Phase II, Quarter 1 was focused on calibration and correlation of Clean Tech's equipment with others in the industry to further validate the successful work in Phase I. We have performed additional tests to those in Phase I which have validated the earlier work. For example, a weak gel was loaded into the sand pack containing 100 mesh a ceramic proppant, Carbo Prop 70 – 170 mesh, at 204 ^{o}C at a rate of 1 ft/day. It was held there for about an hour with a ΔP of 31 psi. This ΔP was a duplicate of a previous run. The rate was increased to 5.35 ft/day with a ΔP of 144 psig before decreasing the rate back to 1 ft/day at a ΔP of 32 psi. In

essence, the rate held. We are still investigating, but believe with a few more runs, our system will be correlatable and the data generated will be viable. The chamber was shut in over the weekend and brought back to a 1 ft/day rate with no back pressure at room temperature. The gel pressure at 1 ft/day under these conditions was 62 psi.

4.2.2 Gel Stability Testing – Dynamic System Improvements

In 2013, efforts were performed to make sense of the results obtained with the pack. To get meaningful results, it was important to understand and make sure that some areas are being included in the project that could give what appears to be negative results. As the runs were performed, potential error elimination occurred to give a confidence level supported by accuracy. For example, we learned that the flow was linear. There was no issue with fluid bypass down the side or channeling through the pack. The tests confirmed that the SPI gels all trailed off to a specific effectiveness over time. We knew the pack was identical with each and every run to a better than 1% accuracy which allowed for the data to be compared directly to the previous test results because of the spherical nature of the proppant

Based on the prior work as outlined in Task 2.0 and building on the key learning from Task 3.0, we proceeded with improving the dynamic system to operate at HPHT in Task 6. Task 3.0 revealed SPI gel formulations that maintained integrity at the maximum pressure and temperature of the system at that time. Thus, for Task 6.0 we

1) Started current system modifications to get to the appropriate HTHP, and
2) Completed verification experiments on the current successful gel formulations on select matrix media.
3) Used the results to modify testing procedure and plan for equipment modification to ensure reliable experimental results at elevated temperatures and pressures.

Figure 24. Hydrostatic Core Holder Showing the Top and Bottom Section.

Modifications include the purchase of a new DAQ system that would allow for improved and more accurate measurements at HPHT. These improvements included the purchase of all equipment, equipment pieces (valves, fittings, pressure regulators, etc.) wiring, and other instrumentation to ensure successful and safe operation, and purchase of equipment pieces that would allow safe HPHT operation.

The high pressure system modifications were completed and we started running tests to verify similar data with new design. The results mimic the testing done previously and therefore can state that the results of the new system are comparable to the old design. Then runs were performed moving to higher temperatures and an evaluation of a new RAA initiator system. At this point the pack load (Carbo ceramics) was the same. Figure 27 shows the results of porosity of Carbo Prop,70-100 mesh material, at three different pressures. The graph shows the standard

volumes of Ar as measured by a wet test meter. The relative porosity was measured by dividing A) Standard volume of Ar from the chamber filled with three separate loadings of the same

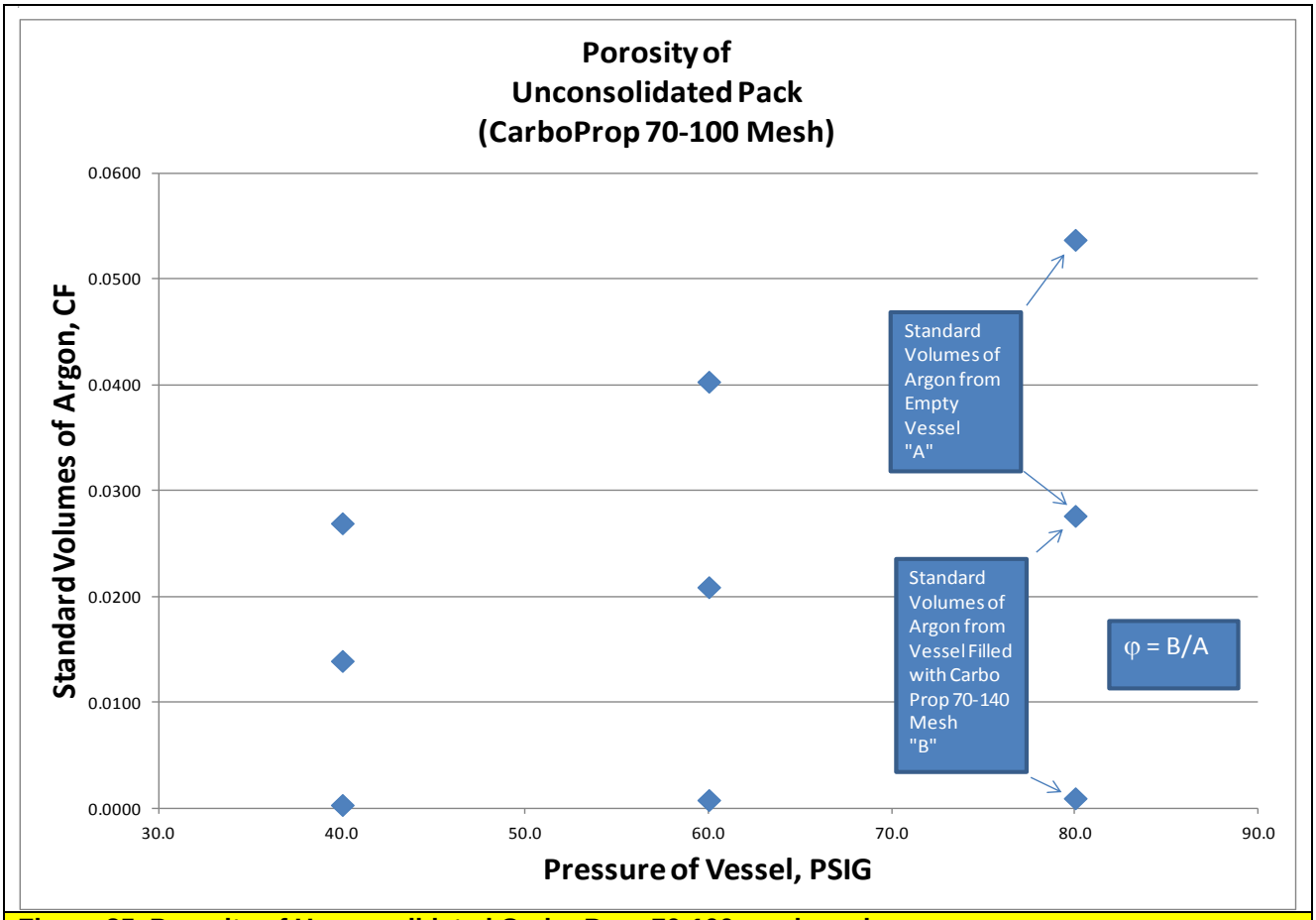


Figure 25. Porosity of Unconsolidated Carbo Prop 70-100 mesh pack.

proppant were tested. The porosity was measured in each case and these results are shown in Table 18. For the first test, after the porosity measurement was completed, tap water was flowed across the proppant (5.6 PV) until the complete saturation of the proppant was accomplished. Next, an internally initiated SPI gel (Phase I preference) was mixed and injected across the Carbo Prop pack. Inlet pressure was stabilized at 30 psig and the SPI gel mix was rushed into the pack. The system was allowed to settle overnight. The next day tap water was flowed across the pack and permeability was measured at different flow rates. Table 19 shows the results of that effort. The Darcy velocity divided by the porosity yields the interstitial velocity. Figure 25 shows real-time pressure drop measurements at different flow rates.

Table 18. Measured Porosity of Unconsolidated Carbo Prop 70-100.

Media	% Porosity
Carbo Prop 70-100 mesh (Test 1)	42
Carbo Prop 70-100 mesh (Test 2)	41
Carbo Prop 70-100 mesh (Test 3)	45
Standard Sand	33
San Andres Limestone/Dolemite	43
Cotton Valley Sandstone	30

Table 19. Verification Experiments on the Unconsolidated CarboProp 70-100.				
Q	**Darcy Velocity**	**Interstitial Velocity**	**Mean ΔP**	**Standard Deviation**
Cc/min	**Ft/day**	**Ft/day**	**Psi**	**St. Dev.**
Tap Water Flowed Across Carbo Prop 70 – 100 Mesh				
0	0	0.0	-0.017	0.40
0.12	0.50	1.2	0.510	0.289
0.24	0.99	2.4	0.528	0.270
1.29	5.35	12.7	0.767	0.273
2.58	10.69	25.5	0.738	0.205
After 1 treatment volume of SPI Gel				
0	0	0.0	0.023	0.67
0.12	0.50	1.2	38.0	9.5
0.24	0.99	2.4	66.0	8.3
1.29	5.35	12.7	138	24
2.58	10.69	25.5	122	31

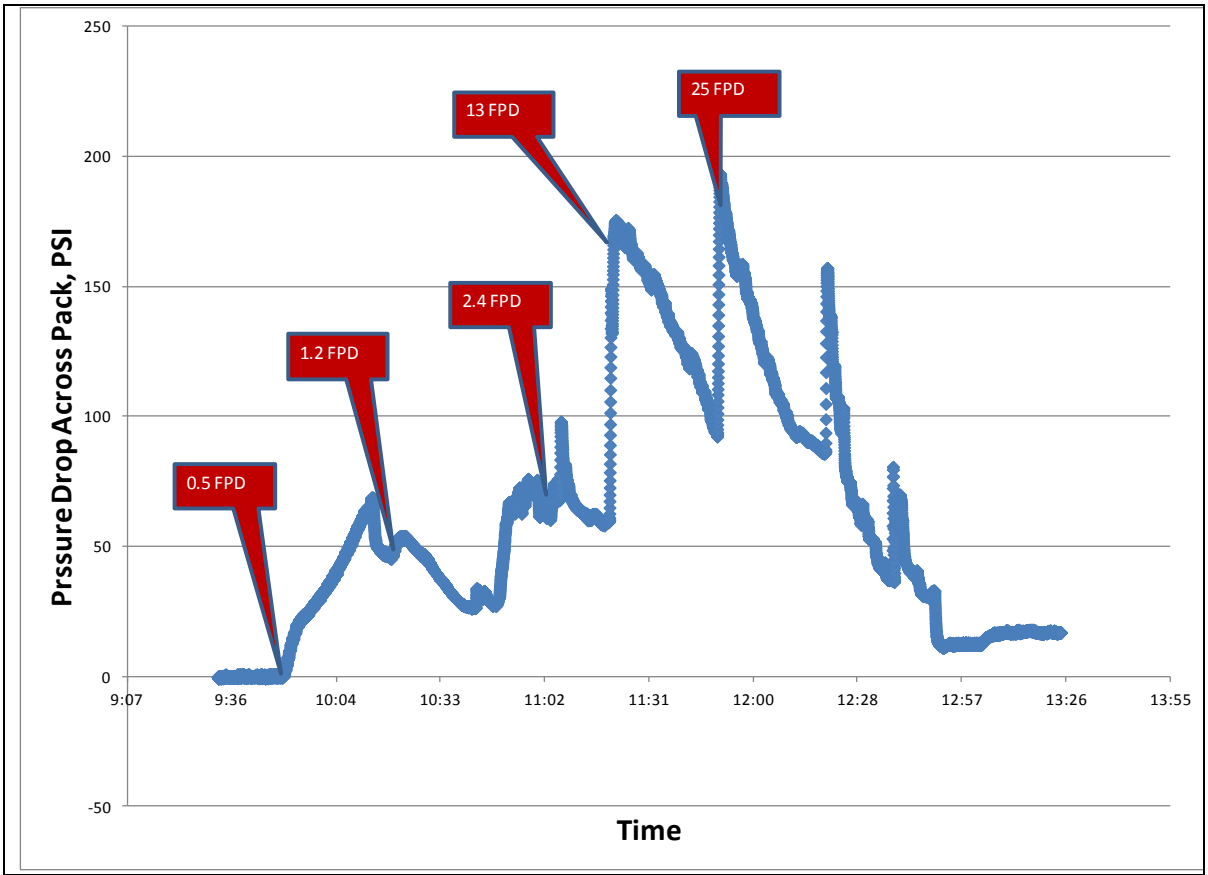


Figure 25. Ambient Pressure/Temperature Permeability of Tap Water Across Unconsolidated Carbo Prop 70-100 Mesh Core at Various Flow Rates.

As we have seen in previous work to test SPI gels to improve conformance in production zones, the improvements fall off rather rapidly, but eventually tend toward an asymptotic result (as we shall see in the 5 day test using proppant and SPI gel formulations). First the internally initiated

SPI gel was injected at a stable inlet pressure of 30 psig; this resulted in the SPI gel mix being pushed through the pack in a relatively short amount of time. Table 20 shows the Residual Resistance Factor (F_{rr}[1]), or the improvement for Carbo Prop proppant treated one time with SPI Gel technology. These results showed the reduction in permeability and the improvement in residual resistance factor, $F_{rr=}$, for one treatment with SPI gels, at ambient temperature and pressure.

Table 20. Water Permeability Before and After SPI Treatment on Unconsolidated Core.

	Carbo Prop 70-100 Mesh Core Packing	
	Without Treatment	One Treatment
A, ft^2	1.27E-02	1.27E-02
Effective Area A/Φ, ft^2	3.02E-02	3.02E-02
DX, 1ft	0.83	0.83
Q[cc/min]	0.12	0.12
Q[bbl/day]	1.09E-03	1.09E-03
Darcy Velocity, fpd	0.50	0.50
Interstitial Velocity, fpd	1.2	1.2
Δ P, psi	0.51	38
μ = Viscosity of Water, cp	1	1
$K=(Q\ \mu L)/((P_1-P_2)A)$= Perm., md	52	0.70
F_{rr} = Residual Resistance Factor		75
F_{rr} = Perm to water before polymer/Perm to water after polymer		
Sheng, J.J. Modern Chemical EOR, Theory & Practice, 2011, Gulf Publishing, p169.		

The next series of tests used a new Carbo Prop 70 -100 proppant pack after the porosity was measured. The system was saturated with tap water and followed by a two dilute 3 cp polyacrylamide (PAM) polymer runs in tap water and then one treatment with a very weak internally initiated SPI gel formulation. We purposely used a very weak gel to verify the dynamic system. We know the gel will fail, but this is not the point since we are testing the system. In Phase I, we made an SPI gel with a Δ P of over 1,000 psi which is generally good enough for field purposes. The permeability was determined. The results are shown in Table 21. The highlighted lines in Table 21 show what levels are injectable at 1 ft/day under practical circumstances in the field.

Table 21. Further Verification Experiments - Unconsolidated CarboProp 70-100.

Q Cc/min	Darcy Velocity, Ft/day	Interstitial Velocity, Ft/day	Mean ΔP Psi	Standard Deviation (St dev)
Tap Water Flowed Across Carbo Prop 70 – 100 Mesh				
0.00	0.00	0.0	0.00	0.44

[1]Betty Felber, PhD., Consultant, "Core Analysis Definitions, Study Conducted for Impact LLC In Support of DE-EE0005958," Oct 28, 2011

0.05	0.21	0.5	0.07	0.40
0.12	0.50	1.2	0.051	0.394
0.24	0.99	2.4	0.068	0.392
1.29	5.35	13.0	0.023	0.356
2.58	10.69	26.1	1.436	0.274
5.17	21.43	52.3	3.108	1.210
After 3 cp PAM polymer, 1st Run				
0.00	0.00	0.0	0.00	0.33
0.05	0.21	0.5	0.21	0.34
0.12	0.50	1.2	0.50	0.40
0.24	0.99	2.4	0.63	0.50
1.29	5.35	13.0	2.40	0.73
2.58	10.69	26.1	3.50	0.70
5.17	21.43	52.3	5.58	0.62
After 3 cp PAM polymer, 2nd Run				
0.05	0.21	0.5	0.22	0.47
0.12	0.50	1.2	0.29	0.44
0.24	0.99	2.4	0.49	0.46
1.29	5.35	13.0	2.70	0.74
2.58	10.69	26.1	5.24	0.68
5.17	21.43	52.3	8.83	0.83
Weaker SPI Gel – One Treatment Only (#113-66-41)				
0.05	0.21	0.5	0.26	1.5
0.12	0.50	1.2	9.0	6.4
0.24	0.99	2.4	41.	7.0
1.29	5.35	13.0	156	22
0.24	0.99	2.4	38	14

The resulting residual resistance factor, F_{rr}, (Table 22) demonstrates the unconsolidated core pack obeys Darcy's law. As the viscosity of the polymer approaches 3, the permeability of the pack and the F_{rr} become the same at 150 md and 1.0 respectively. With the weak SPI gel held until the Δ P exceeded 0.26 psi.

Table 22. Further Verification Experiments - CarboProp.

	Carbo Prop 70-100 Mesh Core Packing			**SPI Gel Treatmt**
	Tap Water	3 Cp PAM	3 Cp PAM	Tap Water
A, ft^2	1.27E-02	1.27E-02	1.27E-02	1.27E-02
Effective Area A/Φ, ft^2	3.02E-02	3.02E-02	3.02E-02	3.02E-02
DX, 1ft	0.83	0.83	0.83	0.83
Q[cc/min]	0.05	0.5	0.5	0.5
Q[bbl/day]	4.53E-04	4.53E-04	4.53E-04	4.53E-04
Darcy Velocity, fpd	0.21	0.21	0.21	0.21
Interstitial Velocity, fpd	0.5	0.5	0.5	0.5
Δ P, psi	0.07	0.21	0.22	0.26
μ = Viscosity of Water, cp	1.00	3.00	3.00	1.00
$K=(Q\mu L)/((P_1-P_2)A)$= Perm, md	154	154	147	42
F_{rr} = Residual Resistance Factor		1.0	1.0	4.0
F_{rr} = Perm to water before polymer/Perm to water after polymer				
Sheng, J.J. Modern Chemical EOR, Theory & Practice, 2011, Gulf Publishing, p169.				

The results of real time pressure drop across the Carbo Prop pack are also consistent with the results of previous work, including the Phase I "Proof of Concept" runs. Figure 26 shows a real time plot of pressure drop across pack versus the time on stream. These results are consistent and are perceived to be a result of adequate saturation of the dry pack with tap water at slow rates prior to determining the permeability improvement with dilute PAM polymer mix and tap water. As Figure 26 shows, the results are very favorable and consistent between the first set and the second set of tests (both shown on the plot in Figure 26). These consistent results

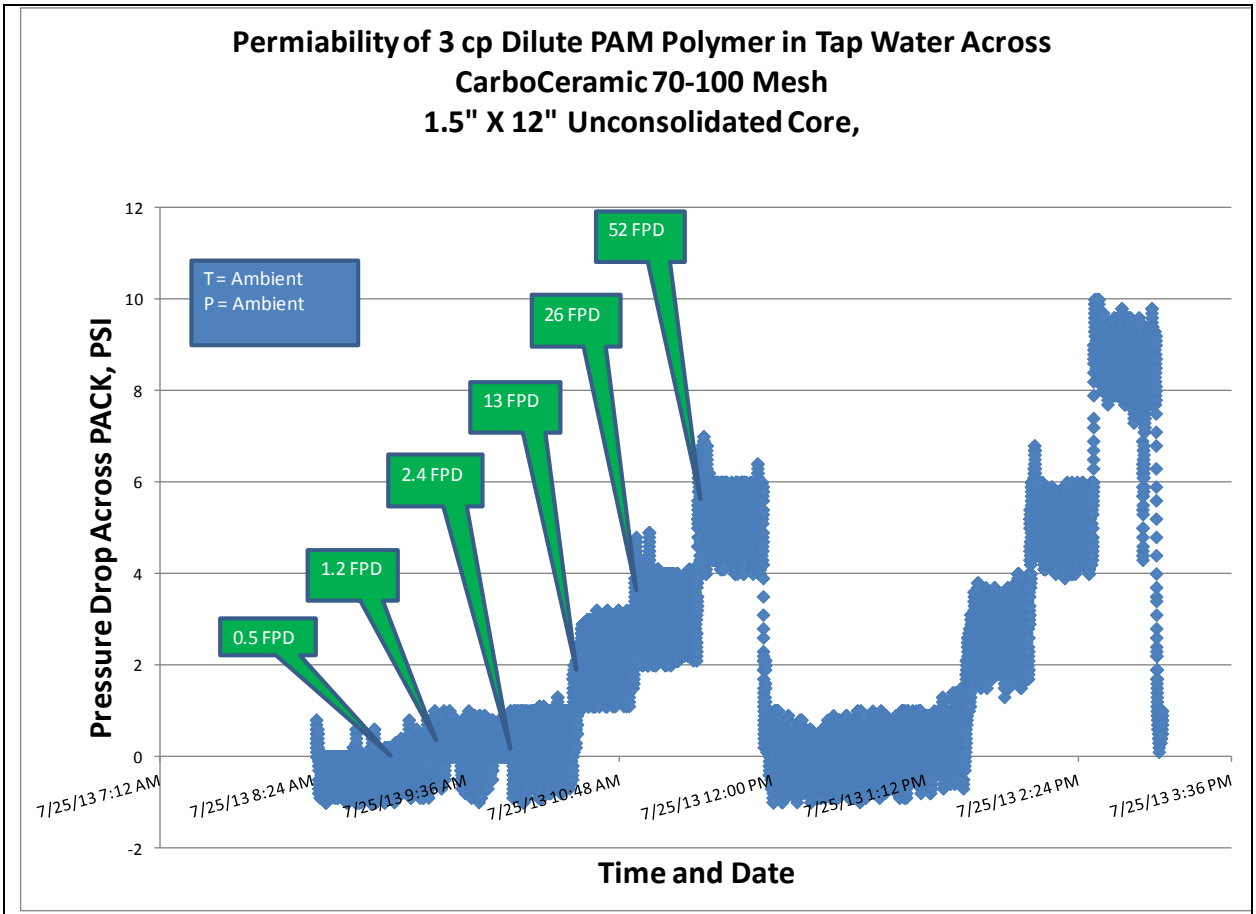


Figure 26. Real Time ΔP Across Carbo Pack System at Different Velocities.

Following the dilute PAM polymer flow, the Carbo Prop pack was treated with SPI gel technology. A weaker SPI gel formulation was chosen because the investigators wanted to see if consistent permeability measurements could be achieved (as compared to the "Proof of Concept" phase of this project where tests had to be stopped because the maximum system pressure (at that time, $\Delta P > 1000$ psi) was reached). Again, the F_{rr} result and the permeability improvement was not optimum since we purposefully chose a weaker gel.

Next, the permeability from a pack made from 1) Carbo Prop 70-100 mesh and 2) Standard sand pack sieved to 20-40 mesh was tested. In this test, dilute PAM polymer in water (3 cp) was flowed across a dry pack and the permeability was measured. Figures 27 and 28 show large pressure drop variations, bypass, and internal plugging and breakthrough with dilute PAM polymer across a dry pack. During the 5 day tests, the pressure drop in either test never

stabilized. The important point in this experiment is we did not pre-flush with water on either the 70/100 Carbo Prop or the 20/40 sand.

The last series of tests, we retrieved a core sample of a commercial consolidated sandstone chosen for SPI Gel treatment for conformance control. This commercial Cotton Valley sandstone was crushed and sieved to 20-40 mesh and loaded into a 1.5" X 12" overburden core holder. After the porosity was measured (Table 24) the dry pack was immediately flushed with dilute 3 Cp dilute PAM polymer (3cp) and the permeability measured. The pressure never stabilized after 5 days

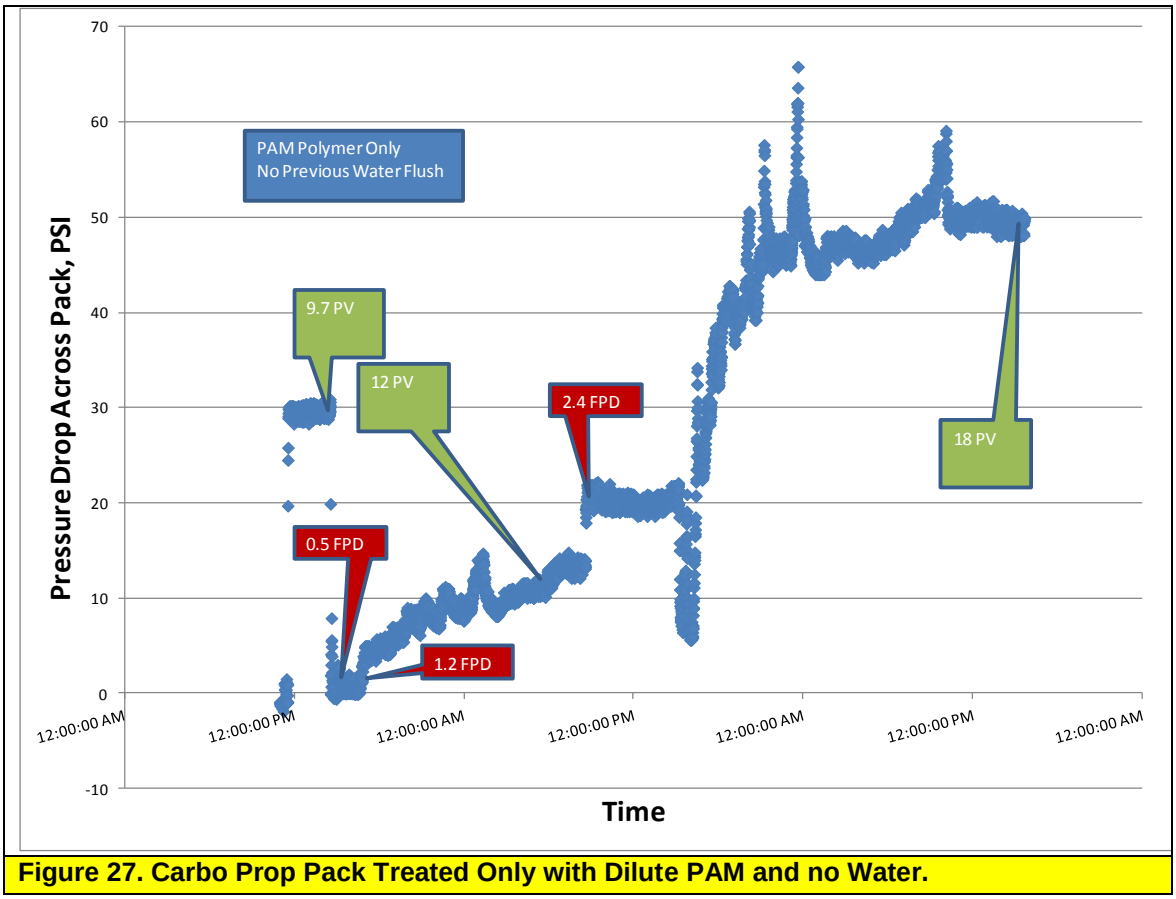


Figure 27. Carbo Prop Pack Treated Only with Dilute PAM and no Water.

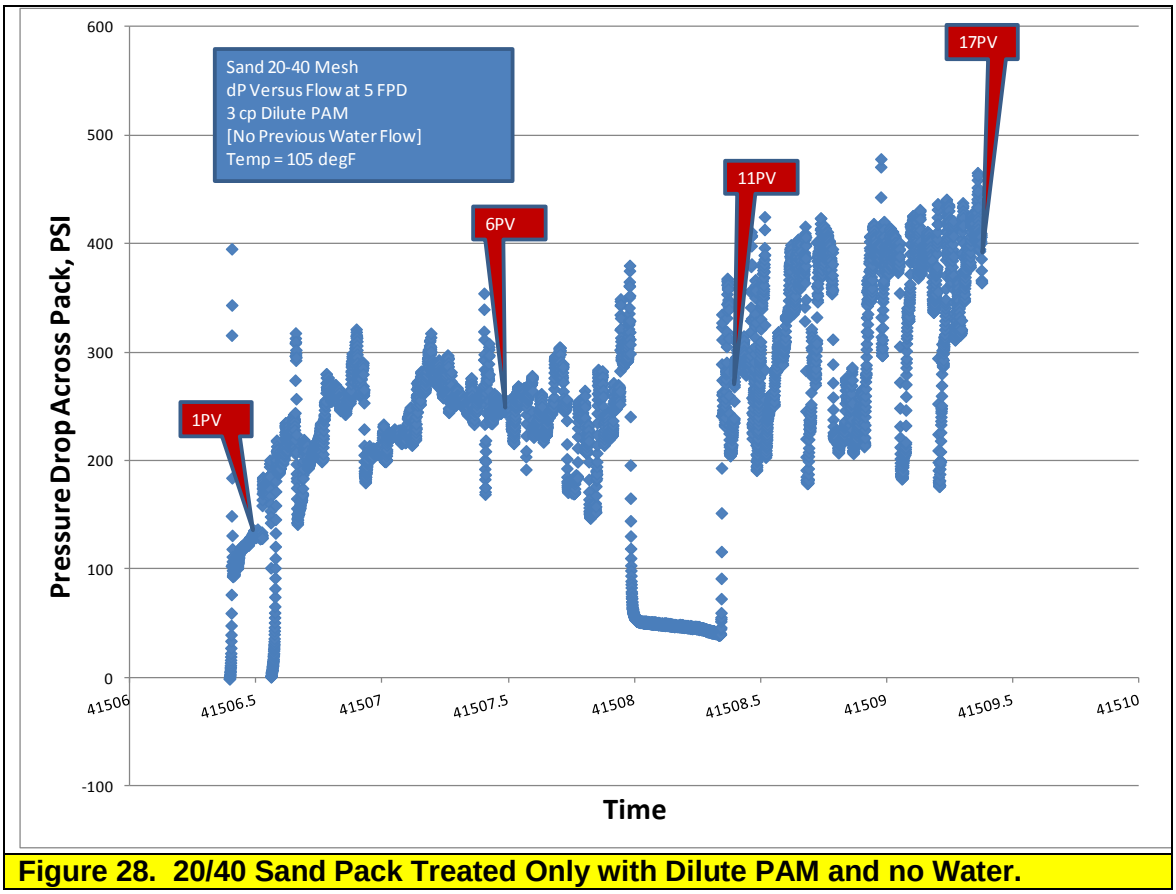


Figure 28. 20/40 Sand Pack Treated Only with Dilute PAM and no Water.

Later the commercial 20/40 sandstone unconsolidated core was treated with SPI gel technology and allowed to sit over night. The permeability was measured and these improvements are shown in Table 23. Table 23 also demonstrates that both dilute PAM polymer improvement for mobility improvement and treatment of SPI Gels on the sandstone make a great improvement over conventional water sweep only.

Table 23. Unconsolidated 20/40 Sandstone Teated with SPI Gel.

	Unconsolidated 20/40 Sandstone Mesh Core Packing			SPI Gel Treatmt
	Tap Water	3 Cp PAM		Tap Water
A, ft^2	1.27E-02	1.27E-02		1.27E-02
Effective Area A/Φ, ft^2	4.23E-02	4.23E-02		4.23E-02
DX, 1ft	0.91	0.91		0.91
Q[cc/min]	0.05	0.05		0.5
Q[bbl/day]	4.53E-03	4.53E-03		4.53E-03
Darcy Velocity, fpd	2.07	2.07		2.07
Interstitial Velocity, fpd	6.9	6.9		6.9
Δ P, psi	0.07	38		64.2
μ = Viscosity of Water, cp	1.00	3.00		1.00
$K=(Q\mu L)/((P_1-P_2)A)$= Perm, md	1234	6.82		1.35
F_{rr} = Residual Resistance Factor		181.0		917

The benefits of using SPI Gel have been demonstrated for internally initiated systems for Carbo Prop, and sandstone reservoirs. Investigators will also determine the performance of SPI gels candidate formulations as discovered in Task 4.0 and also determine the performance of these formulations in EGS matrices.

In conclusion for this section, the progress made for Task 6.0 includes:

1) Improvements planned and ongoing will ensure safe and reliable operation of the dynamic system at HPHT,
2) Verification permeability tests were completed using a weaker gel formulation and tested at lower temperature and pressure for select unconsolidated matrices. These unconsolidated packs include Carbo Prop proppant (70-100 mesh), standard sand (20-40 mesh), and a commercial Cotton Valley sandstone from an actual oil production site (20-40 mesh). Resulting permeabilities measured for these matrices with a weaker gel formulation, and at lower temperature and pressure conditions, were commensurate with permeabilities investigated elsewhere.
3) Therefore, these results give the investigative team the confidence to begin testing for permeabilities (and then zonal isolation) for select matrices and formulations targeting 600°F and 6000 psig. Together with the DAQ system modification nearing completion, the design and installment of equipment and instrumentation to operate at HPHT will follow directly.

4.2.3 Verification of Contacting

Most of the work in Quarter 4, 2013 was focused on developing a proper testing sequence to ensure a more consistent permeability measurement and to validate the testing sequence at lower conditions before embarking at higher pressure and temperature regimes.

In the third quarter, SPI gels were tested in sandstone and limestone/dolomite reservoir formations mainly for oil and gas work. First quarter results, although beneficial, showed inconsistent permeability of SPI gels in the experimental core that was not seen in outside work. [11] Namely, the permeability would fall off during the experimental run. First quarter results also showed that when investigators inadvertently allowed a longer presoaking of the core with tap water (tap water inadvertently left on over the weekend), a more consistent permeability measurement was the result (Compare Figure 8 with Figure 9). Thus, it was felt an experimental artifact of permeability fall off could be eliminated, and a more phenomenological permeability measurement using the core apparatus would result, with additional presoak time.

To develop an effective presoaking sequence targeted at eliminating this artifact of permeability fall off, a series of experiments were completed in the 4th quarter. An initial sequence, outlined below, was established for permeability experiments using our HPHT experimental coreholder:

Experimental Sequence

1. Load core holder with sandstone, granite, limestone, Berea, or other commercial material.
2. Measure porosity (each flow rate was held for 1 hour).
3. Presoak the core material with tap water at 0.05 cc/min tap water across pack (initially 1 day).
4. Measure permeability at various space velocities (each flow rate was held for 1 hour).

5. Presoak with water/PAM polymer mix (1 day soak time).
6. Measure permeability with water/PAM polymer mix (each flow rate was held for 1 hour).
7. Inject internally initiated SPI Gel mix (1 day soak time).
8. Measure permeability of SPI Gel in core with tap water (each flow rate held for 1 hour).

To determine the effect of presoak and its effect on measured permeability, the investigators choose Carbo Ceramic proppant as the core matrix since this proppant is high crush strength, very consistent sieve size, low inter-particle porosity, and less friable than either sandstone and other commercial material.

First quarter results also indicated that gel strength was maintained for a short time for our strongest candidate SPI gel formulation at elevated temperature. Eventually we stopped our experiment when system pressure was reached. So, to develop a proper testing sequence to allow for adequate soaking in our coreholder apparatus and to validate our system for HPHT operation, a weaker gel formulation was chosen (about ¼ of the SPI gel formulation mixed in water of the strongest SPI gel formulation).

A method was devised to measure porosity in Quarter 3, 2013. Table 24 shows the measured porosity of Carbo Prop, 70-100 mesh material used for experiments conducted in Quarter 3, 2013. The mass of proppant loaded into the coreholder, and the pack dimensions for all three experiments, were essentially identical.

Table 24. Measured Porosity of Unconsolidated Carbo Prop 70-100.

Media	% Porosity
Carbo Prop 70-100 mesh (Test 1)	36.0
Carbo Prop 70-100 mesh (Test 2)	36.2
Carbo Prop 70-100 mesh (Test 3)	36.0

Three separate tests were completed using the same experimental sequence as listed above. The only parameter changed was the time allowed for the proppant to soak with tap water at 0.05 cc/min from 1-3 to 1-5 days. Table 25 shows that although the same weak SPI gel formulation was used for all tests, the permeability drastically changed (signified by the delta pressure change).

Comparing the pressure drop for the water/PAM polymer mix across the water soaked pack, the pressure drop was not consistent as the soak time increased (from 1-3 to 1-5 days). Our team will continue to develop experimental changes to ascertain the appropriate soak time for the water/PAM polymer mix.

Table 25. Measured Porosity of Unconsolidated Carbo Prop 70-100.

Q	Darcy Velocity	Interstitial Velocity	1 Day Soak w/ H_2O		3 Day Soak w/ H_2O		5 Day Soak w/ H_2O	
cc/min	fpd	Fpd	Mean dP, psi	Stdev	Mean dP, psi	Stdev	Mean dP, psi	Stdev
Tap Water Only								
0	0	0.0						
0.1	0.41	1.2	1.040	0.48	0.850	0.27	1.61	0.55

3 cp Superfloc PAM Polymer, 1st Run								
0	0	0.0	-0.7	0.27	-0.5	0.31	0.04	0.74
0.05	0.21	0.6	1.09	0.27	1.72	0.27	1.18	0.34
0.12	0.50	1.4	1.87	0.60	1.81	0.27	0.54	0.31
0.24	0.99	2.8	3.01	0.28	1.62	0.31	0.31	0.27
0.48	1.99	5.5	2.61	0.37	2.01	0.36	0.51	0.28
Weaker Gel 1 Treatment Only (#113-66-41)								
0	0	0.0	-0.7	0.27			Max System Pressure	
0.05	0.21	0.6	23.0	10	174.0	123		
0.12	0.50	1.4	68.3	6.3	396.0	21.0		
0.24	0.99	2.8	84.1	4.7	403.0	14.0		
0.48	1.99	5.5	92.4	6.1	415.0	17.0		

4.2.4 Remodeling Effort for the Dynamic Gel Testing Apparatus for HTHP Conditions. (June 30, 2014)

Parts lead time, pump breakdowns, and sheer raw configuring of the system for the HTHP configurations has been very challenging. This is due to the changes in the limitations of seal design since the original proposal and components said to be available at that time on a lab scale. Progress is being made daily and the system is coming together. It seems all major hurdles have been overcome.

Most all of the component parts to run HTHP have been received and installed. The water side of the pack is holding over 6000 psi H_2O at a loss of 0.000150 ml/min. The anticipated flow rates of the experiment will be at .01 to .05 ml/min. The leak rate will be inconsequential to the experiment. The silicon oil has arrived so work will commence on the overburden pressure side that must be at or less than the leak rate of the pack. The overburden pump will be rewired in approximately three weeks by an electrical company. The new HTHP system will be tested at lower pressures and a couple runs must be completed for baselines with the new equipment so that there is an operational understanding of how the system will perform. If all goes well, the pumps function correctly, data collection is flawless, and the system works as planned, data should begin to be collected in Quarter 3 of 2014.

Task 7 - Dynamic/Field Testing and Candidate Verification

4.2.5 Summary of HTHP Flow Tests with Carbo Ceramic Packing

The flow tests were conducted utilizing Carbo Ceramics CarboProp 70-100 to create the porosity in the heterogeneous unconsolidated sleeve. The Carbo Ceramics material was contained in a 1.5” ID silicon sleeve of 3.5” X 12” Stainless Steel core holder pack used as a pressurized chamber. End caps were applied at the entrance and exit. This core holder was placed into a heating jacket with a thermocouple to detect the reaction temperature. The temperature was raised to the targeted range. In all tests overburden pressure was applied so that water would not vaporize. The overburden pressure varied from 500 to 2,000 psi depending on the test temperature. After the reaction vessel was at a stabilized temperature, three pore volumes of the selected gel solution were injected into the reaction vessel. The solution was over displaced at the entrance and exit ends so that the gel would not form in the flow lines. (The exception was when one solution reacted before the 3 pore volumes could be injected.)

Once the gel was formed then water was injected into the reaction vessel at constant rate of 0.24 ml/min. The 0.24 ml/min injection rate was too high for the 360°F second test, thus the rate was decreased to 0.01 ml/min in an attempt to keep the delta pressures below the overburden pressure.

A gas was not used as a back pressure in the previous flow tests. The pressure drops were measured and the raw data analyzed to determine the F_{rr} (Redisual Resistance Factors). The F_{rr} is defined as the pressure after the gel has formed divided by the initial pressure. Weak gels have F_{rr} values in the range of 5 to 20.

In order to calculate F_{rr}, the viscosities of water at the test temperatures were used as shown in Table 26. The viscosities above 320°F were extrapolated from the curve. These viscosities were used to calculate the initial sand pack permeabilities shown in Table 26.

Table 26. Viscosities At Temperature & Initial Reaction Vessel Permeabilities.

Test Date	Formulation	Temp., Deg F	H_2O Vis., cp	Initial Permeability, D
Sept 5, 2014	113-66-41	RT	0.80	412.2
Sept 16, 2014	113-66-207	RT	0.80	412.2
Sept 25, 2014	113-66-207	180	0.35	179.2
Oct 8, 2014	113-66-202b	180	0.35	179.2
Oct 24, 2014	117-46-347	180	0.35	179.2
Nov 6, 2014	117-46-347	360	0.16	82.4
Dec 4, 2014	117-46-347	360	0.16	82.4

These initial permeabilities were the basis for determining the $F_{rr's}$ shown in Table 27.

Table 27. Summary Flow Test Results From Table 26.

Test Date	Formulation	Temp., Deg F	Results
Sept 5, 2014	**113-66-41**	RT	Flow test had final F_{rr} of 65; Strong gel
Sept 16, 2014	**113-66-207**	RT	Strong gel— F_{rr} 143; Chased with 2 N NaOH; Successful BD*
Sept 25, 2014	**113-66-207**	180	Suspect solution gelled in flow line
Oct 8, 2`014	**113-66-202B**	180	$F_{rr's}$ are 19, 22, & 15; Weakest tested; Old activator
Oct 24, 2014	**117-46-347**	180	$F_{rr's}$ are 112 & 129, strong gel; RAA Activator
Nov 6, 2014	**117-46-347**	360	Very high pressure; F_{rr} 1,363, stronger gel; RRA Activator
Dec 4, 2014	**117-46-347**	360	Changed entrance bypass; F_{rr} for 1st section was 448; Second section was 18,577 and 3rd section was 24,150
Dec 19, 2014	**117-46-347A**	180	1st test diluted RRA; F_{rr} 1st section was 163; 2nd section was 673, and 3rd section was

			1040
Dec 23, 2014	**117-46-347A**	180	Continuation of Dec 19th test; F_{rr} 1st section was 846; 2nd section was 1343
Dec 26, 2014	**117-46-347A**	180	Continuation of Dec 19th test; F_{rr} was 1270
Dec 30, 2014	**117-46-347A**	180	Continuation of Dec 19th test; F_{rr} was 1228
*BD = Breakdown of gel, Section 3.0.			

Using formulation 117-46-347 an RAA gel system only, the temperature dependence is shown in Table 28. This gel at room temperature bench tests was described as weak; however the flow test results at 180°F and above indicate that it forms strong gels and that these fluids do not set into gels so fast that they can't be displaced.

Table28. Temperature Comparison Of 117-46-347 Formulation Results

Test Date	Temp., Deg F	Results
Oct 24, 2014	180	Two after gel flow sections analyzed; F_{rr} numbers were 112 & 129 respectively
Nov 6, 2014	360	One after gel flow section was analyzed; F_{rr} number was 1,363
Dec 4, 2014	360	Three sections analyzed; F_{rr} numbers were 448, 18,577 & 24,150 receptively

These tests demonstrate that the gel strengths formed using the 117-46-347 formulation is directly proportional to temperature. Time dependence data is shown in Table 29. It also shows that this formulation is stable up to and including 360°F. The following Figures are plots from the various pressures recorded. Individual flow test results are summarized below.

Table 29. Time Dependence Of 113-46-347A--Diluted RAA 180 Deg F.

Test Date	Temp., Deg F	Results
Dec 19, 2014	180	Three after gel flow sections analyzed; F_{rr} numbers were 163 @ 0.24 ml/min, 673 & 1040 @ 0.01 ml/min respectively
Dec 23, 2014	180	Two after gel flow sections analyzed; F_{rr} numbers were 846 & 1343 @ 0.01 ml/min respectively
Dec 26, 2014	180	One section analyzed; F_{rr} was 1270 @ 0.01 ml/min
Dec 30, 2014	180	One section analyzed; F_{rr} was 1228 @ 0.01 ml/min

These tests indicate the flow system, even when exposed to 180°F for extended periods of time, continues to remain intact. No leaks were detected throughout the 272 hour test period (11.3 days) and the gel remained undamagedl. The fact that no temperature degradation occurred to the gel is significant because many other gel systems cannot withstand these temperature conditions for extended time periods. Also the F_{rr} numbers for all of the reduced concentration tests were greater than the higher concentration F_{rr} numbers shown in Table 29 at 180°F.

September 5, 2014 Test—113-46-41 Formulation—Room Temperature

The pressure across the reaction vessel is shown in the Figure 29. The analysis shows that the F_{rr} is 65. Even though the bench test results describe this as a weak gel, the flow test indicates that it isn't since weak gels have F_{rr} values in the range of 5 to 20.

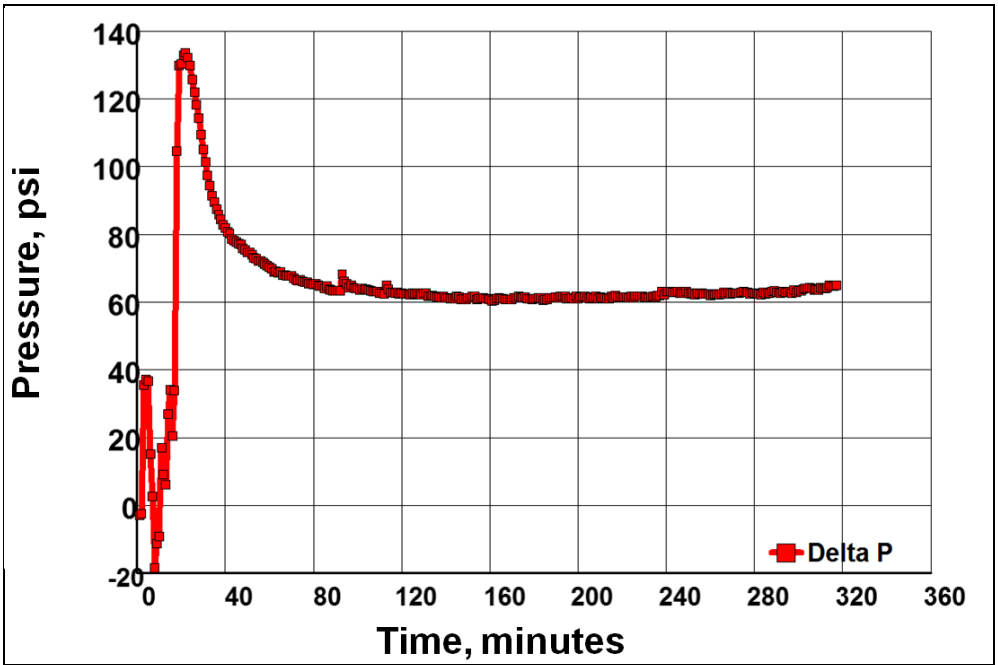


Figure 29. Room Temperature Weak Gel Flow Test.

The maximum pressure change across the sand pack was 135 psi and the minimum was zero. The average pressure was 65 psi. Using this number and the pressure drop across the sand pack at 0.24 ml/min of 1 psi, the F_{rr} was determined to be 65. The maximum pressure was 1,358 psi while the minimum pressure was 46 using an Eldex pump as shown in Figure 30. The average inlet pressure was 1,232 psi. This test was conducted using on overburden pressure of 200 psi.

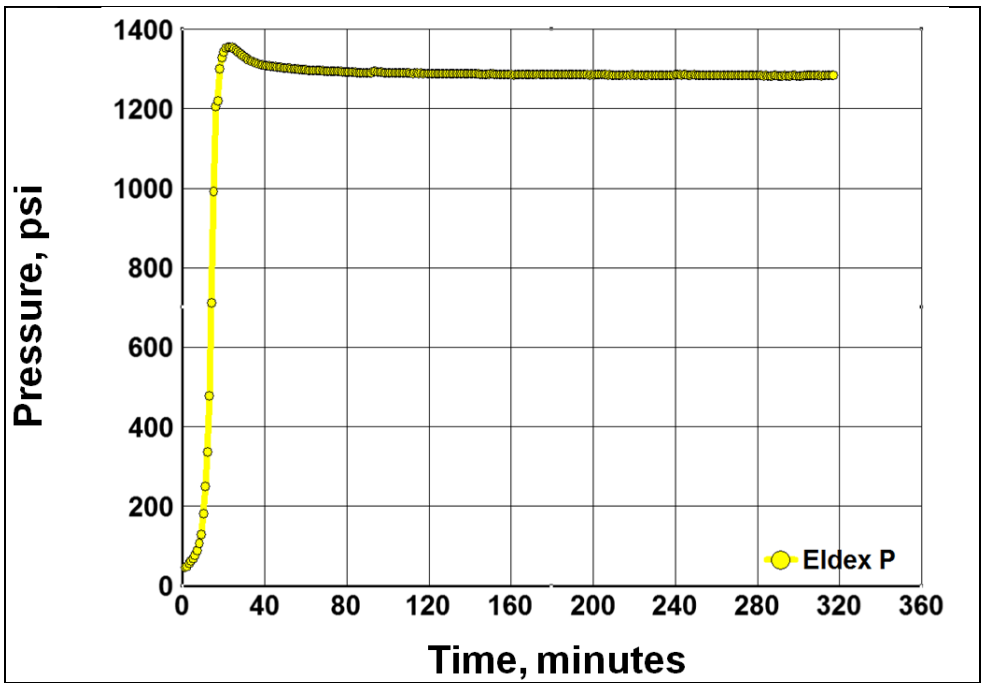


Figure 30. Room Temperature Eldex Injection Pressure.

Both pressure drops are shown in Figure 31. By putting both of the pressure responses on the same plot, the cycling from the syringe injection is not as distinct.

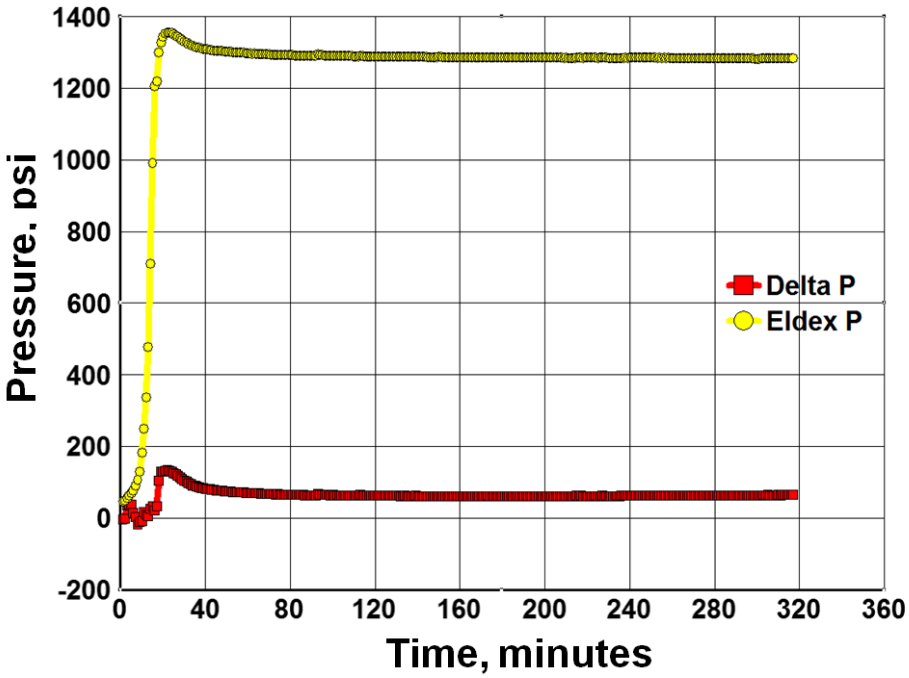


Figure 31. RT Eldex Injection Pressure & ΔP Across Reaction Vessel.

September 16, 2014 Test—113-66-207 Formulation—Room Temperature

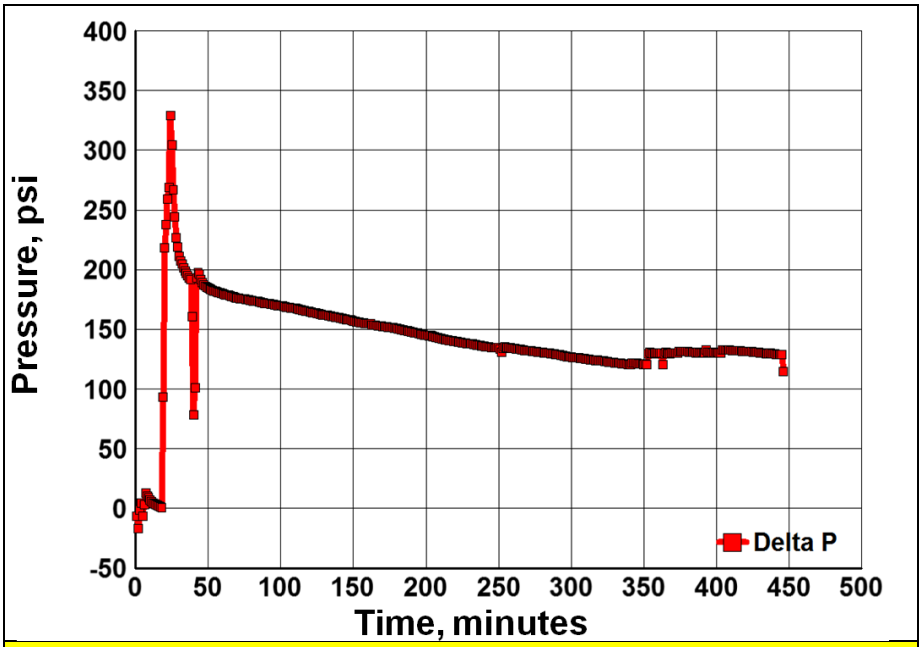


Figure 32. Delta Pressure Across Reaction Vessel At Room Temperature--Stronger Gel.

The second flow test in this series, shown in Figure 32, was conducted on September 16, 2014.

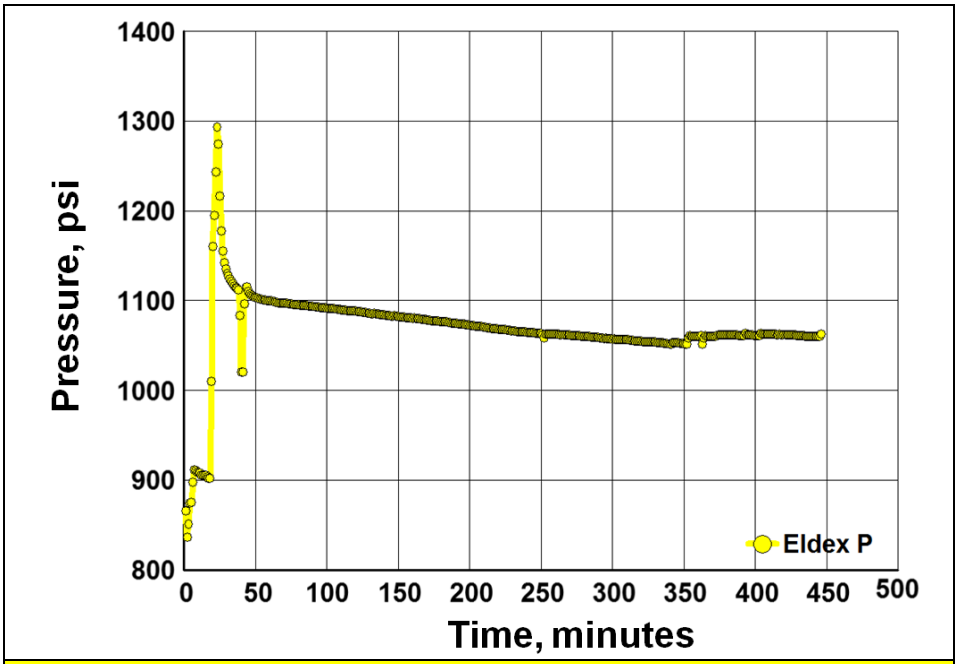


Figure 33. Eldex Injection Pressure Strong Room Temperature Gel.

This was to test a strong room temperature gel based on the bench tests reported previously. The maximum pressure in Figure 33 was 373 psi. The minimum pressure recorded was zero.

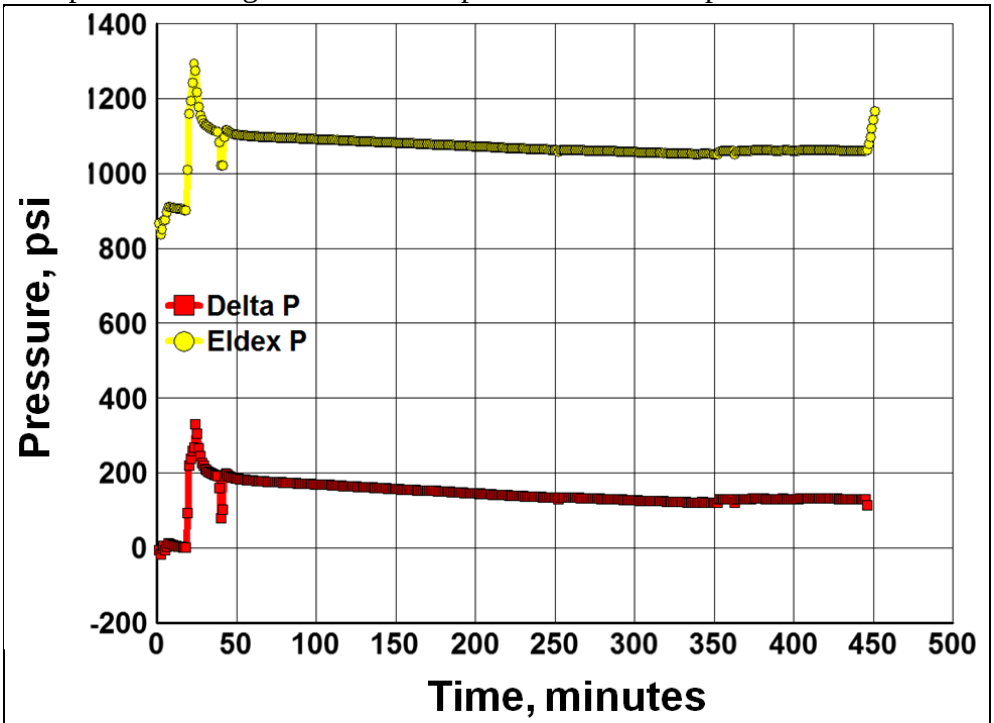


Figure 34. ΔP & Injection Pressure Strong RT Gel.

The average pressure was 143. Using 1 psi as the base pressure drop at 0.24 ml/min, the F_{rr} was determined to be 143 making this a strong gel. The inlet pressure ranged from 43 to 1,393 psi in Figure 34. The average inlet pressure was 1,073 psi. The overburden pressure was 350 psi. Figure 35 depicts the test pressure responses from the inlet pressure. Figure 36 contains both of the above pressure responses. Notice that the syringe cycling is not as noticeable.

September 25, 2014 Test—113-66-207 Formulation—180°F

This first elevated temperature attempt failed. The gel solution set up in the flow lines before the injection could be completed.

October 8, 2014 Test—113-66-202b Formulation—180°F

The first successful flow test at 180°F was conducted using SPI gels. The core media was Carbo Prop 70-100 mesh. This unconsolidated flow test consisted of saturating the Carbo Prop with Bartlesville tap water to determine the permeability. The test system was heated to 180°F. The overburden maximum pressure was 1,841.4 psi.

After the flow system reached temperature stability, the activated SPI weak gel system solution was injected through it. Three pore volumes were injected to increase the probability that the core was saturated. This gel system had a gel time long enough to complete the three pore volume injection at 180 ^{o} F. Bench tests indicate that a medium non-ringing gel is formed over night; therefore it was allowed to set up over night in the pack. The next morning Bartlesville tap water was injected at approximately 1 foot per day to determine the amount of flow reduction achieved from this weak gel system. Figures 35, 36, and 37 depict the pressures measured during the flow test.

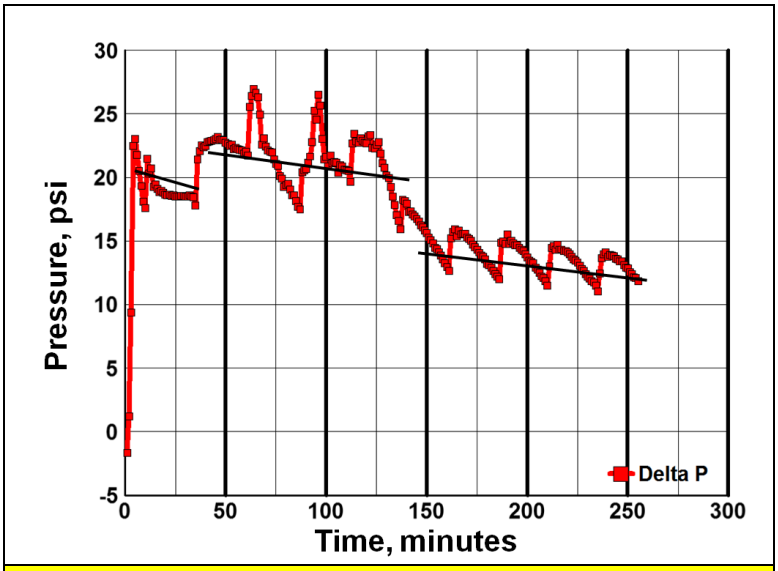


Figure 35. Delta Pressure Across Ceramic Pack 180 Deg F--Weak Gel System.

The plot in Figure 35 depicts the average pressure over one minute. The cyclic pressure responses are the result of the stroke in the pump used to inject the water into the core not necessarily the response from the gel in the media. The maximum Δ P is recorded as 29.4 psi. The minimum pressure recorded was -3.4 which is impossible. One has to assume that the initial Δ P is zero.

The average pressures are shown by lines for the three distinct sections of the flow test. The average pressure for the first section is 19.2 psi. The average pressures for sections 2 and 3 are 21.9 and 14.7 respectively. The ~67% reduction between sections 2 and 3 are characteristic of this gel system and this activator.

The flow reduction factors for this gel by section were 19, 22, and 15 respectively are shown in Figure 36. These high flow reduction factors indicate that the gel formed was a "weak" gel and is consistent with the bench tests. Further evaluation of the flow test was targeted the inlet flow characteristics. Figure 38 shows the pressures recorded for the inlet. The inlet pressure was designed to be ~265 psi greater than the overburden pressure. The maximum inlet pressure recorded was 1,575.6 psi. The minimum pressure was 1,480.5 psi. Again the average pressures are shown by the black lines. The first section average is 1,562 psi which section 2 is 1,566 and section 3 is 1,553.

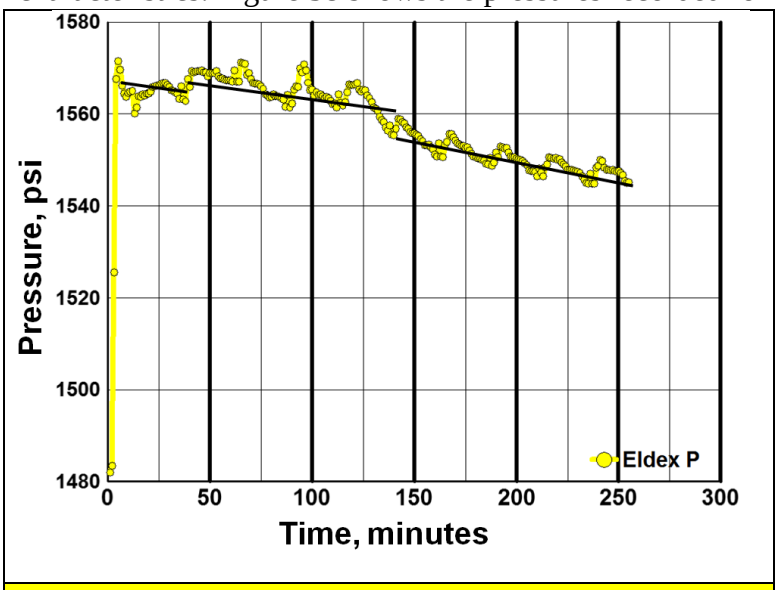


Figure 36. Inlet Pressure For Ceramic Pack At 180 Deg F Weak Gel System.

Figure 36 shows the two pressures together. Note that because of the differences in these pressures, the surging of the injection pump is dampened. This test was successful both from the equipment being tested for the first time at elevated temperatures and the gel system lowering the flow pack permeability significantly. Other elevated temperatures will be tested with gel systems initiated by different activators.

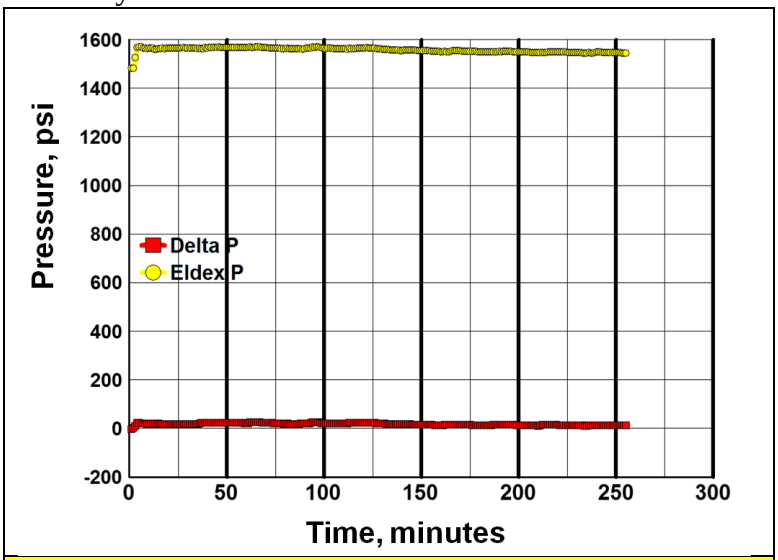


Figure 37. Delta P & Eldex Pressure 180 Deg F RAA Activated Gel

October 24, 2014 Test - 117-46-347 Formulation - 180°F

This is the first test conducted with the Reduced Acid Activator (RAA) system. It was successful. Figure 40 shows the results. The maximum pressure across the reaction vessel was 695 psi and the minimum was 39 psi. There are two sectors which were analyzed separately. In

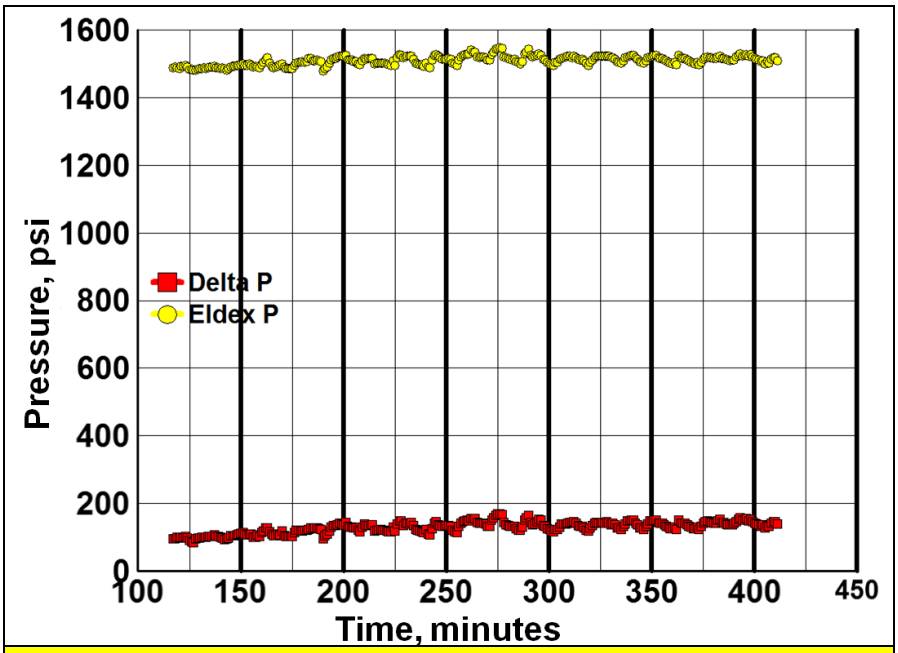


Figure 38. Δ P & Eldex Pressure at 180 F for an RAA Activated Gel.

the first one, the average pressure was 112 psi. This yielded an F_{rr} of 112. The second section had an average pressure of 129 which means that the F_{rr} was 129. The inlet pressure in the Figure 38 shows that the maximum was 1550 psi with a minimum pressure of 1480 psi. The overburden pressure was approximately 600 psi. The figure above depicts the inlet and **Δ** P. Even Even with these two plotted together, the cycling of the syringe pump is evident.

November 6, 2014 Test—117-46-347 Formulation—360°F

This is the first attempt at conducting a flow test at 360°F is shown in Figure 39. It was very

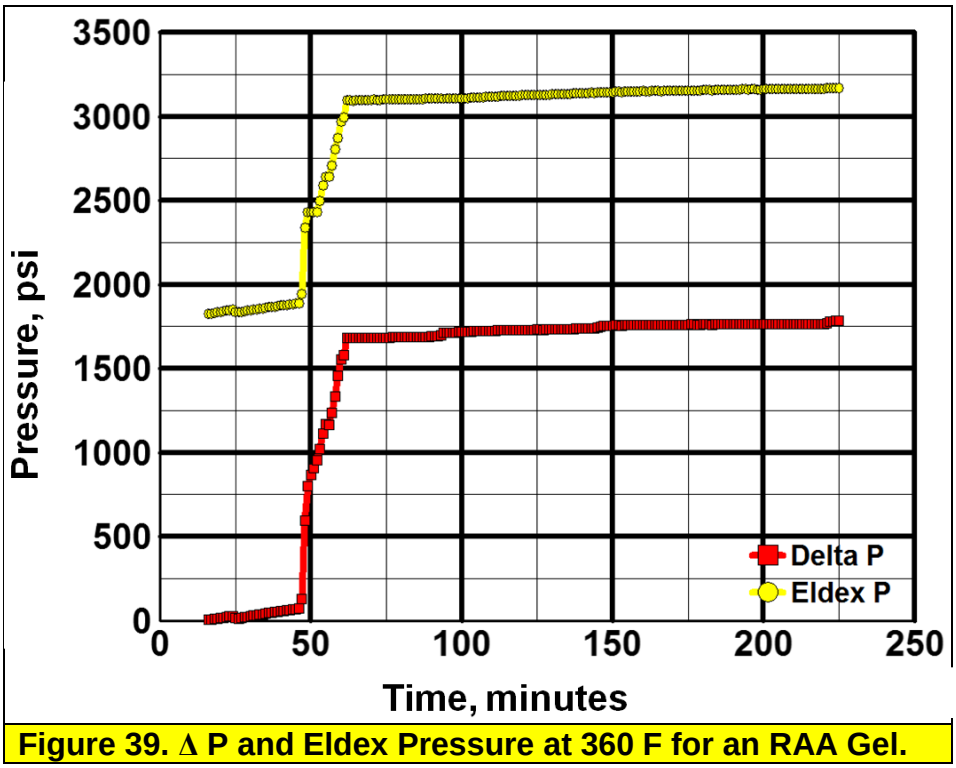


Figure 39. Δ P and Eldex Pressure at 360 F for an RAA Gel.

successful. Note that the pressure across the reaction vessel continues to increase throughout the test. This is the first gel system to ever respond in this manner.

The maximum pressure drop across the reaction vessel was 1,785 psi and the minimum was zero. The overall average Δ P was 1,363 psi. The F_{rr} is 1,363. This is an extremely strong gel. The best characteristic of this formulation was that it could be injected in an appropriate amount of time at this temperature. The pressure response at the inlet of the flow system is also shown in Figure 39. The maximum pressure was 3,167 psi and the minimum was 1,825 psi. The overburden pressure was about 110 psi. This was necessary because the inlet pressure was so high.

Figure 39 shows both of the pressure tracts. Note that the typical syringe cycling was essentially absent. The high pressure on both curves serves to dampen the cycling.

December 4, 2014 Test—117-46-347 Formulation—360°F

The second run conducting a flow test at 360°F was also very successful. During the gel solution saturation of the unconsolidated flow pack, the pressure continued to increase to 62 psi four minutes after the injection ceased. Six minutes after the injection creased the Δ P across the pack was 20 psi. It then decreased rapidly until the pressure drop was less than 1 psi. The increase in pressure is the result of inertia during the rapid injection rate during gel solution placement. The solution was then allowed to react overnight to form the gel throughout the flow pack.

When water injection began after gelation, the gel was so strong that the pressure across the reaction vessel continued to migrate toward the overburden pressure so that the test had to be halted several times. The flow rate also had to be decreased to 0.01 ml/min as a result. The final flow mirrors the first 360°F test since it continues to increase in pressure rather than reach a maximum and decrease to approximately 50 % of the maximum per gel systems with different activators. This confirms that the previous 360°F results of increasing Δ P across the sand pack with no pressure drop. Figure 40 depicts these results based on one minute averages.

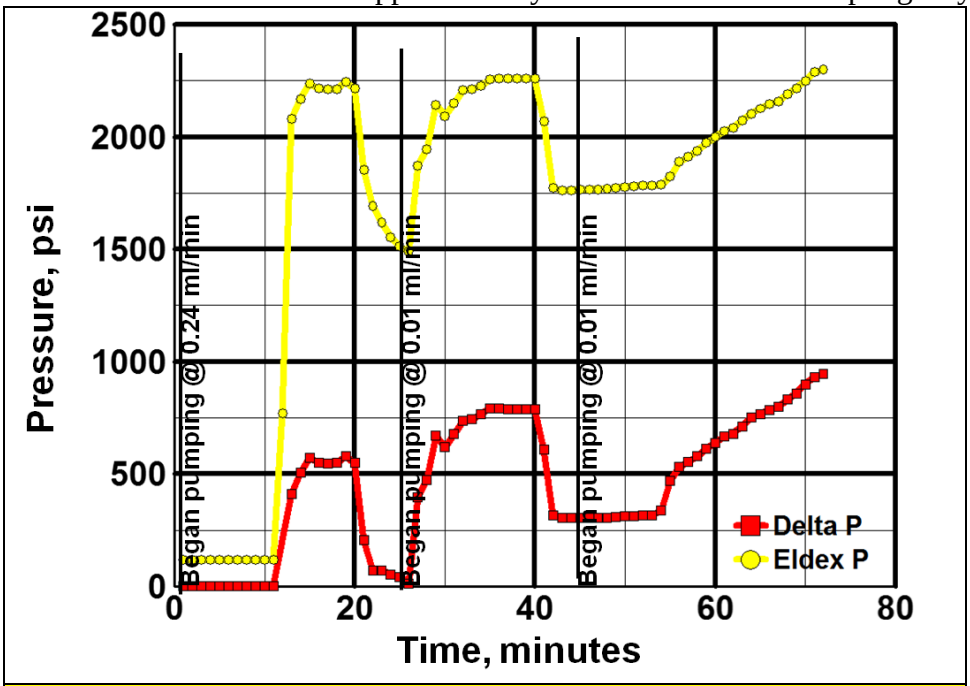


Figure 40. Δ P and Eldex Pressure At 360 F - Second Test.

The maximum pressure in the first section was 772 psi while the average at the top was 533 psi. The second section maximum pressure was 824 with the average being 725

psi. The third section continues to increase even at the very low injection rate of 0.01 ml/min. The maximum pressure reached 966 psi. The respective RRF numbers are 448, 18,577 and 24,150. This means that the gel never did break down. This is similar to the same gel system tested on November 6, 2014. The Eldex pressure mirrors the Δ P plot with respect to pressure variances. Note that the surge pressure is not visible because of the high pressure.

When both pressures are plotted on the same graph the results look like this. Note that there is no lag time between the Eldex and the change in the pressure across the pack as the injection rates were changed. This means that the system was liquid filled. This group of plots confirms the November 6, 2014 experiment that a very strong gel was produced at 360°F.

December 19, 2014 Test—117-46-347A Formulation—180°F

This was the first test conducted with a reduced concentration of the gel system because the previous concentrations produced very strong gels. The purpose was to determine if a weaker gel could be produced using the basic gel formulation. The "saw tooth" nature of the pressure responses are produced as the flow test pressures recorded continues to approach the pressure differential limits of the ceramic pack container. It was necessary to stop the flow to adjust the pressures. This indicates that a very strong gel was also produced with this reduced concentration

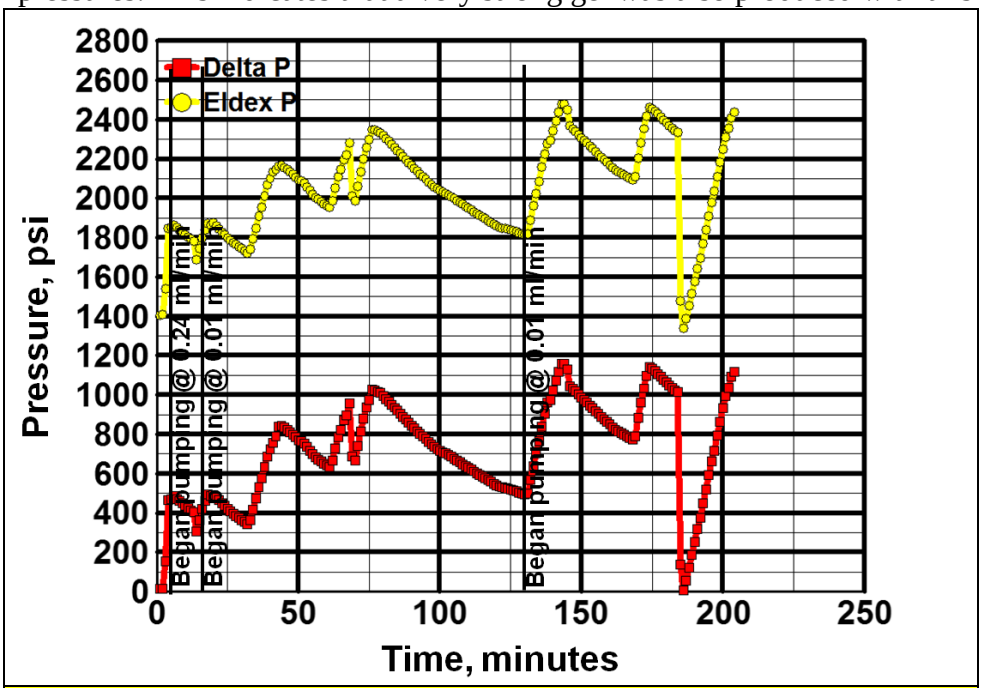


Figure 41. Δ P and Eldex Pressure Tracts For 12-19-14 Test.

0.24 ml/min could not be tolerated except for a few minutes. It became necessary to decrease the rate to 0.01 ml/min and even then it was impossible to inject the chase water continually. Both pressure tracts are depicted in the Figure 41. This Figure is included to easily view the pressure tract similarities.

gel formulation. The pressure continues to increase throughout the test rather than reaching a maximum and declining to approximately 50% for the remainder of the test. The Eldex pressure mirrors the "saw tooth" pressure responses of those across the flow pack. The higher flow rate of

December 23, 2014 Test—117-46-347A Formulation—180°F

The pressure tract is shown in the Figure 43. Even though it was necessary to start and stop the flow test several times, there was essentially two major pressure breaks as the pump is turned off

and on. The center section represents the pressure maintained while the pump was shut-off for about one hour. The final flow also is characterized by continuing to increase in pressure rather than decline as it had in the earlier tests with other activators. The Eldex pressure parallels the pressure responses for the pressure drop across the flow pack. Both pressure responses are illustrated in Figure 43. Figure 43 is included to demonstrate how the pressure responses mirror each other.

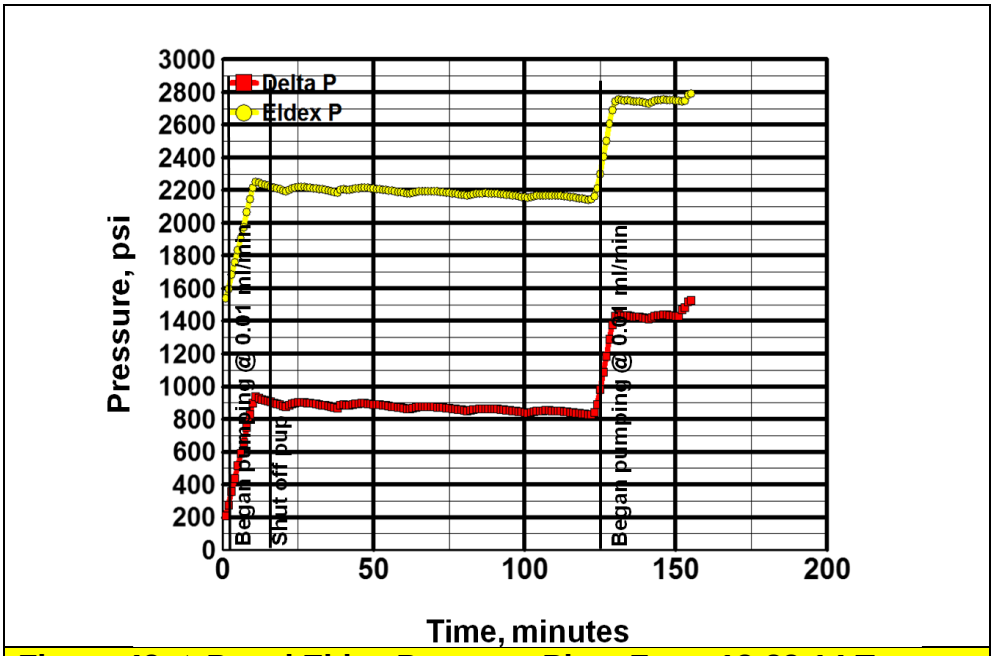


Figure 43. Δ P and Eldex Pressure Plots From 12-23-14 Test.

December 26, 2014 Test—117-46-347A Formulation—180°F

To further test the system, water was injected into the flow pack at 0.01 ml/min on the subject date. The Δ P across the flow pack is shown in Figure 44. Note that it took only 6 minutes to reach the pressure limit. Also note that the cycling usually seen during testing is absent from this test. The Eldex pressure tract doesn't have the cycling that is usually present. It could be that the injection container didn't need to reload since the test length was so short. Certainly they are parallel and smooth throughout the six minute test.

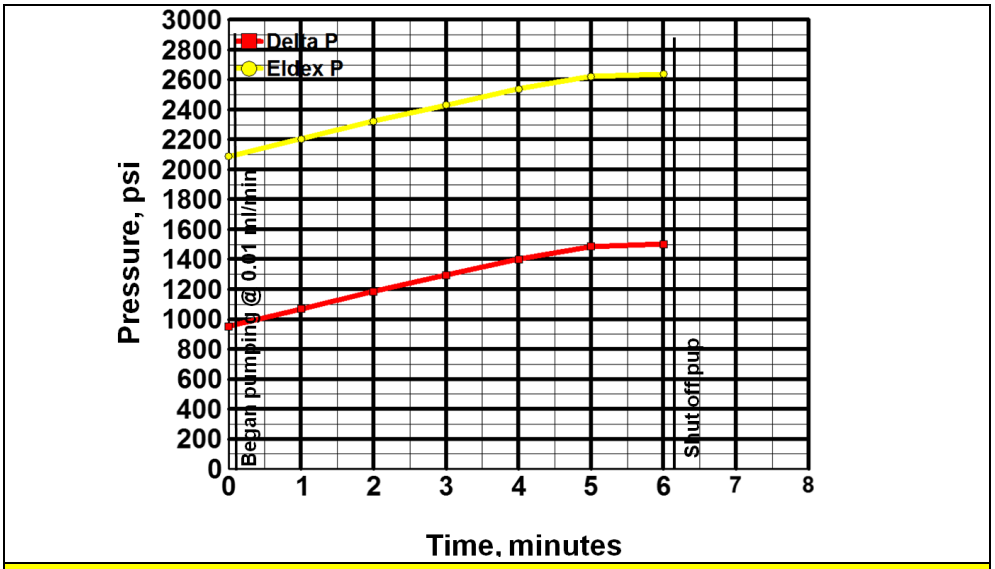


Figure 44. Δ P and Eldex Pressure Plots From 12-26-14 Test.

December 30, 2014 Test—117-46-347A Formulation—180°F

This is the final flow test for the gel formed by this formulation. It continues to show that the gel system hasn't broken down by being exposed to this relative high temperature. The Δ P plot is shown in Figure 45. It took only about 8 minutes for the pressure to build up near the limit. The Eldex pressure is included in the Figure 45. Since this injection is short, the cycling from the injection pump is not observed. This short test was necessary because the pressure limit was approached during it.

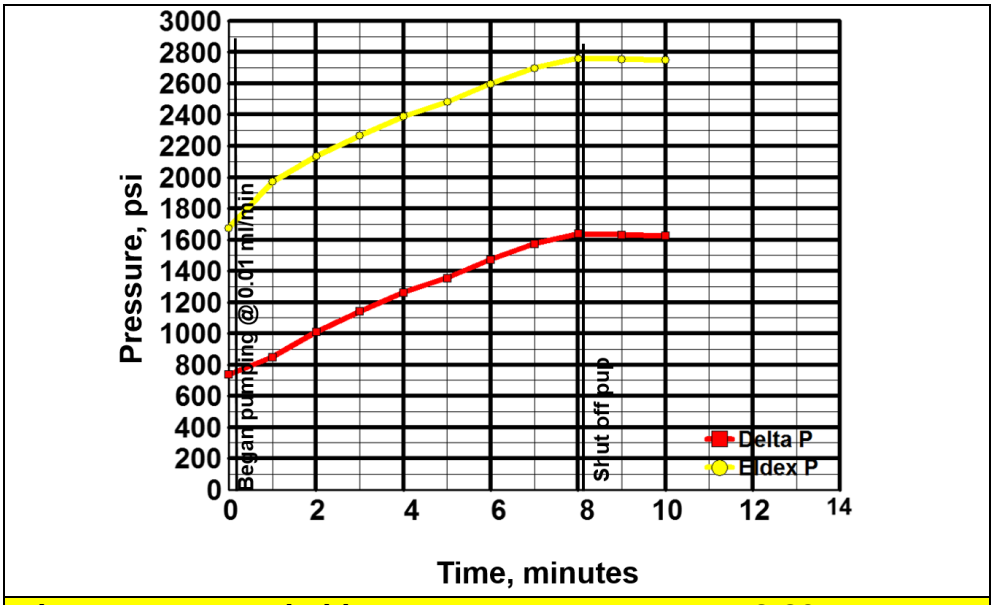


Figure 45. Δ P and Eldex Pressure Tracts From 12-30-14 Test.

The final two data points are included to show the slow decline in pressure after the pump was shut-off. Remember that this test was monitored for seven hours before the temperature was turned off. The pressure was still high before the termination.

April Flow Test Summary

Two high temperature flow tests were conducted during April 2015. These are the first ones to be conducted since the new high temperature, high fluid resistant end caps were installed. The new bypass valve was also tested to determine if it worked as designed. This is also the highest temperature to be attempted: 480 ± 5 ^{o}F. The gel formulation was the same in both of these tests. The flow media was Carbo Prop 70-100 mesh. This unconsolidated flow test consisted of saturating the Carbo Prop with Bartlesville tap water to determine the initial permeability of 1,234 mD and then increasing the system temperature to near 480 ^{o}F.

April 10, 2015 SPE-RAA Activator Flow Test #1

On April 10, 2015 the first flow test was conducted. The average temperature for this test was 479°F. The goals were to determine if the SPI-RAA gel system could be controlled at these temperatures and to test the new flow test equipment configuration.

After the flow system reached temperature stability, the internally activated SPI gel system solution was injected through it. Three pore volumes were injected to increase the probability that the core was saturated. This gel system has a gel time long enough to complete the 3 pore volume injection at elevated temperatures. The gel system was allowed to set up overnight. The next morning Bartlesville tap water was injected in the gelled flow pack in order to determine the

the amount of flow reduction achieved from this gel system. Figures 46, 47, and 48 depict the pressures measured during the flow test.

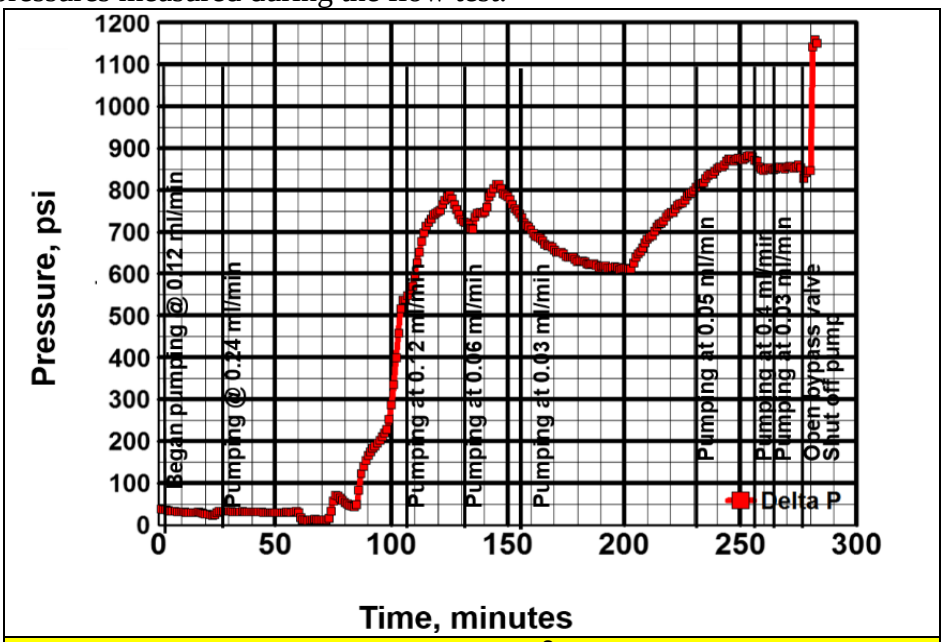


Figure 46. Δ P Across Pack at 479 °F from 4-10-15 Test.

During this test the flow rate was changed eight times as shown by the delineators. The purpose for this was to determine the pressure reaction to the various rates. Sometimes during the flow testing the back pressure needed to the lowered in order to maintain integrity of the inter-sleeve holding the flow media in place. It is unknown why the lower flow rates --0.03 ml/min produced higher pressure drops than the higher rates. It could be that the gel strength continued to increase as the test was in progress or that the overburden pressure which is higher than the initial ones contributed to these higher pressures. There was no gel breakdown during the testing.

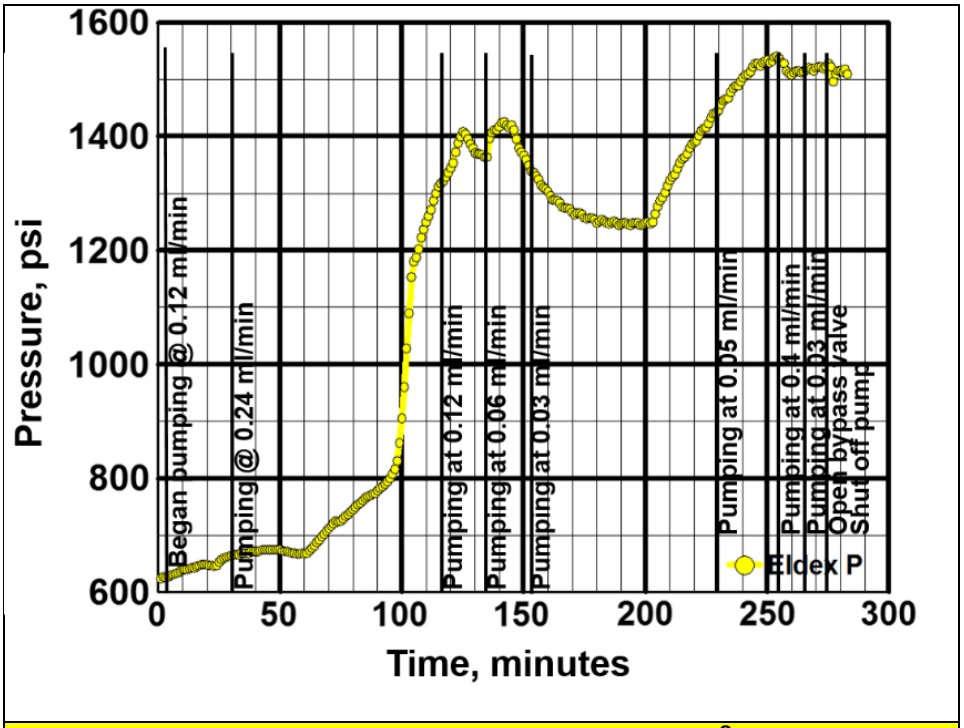


Figure 47. Eldex Pressure Across Pack at 479 °F from 4-10-15 Test.

During the after gelation flow testing, the overburden maximum pressure was 1751 psi. As the flow system was broken down, no gel was observed in the entrance or exit flow lines so this did not contribute to the higher pressures across the flow pack. Eight flow reduction factors were determined. In the Sections the first three F_{rr} values were 61, 81 and 1,359 respectively. These flow reduction

factors indicate that the gel formed was a strong one. The other Sections had F_{rr} values of 3,006, 5,392, 3,888, 5,259 and 7,078 respectively. These flow rates also demonstrate that the gel is a strong and can be utilized at these temperatures and pressures.

The Eldex inlet pressure is shown on Figure 47. Note that the pressure drops in Figure 47 resemble those of that measured across the flow pack. The maximum inlet pressure was 1,543 psi while the minimum was 622 psi.

These pressures also change as the rates vary. Section 1 recorded an average inlet pressure of 639. Sections 2, 3 and 4 recorded average inlet pressures of 648, 729 and 1154 respectively. Sections 5, 6 and 7 recorded 1299, 1396 and 674 respectively. The final Sections recorded 816, 877, 885 and 1518 respectively.

As noted in the pressure drop explanation above, the final flow of 0.03 ml/min pressure drops were greater than the higher rate pressure drops early in the test procedure possibly due to the increased overburden pressures later in the testing procedure. However, it can be a positive in the field application because the longer the gel is exposed to the higher temperatures the stronger it becomes.

Figure 48 has both of the pressure traces on it. The purpose is to show that each pressure tracks the other even as the injection rates are changed several times.

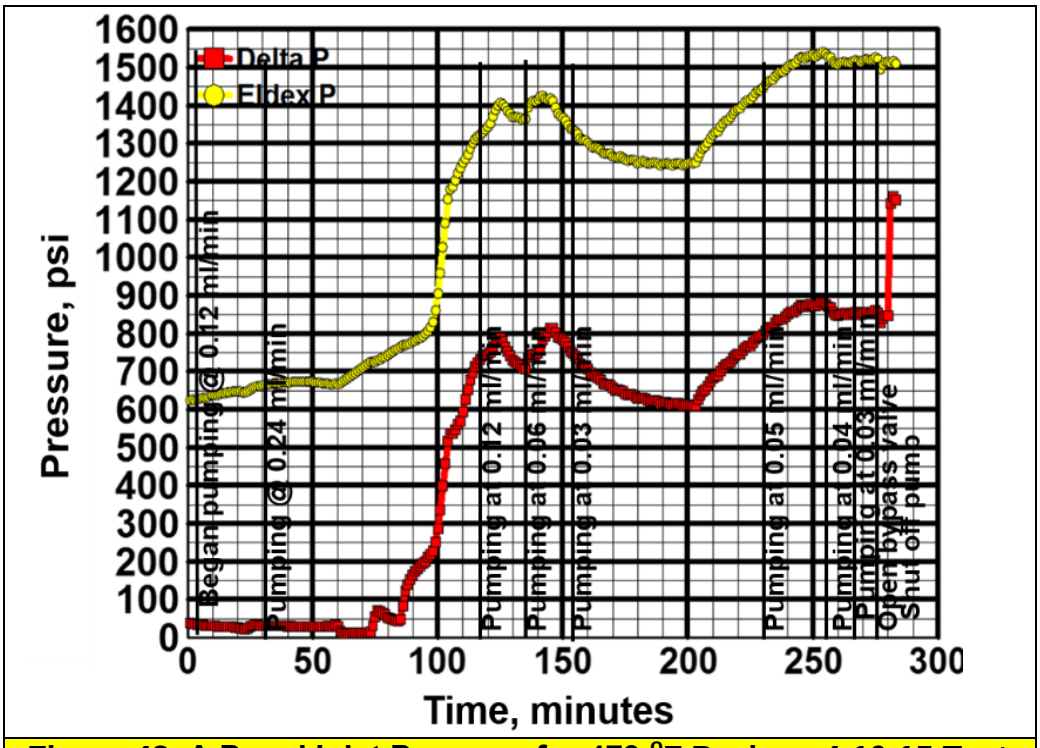


Figure 48. Δ P and Inlet Pressure for 479 °F Pack on 4-10-15 Test.

This test has shown that the new equipment configuration is viable for use at temperatures near 480°F and that the SPI-RAA gel solutions continue to perform at these elevated temperatures. The gels continue to meet and exceed xpectations. They should certainly be considered for high temperature applications. They form very strong gels that are stable at elevated temperatures.

Another flow test at ~480°F will be conducted to confirm that the equipment and the gel system continue to meet high temperature applications requirements.

April 22, 2015 SPI-RAA Activator Flow Test #2

On April 22, 2015 the second (confirmation) flow test at 474 ± 1°F was conducted using SPI gels with the internal RAA activator and the revised flow system - new end caps and fluid bypass at the entrance. After the flow system reached temperature stability, the activated SPI gel system solution was injected through it. Three pore volumes were injected to increase the probability that the core was saturated. This gel system has a gel time long enough to complete the 3 pore volume injection at 474°F. The gel system was allowed to set up overnight. The following morning Bartlesville tap water was injected in the gelled flow pack in order to determine the amount of flow reduction achieved from this gel system. Figures 49, 50 and 51 depict the pressures measured during the flow test.

The plot depicts the average pressure over one minute. The injection rate began at 0.03 ml/min. After 30 minutes the injection rate was reduced to 0.01 ml/min. This is indicated by the pressure drop from ~2,200 psi to 2,000 psi in Figure 49. The final injection rate change was conducted at 42 minutes. This injection rate was once again set at 0.03 ml/min. A maximum constant pressure was not attained because the injection pressure reached the maximum pressure differential that the equipment allowed at these temperatures. This indicated that a very strong SPI gel was formed. There was no gel breakdown during the testing. During the after gelation flow testing, the overburden maximum pressure was 3454 psi.

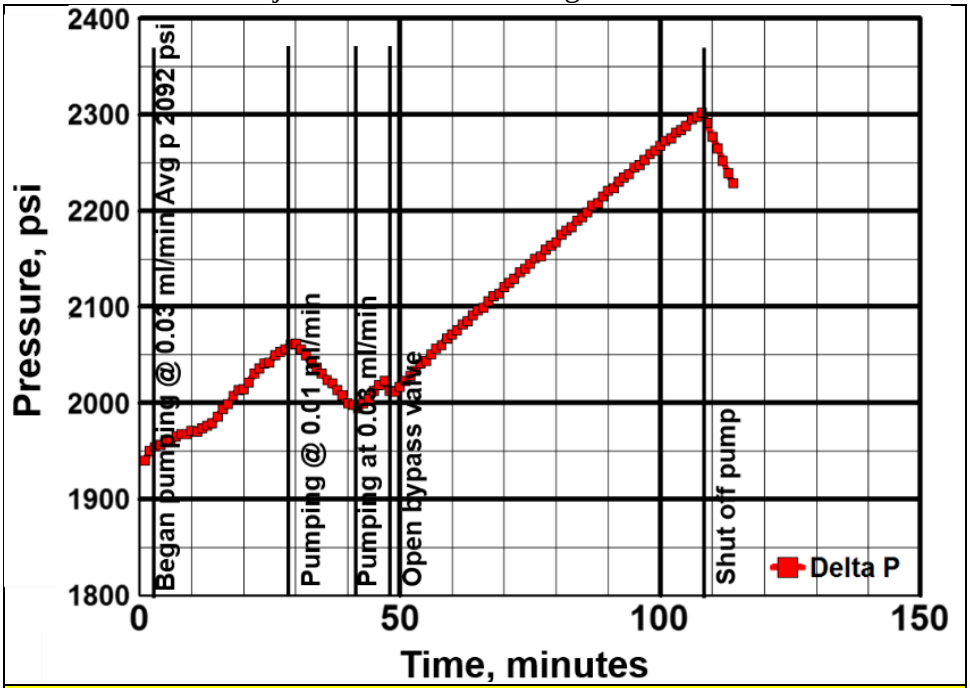


Figure 19. Δ P for 474 °F for Pack on 4-22-15 Test.

Three flow reduction factors were determined. In the sections, the Frr values were 15,700, 16,198, and 17,182 respectively. These high flow reduction factors indicate that the gel formed was really strong.

Further evaluation of the flow test was targeted the inlet flow characteristics. Figure 50 shows the pressures recorded for the inlet. The inlet pressure was designed to be ~500 psi greater than the overburden pressure. The maximum inlet pressure recorded was 2,808 psi. The minimum pressure was 2,426 psi.

The Section 1 average pressure was 2,455 psi, Section 2 was 2,520 and Section 3 was 2,649. During the Section 3 flow test, the overburden pressure had to be partially released in order to maintain test integrity so that the internal sleeve would not burst at this temperature and pressure. This is noted at the "open bypass value" 50 minutes into the test.

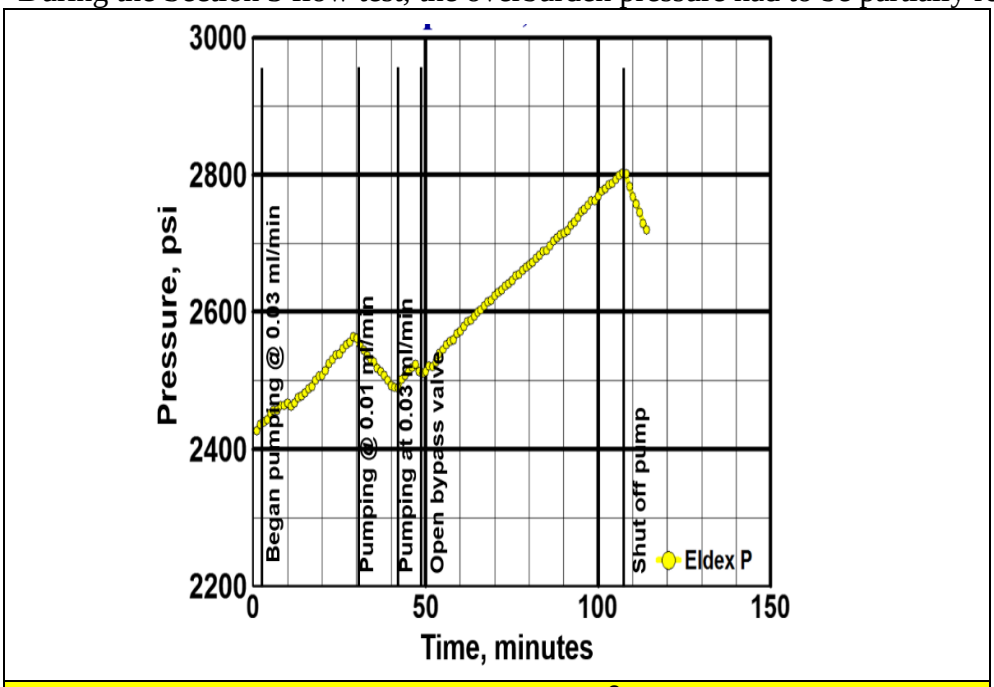


Figure 20. Eldex Inlet Pressure for 474 °F Pack on 4-22-15 Test.

Figure 51 shows the two pressures together. The pressures track each other very well throughout the test.

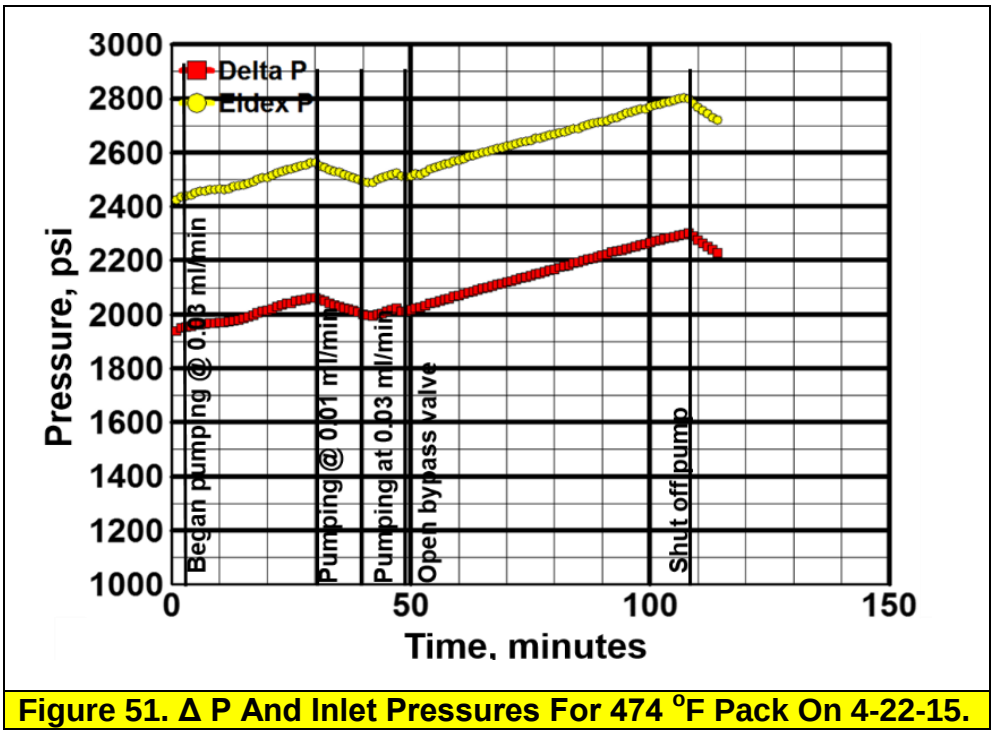
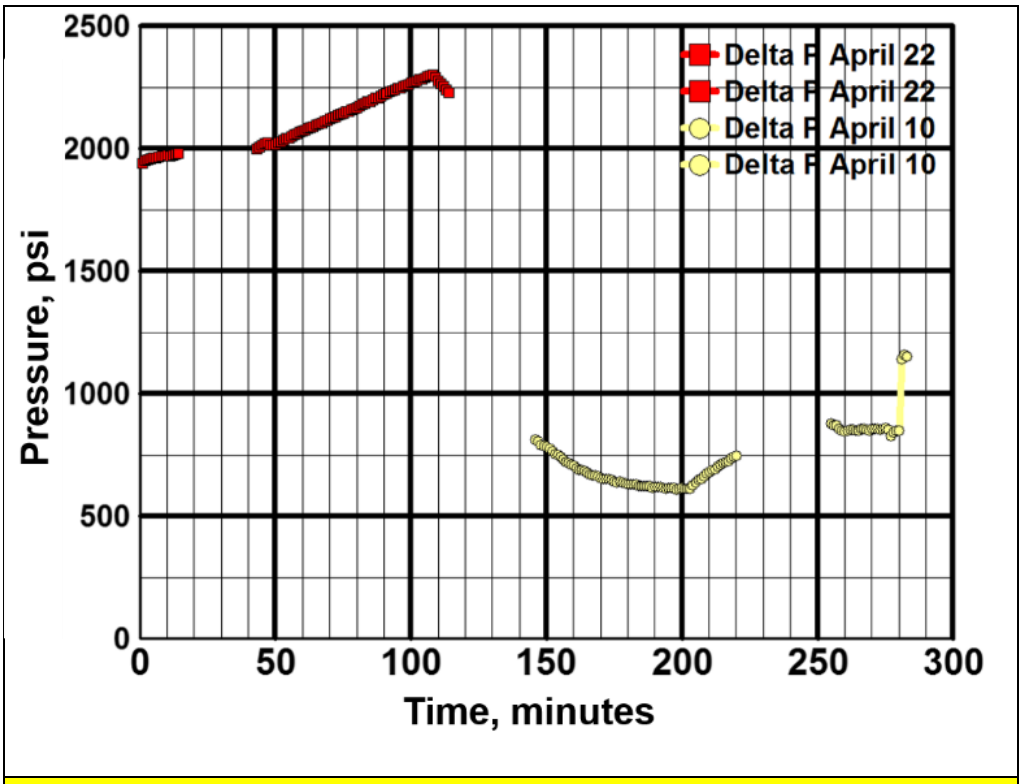


Figure 51. Δ P And Inlet Pressures For 474 °F Pack On 4-22-15.

This test was successful both from the equipment being tested for the second time at this elevated temperature and the gel system lowering the flow pack permeability significantly. The temperature for the flow system cannot safely be increased above 474°F so this is likely the highest temperature that will be tested. If modifications can be made, then higher temperatures might be tested.

Summary and Comparison

The following plot depicts both of the pressure changes across the flow media after the gels were in place. Only the 0.03 ml/min rate which was equivalent in the two tests are included on this plot. The delineators are omitted in order to be able to evaluate the pressure changes. It is unknown if the temperature variance of 5°F has played a role in the pressure differences noted or not. The second test—April 22—had much higher pressure drops than the initial test did. See the April 10, 2015 data on the plot. This is attributable in part to the differences in overburden pressures—3,455 for the April 22nd test and 1,752 for the April 10th test.



igure 52. Comparison Of April 10th and April 22nd Flow Tests

This ~1700 psi pressure difference is the major contributor to the lower pressure drops observed in the April 10th test. They are approximately 50 % lower than the April 22nd pressures. Each test showed that strong gels from the SPI-RAA system can be formed.

Conclusions and Further Work

These are the summaries from the flow tests conducted. The flow tests have demonstrated that the gel formulations have a wide range of flow reduction factors from 19 to 24,150. They have also shown that these systems can be controlled at elevated temperatures and that the flow system can be utilized for long time periods at elevated temperatures and continue to remain leak proof.

Flow test of the RAA gel system on 4-10-15 at 480˚F is a duplication of a gel test done on 3-6-15 performed at 180˚F. Gel was injected to the pack at a temp of 180˚F on both tests. On 4-10-15, the pack was taken to 360˚F and shut in overnight. Then the pack was taken to 480˚F the next morning. When internal temperature reached 477˚F, water flow was started. Initial pack Over Burden (OB) was only 700 psi between OB side and pack outside. This affected the ΔP of the pack since the sleeve was of a thicker material and the OB pressure had to be increased to keep bypass down. Once the bypass was minimized, the pump rate from max of 0.24 ml/min (1 foot

per day) was reduced every time the ΔP of the pack reached 800 psi. The pack was holding ΔP at a rate of 0.03 ml/min of about 650 psi. This rate correlates to a velocity of 0.125 foot per day flow of injected water. The ΔP of the pack with no gel is approximately 1 psi at a flow rate of 1ml/min. At a rate of 0.03 ml/min the ΔP is indistinguishable from 0 psi.

During the week of 4-20-15 a flow test of RAA initiated SPI gel system duplicated the 4-10-15 run at 480˚F is a duplication of a gel test done on 3-6-15 performed at 180˚F. Gel was injected to the pack at a temp of 180˚F on all three tests. On 4-10-15, the pack was taken to 360˚F and shut in overnight. Then the pack was taken to 480˚F the next morning. When internal temperature reached 477˚F, H_2O flow was started. Initial pack OB was only 700 psi between overburden side and pack out. This affected the ΔP of the pack since the sleeve was of a thicker material and the OB pressure had to be increased to keep bypass down. Once the bypass was minimized, the pump rate from max of 0.24 ml/min (1 foot per day) was reduced every time the ΔP of the pack reached 800 psi. The pack is holding ΔP at a rate of .03 ml/min of about 800 psi. This rate correlates to a velocity of 0.125 foot per day flow of injected H_2O. The ΔP of the pack with no gel is approximately 1 psi at a flow rate of 1 ml/min. For a pack with no gel in it at a rate of 0.03 ml/min, the ΔP is indistinguishable from 0 psi.

4.3.0 Gel Reversibility

During the experimental runs with the SPI gels, the use of 2 N NaOH caustic is used to remove the gels from the consolidated proppant pack. It took about 5 – 6 hours of pumping into the gel plugged sandpack to remove all Δ P from the plug. Thus, this is a technique for plug removal that is unique to the SPI gels. Section 4.2.6, Table 11 gels were broken with 2N sodium hydroxide.

4.9.1 Explanation of Variance:

No significant variances have been necessary at this time.

5.1. Milestone Log

Title: Milestone 1 – PMP approval - Accomplished
Phase I, Task 1, Year 1
Planned Date: 2 months from start of project
Verification Method: Final DOE approved PMP in place DE-FOA-0000522 Clean Tech Innovations, LLC Control No. 0522-1557 Project Management Plan.pdf Page 7

Title: Milestone 2 – Suitable SPI Formulations Determined – Accomplished with One Formulation Over the Whole Temperature Range
Task 2, Year 1
Planned Date: End of the 1 year (12 month from start of project)
Verification Method: Listing of up to 3 candidate SPI formulations that have potential for geothermal temperature ranges between 150^{o}C – 250^{o}C from bench scale tests, i.e. “proof of concept”

Title: Milestone 3 – Suitable SPI Formulations Determined and Verified
Phase II, Task 5, Year 2
Planned Date: End of the year 2 (24 month from start of project)

Verification Method: Listing of up to 10 candidate SPI formulations that have potential for geothermal temperature ranges between 150°C – 300°C from bench scale tests, i.e. "proof of concept" verified and ready for Dynamic testing in the same year. Report on lab tests.

Title: Milestone 4 – Dynamic Testing Confirms Suitable SPI Formulations
Task 6, Year 2
Planned Date: End of the year 2 (24 month from start of project)
Verification Method: Sand pack data to support gel stability for zonal isolation over the range of 150°C – 250°C to verify bench tests.

Title: Milestone 5 – Dynamic Testing Confirms Suitable SPI Formulation
Task 9, Year 3
Planned Date: End of the year 3 (33 month from start of project)
Verification Method: Sand pack data to support gel stability for zonal isolation over the range of 150°C – 250°C to verify bench tests.

Title Go/ NO Go Decision #1- Proceed to Dynamic Tests – Accomplished with a GO Decision Confirming the One Formulation Up to 305 °C in the Oven.
Planned Date- End of Year 1 (12 months into project start)
Verification Method: Approval by Clean Tech, Impact, and DOE before proceeding DE-FOA-0000522

Title: Milestone 6 – Discovery of RAA as New SPI Gel Initiators.

Title: Milestone 7 – Discovery of Flow Reduction Factors with the RAA SPI Gel Initiators at 475 °F. Flow tests have demonstrated that the RAA gel formulations have a wide range of flow reduction factors from 19 to 24,150 and are stable at temperatures up to 475 °F.

6.0 Funding and Costing Profile (in 000s)

The cost share (20%) commitments come from the four entities participating in the project, Clean Tech Innovations, Impact, and Felber. The budget justification shows the spending breakdown as per task and year.

Table 32. Phase II Funding and Cost Profile.

Organization	Cash/In-Kind Type	Match Value, Subtotal	Value Basis
Clean Tech Innovations	Cash/in-Kind	$64,793	20%
Felber	Cash	$17,580	20%
Impact Technologies	Cash	$2,632	20%
Felber	Cash	$894	20%
Total Match		$85899	
Total Funding & Match	$429,493	$85,898.60	

7.0 Products/Deliverables

7.1 Training and Professional Development:

None Occurred

7.2 Publications, Conference Papers, and Presentations:

None occurred yet.

7.3 Patents and IP:

Patents are planned from the data generated in this project and another project on Carbon Storage Technologies-Advanced Geologic Storage Technologies

7.4 Other Products/Deliverables:

Lyle Burns, Ken Oglesby and Betty Felber all attended the SPE IOR conference in Tulsa, OK from April 12-16, 2014. Mr. Burns assisted Mr. Oglesby at the SPI exposition booth at the conference. The booth focused on the good field test results obtained so far from 7 tests on five wells. Lots of good CO_2 contacts were made with addition operators to work on additional field tests to support product commercialization. Dr. Felber was the first female to receive one of the five 2014 IOR Pioneer Awards for her significant contributions to the fields of Improved Oil Recovery (IOR) and Enhanced Oil Recovery (EOR). Plans are in place for Mr. Oglesby to present an SPE paper on the SPE gels for CO_2 flooding at the Spring 2016 IOR conference in Tulsa, OK.

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APPENDIX I

SPI Technologies LLC

(wholly owned subsidiary of Impact Technologies LLC)

Commercialization Plan (Note: This is a Work In-Progress)

1. Market Opportunity

Product or Service Delivered: A cross-industry-cutting specialized SPI chemical treatment (i.e. gel product and pumping service) for conformance control and plugging /sealing-off in wellbores. These gels have been used in casing leak plugging, water flooding, CO_2 flooding, and it is anticipated they will work well in zonal isolation for geothermal or regular drilling applications and CO_2 storage remediation. See Figure 1 below for what the gel looks like with green coloring added. See Figure 2 for a schematic drawing of one SPI application.

Figure 1. SPI Gel in a Jar

Value Proposition: SPI gels are innovative sealing systems offering promising solutions to the geothermal (hydrothermal and EGS) and the oil & gas industry sectors. *This environmentally "Green" gel system remains at a low viscosity fluid (like water) until an (internal or external) initiator triggers gelation.* Gels may be formulated to be weak or strong and elastic. SPI gels are up to 10 times stronger than conventional cross-linked polyacrylamide polymer systems meaning that when placed they will hold pressure and flow and not wash out. SPI gels are near permanent once set, such that they are not reduced or removed by acid treatments or acid gases such as carbon dioxide and hydrogen sulfide (CO_2 and H_2S). However, they can be dissolved with alkaline solutions if needed. SPI gels can (if so designed) enter even small pathways since they do not have internal solid particles that filter out and plug off flow- but they can be so designed if desired. SPI gels can seal off zones but do not require costly and potentially damaging drill-out as do cements. SPI gel, by its chemical nature, immediately reacts with CO_2 already in the reservoir or injected after the treatment to form a strong firm gel. SPI gel treatments may also be up to 50% lower cost and more effective than other chemical and mechanical sealing methods

now utilized. SPI gel systems are versatile in their formulations to fit a variety of budgets and applications.

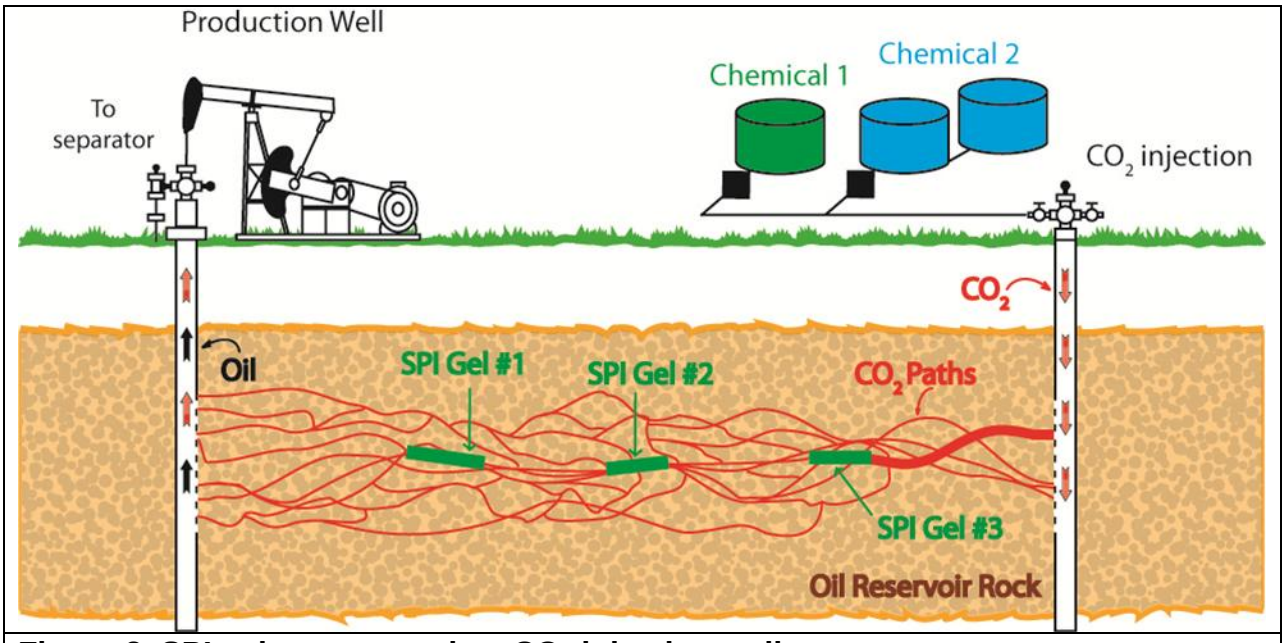

Figure 2. SPI gel treatments in a CO_2 injection well.

Problem Addressed: Portland cement, cross-linked polyacrylamide polymers, foams and mechanical plugs are now used in wellbore / reservoir plugging, sealing and conformance improvements. Each current method has problems in effectiveness, strength, sealing and corroding against CO_2. SPI gels are up to 10 times stronger than PAM systems per lab testing-important in high flow channels. Carbon dioxide actually can set SPI gels immediately upon contact, instead of harming the gel. Per lab tests and field results, SPI gels provide good solid seals against flow.

Note- carbon dioxide CO_2 has been proven in the field to be an effective external initiator for SPI gels allowing a position/contact gelation process to occur. An internal initiator allows a time/temperature gelation process with sufficient delayed gel time to allow the SPI mix to be fully injected before gelation begins. This currently works best for lower temperature applications and we are working to extend those delayed gel times. The combination of initiator types will provide extra versatility to the SPI gel system.

Natural or created high permeability paths in the reservoir allow unimpeded flow of injected fluids between wells and leads to inefficient operation in geothermal and many oil and gas operations. Conformance control means that these high flow paths are restricted to allow for improved efficiency. SPI gels can be used to prevent or remediate problems in different applications, such as:

1) Drilling wells – LOSS of WELL- Drilling applications are found in both oil & gas industry and geothermal sectors. In overbalanced drilling with mud systems, lost circulation zones consume expensive mud, endanger the well, risking an environmental blow-out, and endanger lives. Conversely, in underbalanced drilling where the rock pore pressure is greater than the wellbore pressure (at any point in the wellbore) then water/steam/fluid influx can

cause higher costs and even require a halt to drilling. In these cases, a strong SPI gel system with an internal initiator causing a short gel time would be pumped into place and allowed to gel and plug up those zones sufficiently and for long enough for drilling to proceed until casing is set. The step up to HTHP environments are now being explored for SPI gel applications in the Geothermal and Oil and Gas Industry sectors, especially for zonal isolation while drilling.

2) Completions – ONE OF A KIND PRODUCT - Zonal isolation and production well casing repairs are also applications of the SPI gel product in geothermal and oil & gas industries. Placement would be the same as in the drilling section above. The competitive metal crosslinked gel systems for lower O & G applications cannot approach the level of hardness possible with the SPI gels. Thus, the only other options for geothermal zonal isolation are mechanical or cement placement.
3) CO_2 EOR floods - LOW EFFICIENCY - Cycling CO_2 (injection to production to reinjection, etc…) is expensive. It also allows bypass of contacting the remaining crude oil in the rocks - called 'low conformance'. SPI gels can enter the primary path(s), then gel to block that/those paths from future CO_2 cycling.
4) Waterfloods- LOW EFFICIENCY- the same cycling of injected water causes increased costs and low oil recovery. SPI gels with an internal initiator will allow treatments in these wells.
5) EGS or Hydrothermal Reservoirs – LOW EFFICIENCY - flow short-circuiting from injector to producer causes low heat mining efficiency and shorter project lives. Conformance control in these systems would follow the same process as described in the CO_2 floods or in waterflooding. For systems utilizing an internal initiator for a time-temperature set, a volume of SPI gel solution with appropriate initiators would be pumped, flow would be stopped at the correct time and the gels would set blocking that pathway. The predominate flow path would take the most SPI solution and thus would set the most, diverting the injected water into newer hotter zones. Alternatively, alternating SPI solution and external initiators would allow sealing at any temperature (limited only to the polymer temperature limit). The potential use of CO_2 as an EGS working fluid opens up the potential to use SPI gels (and the CO_2 an external initiator again) on a routine basis to maintain reservoir conformance.
6) Carbon Sequestration- PROTECTION- injected CO_2 with water forms carbonic acid which will corrode the protecting steel casing and cement. This can cause loss of CO_2 containment. SPI gels with the proper internal initiator can provide a long term barrier between the stored CO_2 and the casing/cement. MITIGATION- SPI gels with an internal initiator can be pumped down a leading well with plugs or casing leaks to set up and seal off the pathway.

The service needed to properly design, formulate, pump, place and set SPI gels in each application are different. Specifically, this deals with the equipment to pump at the rates needed and with the appropriate pressure capabilities and crew training, Geographical areas also play a role in the service needed. Shallow, cooler applications of drilling and reservoir conformance need a focus on providing lower cost SPI solutions.

HTHP applications require specialized equipment and crews that are trained for these harsh environments. It is envisioned that certain standard service company pumping equipment can be contracted to pump SPI solutions in HTHP well drilling and reservoir conformance, allowing only a design, formulation, providing the solution/chemicals and supervision of the pumping and placing of the product.

Market Targeted and Size: See attached Spreadsheet on Markets Identified, Targeted and Size for using SPI. Table 1 below shows the largest to smallest markets identified with the initiator type needed and the estimated 10 year net profit that can be obtained versus the total revenue possible from those markets:

Table 1. Markets and Size.

Market	Initiator Type Required	Targeted/Total $MM/$MM
CO_2 Flood EOR Injection Wells	External Initiator	16 / 48
CO_2 Flood EOR Production Wells	Internal & External Initiators	18 / 54
Water Flood (Inject & Prod Wells)	Internal Initiator only	104 / 312
Drilling (Air & Mud Systems)	Internal Initiator only	39 / 46
Carbon Sequestration	Internal & External Initiators	9/ 27
EGS or Zonal Isolation	Internal & External Initiators	? / ?

These markets are in various geographical areas- Mid-Continent (OK, KS, AR), Permian Basin (W. Texas, NM), Gulf Coast (E. Texas, LA, MS), Rocky Mountain (WY, CO), and other areas (CA, Canada, Mexico, Europe, China).

Overall the largest general market ($104MM over 10 years) is for water floods that are spread out across all oil producing states. The problem is that water is cheap and cycling it is not as expensive as for CO_2, thus it is less of a concern. However, most water floods in the US are very mature and close to the end of their lives, unless the flood efficiency is substantially improved with SPI gels. But, still most operators of those properties are very financially conservative and thus the profit margin on those treatments would be low. Existing CO_2 in the reservoir is not there and so an internal initiator must be added at additional cost. The proof, acceptance and widespread adoption of SPI gels would also be slower than in the other markets. There are also thousands of operators of these water flood properties, instead of the 10 major operators for CO_2 EOR flood fields, thus marketing is more difficult and expensive.
Drilling market applications require 24/7 offices with fast response times where marketed. This requires special setup and manning operations that necessitate 4X pricing over normal. It may also allow for smaller treatment volumes for some savings to the operator. It will require a shorter time, but more tightly controlled delayed internal initiator to ensure strong gelation that allows drilling to quickly resume. This is too small a market to have a presence in all regions possible, thus only where sufficient SPI pumping units are located can this market be addressed. There may be some overlap in the SW where geothermal activity is prominent. Zonal isolation is very important in geothermal exploration and development due to its impact on sealing lost circulation zones during drilling. Highly fractured, weak zones may be encountered that cannot contain the wellbore pressure, allowing significant amounts of expensive drilling mud to be lost to the formations. If not controlled, this can stop drilling development of that resource.

The previous performance level in conformance control was at temperatures < 200^{o}F only because of the targeted CO_2 demonstration reservoirs. The on-going geothermal laboratory project DE-EE-0005508 demonstrated “proof of concept” this system is capable of tolerating much higher temperatures under pressure and it seeks to improve SPI gel integrity further by modifying various components to impart HTHP stability for longer periods. The other primary

aspect of this project is to enhance the gel delay to a desired time after placement. The goal of '5508 is to have one to as many as three hard SPI gels with elastic gel properties for operations tolerant up to 6,000 psi at 600°F for a period of up to two months. The new SPI products would become field demonstration candidates in a future, project, such as ARPA-E. Chemistry suggests HTHP SPI formulations could be used in zonal isolation applications and can solve this problem. Although the EGS market has a substantial growth rate between 8 - 12 percent/year, we are unsure what the dollar ($MM / $MM) requirements are at this time for Table 1.

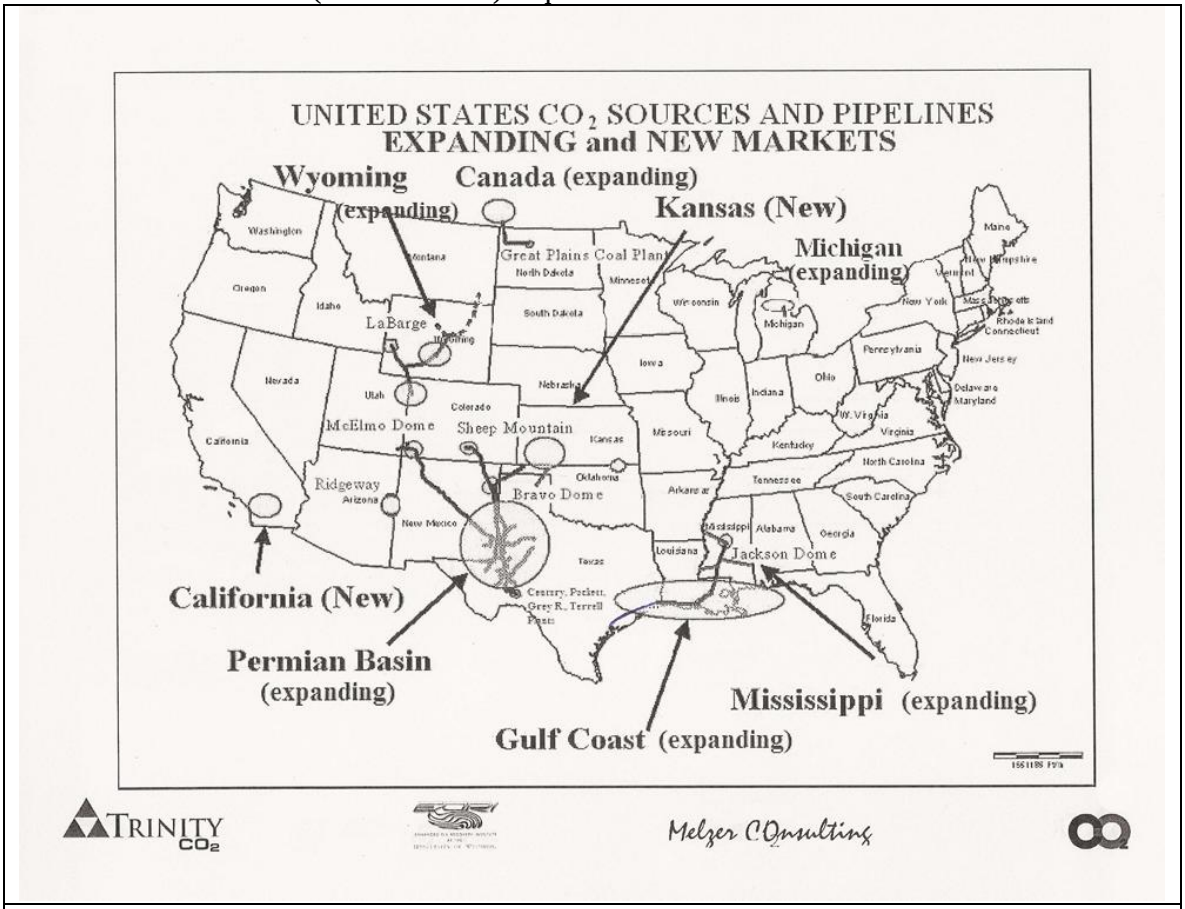

Figure 3. CO_2 Pipelines and CO_2 Waterflood Fields Using the Gas. [1]

Carbon Sequestration is also a small market since no projects are anticipated until demonstrations begin in 2020 (or 6 years away). Once they begin, due to regulatory or CO_2 EOR depletion, the number of treatments will soar, but this is at the end of the evaluation period used herein. SPI gels are a natural fit for CO2 sequestration since it gels the SPI mix upon contact, forming a prefect rejuvenating and living seal. SPI gels must be proven in other applications so that they are proven and ready when that growth occurs.

This leaves the last primary market as injection and production wells in CO_2 EOR floods. These are mostly along the Gulf Coast states (Mississippi, Louisiana, south east Texas), in the Permian Basin (west Texas, New Mexico) and in Oklahoma (Figure 3). This market can provide $34MM profit over 10 years out of an estimated $102MM in the targeted market areas. This market provides a natural fit to SPI gels which set upon contact with CO_2 in the reservoir and plugs the flow path. Injection well treatments can use the pre- and post- CO_2 injection to set the SPI gels-

being done now in the field. However, an internal initiator is needed in very high rate wells to provide a 'brake' to SPI movement relative to the injected CO_2 to cause penetration, contact and gelation. Production well treatments need the internal initiator in the last SPI portion pumped to form a 'brake' when flow is reversed back toward the well.

Geothermal development has long been centered in western states. But according to Geothermal Energy Association, "developers are increasingly exploring for and developing conventional hydrothermal geothermal resources in areas where little or no previous development has taken place." The number of states with projects in development (15) compared to those with operating plants illustrates the trend of geographical expansion of the market (9) as shown in Figure 4.

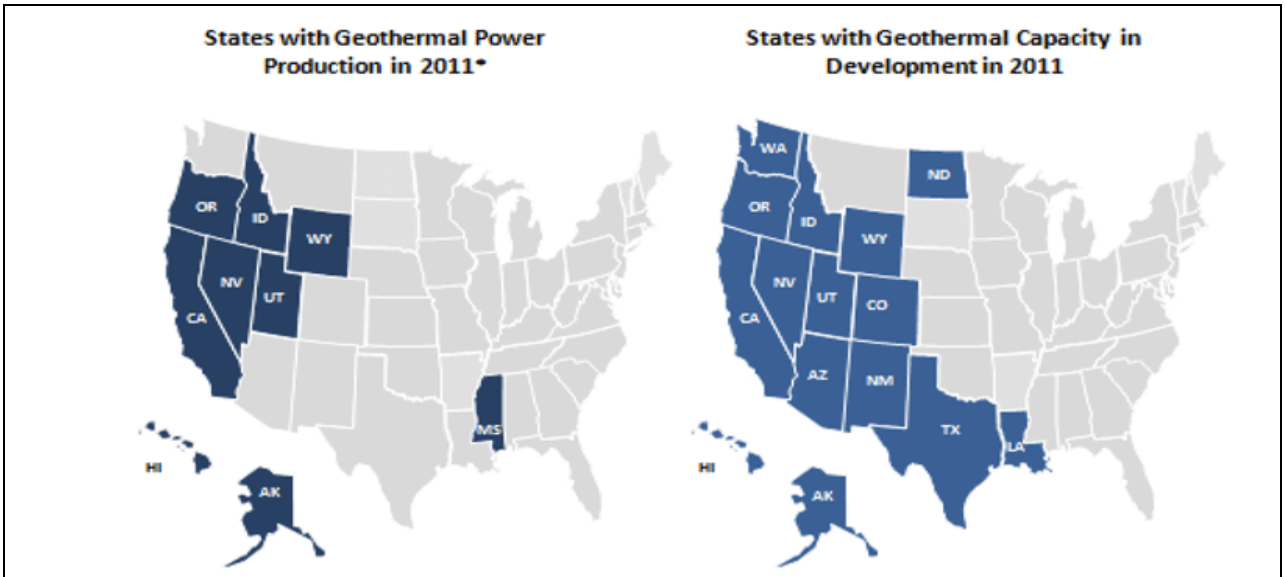

Figure 4. Geothermal Capacity Online (Left) and Under Development (Right) in 2011. [2]

Customers: SPI will sell its products and services directly to the customers- operators of the wellbores. The number of customers in the key targeted United States market (CO_2 EOR Floods) is fairly limited-

1) Occidental Petroleum (OXY) in based in Houston, Texas- world's largest injector of CO_2;
2) Denbury Resources in Dallas, Texas;
3) Kinder Morgan LLP (KMP) based in Houston, Texas- operates the world's largest CO_2 flood, SACROC;
4) Whiting Petroleum based in Denver, Texas;
5) Chevron USA, based in Houston, Texas;
6) Other smaller players

Table 2. CO_2-EOR Producing Companies in the US in 2009. [3]

Company	No. of Projects	CO_2-EOR Production Bbls/day	Locations

Occidental Petroleum	32	108,207	TX, NM
Denbury Resources	18	43,050	MS, LA
KinderMorgan	1	26,530	TX&NM, SACROC World's Largest CO_2 EOR
Chevron	7	24,221	TX, CO, NM
Hess	4	20,400	TX
Whiting Petroleum	4	20,000	TX, OK
Merit Energy	7	13,640	WY, OK
Anadarko	5	12,600	WY
ExxonMobil	2	5,450	TX, NM
ConocoPhillips	2	5,450	TX, NM
Apache	4	4,580	TX

Most of these companies have a high level team of conformance experts that must be convinced of a product before the field office will adopt it. Mr. Oglesby has contacts within most of these companies at those high levels from his attending numerous industry meetings and trade shows. He has contacts and has talked to most of those key groups in the commercialization of the external initiated SPI formulation. Mr. Oglesby will be exhibiting SPI products at the IOR meeting in Tulsa, OK in April 2014 to make additional contacts. Furthermore, Impact has consultants available for introductions into other companies.

The operators of the current USA waterfoods are too numerous to list herein, but it would include most of the larger oil operating companies- Chesapeake, Devon, Apache, Chevron USA, Exxon/Mobile, ConocoPhillips and others. State electronic records will easily identify the operators of larger fields in a given area targeted for marketing. Operators of the Geothermal and Sequestration projects wells are not yet identified, but for sequestration would most likely include those CO_2 flood operators since they have the operating expertise to perform that service. Operators for Geothermal may be different. Operators of wells being drilled cover a full range of small independents to major operators. State drilling permits are always posted electronically and experience will narrow down the geographic area and operators that would utilize SPI services.

Competition: There are limited competitors in delivering conformance or sealing treatments for wellbores- most of them do treatments in primary wells with high water production, waterfoods and CO_2 floods. Most of them use weaker gels at the forward edge to allow the days pump times required. Toward the end of the job they increase the strength of the gels that are left near the wellbore.

The companies are: Halliburton who is located everywhere; Schlumberger (Dowell) in France/Houston, Texas; Gel Systems in Wichita Falls, Texas; Polymer Systems in Hayes, Kansas; and Tiorco in Denver, Colorado. Mr. Oglesby knows many individuals in each of those companies. Halliburton and Schlumberger are not strong competitors in the US due to their high cost structure. Each company has their strengths in their nearby area. Our main competitors will be Gel Systems and Tiorco in the west Texas area. General Electric has a foam system for increasing CO_2 apparent viscosity, but it does not plug nor seal off zones.

The top featured companies for geothermal and oil & gas drilling services are Halliburton, Schlumberger, Thermal Source, Inc. and Geothermal Resource Group. Baker Hughes, GEO Drilling Fluids and Newpark Resources Inc. are the three fluids companies. Schlumberger and

Halliburton also have their own drilling fluid loss agents. Many of these companies also provide pumping services to these high end, HTHP, high pump rates, high markup) and international markets. Lower end (shallower, low pressure, low rate and more price sensitive) markets are rarely served by these larger service companies.

Baker Hughes states widely in their web pages that "Our reliable, high-temperature products and services have been used on 95**%** of the ***geothermal*** wells ever ***drilled [4].***" This suggests Baker Hughes is claiming 95% of the worldwide market share of geothermal drilling fluids. Newpark Resources stated at its February 2012 Investor Presentation [5] that the total worldwide drilling fluids market was $10.0 billion in 2011 and Newpark had 8.1% market share Baker Hughes (10.1%), Halliburton (23.7%), Schlumberger (35.7%) and Others (21.5%). An effort was made to define the geothermal market share of the total drilling fluids market, but no records were found. Assuming that the geothermal drilling fluids market is 10% of the total market, then either Baker Hughes claims $950,000 of that market or it is divided up among the others in a more proportional rate.

2. Company/Team

SPI Technologies LLC (SPI-T) is a wholly owned subsidiary of Impact Technologies LLC, incorporated in 2008. Impact has and will provide initial funding to get SPI-T started, but outside investors will be needed to obtain the strong growth possible as shown in the Financial Cash Flow Analysis provided in field. SPI-T's initial office will be in Tulsa, OK in the office space of Impact Technologies LLC. The back office functions will be shared with Impact to save on cost. An independent CPA group will do the books and taxes for the corporation. Impact / SPI-T is currently working to commercialize SPI gels in CO_2 floods for injectors, since such jobs do not need an internal initiator. That external initiated product has been field tested with 8 treatments in 6 wells and in 2 fields (Mississippi sandstone/ Gulf Coast and west Texas dolomite/ Permian Basin). Impact/ SPI-T is now awaiting the full results of those treatments. Initial results show strong and good responses in the treated injector, but it is too early to determine if it makes a difference in offset production wells. More will be known by mid-year. .

Mr. Ken Oglesby will initially serve as President of SPI-T. He will also serve as Chief Technical Officer initially. Ken has extensive business experience and capabilities with 35 years in oil and gas, covering almost all upstream sectors (production, EOR and drilling). He has been owner and officer in 4 companies including investments, real estate, oil and gas and technology development. He has 10 patents and numerous patents pending in the US and internationally. He was General Chairman of the 2004 Improved Oil Recovery Symposium and Conference in Tulsa OK. Mr. Oglesby has developed several technologies into commercial products and he has contacts within most all CO_2 operating and many oil & gas operating companies.

Mrs. Pat Oglesby will initially serve as Vice President Administrative, Financial and Legal. Pat is an attorney with 23 years' experience in managing four businesses.

Marketing/ Sales position will be filled as soon as possible by someone knowledgeable in the EOR CO_2 chemicals or services industry.

Mr. Bryan McCollam will be the Manager of SPI Field Operations. He has more experience in SPI treatments in Mississippi and west Texas than anyone else, except Mr. Oglesby.

Technical Consulting: Mr. Lyle Burns- SPI co-inventor and chemistry consultant for SPI-T and an investigator in this SBIR project; Dr. Betty Felber- chemistry consultant, and Dr. Rychel- CO_2 consultant.

SPI-T has no employees now, but will need to expand by a multiple of 4 people for each unit in the field, 2 or 3 in the field and 1 in the office for scheduling, designing, and marketing. The whole management team will step down to allow outside investors to select their own people when that time comes.

Impact/ SPI-T already has a verbal strategic agreement with the world's second largest supplier of the key chemical used in our SPI treatments. It will not take much sales volumes to obtain large discounts on the product to improve our profit margin or to meet the competition pricing.

Each pumping/ service unit will cost about $250,000 to purchase pumps/tanks/ lines/trucks and initially fund the operating cost for that unit. Each unit can perform about 4 treatments per month. SPI-T will not make our own chemicals or our own equipment. We will take most/all chemical deliveries in the field and mix them up onsite or near the treatment site. It will be planned to perform multiple treatments (i.e. 5 pumping service units) in one area to leverage the chemical delivery and mixing functions. Initially the Tulsa shop will be the only equipment and personnel staging area. Later field offices will be setup where the activity is strongest and delivery locations are optimal.

3. Intellectual Property

Impact and Clean Tech Innovations have reviewed the existing patent literature and believe that the SPI product and placement method is novel and substantially different from all existing approaches. SPI gels are in patent pending state in the US and internationally. It was filed on 28 November 2006 and published as US2008-0125334 A1. The patent rights are owned by Regency Technologies LLC which will exclusively license the IP (now in pending status in the US and elsewhere) to SPI-T once funded, for a low (confidential), variable royalty, per an existing agreement. Note- Owners in Impact are also majority owners in Regency. This arrangement allows for a service company option to proceed or a licensing option to an existing service provider. Impact and SPI-T also has extensive trade secrets that will be kept proprietary.

4. Revenue Forecast - Pending

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