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Chemical Method to Improve CO_2 Flooding Sweep Efficiency for Oil Recovery Using SPI-CO_2 Gels

Final Report for SBIR Phase I (Topic 60), ENHANCED OIL RECOVERY, OIL SHALE, OIL AND NATURAL GAS TECHNOLOGIES,

(Subtopic a)
CO_2 Flooding For the Recovery of Oil

By
L. D. Burns, PI and Bill Johnson, Project Director
RTA Systems, Inc. - Bartlesville, OK and Oklahoma City, OK

Teaming Members
Ken Oglesby
Impact Technologies - Tulsa, OK

And

Dwight F. Rychel
Consultant - Tulsa, OK

Prepared for
U.S. Department of Energy
Peter R. Waldman
Contract Specialist Operations Division
Office of Acquisition and Assistance

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Executive Summary

The problem in CO_2 flooding lies with its higher mobility causing low conformance or sweep efficiency. This is an issue in oilfield applications where an injected fluid or gas used to mobilize and produce the oil in a marginal field has substantially higher mobility (function of viscosity and density and relative permeability) relative to the crude oil promoting fingering and early breakthrough. Conformance is particularly critical in CO_2 oilfield floods where the end result is less oil recovered and substantially higher costs related to the CO_2.

The SPI-CO_2 (here after called "SPI") gel system is a unique silicate based gel system that offers a technically effective solution to the conformance problem with CO_2 floods. This SPI gel system remains a low viscosity fluid until an external initiator (CO_2) triggers gelation. This is a clear improvement over current technologies where the gels set up as a function of time, regardless of where it is placed in the reservoir. In those current systems, the internal initiator is included in the injected fluid for water shut off applications. In this new research effort, the CO_2 is an external initiator contacted after SPI gel solution placement. This concept ensures in the proper water wet reservoir environment that the SPI gel sets up in the precise high permeability path followed by the CO_2, therefore improving sweep efficiency to a greater degree than conventional systems. In addition, the final SPI product in commercial quantities is expected to be low cost over the competing systems. This Phase I research effort provided "proof of concept" that SPI gels possess strength and may be formed in a sand pack reducing the permeability to brine and CO_2 flow. This SPI technology is a natural extension of prior R & D and the Phase I effort that together show a high potential for success in a Phase II follow-on project.

Carbon dioxide (CO_2) is a major by-product of hydrocarbon combustion for energy, chemical and fertilizer plants. For example, coal fired power plants emit large amounts of CO_2 in order to produce electrical energy. Carbon dioxide sequestration is gaining attention as concerns mount over possible global climate change caused by rising emissions of greenhouse gases. Removing the CO_2 from the energy generation process would make these plants more environmentally friendly. In addition, CO_2 flooding is an attractive means to enhance oil and natural gas recovery. Capture and use of the CO_2 from these plants for recycling into CO_2 flooding of marginal reservoirs provides a "dual use" opportunity prior to final CO_2 sequestration in the depleted reservoir. Under the right pressure, temperature and oil composition conditions, CO_2 can act as a solvent, cleaning oil trapped in the microscopic pores of the reservoir rock. This miscible process greatly increases the recovery of crude oil from a reservoir compared to recovery normally seen by waterflooding. An Enhanced Oil Recovery (EOR) project that uses an industrial source of CO_2 that otherwise would be vented to the atmosphere has the added environmental benefit of sequestering the greenhouse gas.

Notices

P.O. Box 721985
Norman, OK 73070
www.rtasys.com

4.0 Actual Accomplishment Comparison with the Project Objectives and Goals

The objectives and actual accomplishments are summarized in Table 1.

Table 1. Objectives and Accomplishments Comparison.

Objective	Accomplishment
Demonstrate utility from gel strength and stability for a modified *in situ* SPI gel system using CO_2 as an initiator.	1. Using the Bulk Gel Strength Tester, the external CO_2 initiated SPI gels showed superior "proof of concept" gel strength to aluminum crosslinked polyacrylamide and silicate alone without polymer. 2. The CO_2 stochiometry was found to not be a critical variable in forming a strong gel and the CO2 concentration is minimal.
Perform sand pack tests exposing the SPI fluids to a CO_2 -rich environment for "proof of concept" and pressure test the resulting gels.	1. Using the sand pack, the external CO_2 initiated SPI gels demonstrated "proof of concept" permeability reduction to brine and CO_2 flow.
Identify an oil operator willing to support field-testing of the SPI-CO_2 system in a Phase III project, and perform a preliminary design for a specific field test.	1.Whiting Petroleum has experessed interest in working with RTA to perform evaluate their CO_2 flood wells as candidates in Phase II for a Phase III field testing. 2. Other operators have expressed similar interest.

5.1.0 Technical Summary

The overall Technical Objective of this Phase I project was to provide "proof of concept" research demonstrating that the internal initiated SPI gel system can be modified for external initiation by CO_2 for effective use in CO_2 flooding or sequestration.

5.1.1 Technical Questions and Objectives

The Phase I goal was to demonstrate "proof of concept" research supporting the gel strength and long term compatibility of a SPI – CO_2 initiated gel system. The *in situ* gel process will utilize carbon dioxide (CO_2) as the external initiator to create a gel in the swept out portion of the reservoir. The questions and technical objectives for Phase I were:

Question #1. Can the SPI gel system be modified to utilize CO_2 as an external initiator and can this modified system be suitable to produce *in situ* strong gels?
Technical Objective #1: Demonstrate "proof of concept" utility from gel strength and stability for a modified *in situ* SPI gel system using CO_2 as an initiator.

Question #2. Will the SPI - CO_2 gel strengths be substantial and long lasting in a typical reservoir environment to improve reservoir sweep efficiency in a sequestered CO_2 flood?
Technical Objective #2: Perform sand pack tests exposing the SPI fluids to a CO_2 -rich environment for "proof of concept" and pressure test the resulting gels.

Question #3. What is the best possible method for a successful field test in Phase II?
Technical Objective #3: Identify an oil operator willing to support field-testing of the SPI-CO_2 system in a Phase III project, and perform a preliminary design for a specific field test.

The following top-level tasks were identified to accomplish these technical objectives. The results of the work plan for these tasks will be discussed below.

Task 1 – SPI - CO_2 Gel System Strength and Stability
Task 2 – SPI – CO_2 Gel Performance in Sand Packs
Task 3 – Site Identification, Preliminary Design of Potential SPI –CO_2 Gel Field Tests
Task 4 - Reporting

In order to achieve the Technical Objectives, RTA investigated the feasibility of using CO_2 as an external initiator instead of the traditional internal chemical initiator to create a stable SPI gel capable of deep placement in the reservoir. The basic expertise and knowledge spans from developing the original SPI products using internal initiators for in-depth placement for reservoir water diversion on injectors and casing leak plugging. SPI stands for Silica Polymer Initiator. Thus, it was a natural succession to evaluate the SPI – CO_2 gel system in the laboratory to evaluate "proof of concept" for CO_2 floods.

The lab work was accomplished by RTA Systems Inc. in its Bartlesville, OK laboratory. This approach was similar, but different from that used to develop the original SPI gel systems because the original initiators were stable liquid organic chemicals boiling significantly above room temperature. In this study, the initiator was gaseous CO_2 or aqueous CO_2 (carbonic acid).

5.1.2 Phase I Background

Formation of Gelled Silicate Polymers

Carbon dioxide dissolved in water is in equilibrium with carbonic acid (H_2CO_3), and the concentration of H_2CO_3 is much lower than the CO_2 concentration, thus reducing the measured

Equation 1.

$$CO_2 + H_2O \quad \leftrightarrow \quad HCO_3^- \quad + \quad H_2CO_3$$

acidity. Henry's Law states the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas above the liquid. Thus, at high pressures, H_2CO_3 becomes the dominant species over CO_2.

Sodium silicate is a complicated system of various molecular weight silica polymers in an alkaline solution. Aside from requiring a certain minimum amount of buffered alkalinity, sodium silicate has no definite chemical combining numbers. Anhydrous sodium silicate contains a chain polymeric anion composed of corner shared (SiO_4) tetrahedra, and not a discrete SiO_3^{2-} ion. The sodium silicates of common interest to this project have a molar ratio of silicon dioxide to sodium oxide of about 3.22 and for convenience are written as $Na_2O:SiO_2 \cdot xH_2O$ or $Na_2SiO_3 \cdot xH_2O$ where $x = 5, 6, 8$, or 9. Often when neutralizing, one can consider that they are essentially neutralizing the alkaline base portion, sodium oxide (Na_2O) of the sodium silicate.

When sodium silicate is acidified by carbonic acid to a pH of less than about 10, the sodium silicate is converted partially to a silicic acid $Si(OH)_4$ monomer as shown in Equation 2. Silicic acid exists at these alkaline pH's as it is a very weak acid. Instead of precipitating and making silica, SiO_2, the silicic acid remains hydrated and forms a three-dimensional network trapping the solvent water. This network is a gel since both phases are continuous. Although short-lived, the silicic acid monomer quickly undergoes condensation with another molecule of silicic acid,

Equation 2.

$$Na_2SiO_3 + H_2CO_3 + H_2O \rightarrow Si(OH)_4 + Na_2CO_3 \text{ (pH > 8.3) or } 2NaHCO_3 \text{ (pH <8.3)}$$

eliminating water, to form dimmers, trimmers and polysilicic acids up to 100,000 in molecular weight as indicated in Equation 3. [1]

Equation 3.

$$HO\text{-}Si(OH)_2\text{-}OH + HO\text{-}Si(OH)_2\text{-}OH \rightarrow HO\text{-}Si(OH)_2\text{-}O\text{-}Si(OH)_2\text{-}OH + H_2O$$

The polymeric aggregates grow in size until (depending on the environmental conditions, temperature, salt concentration, pH etc.) at a particular size, the hydroxyl groups on the surface of the aggregates begin to condense. The aggregates adhere to one another and the liquid is observed to form a gel. [2] The aggregates form a network of silicic anhydride groups with hydroxyl groups covering the external surface. The silicic acid polymerization process can be divided into three steps:

1. A reaction between monosilicic acids,
2. A reaction between monosilicic and polysilicic acids, and
3. A reaction between polysilicic acids.

The reaction rates between monomer-monomer, monomer-polymer and polymer-polymer are very rapid at pH values around 9.3, 8.5, and 6.8 respectively. [3] Silicic acid and it's polymers form a variety of complexes with ions and organic molecules, including mucopolysaccharides, glycoproteins that are enriched in hydroxyl amino acids (serine and threonine), glycine, aspartic and glutamic acids. Additionally, silicic acid is expected to form organic silicate complexes (Si-O-C) with hydroxyl centers from cis-1, 2-diols. From these examples it is possible to see how various organic compounds, bacteria and fungi, or their remains, can make Si-O-C complexes with silicic acid and contribute to the crosslinking and hardening (by elimination of water) of the silicate polymers. [4] Significantly, silicic acid also makes Si-O-metal complexes, such as the Si-O-Fe complex with ferrihydrate. This means that not only organic substances, but metals as well, can participate in polymerizing, crosslinking and hardening (by elimination of water) of silicic acid.

One could envision in the SPI system that the long molecules of the polyacrylamide (PAM) are surrounded by polysilicic acid (PSA). Iler, [5] suggests logical interactions between the intertwined PSA/PAM polymers are association complexes that are the result of hydrogen bonding with the PAM electron-donor atoms from the amide functional group and the silanol (Si-OH) groups on the PSA. As it applies to this work, one could conclude that there is an interaction between the PSA and PAM that is responsible for the observed stability and enhanced elasticity of the SPI gels formed.

5.1.3 Task 1 – SPI - CO_2 Gel System Strength and Stability

RTA Systems, Inc. personnel in its Bartlesville, OK laboratory accomplished the work on this task. The parameters of interest when evaluating the gel formulations are normally: gel time, gel strength and gel stability, but in this work delayed gel time is not as important as the fact that CO_2 causes gelation in a reasonable period of time after placement. Extrapolating to a field environment, these gel characteristics correlate with gelling after appropriate placement, degree of permeability reduction and gel treatment longevity. Achieving a significant level success in gel strength and gel stability will constitute milestones for “proof of concept” in Task 1.

Effect of CO_2 on pH - Stoichiometry

The first effort was to compare the results of acidification by bubbling CO_2 in water (Experiment 1) compared with bubbling CO_2 into a sodium silicate solution (Experiment 2) as shown in Table 2. The pH was followed by a pH meter. In Experiment 1, note the most significant pH drop occurred in the first 3 minutes down to a pH of 2.00 and continued to drop to a pH of 1.67 over the next 3 minutes. In both experiments, atmospheric pressure was 1.01 atm., temperature was 25^{o}C, the CO_2 flow time was 10.00 minutes at a rate of 0.430 L/min. Using the Ideal Gas Law, PV = nRT, a total of 0.178 moles of CO_2 was introduced into each of the solutions. If one considers the neutralization occurring in Experiment 2 was essentially that of the Na_2O component of the sodium silicate, then there are 0.05938 mmoles (millimoles or 1 mmole = 0.001 mole) of Na_2O being neutralized. Na_2O must accept two protons for neutralization and carbonic acid has the capacity to generate 2 protons, therefore the charge was balanced. The ratio of moles of CO_2 required to approximately neutralize a mole of Na_2O in Experiment 2 was 2994:1. The word approximately is used because the CO_2 flow stopped at 10 minutes at a pH of 8.14 and the sample gelled at 15 minutes at a pH of 7.84. In these atmospheric pressure experiments, the CO_2 was bubbled into the solution and much of the excess CO_2 was simply lost to the air. Thus, the actual number of moles of CO_2 consumed by the Na_2O was significantly less.

Table 2. Effect of CO_2 on pH of Water and a Diluted Sodium Silicate.

	Experiment 1* No Mmoles Sodium Oxide In 281.86 g water			**Experiment 2* 0.05938 Mmoles Sodium Oxide in 281.86 g water**		
Time, min.	**Moles CO_2**	**pH**		**Moles CO_2**	**pH**	**Comments**
0	0.0000	5.77		0.0000	10.45	
1	0.0178	3.25		0.0178	9.26	
2	0.0356	2.26		0.0356	9.15	
3	0.0534	2.00		0.0534	8.91	
4	0.0712	1.82		0.0712	8.76	
5	0.0890	1.71		0.0890	8.54	
6	0.1068	1.67		0.1068	8.40	
7	0.1246	1.67		0.1246	8.29	
8	0.1424	1.67		0.1424	8.22	
9	0.1602	1.67		0.1602	8.16	
10	0.1780	1.67		0.1780	8.14	Stop CO_2 Flow
11	0.1780	1.67		0.1780	8.06	
12	0.1780	1.67		0.1780	8.06	
13	0.1780	1.64		0.1780	8.04	

14	0.1780	1.57		0.1780	7.95	
15	0.1780	1.56		0.1780	7.84	Sample Gelled
16	0.1780	1.54		0.1780	7.80	
17	0.1780	1.54		0.1780	7.79	
18	0.1780	1.55				
19	0.1780	1.53				
20	0.1780	1.54				
*These solutions contained no polyacrylamide.						

The acid concentration [H^+] generated in solution from the CO_2 at the pH of 1.67 (Table 2, Experiment 1) is calculated from the definition of pH = $-\log_{10}[H^+]$ to be 0.0214 moles/l. Since the solution contains only 281.86 ml (density ~ 1), the actual number of moles of H^+ generated in this solution volume was 0.0060 moles or a ratio of moles of CO_2 to the moles of Na_2O = .0060/0.00005938 = 101. The 0.0060 moles CO_2 from Experiment 1 is an equilibrium value and obviously if the base (Na_2O) is present for neutralization as in Experiment 2, more H^+ will be produced from CO_2 for neutralization. In fact, the moles of CO_2 should be slightly less than the total moles of Na_2O, because the pH when the sample gels was designed to be just slightly lower than the pH = 8.14 when the CO_2 flow stopped. Therefore, the actual number of moles of [H+] required for the gel formation in this atmospheric experiment is equal to the number of moles of CO_2, which for Experiment 2, was just slightly less than 0.0060 moles. *This is an insignificant quantity of CO_2 to form an SPI gel in the laboratory and is dwarfed by the CO_2 present in a CO_2 flooding operation. Therefore, CO_2 stochiometry is not considered a significant variable, which is a significant milestone.*

Penetrometry Experiments Related to Stoichiometry

Procedure:

The samples were prepared by using N-sodium silicate from PQ Corporation, a nonionic PAM, and water. A few runs included a small amount of a component originally thought to provide additional gel stabilization or enhancement. The PAM used in the dry powder form. The PAM was pre-mixed according to standard procedures to a 5000 ppm concentrate and let down into the formulation. The order of mixing was first water, then PAM, then the optional stabilizing component, and the sodium silicate, making sure homogeneous solutions were obtained before the next feedstock was added. A jar containing the formulation was placed under a CO_2 manifold with a flow meter and CO_2 was bubbled into the solution through a glass frit over a set period of time at a given flow rate at room temperature and atmospheric pressure, which were recorded. The CO_2 tube was removed just minutes before the samples start to gel as by evidence of cloudiness. The gels were set-aside until gelling occurred. Standard aging was 24 hours before testing.

The atmospheric pressure P_{atm} in inches of Hg was converted to atmospheres, the temperature in ^oC converted to ^oK, the CO_2 flow rate in L/min over a set time to L_{CO2}, and the ideal gas law (Equation 4) was used to calculate the number of moles of CO_2 bubbled into solution. This is not the number of moles in solution as defined in the previous stoichiometry discussion since most of the CO_2 escapes, but it does significantly lower the solution pH.

Equation 4.

$$n = (PV/RT)$$

where n = moles, P = pressure in atm, V = volume in L, R = a constant 0.08206 L atm $K^{-1}mole^{-1}$, and T = temperature in ^{o}K.

Results

A GCA Precision Scientific Precision Cone Penetrometer was used according to ASTM D-217-68. Fifteen samples were gelled by bubbling CO_2 into the pre-gel SPI mixture and the gel strength results using penetrometry are presented in Table 3. The penetrometer measurements are an average of those obtained in three gel samples of the same formulation. Minor differences in the moles of CO_2 received by the formulation are due to atmospheric pressure and temperature differences when the experiments were performed. The moles of CO_2 are calculated from the Ideal Gas Law. Table 3 is divided into two sections in order to display the data.

The first three formulations were designed to establish a baseline for carbonating a sodium silicate solution without any other formulation component using penetrometer data for gel strength. Sodium silicate concentrations ranging from 3.2 – 4.3 weight percent provided cone penetration depths of 196.00 – 214.33 tenths mm for Formulations 1 - 3. Sodium silicate formulations alone form brittle gels that are susceptible to cracking when pressure exerted on the gel. In previous studies, chromium crosslinked polyacrylamide gels perform poorly in this test with cone penetration of over 340.00 tenths mm. The cone essentially sinks into the gel the full depth.

The PAM used in these experiments is a nonionic blend of commercial polymers. When PAM is incorporated to form the SPI gels, a significant effect is observed attributed to gel elasticity. When pressure is exerted on SPI gels, the gel flexes and sometimes produces a vibrating or ringing sensation. The gel recovers when the pressure is removed. When the penetrometer cone is released on an SPI gel, the cone tends to bounce on the surface of the gel. Generally, a very low level of PAM, between 0.10 to 0.20 weight percent, is sufficient to impart these properties. Formulation Nos. 4 – 6 contain are SPI gels with PAM. Formulation 4 had 20 tenths mm less penetration than Formulation 3. Formulation 5 was 9 tenths mm better than formulation 3 even with 40% less CO_2.

In previous research the addition of a third component, often called a very low concentration stabilizer, previously contributed enhanced features to the internal initiated SPI gel such as minimal syneresis and slightly better gel strength. In these tests, Formulations 7 – 16, the third component did not stabilize or enhance the formulations in these experiments much above the contribution of the PAM. However, the gels had better properties than just sodium silicate alone.

Poor gel stability is most often caused by syneresis. Syneresis is defined as shrinkage of the gel that forces out the liquid held in the lattice. With the SPI gels, RTA Systems has found that syneresis is minimized or eliminated when the optimum stoichiometry of the gel components are obtained. The data seems to suggest that when the moles of CO_2 were reduced (Nos. 5 and 7, Table 3) or increased (No. 14) from the standard 0.180, there was probably not a consistent relevance to gel stability. As long as there is a significant excess of CO_2, this variable may become relatively unimportant. Low or negligible gel syneresis is a measure of SPI gel stability. The syneresis that occurred after 48 hours was low, on the order of less than three weight percent in all of these formulations. This could be considered a success milestone, although it could also be related to the procedure used to make the gels. There seems to be no correlation with syneresis and CO_2 concentration, which is good because in the real world, there will be no control over the CO_2 concentration the SPI gel encounters other than hopefully “in excess”.

Delayed gel times are not as important in this research project, since they are generally less than one hour and the pre-SPI gel is properly placed before gelling with an external source of CO_2. This assumes gel solution compatibility with the rock formation has been taken into consideration. The pH measurements are slightly higher than one would expect based on the data in Table 2. These pH measurements were taken after the gel had formed and aged using pH paper, therefore they are not a direct comparison to those in Table 2.

Table 3. Stoichiometry of CO_2 Initiated SPI Gels and Stability by Penetrometry.

Formulation No.	Si/PAM/Stab Wt. % Ratio	CO_2 Rate, L/min.	CO_2 Time, Min.	Moles CO_2	Mmoles Na_2O
1	3.2/0/0	0.43	10	0.182	0.0445
2	3.7/0/0	0.43	10	0.187	0.0520
3	4.3/0/0	0.43	10	0.182	0.0594
4	4.3/0.089/0	0.43	10	0.179	0.0594
5	4.3/0.14/0	0.29	10	0.115	0.0594
6	3.3/0.111/0	0.43	10	0.180	0.0463
7	4.3/0.142/0.035	0.43	7	0.123	0.0594
8	4.3/0.142/0.018	0.43	10	0.173	0.0595
9	3.8/0.0125/0.015	0.43	10	0.181	0.0525
10	3.3/0.111/0.027	0.21	10	0.088	0.0463
11	3.3/0.111/0.027	0.43	10	0.181	0.0463
12	3.3/0.110/0.014	0.43	10	0.181	0.0460
13	3.3/0.110/0.014	0.43	15	0.272	0.0460
14	3.1/0.100/0.013	0.43	10	0.181	0.0433
15	1.3/0.103/0.018	0.43	10	0.181	0.0215
Same Samples	**Data**	**Continued**			
Formulation No.	**Si/PAM/Stab Wt. % Ratio**	**Gel Time, Min.**	**Syneresis Wt., %**	**pH**	**Penetrometer, Tenths mm[1]**
1	3.2/0/0	24.1	2.13	9	214.33
2	3.7/0/0	36.8	1.40	10	200.33
3	4.3/0/0	43.0	0.89	10	196.00
4	4.3/0.089/0	19.9	2.66	10	173.33
5	4.3/0.14/0	16.3	1.48	10	187.00
6	3.3/0.111/0	45.1	2.07	10	224.67
7	4.3/0.142/0.035	12.8	1.71	9	170.00
8	4.3/0.142/0.018	13.3	2.28	9	179.00
9	3.8/0.125/0.015	19.8	0.01	9.5	191.67
10	3.3/0.111/0.027	15.2	2.07	9.5	185.00
11	3.3/0.111/0.027	14.8	2.90	9.5	220.00
12	3.3/0.110/0.014	20.0	0.49	9.5	206.33
13	3.3/0.110/0.014	14.2	1.00	9.5	200.67
14	3.1/0.100/0.013	19.5	0.71	9.5	209.00
15	1.3/0.103/0.018	64.0	2.32	9	300.00

1. Average of 3 samples.
2. Formulation No. 3 cracks when applying pressure on the surface.

3. Formulation Nos. 6 and 11 do not crack when applying pressure on the surface. Instead they resonate and spring back when the pressure is removed. Sample 5 appears slightly more firm.

Effect of viscosity

A common method for measuring gel times uses a Brookfield Viscometer or the like to follow how solution viscosity increases over time, however, this procedure was not feasible with SPI gels and especially when CO_2 gas is introduced. Internally initiated SPI gels typically remain at constant viscosity until the pH drops to the point where gelation occurs and a sharp increase to thousands of centipoises (cp) viscosity is observed at that point over a short time interval.

The Brookfield viscosity of these pre-gel solutions containing sodium silicate and PAM are relatively low. The viscosity at 3, 6, and 12 RPM for Formulation 5 was 18, 9, 7.5 cp and for Formulation 7 was 28, 14 and 11.5 cp respectfully.

Pressure Bottle Studies

A gas pressure bottle (rated to 100 psig) was configured for preliminary stoichiometry evaluations of SPI gels initiated with CO_2 under pressure as shown in Photo 1. The vessel containing a magnetic stir bar and the associated SS connections were found to have a volume of 0.1812 L. The SPI formulation chosen for these experiments was No. 11, Table 3 reduced in volume by a factor of 9 making a new pre-gel aqueous volume of 35.2 g or ml (d = 1.00) containing 0.00660 mmoles of Na_2O. This leaves 0.1460 L of volume for the CO_2. The pressure bottle was evacuated using vacuum aspiration and filled to 68 psi (4.62 atm) of CO_2. Using the Ideal Gas Law (Equation 4), this volume contains 0.027 moles of CO_2 added to the bottle or a mole ratio of 4,183/1 for CO_2/Na_2O, just slightly higher than that used in Table 3.

Photo 1. Pressure Bottle Apparatus.

The first experiment was conducted without stirring. After 1 hour, the CO_2 was released and a soft gel formed in the top 2 mm of the liquid. In the second experiment, the mixture was stirred at low speed for 15 minutes, then the mixture was allowed to set for observations. After 1 hour, the pressure was released and a weak gel had formed on the bottom and a harder gel formed on the top 2 mm of the SPI liquid. Experiment 3 was conducted with stirring for 40 minutes and 10 seconds. Soon after stirring stopped, a firm gel formed. The pressure was released and after 18 hours, no syneresis was observed, but when the gel was removed it was not as firm and hard as those that formed by bubbling the CO_2 into solution at atmospheric pressure. A fourth experiment was conducted where the system was not stirred and exposed to the CO_2 for 48 hours. A firm hard gel had formed in the pressure bottle similar to those formed by bubbling CO_2 into the solution. Less than 0.1 ml (0.28 wt. %) of syneresis was observed, which is a stability milestone. *This milestone experiment is the first* *indication of "proof of concept" that CO_2 under pressure and static conditions may be used to form firm SPI gels.*

Bulk Gel Strength Tester - Background

Gel strength is important in diversion of CO_2 from thief zones into areas of lower permeability to improve sweep efficiency. Gel strength is also relevant to long term stability. A milestone for gel strength is achieving performance greater than a competitive technology for water conformance such as an acrylamide metal crosslinked gel. Historically, early tests on the cross-linked PAM gels were based on comparison of their "tongue" size or drawback ability. Silicate gels do not posess the "tongue" flow capacity, but are hard and often have a ringing sensation when the jar containing the gel is thumped with a finger. Gels containing only silicate are brittle and susceptible to fracture when pressure is exerted on the surface. With the presence of a small concentration of PAM, the gels do not fracture. In fact these gels possess a level of elasticity imparted to the silicate polymer by the PAM.

The final gel strength is a parameter of interest for the determination of the suitability of a gel for a given application. For example a strong gel is better than a weak gel for plugging large fractures. Several early attempts in this laboratory focused on the design of an inexpensive extruder device to determine the pressure and rate to extrude the gel through a small opening. It served its purpose, but meaningful data beyond an extrusion time was not possible. Other published methods [6] proposed for evaluating gel strength include a Bulk Gel Strength Tester (BGST), which is based on determining the yield pressure which is required to extrude the gel through a 30 mesh SS screen. The BGST measured the gels extrusion rate (m) at a given pressure drop (ΔP) to extract a yield pressure (ΔP_y), which is the measure of gel flow resistance at rest and the gels apparent viscosity (μ_{app}) is the flow resistance while in motion.

Equations derived from Armour and Cannon's model for flow through a plain square screen were used to calculate the μ_{app} from a linear least squares plot of the gel strength curves (ΔP and m) extrapolated to the y-axis to find ΔP_y. The apparent viscosity term is calculated from Equation 5.

Equation 5.

$$\mu=(5.151 \text{ X } 10^4)(\Delta P/m) - (4.02\text{X}10^{-3})m$$

where μ is viscosity in cp, ΔP is pressure drop in psi and m is flow rate through the BGST screen in g/sec for each data set. Incorporating ΔP_y, the corresponding shear rate (γ) is calculated from Equation 6 where $c = 1.45 \text{ X } 10^{-7}$ psi · sec/cp.

Equation 6.

$$\gamma = (\Delta P - \Delta P_y)/\mu_{app}\, c$$

The Ostwald-de Waele flow behavior index (N') and the flow consistency index (K') are derived from the linear least squares fit of the logarithm of the power law form of apparent viscosity according to Equation 7.

Equation 7.

$$\log \mu_{app} = (N'-1) \log \gamma + \log K'$$

By plotting the log of μ_{app} vs log γ, then the slope = $(N - 1)$ and log $K' = 10^x$.

Bulk Gel Strength Tester - Equipment and Procedure

The BGST is a screen extrusion rheometer designed and published by J. Meister (6). It is a simple device to measure gel strengths using compressed air to force the gel through a screen. The device used in this work, shown in Photos 2 and 3, was modified slightly from that of Meister. The BGST was made from a 2 inch inside diameter polyvinyl chloride (PVC) pipe union glued to an 8-inch length of PVC 2 inch pipe on one side of the union. The other side of the union had a 3 ¾ inch diameter, 30 mesh, 0.012-inch wire diameter, stainless steel (SS) screen fitted inside the screw cap. This leaves a cylinder opening of 1 7/8 inch covered by the screen for gel extrusion. The pipe end of the BGST has a PVC cap with a threaded center hole fitted with a tee. One end of the tee has a pressure gauge and the other end has a toggle valve leading to an air compressor quick disconnect. The tube then serves as a holder for the gel and the volume above the gel serves as a small air pressure cylinder. The gel was made in a Playtex® Drop-In system baby bottle liner that holds up to about 150 ml of gel fluid. The collapsible plastic liner has a circular rim that conveniently fits perfectly inside the PVC union against the screen. The liner is secured in place when the PVC union is screwed together hand-tight.

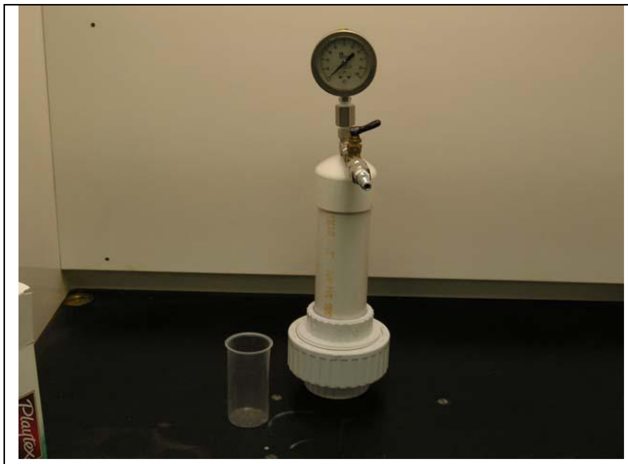


Photo 2. BGST in Upright Position with Adjacent Playtex Drop-In.

Photo 3. Unassembled BGST Showing Playtex Drop-In and SS Screen Position.

The BGST is in the upside down position when the Playtex® Drop-In containing the gel is loaded (filled to the rim with gel). The BGST is carefully turned 180 degrees to right side up and clamped to a support stand above a 600 ml tarred beaker on an electronic balance. At this time, the gel is upside down. If the gel has syneresed, the water weight will be measured as it drips into the beaker over a 2 minute time period.

The air compressor is calibrated with a second pressure gauge to the desired air pressure for the experiment. The air compressor hose is quick connected to the BSGT with the toggle valve in the closed position. Simultaneously, when BGST toggle valve is opened, a timer is started. As the gel is extruded through the screen, the timer is stopped when the gel has finished extrusion and the time is recorded. The BGST union cap is unscrewed, the wire screen is cleaned and the Playtex® Drop-In is discarded.

The extrusion rate (m) is calculated from the weight of gel extruded over the period of time at a given ΔP and plotted to give a gel strength curve of a series of gelling formulations. The desired flow properties are calculated according to Equations 4 – 6.

Bulk Gel Strength Tester - Sample Preparation

The samples were prepared by using N-sodium silicate from PQ Corporation, a nonionic PAM, and water. A few runs included a small amount of a component originally thought to provide additional gel stabilization or enhancement. The PAM used in the dry powder form. The PAM was pre-mixed according to standard procedures to a 5000 ppm concentrate and let down into the formulation. The order of mixing was first water, then PAM, then the optional stabilizing component, and the sodium silicate, making sure homogeneous solutions were obtained before the next feedstock was added. A beaker containing the formulation was placed under a CO_2 manifold with a Flocat LA10 volumetric gas flow meter and CO_2 was bubbled into the solution through a glass frit over a set period of time at a given flow rate at room temperature and atmospheric pressure. Just prior to gelation, the solution was removed from the CO_2 sparge and transferred to the Playtex® Drop-In supported in two 1 7/8 inch SCH40 PVC couplings (1 atop the other) for gelling in the upright position. The formulations gelled over a period of minutes up to an hour and were left for set time periods before being extruded in the BGST.

The exact atmospheric pressure P_{atm} in inches of Hg was converted to atmospheres, the temperature in ^oC converted to ^oK, the CO_2 flow rate in L/min over a set time to L_{CO2}, and the ideal gas law (Equation 4) was used to calculate the number of moles of CO_2 bubbled into solution. Remember as before, this is not the number of moles in solution since most of the CO_2 escapes, but it does significantly lower the solution pH. The number of moles of CO_2 required to neutralize the Na_2O is very small in comparison to the overall amount of CO_2 bubbled into solution.

As a control, a 30 percent PAM, Superflock 1986 emulsion (31% active) polyacrylamide from Kemira Water Solutions was crosslinked with aluminum citrate solution according to the procedure in SPE 135697 [6]. Using the aluminum citrate gel as a control is an attempt to tie the RTA Systems results to the SPE 13567 results. Upon setting, this gel appears to not have a high viscosity, but if the container is shaken hard, it quickly gains a very high “tongue-like” viscosity. To explain this phenomena, Meister suggests the aluminum gels thicken with continued constant stress in the manner of a rheopectic behavior. To be consistent in this work, the aluminum citrate gel was placed in the BGST without shaking and evaluated in the same fashion as the other silicate and SPI gels.

Results

Complete data are available in Tables 3 – 12 for eight experimental silicate formulations and one control aluminum citrate cross-linked PAM formulation. Graphical presentations of the data are shown in Figures 1 and 2 to derive the data for Equations 1 - 3. The formulations consist of four types: 1) Aluminum Citrate gel produced according to SPE 13567, 2) Silicate and CO_2, 3) Silicate, PAM, and CO_2, and 4) Silicate, PAM, a Stabilizer, and CO_2. Two other formula variations were investigated, but they were deemed unsuccessful and are not reported. The tables present data relative to the formulation in the top portion of the table such as composition, pH of the final gel, CO_2 time, flow rate, and volume, Na_2O moles and experimental parameters for the ideal gas law calculation of CO_2 moles. The bottom section of each table contains the relevant parameters from the BGST experiments such as the pressure drop, extrusion time, syneresis level, gel weight, and the calculated extrusion rate, apparent viscosity, shear rate, and the graphically derived values for the yield pressure, flow behavior index, and flow consistency index.

The control aluminum citrate - PAM gel (Photo 4) and the SPI gel (Photo 5) physically appear quite different when extruded through the BSGT. The aluminum citrate - PAM gel is a formless tongue that seems to hang from the screen after it is extruded. The SPI gel extrudes and stays together in a cylinder like form after extrusion.

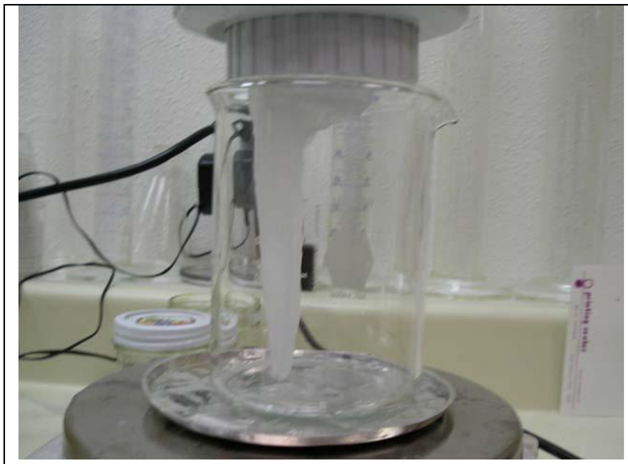


Photo 3. Aluminum Citrate/PAM Gel After Extrusion Through the BSGT.

Photo 4. SPI Gel After Extrusion Through the BSGT.

There is a lot of information in the following tables describing the formulation differences and the flow behavior of the gels. The values for flow behavior index, N', were less than 1, which is indicative of pseudoplastic or shear thinning behavior. If N' is = 1, the fluids are considered to be Newtonian, and if N' is > 1, the fluids are indicative of a dilatent shear thickening fluid. The flow behavior index (N') of all the samples ranged between 0.39-0.80 and the consistency index (K') for all samples was >1 ranging from 0.35 – 10.96 (E^5). Therefore, it is concluded that all samples exhibit pseudoplastic behavior in these experiments.

Several interesting trends regarding the gel strength become apparent when interpreting the BSGT data. These trends are summarized below.

1. The control aluminum citrate gel seemed to approach Newtonian flow from the flow behavior index (N' = 0.80) under the conditions of extrusion in the BGST. The apparent viscosity was moderate, averaging around 6,000 cp and not very sensitive to shear thinning.

2. The silicate gels were non-Newtonian from the flow behavior index (N') ranging between 0.39 – 0.68 with one out lying value at 0.85. Generally, the apparent viscosity was 6 – 10 times higher than the control under low shear and up to 3 times greater under high shear conditions.
3. Longer exposure time to CO_2 at lower flow rates provides silicate gels that are less shear thinning and have a higher viscosity in the higher shear regime. The ratio of the moles of CO_2 bubbled into the solution to the mmoles of Na_2O present in the solution ranged in excess by 2,525 - 687 times that of Na_2O.
4. The presence of low levels of PAM in the silicate formulation produced higher apparent viscosity gels at high shear than the control supporting the observation that the silicate – PAM gels are more elastic compared to the brittle (silicate only) gels.
5. The presence of low concentrations of an experimental stabilizing agent in the silicate – PAM formulation did not appreciably alter the gel stability.
6. Gel syneresis is reduced with slower CO_2 flow rates.

The complete data set for the aluminum citrate – PAM control gel is provided in Table 4. This gel had the lowest ΔP_y corresponding to a high N' which suggests it is approaching a Newtonian fluid and it showed very little shear thinning effect from the μ_{app} over the range of ΔP. There was no syneresis in this gel. The aluminum citrate gels apparent viscosity is in the 5000 – 6000 cp range through out the ΔP range.

Table 4. Aluminum Citrate Gel Formulation and BGST Rheological Performance.

Formulation Control	**Al Citrate, Wt % Al**	**Polymer, Wt. %**	**Synthetic Brine, TDS ppm**	**Gel Time**	**pH**	
Formulation	0.1772	0.3800	64,891	5 days @ 49C	7	
			BGST Rheology Data			
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Weight, g**	**Extrusion Rate, g/sec**	**$Viscosity_{App}$, μ, cp**	**Shear Rate, γ, sec^{-1}**
8	1.5	0.00	95.80	63.87	6,452	5,975
8	1.5	0.00	94.16	62.77	6,564	5,873
10	1.0	0.00	95.58	95.58	5,389	9,714
18	0.6	0.00	93.87	156.45	5,926	18,144
18	0.5	0.00	95.60	191.20	4,849	22,175
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**$Viscosity_{App}$ Average μ, cp**	**$Viscosity_{App}$ Range μ, cp**		
2.41	0.80	0.35481	6,083	1,715		

Tables 4 and 5 compare the rheology of sodium silicate gels without PAM at 0.150 and 0.0408 total moles of CO_2. The ratio of the moles of CO_2 bubbled into the solution to the mmoles of Na_2O present in the solution is 2,525 for Formulation 1 (Table 5), whereas for Formulation 2 (Table 6), the mole ratio of CO_2 to Na_2O is 687. One might anticipate the Formulation 2 gel might be a weaker gel because of its lower CO_2 concentration, but this is not reflected in the viscosity data when Formulations 1 and 2 are compared over the range of ΔP. In fact, Formulation 2 did not extrude at the lower ΔP over 60 seconds and had there been a data point at 8 psi, it would likely be at a much higher viscosity. Therefore, the lower level of CO_2 bubbled into Formulation 2 was sufficient to form a stable gel and perhaps one that is not as shear thinning as Formulation 1.

Formulation 2 had a significantly higher apparent viscosity at higher shear rates than the control in Table 5. Formulation 1 had an N' of 0.39. This value is reflected in the viscosity data shown in Table 6 that shows a higher level of shear thinning in the gel. It could also be a reflection of the tendency for silicate gels without polymer to be very brittle and non-elastic. Syneresis was lower in Formulation 2. Both gels had a pH between 9.5 – 10 after gelation.

Table 5. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 1	**Silicate, Wt.%**	**Polymer, Wt. %**	**Stabilizer, Wt. %**	**pH**	**CO_2 Time, Min.**	**CO_2 Flow Rate, L/min**
Formulation	4.27	0.00	0.0	9.5-10	6.00	0.60
Parameters	**Gelled**	**P, atm.**	**Temp., ^oC**	**CO_2 Vol, L**	**CO_2, moles**	**Na_2O, mmole***
	3 min	1.01	23	3.60	0.150	0.05940
			BGST Rheology Data,			
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**$Viscosity_{App}$ μ, cp**	**Shear Rate, γ, sec^{-1}**
8	14.0	0.00	150.00	10.71	38,461	81
10	10.0	0.00	150.00	15.00	34,340	311
12	1.0	2.00	150.00	150.00	4,120	5,952
14	1.0	11.00	150.00	150.00	4,807	7,963
16	0.8	11.00	150.00	187.50	4,395	11,848
18	Gelled	Prematurely				
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**$Viscosity_{App}$ Average μ, cp**	**$Viscosity_{App}$ Range μ, cp**		
8.45	0.39	10.96	17,255	34,341		
* mmole = 0.001 mole.						

Table 6. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 2	**Silicate, Wt.%**	**Polymer, Wt. %**	**Stabilizer, Wt. %**	**pH**	**CO_2 Time, Min.**	**CO_2 Flow Rate, L/min**
Formulation	4.27	0.00	0	9 - 10	12.00	0.0830
Parameters	**Gelled**	**P, atm.**	**Temp., ^oC**	**CO_2 Vol, L**	**CO_2, moles**	**Na_2O, mmole**
	3 min.	1.002	25	0.996	0.0408	0.05940
			BGST Rheology Data			
ΔP, psi	**Time, sec.**	**Syneresis Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**$Viscosity_{App}$ μ, cp**	**Shear Rate, γ, sec^{-1}**
8	>60	0.00	0	0	-	-
10	5.4	0.00	132.2	24.48	21,040	734
12	5.0	0.00	87.1	17.42	35,483	824
14	4.2	0.00	103.2	24.57	29,349	1,466
16	3.5	0.00	100.9	28.83	28,588	1,988
18	2.4	0.00	97.6	40.67	22,799	3,098
ΔP_y	**Flow Behavior**	**Flow Consistency**	**$Viscosity_{App}$ Average**	**$Viscosity_{App}$ Range**		

	Index, N'	Index, K' E^5	μ, cp	μ, cp		
7.76	0.68	3.02	27,452	12,684		

Tables 7, 8 and 9 compare the rheology of SPI sodium silicate gels with low concentrations of PAM treated with 0.150, 0.075 and 0.814 total moles of CO_2 (Formulations 3, 4 and 5). The viscosity shear-thinning pattern of SPI Formulation 3 with silicate, PAM and 0.15 mole of CO_2 is very similar to Formulation 1 without PAM, except the gel has a much higher apparent viscosity level at higher shear rates supporting Trend No's.2 and 4 above. At the higher ΔP, Formulation 3 has almost 2.5 times the viscosity as Formulation 1. The high viscosity, low shear-thinning pattern of Formulation 4 is similar to the pattern of Formulation 2, without the PAM, except that like Formulations 1 and 3, the CO_2 flow rate was at 0.6 L/min. When the CO_2 moles (0.0814) and flow rate (0.333L/min) were lowered in Formulation 5, the resistance to shear thinning was even more apparent supporting Trend 3. An interesting note, Formulation 4 has the highest N' of all the SPI and silicate gel formulations supporting the reduced shear thinning sensitivity. Syneresis was generally less in Formulations 4 and 5 at the lower concentration and delivery rate of CO_2 supporting Trend 6 above.

Table 7. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 3	Silicate, Wt.%	Polymer, Wt. %	Stabilizer, Wt. %	pH	CO_2 Time, Min.	CO_2 Flow Rate, L/min
Formulation	4.42	0.147	0	9 – 10	6.00	0.60
Parameters	**Gelled**	**P, atm.**	**Temp., °C**	**CO_2 Vol, L**	**CO_2, moles**	**Na_2O, mole**
	6 min.	1.014	23.5	3.60	0.150	0.0615
			BGST Rheology Data			
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**Viscosity$_{App.}$ μ, cp**	**Shear Rate, γ, sec^{-1}**
8	20	9.32	150.00	7.50	54,944	200
10	3.7	7.18	150.00	40.54	12,706	1,949
12	2.9	11.35	150.00	51.72	11,950	3,226
14	1.9	1.5	150.00	78.95	9,134	5,731
16	1.7	0.0	150.00	88.24	9,340	7,081
18	2.7	5.6	150.00	55.56	10,508	7,607
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**Viscosity$_{App}$ Average M, cp**	**Viscosity$_{App}$ Range μ, cp**		
6.7	0.54	8.32	18,097	45,810		

Table 8. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 4	Silicate, Wt.%	Polymer, Wt. %	Stabilizer, Wt. %	pH	CO_2 Time, Min.	CO_2 Flow Rate, L/min
Formulation	4.27	0.142	0.0	9	3.00	0.60
Parameters	**Gelled**	**P, atm.**	**Temp., °C**	**CO_2 Vol, L**	**CO_2, mole**	**Na_2O, mmol**
	3 min	1.01	25.0	1.80	0.075	0.0594
			BGST Rheology Data			
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**Viscosity$_{App}$ μ, cp**	**Shear Rate, γ, sec^{-1}**
8	12.2	1.50	159.00	13.03	31,619	45.80
10	5.45	1.90	159.00	29.17	17,656	863

12	4.20	0.00	159.00	37.86	16,328	1,778
14	4.20	0.00	159.00	37.86	19,049	2,248
16	3.50	8.20	159.00	45.43	18,142	3,121
18	1.20	0.00	157.00	130.83	7,086	9,937
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**$Viscosity_{App}$ Average M, cp**	**$Viscosity_{App}$ Range µ, cp**		
7.79	0.85	0.55	18,313	24,533		

Table 9. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 5	**Silicate, Wt.%**	**Polymer, Wt. %**	**Stabilizer, Wt. %**	**pH**	**CO_2 Time, Min.**	**CO_2 Flow Rate, L/min**
Formulation	4.27	0.142	0	9-10	6.00	0.330
Parameters	**Gelled**	**P, atm.**	**Temp., °C**	**CO_2 Vol, L**	**CO_2, mole**	**Na_2O, mmol**
	18 min	1.002	24	1.980	0.0814	0.05940
BGST Rheology Data						
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**$Viscosity_{App}$ µ, cp**	**Shear Rate, γ, sec^{-1}**
8	3.5	0.14	133.00	38.00	10,844	1,793
10	5.0	0.10	134.10	26.82	19,206	1,731
12	2.5	0.10	140.00	56.00	11,038	4,261
14	1.6	0.12	138.59	86.62	8,325	7,307
16	1.6	0.22	140.26	87.66	9,401	7,938
18	1.4	0.50	132.09	94.35	9,827	8,997
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**$Viscosity_{App}$ Average µ, cp**	**$Viscosity_{App}$ Range µ, cp**		
5.18	0.58	4.27	11,440	9,805		

Tables 10, 11 and 12 compare the rheology of SPI sodium silicate gels with PAM and an added component originally thought to stabilize the gels treated with 0.150 and 0.075 total moles of CO_2 (Formulations 6, 7 and 8). The viscosity shear-thinning pattern of SPI Formulation 6 with silicate, PAM, stabilizer and 0.15 mole of CO_2 is somewhat similar to silicate only Formulation 1 without PAM, because it shear thins to an apparent viscosity in the range of 4,000 to 5,000. Lowering the stabilizer concentration in Formulation 8 and keeping the CO_2 concentration constant creates a viscosity behavior similar to SPI Formulation 4, which is the same formulation without the stabilizer. At the higher ΔP, Formulation 8 has almost 2 times the viscosity as Formulation 1. When the CO_2 moles (0.075) and flow time (3 as opposed to 6 minutes) were lowered at the same low stabilizer level in Formulation 9, the viscosity resistance to shear thinning was very similar to Formulation 4 without the additive. Thus the stabilizer was not shown to be beneficial to the SPI gels supporting Trend 5 above. Syneresis was generally less in Formulations 6 at the higher stabilizer concentration, which had been observed in previous research.

Table 10. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 6	**Silicate, Wt.%**	**Polymer, Wt. %**	**Stabilizer, Wt. %**	**pH**	**CO_2 Time, Min.**	**CO_2 Flow Rate, L/min**
Formulation	4.27	0.142	0.070	10	6.00	0.60

Parameters	Gelled	P, atm.	Temp., °C	CO_2 Vol, L	CO_2, moles	Na_2O, mmole
	6 min.	1.01	23	3.60	0.150	0.05940
BGST Rheology Data						
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**Viscosity_{App} μ, cp**	**Shear Rate, γ, sec^{-1}**
8	24.0	0.8	150.00	6.25	65,933	20.92
10	3.0	0	150.00	50.00	10,301	1,473
12	2.0	0	150.00	75.00	8,241	3,515
14	2.2	0	150.00	68.18	10,577	4,043
16	0.8	0.28	150.00	187.50	4,395	12,868
18	0.8	0.7	150.00	187.50	4,944	14,228
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K'**	**Viscosity_{App} Average μ, cp**	**Viscosity_{App} Range μ, cp**		
7.8	0.60	2.24	17,399	51,538		

Table 11. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 7	Silicate, Wt.%	Polymer, Wt. %	Stabilizer, Wt. %	pH	CO_2 Time, Min.	CO_2 Flow Rate, L/min
Formulation	4.27	0.142	0.035	8.5-9	6.00	0.60
	Gelled	**P, atm.**	**Temp., °C**	**CO_2 Vol, L**	**CO_2, moles**	**Na_2O, mmole**
Parameters	6	1.014	23.0	3.60	0.150	0.0594
BGST Rheology Data,						
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**Viscosity_{App} μ, cp**	**Shear Rate, γ, sec^{-1}**
8	12.0	4.80	150.00	12.50	32,996	423
10	4.4	3.00	151.00	34.32	15,009	1,847
12	3.0	7.00	150.00	50.00	12,362	3,358
14	2.4	11.50	150.00	62.50	11,538	4,794
16	2.0	7.20	150.00	75.00	10,989	6,289
18	2.2	0.0	151.00	68.64	13,508	6,137
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K'**	**Viscosity_{App} Average μ, cp**	**Viscosity_{App} Range μ, cp**		
7.8	0.58	4.68	16,062	22,007		

Table 11. SPI Gel Formulation and BGST Rheological Performance.

Formulation # 8	Silicate, Wt.%	Polymer, Wt. %	Stabilizer, Wt. %	pH	CO_2 Time, Min.	CO_2 Flow Rate, L/min
Formulation	4.27	0.142	0.035	9	3.00	0.60
Parameters	**Gelled**	**P, atm.**	**Temp., °C**	**CO_2 Vol, L**	**CO_2, moles**	**Na_2O, mmole**
	6.5 min.	0.997	21	1.8	0.075	0.0594
BGST Rheology Data						
ΔP, psi	**Time, sec.**	**Syneresis, Wt., g**	**Gel Wt., g**	**Extrusion Rate, g/sec**	**Viscosity_{App} μ, cp**	**Shear Rate, γ, sec^{-1}**
8	23.0	7.20	149.00	6.48	63,610	3.25
10	8.0	6.50	149.00	18.63	27,656	506
12	3.0	8.56	149.00	49.67	12,445	2,233
14	1.8	1.24	149.00	82.78	8,711	4,774

16	1.8	8.6	149.00	82.78	9,956	5,562
18	1.2	9.2	149.00	124.17	7,467	9,264
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K'**	**$\text{Viscosity}_{\text{App}}$ Average µ, cp**	**$\text{Viscosity}_{\text{App}}$ Range µ, cp**		
7.97	0.54	3.98	21,641	56,143		

Figure 1 shows the linear plot of Extrusion Rate vs Delta P for the formulations. The y-intercept is the yield pressure of the gel useful in calculating the shear rate using Equation 2. Note the control aluminum citrate gel lies on the fringe of the SPI points and has the lowest yield pressure.

Figure 1. Plot of Extrusion Rate vs Delta P.

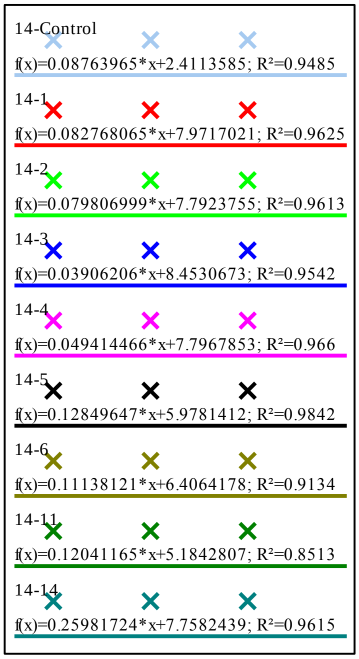
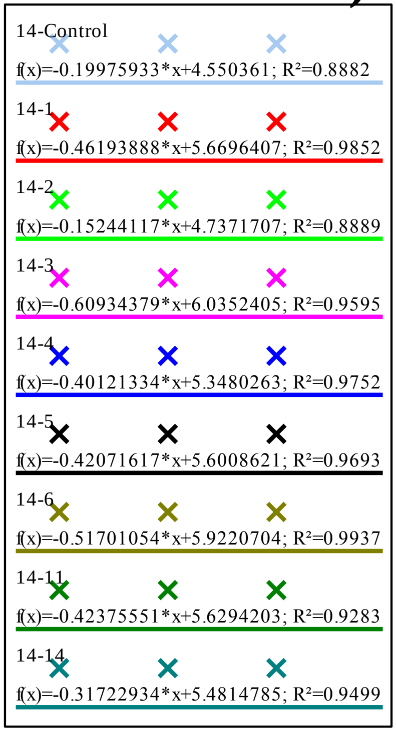


Figure 2 is a linear plot of the log of apparent viscosity vs the log of shear rate. The slope and the y-intercept of these lines are useful in deriving the flow behavior and flow consistency indexes.

Figure 2. Plot of log (Viscosity vs Shear Rate).



Results – Effect of Gel Aging on BGST

The BGST was used to establish an optimum age time after the SPI gel was formed. The Formulation Parameters shown in Table 12 were followed to create a series of SPI gels that were identical except for the time period between gel formation and the time when the bulk gel strength test was performed. The aging times chosen were 1, 2, 3, 5, 7 and 10 days. The BGST rheological data are shown in Tables 13 – 18 for these aged SPI gels.

Table 12. SPI Gel Formulation and BGST Rheological Performance.

	Silicate, Wt.%	**Polymer, Wt. %**	**Stabilizer, Wt. %**	**PH**	**CO_2 Time, Min.**	**CO_2 Flow Rate, L/min**
Formulation	4.27	0.142	0.0	9	3.00	0.60
Parameters	**Gelled**	**P, atm.**	**Temp., ^{o}C**	**CO_2 Vol, L**	**CO_2, mole**	**Na_2O, mmol**
	3 min	1.01	25.0	1.80	0.075	0.0594

The apparent viscosity at the lower extrusion rate shows a distinctive increase throughout the series of aging times ranging from 31,619 – 97848 cp. However, at the higher extrusion rates, this trend does completely hold. A plot of aging time vs average apparent viscosity shows a reasonable fit of the equation y = 1433x + 18628, where the least squares fit, R^2 = 0.8639. The flow behavior index values, N', are reasonable ranging between 0.61 – 0.85, with the highest value representing one day of aging. From the apparent viscosity data (average and range included), it appears that gels aged five days or longer tend to show better gel strength than gels aged less than 5 days.

Table 13. SPI Gel #9 Aged 1 Day Prior to BGST – Rheological Performance.

ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ µ, cp	Shear Rate, γ, sec^{-1}
8	12.2	1.50	159.00	13.03	31,619	45.80
10	5.45	1.90	159.00	29.17	17,656	863
12	4.20	0.00	159.00	37.86	16,328	1,778
14	4.20	0.00	159.00	37.86	19,049	2,248
16	3.50	8.20	159.00	45.43	18,142	3,121
18	1.20	0.00	157.00	130.83	7,086	9,937
ΔP$_y$	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E[5]**	**Viscosity$_{App}$ Average µ, cp**	**Viscosity$_{App}$ Range µ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.79	0.85	0.55	18,313	24,533	0.9613	0.0798

Table 14. SPI Gel #10 Aged 2 Days Prior to BGST – Rheological Performance.

ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ µ, cp	Shear Rate, Γ, sec^{-1}
8	21.00	5.08	150.93	7.19	57,336	105.
10	6.30	3.59	153.74	24.4	21,108	937
12	5.00	4.61	151.50	30.37	20,353	1,650
14	3.00	4.82	150.70	50.23	14,356	3,300
16	2.00	4.91	145.40	72.70	11,336	5,396
18	2.00	8.01	144.90	72.45	12,797	5,858
ΔP$_y$	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E[5]**	**Viscosity$_{App}$ Average µ, cp**	**Viscosity$_{App}$ Range µ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.13	0.61	3.31	22,881	44,539	0.9597	0.137

Table 15. SPI Gel #11 Aged 3 Days Prior to BGST – Rheological Performance.

ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ µ, cp	Shear Rate, γ, sec^{-1}
8	22.00	12.00	150.90	6.86	60,078	24.1
10	7.00	0.90	154.70	22.10	23,308	654
12	2.50	13.14	153.70	61.48	10,054	2,888
14	1.50	0.00	148.80	99.20	7,269	5,892
16	-	1.52	149.00	-	-	-
18	1.10	0.20	151.00	137.27	6,754	10,426
ΔP$_y$	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E[5]**	**Viscosity$_{App}$ Average µ, cp**	**Viscosity$_{App}$ Range µ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.79	0.62	2.19	21,492	53,324	0.9761	0.071

Table 16. SPI Gel #12 Aged 5 Days Prior to BGST – Rheological Performance.

ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ µ, cp	Shear Rate, γ, sec^{-1}
8	22.00	3.48	147.95	6.73	61276	1.46
10	11.80	0.00	152.95	12.96	39,740	349
12	5.00	0.00	150.35	30.07	20,556	1,346
14	4.00	0.00	149.45	37.36	19,301	2,149

16	2.00	1.50	154.65	77.33	10,658	5,185
18	1.90	2.62	153.45	80.76	11,480	6,015
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**Viscosity$_{App}$ Average μ, cp**	**Viscosity$_{App}$ Range μ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.99	0.66	2.04	27,168	50,618	0.9622	0.117

Table 17. SPI Gel #13 Aged 7 Days Prior to BGST – Rheological Performance.

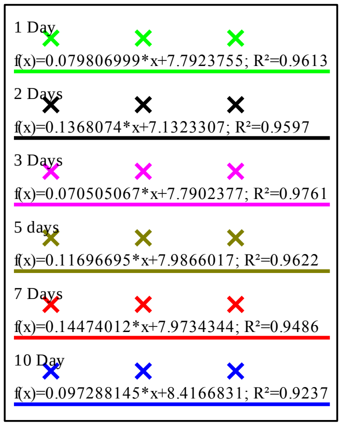
ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ μ, cp	Shear Rate, γ, sec^{-1}
8	30.00	12.00	142.70	4.76	86,632	2.39
10	10.00	0.90	151.30	15.13	34,045	411
12	-	13.14	146.70	-	-	-
14	4.00	0.00	155.50	38.88	18,550	2,242
16	3.20	1.52	146.50	45.78	18,002	3,076
18	1.80	0.2	147.50	81.94	11,314	6,114
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**Viscosity$_{App}$ Average μ, cp**	**Viscosity$_{App}$ Range μ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.97	0.76	1.18	33,709	75,318	0.9486	0.145

Table 18. SPI Gel #14 Aged 10 Days Prior to BGST – Rheological Performance.

ΔP, psi	Time, sec.	Syneresis, Wt., g	Gel Wt., g	Extrusion Rate, g/sec	Viscosity$_{App}$ μ, cp	Shear Rate, γ, sec^{-1}
8	35.00	1.70	147.40	4.21	97,848	4.93
10	10.00	5.27	147.10	14.71	35,017	408
12	5.80	5.01	146.60	25.28	24,455	1,148
14	2.20	1.56	147.20	66.91	10,778	3,884
16	2.00	4.41	146.10	73.05	11,289	4,933
18	1.00	2.75	145.30	145.30	6,381	10,884
ΔP_y	**Flow Behavior Index, N'**	**Flow Consistency Index, K' E^5**	**Viscosity$_{App}$ Average μ, cp**	**Viscosity$_{App}$ Range μ, cp**	**Extrusion Rate vs ΔP, R^2**	**Extrusion Rate vs ΔP, Slope, m**
7.93	0.66	2.04	30,960	91,467	0.9237	0.0973

Although the least squares fit correlation coefficient, R^2, indicate a very good linear fit of the relationship between the extrusion rate, g/sec vs. ΔP over the SPI gel aging times, the expected relationship between the slope of the lines, m, was not apparent. The y-intercept yield pressure values, ΔP_y, were virtually identical ranging between 7.79 – 7.99 (with the exception of 7.13 for 2 days aging), but the higher shear rate data forced the equations to cause the differences in the slopes. At the higher shear rates, the short time measurement during the extrusion process was more difficult to accurately determine. This is borne out by the order of increasing slopes correlated to days aging increases in the order: 3, 1, 10, 5, 2, and 7 which is show in Figure 3, the Plot of Extrusion Rate vs Delta P for the same order of the lines from top to bottom. If one averages the last three extrusion rates for each aging time the order of extrusion rate from lowest to highest is 3, 10, 1, 5, 2, and 7. Only days aged 1 and 10, are switched in the order suggesting fair agreement, that there is a need for triplication in this test procedure to reduce the error.

Figure 3. Plot of Extrusion Rate vs Delta P.



V.1.4.0 Task 2 – SPI - CO_2 Gel System Performance in Sand Packs

The work on this task was accomplished by RTA Systems, Inc. personnel in its Bartlesville, OK laboratory to determine the feasibility of transferring the technology in Task 1 to dynamic testing system in a sand pack.

Sand Packs

Sand pack holders were fabricated from stainless steel for high pressure work with a packed volume of 1.5 inches in diameter and one foot long. The sand pack holders had screw cap ends with threaded holes. A 1.5 inch diameter, 30 mesh, 0.012 inch wire diameter, stainless steel screen was fitted inside each screw cap followed by a steel washer (1/8 inch thick with a ¾ inch hole) to hold the screen flat when the caps are in place. The sand pack threads were Teflon taped (as were all fittings) and sealed with pipe dope. The sand pack holders had four pressure ports incorporated along the length of the holder and one at each end for a total of six pressure ports. Pressure and temperature was monitored by a Fuji Electric PHL Paperless Recorder that displays the data on a color LCD and includes the PC support software to enable the translation to Excel.

Unground Ottawa F-110 ASTM-Graded silica sand (U.S. Silica) was the primary medium in the middle 10-inch length of the sand pack. Coarse silica sand (Ottawa 20-30 mesh, US Silica) was packed in the 1-inch length between the screens and the pack at each end. Both sands were soaked in concentrated hydrochloric acid overnight to remove traces of alkali carbonates and then rinsed with copious amounts of water prior to drying in a forced air oven at 160^{o}F. Dry sands are packed manually in the holder using a vibrator. The pack is saturated with water and water was flowed through the pack at high flow rates while using a vibrator to pack the wet sand further.

The pump was a Cheminert RT Metering Pump manufactured by Laboratory Data Control, a Division of Milton Roy Company. Tubing volumes were measured going into the sand pack and exiting the sand pack. A tracer run was conducted to determine the pore volume of the sandpack. A 1% KNO_3 solution was injected to displace the resident water. KNO_3 concentration in the effluent is measured using Hach AquaChek Nitrate test strips (1 – 50 ppm NO_3^-) for nitrate determination. Flow rates were measured using a balance. Integration of the normalized concentration as a function of grams of fluid produced from the pack gives the pore volume in grams of water and converted to milliliters. Permeabilities of each section and for the overall length of the pack were determined by measuring pressure drops across the sections and the effluent flow rate using a balance. Tracer and permeability runs were conducted at room temperature.

Flow Experiment Procedure

The flow equipment is shown in Photo 5. The data recorder is on the left, adjacent to the CO_2 cylinder. The SS sand pack is in the center with the pressure taps and to the right side is a SPI or brine reservoir (white cylinder) driven by the pump in the bottom right hadn corner. To the left of the CO_2 cylinder, are two 300 ml SS reservoirs, one intended for CO_2 storage and the other for brine storage that could be driven by CO_2 pressure.


Photo 5. Pressure Apparatus For Sand Pack Experiments.

The sand pack was prepared in water and the Pore Volume (PV) of the sand pack was calculated. The SPI gelant was prepared, placed into the white reservoir and 2 - 3 pore volumes is injected into the sandpack by pump. Effluent fractions were collected in weighed vials, and pH was measured. Pressure drops across the sections and the overall length of the pack were recorded. The pump was shut down, the top sand pack valve was closed, and the CO_2 was pressurized into the left SS reservoir and into the sand pack until the pressure reached to 700 – 725 psi (regulator limit). The CO_2 cylinder was shut off and the pressure remained at 700 for 64 hours. Pressure drops across the sections were monitored. After gelation, numerous 2 – 3 PV of 1% KCl brine water was injected monitoring pressure drop and effluent fractions for pH.

The milestone for Task 2 was to demonstrate the SPI gel system was tolerant to continued exposure to multiple pore volumes of CO_2 and brine without significant pressure drop and washout of SPI components.

Experiment Results – Initial Test

A sand pack was prepared according to the procedure disclosed. The pore volume was determined to be 101.58 ml. The sand pack was saturated when approximately 3 pore volumes of SPI Formulation 3, Table 7 were injected into it. The silicate-polymer fluid was then subjected to carbon dioxide and allowed to set for approximate 64 hours.

The sand pack with the gelled solution was chased with 1% potassium chloride (KCl) brine with a green dye tracer. The brine was placed in a SS 300 ml reservoir and driven by CO_2 pressure from the second SS 300 ml reservoir. The pressure was at about 700 psi. No effluent was produced for more than 24 hours. Some of the pressure data are presented in Figures 5 – 8.

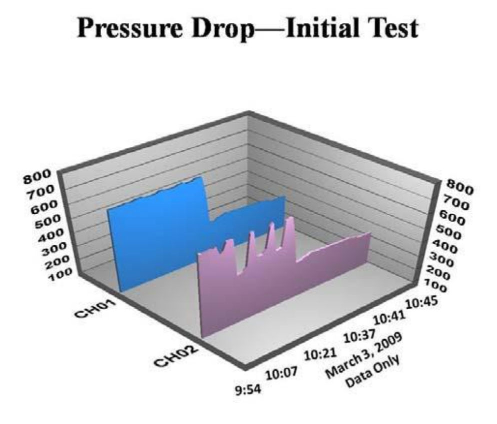


Figure 5. Pressure Drop, Sectors 1 & 2.

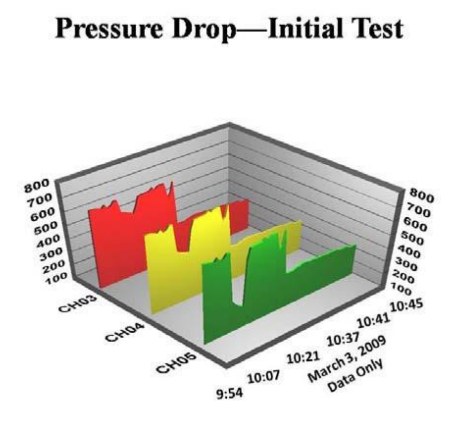


Figure 6. Pressure Drop, Sections 3, 4 & 5.

Figure 5 depicts the pressure drop in the first two sectors. In sector 1 a pressure decrease occurred and held almost constant for the remainder of the time. For sector 2 the saw tooth pressure drops are typical of particle movement. This movement could be the gel, sand rearrangement or a combination of these. Once again the pressure dropped to the 300 psi range where it remained relatively constant for the duration. Both of these sectors show a consistent permeability reduction.

Sectors 3-5 are shown in Figure 6 above. Sectors 3, 4, and 5 all have indications of particle movement. Once again, the movement could be gels, sand or a combination of both of these. The sand movement is not significant enough to be extruded thru the exit port since no sand was observed in the effluent samples collected. Also once the pressure drops to approximately 300 psi it remains there for the duration.

Figure 7 shows the pressure drop recorded for the final sand pack sector. Once again the data show indications of particle movement. This movement could be gel, sand or a combination of both. Still no sand was produced in the effluent samples collected. After the pressure dropped to approximately 300 psi, it remained relatively constant indicating that the particle movement was not significant after initial rearrangement.

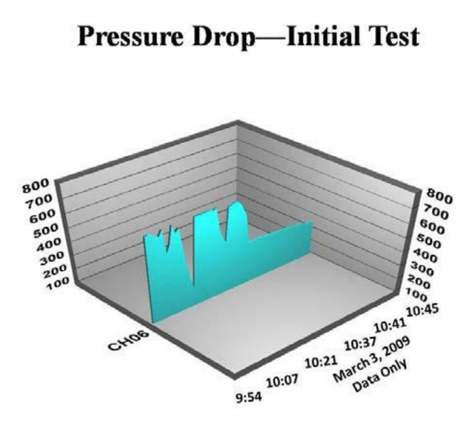


Figure 7. Pressure Drop, Sector 6.

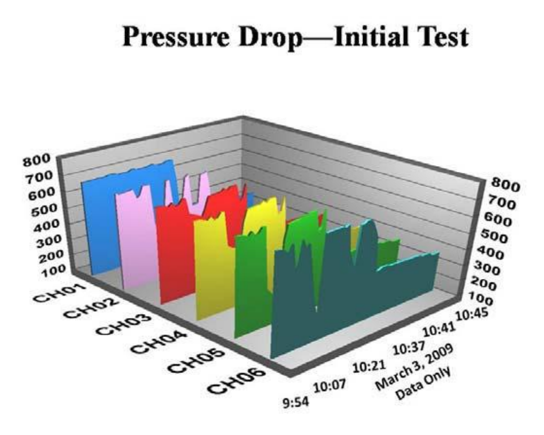


Figure 8. Pressure Drop, All Sectors.

Figure 8 shows the pressure drops in all of the sectors. Note the minimal saw tooth pressure drops occur in Sector 1 compared to the others. Sectors 5 and 6 have the largest saw tooth pressure drops, but all sectors hold relatively constant once the pressures drop to approximately 300 psi. Remember that this means that rearrangement has slowed.

Other observations are reviewed for the effluent fluid produced during the time periods shown in Figures 5 – 8. The first effluent sample collected occurred in a 47 minute period and was measured as 49 ml as shown in Figure 9 where the blue line represents the milliliters collected and the gray line represents the effluent flow rate. This cut is equivalent to 48.4% of the pore volume and was collected after the sand pack was subjected to KCl chase brine for approximately 26 hours. In all cases, the effluent color, pH and volumes were recorded.

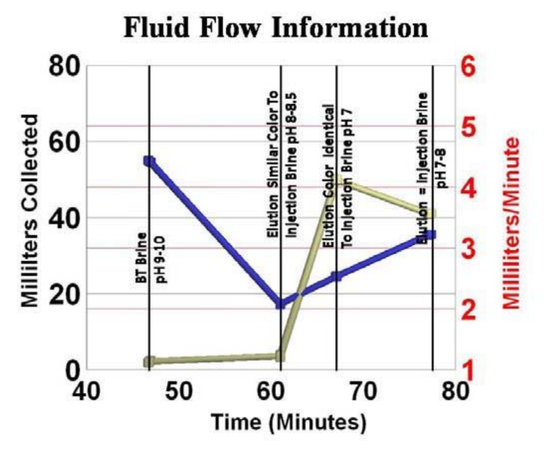


Figure 9. Effluent Sample Results.

The pH of the first effluent was the highest and indicated that chase brine with some SPI gel. The ml/minute calculation showed that the early effluent production rate was approximately 1.5 ml/minutes while the later rates were ~ 4 ml/minute. The last sample was collected at 3 ml/minute. This is encouraging because it could show that the SPI gelled with CO_2 is not breaking down with time.

Samples of Ottawa sand before and after being exposed to a SPI fluid formulation have shown pore throat size reduction in the gelled example. Figure 10 is an example of the Ottawa F-110 sand before gel solution. The red arrows highlight the spaces between the sand grains. Note the size of these spaces.

Figure 11 depicts the effect of a gelled SPI formulation on Ottawa F-110 sand. Note that the number of pore throats was reduced and the open ones appear to be smaller. These pore throats could have been created when the gelled sand pack sample fractured apart during sampling. The red arrow indicates a pore throat. It is reduced in size. The green arrow highlights a black impurity in the Ottawa F-110 sand. It is not a pore throat.

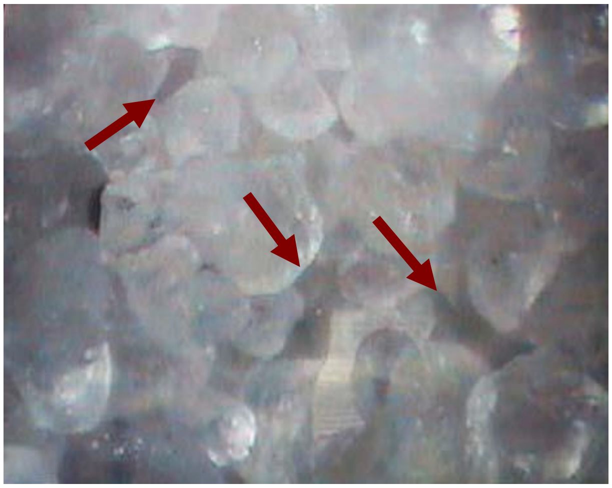


Figure 10. Ottawa F-110 Sand. No Gel, 35 X Magnification

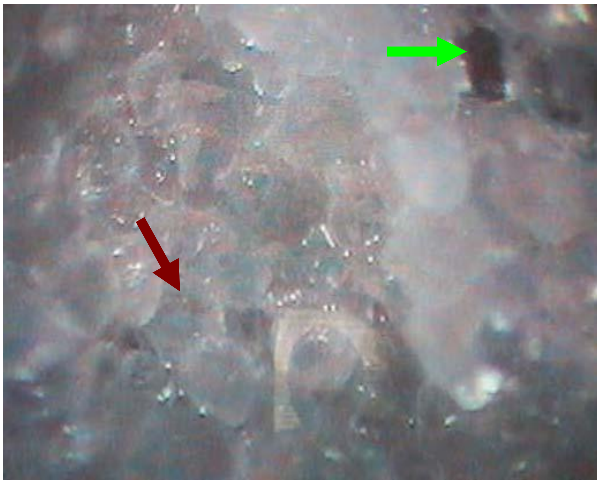


Figure 11. Ottawa F-110 Sand From Center of Sand Pack,

This experiment has provided "proof of concept" that gels can be formed when SPI fluid formulations were activated with carbon dioxide. This is the first of its kind flow test demonstrating that the gel formed could be used to improve oil recoveries by improving reservoir sweep efficiency.

Experimental Sand Pack Results # 2 - Phase I, Task 2

A sand pack was prepared according to the previously disclosed procedure. The pore volume was determined to be 121.37 ml. Approximately 2.6 PV of SPI Formulation 3, Table 7 was injected into the sand pack. The SPI fluid was then subjected to carbon dioxide at 700 psi and allowed to set for approximate 64 hours. The top needle valve was slowly opened over the next seven days to ¼ turn allowing CO_2 to escape. The pressure slowly dropped to 101.5 psi over that period collecting 9.01 ml of pH = 10 fluid, largely toward the end of the period. Much of the fluid was sheared gel. Brine was pumped into the sand pack on the 8th and 9th days at 1 PV/day. On day 8, another 6.04 g of fluid was collected. The pressure fluctuated between 50 – 190 psi. Overnight, a 61.22 ml sample of fluid had been collected for a total of 76.27 ml by morning of the 8th day. The pH of the fluids quickly dropped to between the 7 - 8 range as most of the fluid was brine as indicated by a dye. The pressure fluctuations, although over a smaller range still continued.

A sand pack was prepared according to the procedure disclosed in Experiment 1. The pore volume was determined to be 121.37 ml. Approximately 2.6 PV of SPI Formulation 3, Table 6 (Final Report) was injected into the sand pack. The SPI fluid was then subjected to carbon dioxide at 700 psi and allowed to set for approximate 88 hours. The top valve was slowly opened over the next 168 hours to ¼ turn allowing CO_2 to escape. The pressure slowly dropped to 101.5 psi over that period collecting 9.01 ml of pH = 10 fluid, largely toward the end of the period. Much of the fluid was sheared gel. Brine (1% KCl) was pumped into the sand pack 0.83 PV/day containing a green dye tracer. Another 6.04 ml of fluid was collected, which had not been gelled and the pH dropped to 9. Over the next 72 hours, the pH quickly dropped to 7.5 and a total of 2.39 PV of brine were collected as effluent with lots of CO_2. Then the brine was stopped, the valve closed and the sand pack was again pressured up to 700 psi with CO_2. The valve was again opened slowly and brine was restarted until it was stopped. The pH of the effluent samples was in the range of 6.5 – 7.5 during this time.

Some of the pressure data are presented in Figure 12 that depicts the pressure drop in the first two sectors. Note that the initial pressure drops are almost equal. Also that the pressure decreases occur simultaneously. As in Sand Pack test number 1, the saw tooth pressure changes indicate that there is particle movement. This movement could be sand, gel, or a combination of these, bt more likely, it is CO_2, coming out of solution.

After the second carbon dioxide injection, the lower pressures are higher than those observed before this injection. This means that the second CO_2 injection did react with the gel system already in place. Also note that at about day 10 the pressures, though fluctuating, were consistently higher than even the earlier times after the second CO2 injection. The saw tooth pressure drops even though reduced are typical of particle or CO_2 movement. Both of these sectors show a consistent permeability reduction.

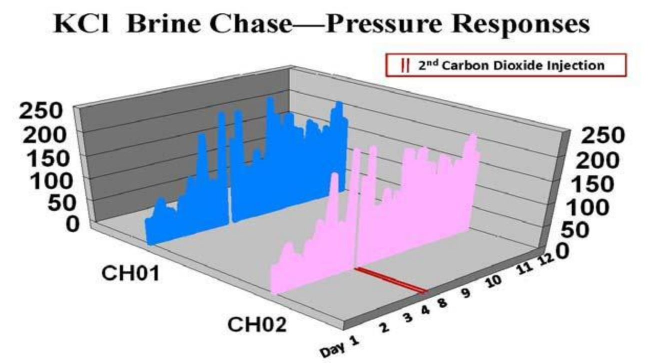


Figure 12. Pressure Drops, Sectors 1 and 2.

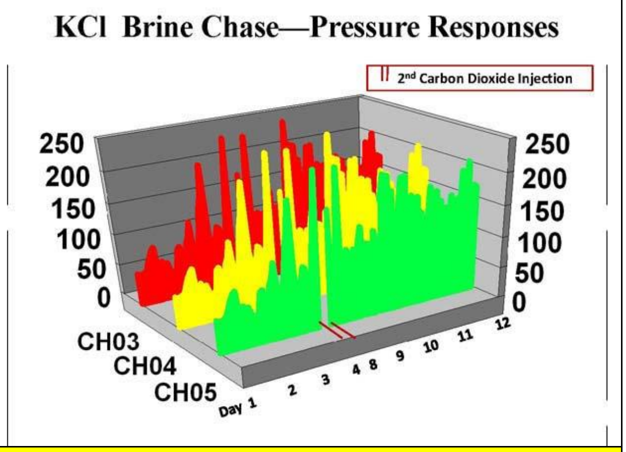


Figure 13. Pressure Drops, Sectors 3 – 5.

Sectors 3-5 are shown in Figure 8. Sectors 3, 4, and 5 all have indications of particle or CO_2 movement. It is more severe than that observed in Sectors 1 and 2. If the movement involved any sand, it was not significant enough to be extruded thru the exit port since no sand was observed in the effluent samples collected. If the movement were gel, no chunks of gel were observed first 9 ml when the valve was initially opened. Also once the second carbon dioxide injection was completed, the lower pressure drops are higher than those recorded prior to it

Figure 14 shows the pressure drop recorded for the final sand pack sector. The pressure changes reflect those observed in Sectors 3, 4, and 5. Once again the data show indications of particle or CO_2 movement. This movement could be gel, sand or a combination of both of them. No sand was produced in the effluent samples collected, but CO_2 was observed in the effluent throughout the test. The lower pressure drops after the second carbon dioxide injection continues to be higher than those before this injection.

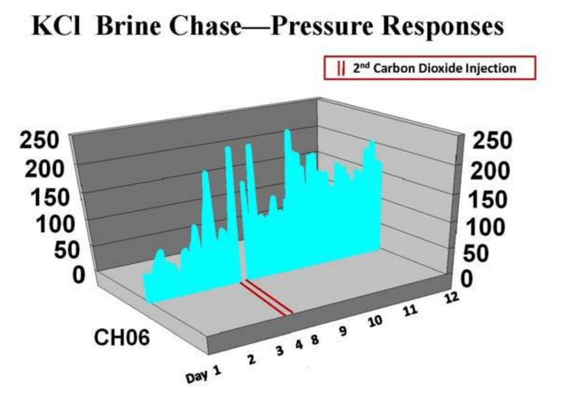


Figure 14. Pressure Drop, Sector 6.

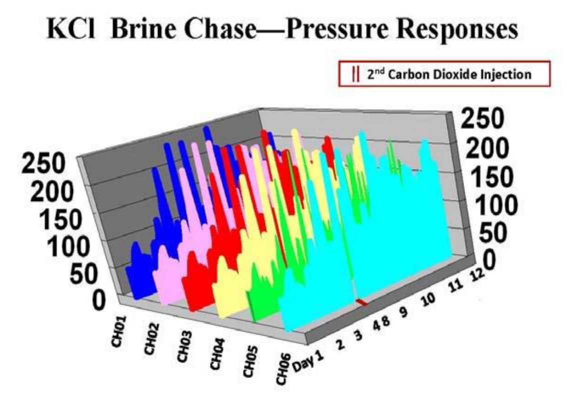


Figure 15. Pressure Drop, All Sectors.

Figure 15 shows the pressure drops in all of the sectors. Note that the saw tooth pressure drops seem to occur in all sectors simultaneously. Sector 1 has slightly higher pressures than the other sectors especially immediately after the second carbon dioxide injection when compared to the others. Sector 5 seems to have the most saw tooth pressure changes especially as the days approach the day 10 – 12 time line. This is the last section, which is completely in the sand pack so it is not unexpected that it would be most influenced by particle movement from the previous sectors. Still all sectors have experienced permeability reduction.

The second sand pack test re-enforced the fact that gels were formed when SPI fluid formulations were activated with carbon dioxide. This is also the first test where a two carbon dioxide injections followed by two chase brine sequences occurred. This sequence demonstrates that in the field if carbon dioxide contacts the gels during subsequent injections then the gels can be reinforced to form even stronger gels, which could improve reservoir sweep even more.

4.1.3 Task 3 – Site Identification and Preliminary Design of Potential Field Test of SPI Gel System

The work on this task was primarily conducted by Impact Technologies, LLC personnel at its Tulsa, OK office with support from the RTA Bartlesville personnel and Dwight Rychel, consultant. This task includes evaluation of the literature and DOE reports on what are ‘typical’ CO_2 flood characteristics. This will be used to set the Phase II lab test specifications. Further, this work will perform site identification and planning for a specific field test of the SPI gel system in a specific oil field CO_2 EOR flood in Phase III.

Site Identification

The most recent (April 21, 2008) Enhanced Oil Recovery Survey published by the Oil and Gas Journal [7] lists 77 miscible and 5 immiscible CO_2 projects in the United States. A number of "projects" have multiple leases and may have more than one reservoir being flooded. Fifty-one of the 82 projects are in the Permian Basin of West Texas and Southeastern New Mexico. The other two producing areas of note are Mississippi (11) and Wyoming (6) with Michigan emerging (2 plus 3 planned). Each of the areas have their own unique source of CO_2 and each have their own reservoir and fluid characteristics. Wyoming and Michigan are supplied with anthropogenic CO_2 from gas processing plants, Antrim Shale in the case of Michigan and the Shute Creek (LaBarge) gas plant in Wyoming. Mississippi and the Permian basin are supplied by large domes of geological sources of CO_2, Jackson Dome in Mississippi and McElmo, Sheep Mountain and Bravo domes in Colorado and New Mexico supplying the Permian basin. While several of these sources have excess producibility, the existing pipeline infrastructure is near capacity, so any large scale projects would require investment in the pipeline infrastructure to bring in the CO_2. Anadarko recently expanded their Wyoming pipeline to add several projects in north and central Wyoming and Denbury recently announced their plans to construct the Green pipeline from Donaldson, Louisiana to near Houston, a total of 314 miles. It will connect to both producing fields and gas plants on the gulf coast. However, beyond these expansions, a substantially less expensive technology to capture the CO_2 will be required to expand CO_2 EOR to other producing areas, such as California. Today, less than 0.5% of the CO_2 emitted from stationary sources is being captured and injected.

The Permian Basin is by far the most prolific CO_2 EOR producing area in the world. Most of the fields undergoing CO_2 flood are large and mature, having already undergone primary and secondary recovery. For the most part, the rocks are limestone/dolomite, naturally fractured, with relatively low porosity and permeability. Porosity can vary from 7 to 20%, averaging 12 – 13%. Permeability can vary 2 to 100 millidarcies with an average around 8 millidarcies. Virtually all the production comes from the Permian San Andres/Clearfork generally found around 6,000 feet. The temperature at that depth is 54.5 ^oC (130 ^oF). Oil gravity is in the 35 – 40^o API range.

The EOR projects in Mississippi are substantially different than those in the Permian Basin. They are deeper, at 11,000 feet. They are small to medium sized sandstone reservoirs, half of which are undergoing CO_2 flooding immediately after primary depletion. They average 20% porosity and 100 millidarcies permeability. Oil gravity averages 40^o API and the temperature at that depth is around 115^o C (240^o F). Denbury Resources, which owns the Jackson dome CO_2, operates all the fields.

The CO_2 projects in Wyoming and Colorado sourced by the Shute Creek (La Barge) plant are also all sandstones at depths ranging from 1,500 to 9,000 feet. They are all mature fields that have been water-flooded prior to initiating the CO_2. Porosity ranges from 10% to 20%, permeability from 10 to 75 millidarcies. The gravity of the oil is around 35^o API.

The potential market for SPI CO_2 treatments is quite large. There are 9,146 producing wells and 6,219 injection wells in the aggregate of all the projects. Over 75% are in the Permian Basin. Well spacing may be as close as 10 acres, but most are 20 to 40 acres. There are a few 3 well projects, particularly on the pinnacle reefs in Michigan and the largest is Kinder Morgan's SACROC Unit with 444 injection wells and 391 producing wells.

The companies that control the bulk of the CO_2 used in these projects include Kinder Morgan, who bought the Shell assets in 2000, including the supply domes, Cortez pipeline and SACROC; Denbury, who bought Shell's assets in Mississippi in 2001 including the Jackson dome, pipeline; and production and Exxon, who owns the Shute Creek (La Barge) gas plant in Wyoming.

Other major operators of CO_2 EOR Projects include:

Anadarko (primarily Wyoming)
Chevron (Colorado)
Conoco Phillips (Permian)
Hess (Permian)
Merit Energy (Wyoming and Oklahoma)
Occidental (Permian)
Whiting Petroleum (Permian)
XTO Energy (Permian)

Nine other small companies have CO_2 EOR operations, primarily in the Permian Basin.
In discussions with several of these operators, there was interest expressed in research and new products to improve reservoir conformance in their projects. In particular, Whiting Petroleum expressed interest in this new SPI conformance/sweep technology.

Specific Whiting field data (pressure and depths) and well spacing size, as well as porosity, permeability and crude oil API data were obtained from the Oil and Gas Journal (April 21,2008)[7]. This data is:

- Ward and Winkler County, Texas
- CO2 injection begun in May, 2007
- 16,300 acres, 816 producers, 816 injectors (10 acre spacing)
- Produces from the Yates Sandstone
- Depth of 2,600 ft.
- Reservoir thickness is 250 feet (gross) and 60 feet (net).
- Porosity 16%,
- Permeability 37 md
- Oil gravity 36 degrees API
- Currently producing 4,225 barrels/, 700 of which is considered tertiary production
- Reservoir pressure is not known, but assumed to be normal hydraulic head of 1,120 psi, which is barely miscible

Based on this reservoir and field data Mr. Oglesby made a preliminary design of a possible field SPI treatment program. This preliminary design will need to be refined with the operator's assistance for a specific well and with additional lab testing, specific to that well/ area in the Phase II project.

Generic Preliminary Design Parameters

The preliminary design assumptions and parameters are:

1. Locate blending site near a rail-head for bulk volume delivery of sodium silicate and PAM (liquid form). Truck transport the feedstocks to the blend site with transport rotation and offload into current mix tank.
2. Assume the operator does not want an injection well down for over a month. This sets the total treatment volume at 20 times the injection rate or about 20,000 bbls.
3. Each 20,000 bbls of premixed SPI mixture treatment contains about 350,000 active # sodium silicate (0.05wt/wt fraction) requiring 10 tank truck transports & 10,500 active # PAM (0.0015 wt/wt fraction) requiring 2 tank truck transports (note road weight limits may increase).
4. Each treatment will be pumped below the fracture gradient of that area, established by the operator.
5. Assume each well will take 1,000 bpd injection rate of SPI gels below the established set maximum pressure, thus 20 days per treatment per well;
6. This design assumes SPI mix directly into the field (or diluted in field) brine to maintain lower cost;
7. Option #1 assumes batch treatments from 500 bbl frac tanks and mixing with high rate pumps OR Option #2 assumes inline chemical additions and inline mixing as a continuous process.

Overall preliminary design program:

1. Monitor and record all rates and surface pressures at the wellhead during all stages and for 6 months after treatment. Monitor offset well production volumes and pressures.
2. Stop CO_2 injection and pump 5,000 bbls of field water (leading spacer) into well below max pressure (est 5 days).
3. Mix and Pump 20,000 bbls of SPI mix (Option #1 or Option #2, see below) into well below max pressure.
4. Pump 5,000 bbls of field water (tail spacer) into well to displace SPI out into formation.
5. Resume CO_2 injection into well

Mixing/Pumping/Measurement Option #1 (Batch)-

- Set three (3) 500 bbl frac tanks and clean thoroughly at each well
- Set two (2) 125 bpm @ 25 ft head centrifuge pumps for full circulation in 10 minutes.
- Set one triplex pump (1000 bpd and max pressure) from the tanks to the wellhead.
- Install 6” headers with welded chain between all pumps/tanks, stingers into tanks and source of base field water
- Set weight scale onsite for transport/batch chemical mixing measurements
- Set tank blade mixers to keep each tank mixed between pumping
- Set doghouse for people, weather and instrumentation.
- Calibrate frac tank volumes with weight scales
- Load 2 frac tanks with field water to set levels.
- Accept transport deliveries of sodium silicate and offload directly into frac with all circulating pumps in operation. Monitor weight changes in truck transports to stop at set delivery weight. Circulate tanks with stingers.

- Accept transport delivery of PAM (diluted and mixed in the transport) directly into the frac tanks with all circulating pumps in operation. Monitor weight changes in truck weights to stop at set delivery weight.
- Mix thoroughly.
- Switch to wellhead triplex pump and pump mix downhole.
- Alternate mixing and pumping each set of tanks until full SPI volume emptied.

Mixing/ Pumping/ Measurement Option #2 (Inline Continuous)-

- Set wellhead triplex pump with field brine source
- Set metering pump for sodium silicate for input into wellhead triplex pump suction.
- Set metering pump for PAM for input into wellhead triplex pump suction.
- Install 60 ft inline mixing section in wellhead triplex pump suction (30 ft between pump and sodium silicate input and 30 ft between sodium silicate input and PAM input)
- Install 60 ft inline mixing section in the discharge line to the wellhead
- Install sampling point at wellhead
- Use weight scales on each Silicate and PAM source to confirm injection rates.
- Stop injection when chemicals are consumed.

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3. Kanichi Shimada and Toshikazu Tarutani, Bulletin of the Chemical Society of Japan Vol.53, No.12(1980) pp.3488-3491 “Formation of Gelled Silicate Polymers in the Presence of Organic Polymers”
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5. Ralph K. Iler, The Colloid Chemistry of Silica and Silicates, Cornell University Press, Ithaca, New York, 1955, p 59.
6. Jean Meister, SPE 13567 “Bulk Gel Strength Tester,” International Symposium on Oilfield and Geothermal Chemistry, Phoenix, AZ, April 9 – 11, 1985.
7. Enhanced Oil Recovery Survey published by the Oil and Gas Journal, April 21, 2008, Vol 106.15 pgs 41 – 59.

6.0 Identify Products Developed under the Award and Technology Transfer Activities:

A. Publications

Publications on the SPI – CO_2 technology have not been prepared at this time. Publication will occur when an opportunity arises.

B. Web Site

No web site is operating at this time. As more development and field-testing experience is incurred, a site will be created under the company name, SPI Technologies, LLC, for licensing/sales opportunities.

C. **Networks or collaborations fostered –** See Section 4.1.3.

D. **Technologies/Techniques –** See Section 4.1.3.

E. **Inventions/Patent Applications, and licensing agreements –** The SPI technology using CO_2 as an external initiator is covered under the original SPI patent application Publication Number US 208/0125334 A1. The international filing has been received by the Patent Cooperation Treaty. RTA Systems, JAG Enhanced Recovery and Impact Technologies are the owners of SPI Technologies, LLC, which was formed in 2006 to hold the SPI intellectual property. JAG is in the process of applying for a license to use the original technology.

F. **Other Products –** Products such as would be useful in technology licensing are in the process of being prepared for licensing of this technology. Appearance SPE paper presentation and promotions at tradeshows such as the Oklahoma Oil and Gas Trade Expo sponsored by the Oklahoma Commission on Marginally Producing Oil and Gas Wells in 2006 - 2008 and the 2008 SPE Improved Oil Recovery Symposium, Tulsa, OK April 19 – 23, 2008 were made.

Computer Modeling Projects Provide the Following Information:
Does not apply.