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Field Test Results of a New Silicate Gel System that is Effective in Carbon Dioxide Enhanced Recovery and Waterfloods

Kenneth D. Oglesby, Impact Technologies LLC; David D'Souza, Denbury Resources; Chad Roller, PhD and Ryan Logsdon, MidCon-Energy Partners LP; Lyle D. Burns, Clean Tech Innovations, LLC; and Betty J. Felber, PhD, EOR Consultant

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Abstract

Field test results of a new silicate based Silicate-Polymer-Initiator (SPI) gel system for zonal conformance control are presented from: 3 treatments in a central Mississippi sandstone carbon dioxide (CO₂) flood, including 1 producer; 5 injector treatments in a mature, west Texas San Andres dolomite, CO₂ flood under Water-Alternating-Gas (WAG) operation; and 2 injector treatments in a northeast Oklahoma waterflood. Gel treatment volumes ranged from 130 to 4,349 barrels of the patented, environmentally friendly, silicate gel system that is pumped at a near water viscosity and density. That pre-gel liquid is triggered to a gel by a pH change caused by external or internal initiation methods. One unique aspect of these silicate solutions is that they can be initiated by both the pre- and post-treatment injected CO₂ itself. Alternately, other external and internal initiators can be used in both CO₂ and water-floods. Targeted gel times ranged from 1 hour up to 6 days, with maximum gel strength generated within 2-4 weeks. The resultant silicate gels are 10 times stronger than any known gelled polymer system, per CTI laboratory Extrusion and Penetrometer testing. Selected additives were utilized in the gel treatment fluids to focus the pre-gelled solutions into the desired high permeability zones. Furthermore, pre-gel fluid entry into water or oil zones will not set the silicate gel, but will instead dilute the leading edge.

Rate, pressure, injectivity and downhole profile surveys were used to evaluate the treatment in injection wells. Oil, water and gas rates, Water: Oil Ratios, Gas: Oil Ratios and CO₂ utilization efficiency were used to evaluate treatments in production wells. Offset production wells were monitored, where possible, for production changes, sometimes seen outside the prior established patterns. Where the data was available, the new silicate gel field treatments were directly compared to prior polyacrylamide and similar conformance systems. In most cases, the new silicate system exhibited positive responses while previous polymer based systems did not respond.

History of Conformance Chemicals

Permeability and reservoir heterogeneity variations significantly affect the sweep efficiency or reservoir conformance of oil recovery processes, especially in enhanced recovery projects. It is also important in other industrial applications, such as drilling and geothermal operations. Before 1922, only mechanical methods were available in the oilfield to seal off unwanted zones. These methods included cement, barite, bentonite and other solid materials inserted into the wellbore. Silicates were the original oilfield conformance fluid with waterflood applications starting in 1922. Acidic systems are the oldest and most commonly employed techniques that employ silicates [13]. Uniform gels are almost impossible to prepare with these early silicate systems because of the very rapid reaction between sodium silicate and its setting agent. Most of these early silicate systems formed very rigid, non-uniform gels subject to fracturing or syneresis with concomitant shrinkage and should be more accurately described as precipitation type gels since they are extremely brittle with no elasticity.

However, the use of silicates for sealing and conformance was improved over time by various groups [17] [10] [8] [60] [18] [43] [25] [26] [24] [69] [53] [23]. After the early 1980's, newer methods to mix and pump silicate systems were devised [14] [38] [20] [11]. New silicate products for a variety of applications, including for high temperatures, have also been developed [6-12] [27] [15] [16/29] [54] [33] [34] [36] [44] [30] [39] [45] [59] [32] [55] [56] [58] [40] [41] [42] [86] [87]. Specifically for this paper, new multi-component silicate (amorphous liquid glass) gels were developed to further improve the use of silicates for sealing in a variety of applications, including reservoir conformance and drilling [46] [2] [47] [48] [50] [63], and for high temperatures (392°F) and extended (14 day) pump times [62] [67] [68].

Although the sodium silicate technology was the first plugging and permeability modification technology largely put to practice, the use of gelled polymers based on polyacrylamide and (heavy metal) chromium VI salts with reducing agents or organochromium compounds became more popular in the 1970's and 1980's because of their unique versatility to make fairly firm and elastic gels rather than the inelastic gels formed using the original sodium silicate chemistry. *The biggest problem with silicate systems from the beginning (until the current SPI version) was the inability to retard the reaction and provide elasticity. The biggest problem with PAM-Chromium gels was the inability to retard the reaction and maintain strength.*

These polymer systems included gelled cellulose and acrylamide polymers, use of chromium proprionate (Phillips Petroleum Company) as a delayed gel complexing agent and later chromium acetate (Marathon Oil Company) [28] for use in gelling polyacrylamides. Key issues with the crosslinked polyacrylamide systems include: (1) environmental and safety issues over the use of the heavy metal crosslinking agent, chromium; (2) limited penetration depth; (3) polymer shear degradation of the weaker gels; (4) polymer adsorption on the reservoir surface; (4) rapid polymer gel time if high concentration / strong gels are desired; and (5) polymer precipitation under harsh reservoir conditions. The need to extend the gel time of polyacrylamide systems requires lowering its concentration and resulting gel strength in the early pumped stages to a point that the gel strength may not be sufficient to prevent reservoir fluid flow, especially in fractured and high conductivity channels. Even near the wellbore, where the highest polyacrylamide concentrations and strength are normally delivered, cement is often used to buttress that polymer plug. This defeats one of the benefits of chemical systems, in that, the cement must be drilled out at additional cost and risk to the well.

Conformance is particularly important in enhanced oil recovery projects, because of the high cost of the initial chemical purchase recycling injectants (CO₂, surfactants or even water) and the growing inefficiencies in any process as projects mature. This is especially true in CO₂ floods with the highly unbalanced mobility (viscosity / density) ratios between crude oil and CO₂. It is because of that reason that numerous chemical methods, including the new silicate gels, have been developed specifically for CO₂ floods [1] [2] [3] [66].

Silicate Gel Chemistry

This new SPI silicate chemistry was developed and reported over 11 years through efforts under two 2005-2008 U.S. Department of Energy (DOE)/ Stripper Well Consortium (SWC) projects [48] [49] for chemistry development and conducting waterflood field tests; and a 2006-2008 Oklahoma Center for the Advancement of Science and Technology (OCAST) [50] project for casing repair and drilling problems. Laboratory testing occurred at RTA Systems Laboratory and at the Tertiary Oil Recovery Project at the University of Kansas. That early base silicate chemistry and field test efforts were reported in 2008 by Burns, et.al. SPE113490 [46].

Laboratory testing at CTI, since 2008, on these silicate gels has included static bottle/ beaker tests, Brookfield Viscosity tests, Penetrometer tests, Bulk Gel (extrusion) tests, and dynamic flow sandpack tests. Many of these tests were performed on actual field core materials and fluids and compared to standard polyacrylamide gels and Ottawa sand data. Results from this testing were reported under: a 2009 DOE Small Business Innovation Research (SBIR) project for using CO₂ as an external initiator [47]; a 2011-2014 DOE CO₂ field test project [63]; and further reported herein; a 2014 DOE SBIR project focused on carbon sequestration [61]; a DOE Energy Efficiency and Renewable Energy (EERE) project for development of high temperature (up to 392°F) silicate gel systems, as well as long delay (up to 14+ day pump time) internal initiators [62]; US patent No.882238 [68], with pending applications; and the official SPI website [89].

The new silicate gel system is a multi-component silicate based gel that can be fully mixed at the surface and pumped as a single stage or pumped separately for reservoir mixing. These new silicate gels are silicate based true gels that are pumped as a high pH, low viscosity liquid. Brookfield Viscosities are near water levels at elevated reservoir temperatures, but in the lab (70°F and 12rpm) measure 7.5 cp and 11.5 cp for low-medium and very high concentration silicate systems, respectively. Specific gravity of the silicate solution ranges from 1.02 to 1.07. Penetrometer gel strength comparisons (following ASTM D-217-68) showed a 2X minimum to 48X times higher silicate gel strength than even the highest, yet unpumpable, 20,000 ppm PAM gel [63]. Bulk Gel Shear Testing (BGST, per Meister SPE13567 entitled "Bulk Gel Strength Tester" [9]) provided extrusion strength comparisons of 2X to 4.5X for low-medium concentration silicate gels over high concentration PAM systems. Note that the higher strength silicate gels could not be forced through the bulk tester. Furthermore, cross-linked PAM systems just flowed through the screen while low concentration silicate gels retained some strength and/ or reformed after passing through the screen. These tests also found that silicate gels initially form within a few minutes of reaching the trigger pH level, but gain additional strength rapidly until day 3-5. Strength continues to slowly improve over the next 30 days.

Dynamic Flow Tests through 0.89 foot long packs were performed using crushed and sorted Ottawa sandstone, Denbury Field A's sandstone and Field B's dolomite. All dynamic testing showed a strong permeability reduction following each 2 PV silicate treatment. However, the strongest result occurred following a 2nd treatment resulting in a residual permeability reduction factor (Frr) of 450 for Ottawa, 123 for Field A sandstone and 2425 for Field B dolomite. This

multiple treatment benefit may be due to the low viscosity of the silicate treatment solution and/ or the unique method of initiation using CO₂. This would then indicate that a second treatment might not be needed if a thicker fluid was pumped, as a more complete coverage into all flow paths, including lower permeability paths, could be obtained with one pumping. However, with a thin solution, only the 1st or 2nd highest permeability flow paths will be filled and sealed. One concept of this multiple treatment option in the field is shown in Figure 1. Of course, viscosifiers can be added for more of a one pass application.



Figure 1. Simplified Schematic of Multiple, Smaller Treatment Volumes in a CO₂ Flood

Once in place in a CO₂ flooded reservoir, the silicate gelation process can be initiated by a reduction in pH via an internal (temperature–time dependency) or external (position/ contact, not temperature sensitive) chemical. The desired initiator in two of the fields reported herein was the carbon dioxide (CO₂) already in the reservoir plus that CO₂ pumped into the well after the silicate mixture. In a CO₂ flood, CO₂ will enter into and dissolve in the water phase of the silicate mixture to form carbonic acid, which causes the drop in pH sufficient to the trigger level and the initiation of the silicate gelation process. Because of its unique initiation methods, the full silicate gel volume (toe to heel) can be at higher strength for treating highly fractured or conductive 'void' zones.

This new silicate gel system is environmentally friendly, a true "green" gel that uses no heavy metals that were developed to solve water and CO₂ conformance problems in injector and producer wells, casing leak repairs, drilling problems and other applications. It is very versatile as it can be adjusted for concentration and strength, addition of sized lost-circulation-materials and polymers for leak off control, mixed and pumped using batch or on-the-fly methods, as well as using different gel initiation methods (internal or external). In addition, the silicate solution will not set and form a strong gel, if it enters water or oil zones.

Field Test Results

A summary of all field silicate treatments are shown in Table 1 and Figure 2, below. Treatment volumes ranged from 130 bbls of a medium concentrated solution into a tighter WAG injection well to 4,349 bbls of a high concentrated solution into a production well. Four different initiators were used in these tests- CO2, strong acid, Initiator A and Initiator B.

				Pre-Treatment Status				SPI		Injectivity Reduction				
SPI	Well		Well	Rock		Rate BPD	WHP	Injectivity	Interwell	Trea	atment	(% of PreTrement)		
#	#	State	Type	Type	Depth	MMCFPD	PSIG	Rate/PSI	Cap- BBLs	Mo/YR	BBLs	3 mo.	12mo.	24 mo.
SPI1	1	cMS	INJ-CO2	sstone	5102	11	1400	7.9	>20,000	Nov-12	950	28%	re-treated	na
SP13	1	cMS	INJ-CO2	sstone	5102	8.26	1500	6.0	>20,000	Feb-13	3842	57%		
											4792		CO2 Overall	58%
SPI4	3	wTX	INJ-CO2-WAG	dolo	5020	1.0	2350	0.43	400	Sep-13	130	47%	re-treated	na
SPI6	3	wTX	INJ-CO2-WAG	dolo	5020	0.5	2200	0.23	400	Sep-13	225	15%		
											355	Overall C	02 & Water=	10%
SP15	4	wTX	INJ-CO2-WAG	dolo	5020	0.92	2371	0.39	2800	Sep-13	705	9%	Evaluate Re	Treat
SP18	4	wTX	INJ-CO2-WAG	dolo	5020	0.84	2365	0.35	2800	Oct-13	0	23%		
											705	Overall C	02 & Water=	No Chg
SP17	5	wTX	INJ-Water	dolo	5020	600.0	1250	0.5	5500	Oct-13	1029	CO2 Injectivity- NA Water Injectivity 50% lower*		
SP19	6	wTX	INJ-CO2-WAG	dolo	5020	1.75	2075	0.84	17500	Nov-13	3265	CO2 Injectivity- No Chg Water Injectivity- 50% lower*		
SPI 10	7	cOK	INJ-Water	sstone	1735	400	0	vacuum	unknown	Dec-14	200	Water Injectivity - No Chg Plugged Thief Zone		
SPI11	. 8	сOК	INJ-Water	sstone	1270	1375	0	vacuum	unknown	Aug-15	279	Water Injectivity - No Chg Slight Change in Profile		
						Pre-Treatment Status					SPI	cum Oil BBLs over Prior Trend		
SPI	Well		Well	Rock		Oil	GOR	Oil	GOR		Treatment	GOR Change over Last Prior		
#	#	State	Type	Type	Depth	BOPD	MSCF/BBL	Trend	Trend		Size- BBLs	3 mo.	12 mo.	24 mo.
SPI2	2	cMS	PROD	sstone	5102	20	450	-78%/yr	+700%/yr		4349	-	750	6,600
			CO Flood	14/0	II Chut in	n riar ta	trantmant	due to eve	accius COP			-649	/ flat	flat





Figure 2. Injection Pressure vs Cumulative Injection Plot Silicate Treatments- Normalized to the Gel at the Perforations

Denbury Field A, Central Mississippi sandstone CO₂ Flood Field A Reservoir Discussion

Field A is located in the Mississippi Interior Salt Basin and is part of the Eutaw sandstone series of reservoirs in Mississippi. The Eutaw reservoir consists of approximately 500 feet (166 m) of consolidated to unconsolidated marine sandstone, siltstone, and shale. Production is primarily from structural fault line traps that have produced more than 299 million barrels of oil and 975 BCF of gas from 39 fields 1997 [64] [65]. Eight Eutaw fields, including Field A, along this fault trend have produced more than 45 million barrels of oil and 2.4 BCF of gas.

Field A is a large salt-formed anticline divided into western and eastern segments due to subsequent faulting. Most of the past and current production comes from the Eutaw (Travis, City Banks, Stanley zones), Selma Chalk and Christmas sands at depths from 3,500' to 5,000'. Geological assessment determined significant heterogeneity in the Eutaw Formation, and documented relatively thin, variably lithified, well-laminated sandstone interbedded with heavily-bioturbated, clay-rich sandstone and shale. Depositional environmental analysis indicates that there are 4 types of sands: Distributary Mouth Bar, Shallow Marine Shelf/ Interridge, Tidal Sand Ridge and Shallow Marine Shelf. A core taken from a Eutaw well in the area with petrographic analysis reveals that quartz overgrowths are more abundant in sandstones without oil than those with oil, due to calcite cementation. The Stanley zone contains glaconite and siderite which, both iron rich clays, which may be problematic in CO₂ floods.

The main Eutaw formation in Field A consists of tight sandstone layers with very high permeability contrast, 4800-5000 foot (1463 meters) depths, a large field with 122 production wells and 47 injection wells, averaging 28% porosity and 300 milli-darcies permeability. The CO₂ flood recovery method is an immiscible gas process.

Field A Well Discussion

Field A wells were first drilled in 1944 with many new drilled wells in the 2011-2013 time period. Both selected wells are newly drilled wells and were completed in one or more of the three zones described above. They were previously water-flooded and much later / more recently placed under carbon dioxide injection. All wells considered for treatment had relatively high CO₂ injectivity of 8 MCFPD/ psi (calculated as Rate/ WHP) of CO₂ and very high calculated 20,000+ bbls inter-well capacities. Most production wells are forced flow from below a packer.

A CO₂ injector, identified herein as Well #1, was selected in the northern part of the field was only open in the Travis (TR) zone, with a sand plug in the casing below this zone. Only 6 feet of the Travis zone was taking injected fluids. A producer, identified as Well #2, was selected in the southern part of the field that was open in all lower Eutaw zones. These two treated wells were at far ends of the field and in different zones, thus the treatments would not interfere with each other. Water injectivity tests at various rates with a downhole pressure and temperature sensors showed that producer Well #2 had 1.6 times higher water injectivity at 1 BPM than the CO₂ injector Well #1.

Due to both wells' high injectivity (allowing high treatment rates) and inter-well capacities (high treatment volumes anticipated), the use of Denbury's high rate triplex pump, 500 bbls square frac tank for fresh water storage and fresh water from nearby supply wells determined that the slipstream method was optimal for both Field A's treatments.

Field A, Well #1 Injection Well Conformance Treatments

Well #1's location and surrounding producers in a northern pattern that is bound by faulting is

shown in Figure 3. Its historical injection plot (CO₂ rate, wellhead pressure and calculated injectivity) is given in Figure 4. Green stars show when the two silicate treatments were performed in this well- SPI1 injected 950 bbls of the silicate mix on 6-11 November 2012 and SPI3 injected 3,842 bbls of silicate mix on 23-28 February 2013. The results of those treatments can be seen in that plot's definitive injectivity reductions for each treatment and in the offset production well data.



Figure 3. Field A, Northern Area showing Well #1 Location

The offset production response to Well #1 treatments can be seen in Figures 5 (oil rate) and 6 (GOR). The silicate treatments in Well #1 affected nearby pattern wells in the same geologic block/ pattern, as well as non-pattern producers 6133 and 6134, from the injected CO₂ following the NW-SE fault. Note that a review of the immediate offset injector to these more distant producers did not show a change in this time period. A lower symbol legend on Figure 5 identifies when any well work was done on the identified wells, but most of these were before or after the treatments and did not impact the results. A total of five wells were identified to have been impacted by the silicate treatments in Well #1 for significant incremental oil recovery and additional savings from reduced gas re-cycling over 2 years time, with those benefits continuing to date.

Figure 7 shows a GOR versus cumulative produced oil plot of the pattern-only production wells around injection Well #1. It does not include outside pattern wells that were identified as being directly impacted by the treatments. The green star and vertical black line show the timing of the silicate treatments. The blue lines show the pre- and post-treatment trends. By projecting each trend line to an economic GOR limit, the significant longer economic life and incremental recovery from the treatments can be identified.

Field A, Well #2 Production Well Conformance Treatment

Well #2 is located in the southern-most part of the field, near the top of the producing zone

structure and in a highly fractured area, see Figure 8. It is not known if these faults are sealing or not, but the very high injectivity (1.6 times higher than the injector Well #1) would indicate they might provide a good flow path back to an unidentified injector(s). This is a forced flow well from under an installed packer with all lower Eutaw zones open. It was shut-in prior to the treatment due to excessive GOR, over 300 MSCF/ BBL and was reactivated just for this field test- our 'Hail-Mary' well treatment!







Figure 6. Field A- Selected Northern Production Wells' Gas: Oil Ratios



Figure 7. Field A, Well #1 Pattern Analysis Plot- GOR vs Cum Oil Prod



Figure 9. Denbury Field A, Well #2 SPI #2 Production Well Treatment

Figure 9 shows Field A, Well #2's production history plot with the SPI2 treatment shown as a green star. Its 4,349 bbls SPI2 silicate treatment was described in prior Figures and Tables. It is important to note that the silicate gel was initiated with a strong acid solution on the tailend of the treatment (i.e., left nearest the wellbore), which is not as effective as using CO₂ or an internal initiator, but it still proved that it can form a strong gel.

From this analysis it can be seen that the pre-treatment declining oil rate trend was stabilized by the silicate treatment at about 10 BOPD. The pre-treatment trend of increasing CO₂ production rate immediately dropped 66% after the gel treatments. The GOR stabilized after the treatments as compared to the increasing trend seen previously. That resulted in significant savings from lower volumes of recycled produced gas through the processing and compression system for that time period.

Field B in West Texas, San Andres Dolomite, Mature CO₂ WAG Flood

By our confidentiality agreement, we are unable to identify the wells, field or the major CO₂ flood operator where these five silicate treatments were performed. However, we were given permission to publish data and some of the operator's analyses. This mature, miscible CO₂ Water-Alternating-Gas (WAG) flood was near Levelland, TX in the San Andres dolomite formation.

Field B Geological and Reservoir Discussion

The San Andres dolomite formation in west Texas is very large and well known. Many SPE papers on the many San Andres CO₂ floods have been published [75][84][85][72][73][76][77] [78][79] [80][81] and for other dolomitic reservoirs [71][74][78][82].

This field was developed on a 5-spot up to a 9-spot pattern as seen in Figure 10 with wells about 900 feet apart. This is a long established, mature miscible CO_2 flood that is under Water-Alternating-Gas (WAG) operation now. There was a 2011 study of conformance problems in the field that was made available for aiding in understanding the field, selecting wells to treat, designing the treatments and in comparing the silicate treatments to prior conformance treatments. The dominate flow path is northwest (NW) toward the southeast (SE), possibly due to orientation of early sand fracturing. Most all production wells utilize beam pumping units with fluid levels that were not pumped down. Well CO_2 injectivities are about 1/8 or less than what was found in Field A.

Field B Well Selection

Only injection wells were treated. Our advocate company engineer(s) wanted to treat at least one producer, but safety concerns required that a 900 foot temporary steel CO₂ line be laid, welded and buried which would take 6 months. Hauling CO₂ by truck and pumping it into the well would have cost almost \$100,000 with many months of planning required, so that effort was stopped as well.

Also, in Field B, a different path in selecting the wells to treat since the developed flow paths were so well defined. Two injection wells (Well #3 and #4) were selected that were in the same zone and in adjacent patterns. In Field B we initially selected 2 injection wells with the lowest injectivity of the initial group of wells provided. Later, two nearby high conductivity injectors were then selected for diversity and these are shown in Figure 19. These are old wells that may have paraffin and oil carryover in the wellbore or deposited on the formation near the wellbore. Many of them also had prior gelled PAM treatments. Core material and core analyses were obtained and analyzed. Open hole and injection profile logs were obtained as well. Field B's wells with low injectivity proscribed lower treatment rates and volumes, as well as lower concentrations.



Figure 10. Field B Map showing the Location of the Treated Injection Wells

Figures 11 to 14 are historical plots of all Field B treated injection wells showing rate (blue solid line), wellhead pressure (red-brown points) and the calculated injectivity (green dashed). Green stars at the top show the treatment dates. Wells #3, #4 and #6 are WAG injection wells, while Well #5 had only water injection for many years due to prior high gas breakthrough. After the treatments and a short shut-in period, only CO₂ gas was slowly injected and shut-in, until

Figures 11-14 Below (grouped). Field B Injection Wells, Injection Rate & Pressure Plots





the normal WAG process was restarted. The field CO₂ supply was always constrained and needed to be spread out (by alternating with water to maintain pressure) to many wells. It should be noted that near the beginning of the treatments the area's gas processing plant went down for maintenance, but Operator B tried to keep a steady CO₂ supply in this area. However, in early 2013 CO₂ injection was reduced and replaced with increased water injection.

In WAG processes, it is important to compare injectivities at the same rate and at the same saturation of CO_2 or water in the flow path. The simplest method to estimate saturation is by injection volume of the given fluid. For Well #3, the pre-treatment injectivity of CO_2 was 0.39 MMCF/Day/ WHP psi and post-treatment it was 0.20; Well #4 pre and post were same at 0.4; Well #5 pre 0.3 and post 0.16; and Well #6 pre and post same at 0.35. Only 50% of the treated injection wells responded with about a 50% injectivity reduction.

Figures 15 (oil rate), 16 (GOR) and 17 (WOR) show the historical plots of selected offset producers to the treated four Field B injectors. Results from these plots show:

- Offset producers did respond to the treatments, showing that previously established flow patterns were changed. Different producers responded in different ways. In one pattern offset Well #6, a 90° flow path change was observed. In all three plots the solid lines were positive responses, while the dashed lines were negative responses. These responses lasted until CO₂ injection was curtailed and water injection increased in 2013.
- An increase in oil production rates over pre-treatment trends was seen in producers A039, A031, A034, A052;
- Reductions in GOR over pre-treatment trends were seen in producers A039, A049, A052, A198- CO₂ injection changes may have impacted these responses. A GOR increase was seen in A360;
- Reductions in WOR over pre-treatment trends were seen in producers A057 and A198, with A039, A049 and A052 showing evidence of pattern redirection;

It should be well noted that this is an active field with much activity, thus it is difficult for the silicate treatments to claim any direct credit for these changes.



Figure 15. Field B Selected Production Well Responses, BOPD



12/23/11 04/01/12 07/10/12 10/18/12 01/26/13 05/06/13 08/14/13 11/22/13 03/02/14 06/10/14 09/18/14 Figure 17. Field B Selected Production Well Responses, WOR

MidCon-Energy Northeast Oklahoma, Cleveland Field Unit Waterflood

The Cleveland Field, see Figure 18, is in Pawnee County, Oklahoma and is a fairly new Cleveland Sand water injection flood. The Bartlesville Sand waterflood began in 1955, with the Cleveland Sand waterflood beginning in about 2013. An East-North-East trending flow was noted in the Bartlesville Sand, but no evidence of directional permeability trends have been found in the Cleveland Sand. Periodic well tests were conducted, although field operating changes did occur due to declining oil prices and waterflood realignment. Two water injectors were treated: Well #7- J.A. Jones #55 (red circle) and Well #8- Mullendore and Berry #39 (green circle).

J.A. Jones #55 had a pre-treatment injection profile log (Figure 19) that showed water injection was going into a previously cement squeezed high permeability interval at 1706-1718 feet within the Cleveland Sandstone interval. The well's injection rate and pressure history is shown in Figure 20. It was treated with 200 bbls medium to very-high silicate concentration (using internal initiator A and B) in SPI10 in December 2014. From the profile logs, the high perm zone was completely sealed off and all injected water was successfully re-directed into the Middle Cleveland Sand Interval. Insufficient time and well tests, as well as waterflood

realignments do not allow for evaluation of offset production responses. Injectivity was only temporarily changed.

Mullendore and Berry #39 was treated with 279 bbls high silicate concentration (internal initiators A&B) in August 2015 for reservoir conformance. A 3 November 2015 post-treatment profile survey (Figure 22) unexpectantly showed that all water was going into an upper perforated Layton interval at 1243-1289 after the treatment. That upper interval had no offset Layton producers, the well was reworked on 18 November 2015 to clean out the Cleveland perforated interval and isolate the Layton zone with opposing cup packers. Another survey was run on 11 January 2016, after the well work, to find all water injection now going into a wider distributed pattern in the Cleveland perforated interval. Only a temporary injectivity change was seen in Figure 21. It is necessary to wait for additional offset production well tests to determine if additional oil will be recovered from the Cleveland sand.



Figure 18. Central Oklahoma, Cleveland Field Map

Field Problems Encountered

In two separate fields and in two separate wells, it was found that if a silicate gel treatment was performed after an XL PAM job that used a chromium initiator a fast pressure response during silicate treatment occurred, since residual initiator apparently remains in the well and near-reservoir. Such a well can be pretreated to reduce the early gelation problem, if that fact is known ahead of time.

Poor/ dirty tankage and mix/ flush water can be a problem with silicate systems. That must be prevented by pre-cleaning and close inspection of the tankage and pre-testing of waters. This was found in the first treatment in west Texas, SPI4, and in SPI9 in JA Jones #55, which found a hard precipitate plug in a short section of the tubing at the tail end of the water displacement of the treatment. Apparently the cause was displacement fluid which had an incompatibility issue with the prior pumped new silicate solution. This reinforced the need to have clean tanks and test all waters that go into the tanks upon delivery and re-test all fluids just prior to use.



Figure 19. JA Jones #55 Pre- and Post-Treatment Injection Profile Logs. Red line is top of perforated zone. Note- Thief Zone Plugged







Figure 21. Cleveland Unit, Mullendore & Berry #39- Water Injection Rate and Pressure History



Figure 22. Mullendore & Berry #39 - Injection Profile Logs. *Note: Red Line is top of Cleveland perforations.*

Some residual solids have been seen in profile logs in the rat-hole of a few wells- all in west Texas. This is thought to be from prior treatments that reacted and formed heavy solids that fell into the rat hole. This did not interfere with zone injectivity. High pH fluids have been known previously to cause field upsets. None were found in these silicate treatments, even in the treated production well, SPI2 in Field A.

Comparisons to Other Conformance Treatments

It was of particular interest that a direct comparison of these silicate treatments to other competitor treatments performed in those same fields and, in some cases, in the same wells could be made. Competitor treatments included one Tiroco MarcitTM treatment, a few PolyCrystalsTM treatments, one foam cement and many high molecular weight cross-linked polyacrylamide (PAM) treatments. In summary for both fields, 29 conformance jobs were performed from 2007 to 2011, but only 4-5 of those treatments were considered by the operators to be successful at some level. Two wells have direct comparisons and will be discussed below.

Well #1 had a 4,180 bbls Marcit[™] treatment in 2011 that did not change CO₂ injectivity nor impact any offset production wells, See Figures 4 and 23. Marcit[™] is an acronym for Marathon Conformance Improvement Treatment. Generally these treatments are composed of a medium molecular weight anionic polymer with an internal chromium cross-linker and are mixed and pumped with fresh water. It is resistant to H₂S, CO₂, high TDS waters and is viable to 210°F. That job had planned to inject a total of 10,000 bbls of Marcit gel, but the job was terminated



early due to a pressure increase. The sum of both SPI1 and SPI3 treatment volumes on this same well totaled 4,792 bbls and both had similar pressure responses.

Field B also had a comprehensive Conformance Study performed in 2012 that reviewed and ranked current conformance problems and evaluated all prior conformance treatments that were performed using a variety of methods. In particular, Field B, Well #3 had PolyCrystal treatments in 2007 and 2008- both with no effect on the injector or offset producers. A 2010 cross-linked PAM gel treatment (3,844 lbs of EOR 204 and 805 lbs of EOR 684 crosslinker) was also performed, which did reduce water injectivity, but not CO₂ injectivity. It adversely increased offset well GOR / GLR, decreased run time and recovered NO incremental crude oil. However, silicate gel treatments SPI4 and SPI6 in that same well showed injectivity decreases and some impact on offset wells, but insufficient time and data is available to determine incremental oil.

Conclusions

- From *laboratory testing*, these multiple component silicate solutions -
 - allow highly variable compositions for creating these pH-triggered strong gels for a variety of applications, affecting cost and gel strength;
 - o are environmentally friendly compositions without heavy metal chrome initiators;
 - allow Internal (composition-time-temperature basis) and External (composition- position/ contact basis) gel initiation methods for a variety of applications. CO₂ is an excellent external external initiator;
 - can incorporate lost-circulation additives and high molecular weight viscosifiers for controlling silicate solution losses into tight permeability zones;
 - o perform in all rock types limestones/ dolomite and sandstones;
 - are pumped at low viscosities (near water at formation temperatures) for good penetration of the highest flow / permeability paths. Laboratory Brookfield Viscosity measurements at 70°F and 12 rpm are- 7.5 for low-medium and 11.5 for high concentration silicate solutions;
 - allow for very high gel strengths, per penetrometer and extrusion tests, that are at least 10X stronger than any PAM based system, but lower than epoxies and cements. Because of

its low viscosity penetration and high strength (toe to heel) sealing capabilities, it can work where gelled PAM systems cannot survive and where cement cannot penetrate;

- o have internal initiators that allow pump times of minutes to 2 weeks forming strong gels;
- are selective where they set and do not set. They will only set in direct contact with an initiator, such as CO₂. If an uninitiated mixture enters a water zone, it will be diluted and form a slush of precipitates in a dilute polymer-like water. If that mix contacts crude oil, it will not set at all;
- obtains a large part of their ultimate strength within a few minutes of reaching its trigger pH level, however, it still gains strength over 3-5 days and reaches its near-term maximum strength in 25 days;
- o produces stronger silicate gels that are not as shear sensitive as the weaker gels;
- are sensitive to high brine and calcium concentrations, thus chemical / water mix water and buffers are required; and
- o are not sensitive to acids once the gel sets.
- From *field testing*, various silicate gel composition and mix/ pumping systems were demonstrated to be effective in sealing treatments in-
 - fractured sandstones along the Gulf Coast, high permeability sandstone in the Mid-Continent and dolomite formations in west Texas;
 - reservoir flow paths lasting for over 2 years;
 - o both field injection and marginal production wells, even with volumes as low as 200 bbls;
 - sandstone and dolomite injection wells where conventional PAM systems did/ could not perform- in direct well comparisons; and
 - o flow paths for significant oil recovery and recycling gas savings over 2 years.
- From the unique and flexible gel formulation and mixing pumping methods possible, it is clear that these gels have a wide range of applications oilfield CO₂ floods and water floods, oilfield high WOR primary production wells, geothermal production operations and problem drilling wells (oilfield, geothermal, other) with lost circulation or high fluid influx.
- From field operational problems, it was found that equipment and mixing/ flush water cleanliness and quality control is extremely important. Silicates are known for their steel protective capabilities, as they were the original corrosion protector and are still used today for that purpose. However, silicate solutions also will clean scale and other deposits and loose coatings off of steel in pipes, tanks and wellbore tubulars. These solids can come loose and be pumped downhole causing injectivity issues.
- Wells with prior PAM treatments need special chemical treatments prior to a new silicate treatment due to potential residual chromium in the wellbore and near-well formation.
- Multiple smaller treatments instead of one large treatment were indicated, from laboratory dynamic flow testing, to be an optimal design with these low viscosity pumped silicate systems. Viscosifiers can be added, if desired, for a more uniform coverage of flow paths for fewer treatments. Such low viscosity fluids will seek out and flow through the highest permeability path(s) and will thus avoid flow through lower permeability/ conductive paths. Furthermore, later lower viscosity/ higher mobility CO₂ injection to set that solution into a gel will also seek out the highest permeability paths, where it will set to form a strong gel. Therefore, multiple smaller treatments allow consecutive sealing from the highest to the lowest permeability flow paths between wells. Furthermore, multiple treatments also allow for intermediate evaluations to prevent over-treatment with such strong gels.

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NOMENCLATURE ACRONYMS AND ABBREVIATIONS

BBL or bbl- industry standard, US barrel, 42 gallons

BCF- billion cubic feet (of gas)

BGST- Bulk Gel Shear Test, method to test and compare gel strengths

BOPD – barrels of oil per day rate

BPD or bpd- barrels per day rate

BPM- barrel per minute rate

BWPD- barrel of water per day rate

cp- centipoise unit of viscosity

CO₂- carbon dioxide

CTI- Clean Tech Innovations, LLC

Denbury Field A- central Mississippi immiscible CO2 flood with SPI1, SPI2 and SPI3

Field B- west Texas miscible CO2 flood where SPI4 - SPI8 per performed

fpd- feet per day of velocity

Frr- residual resistance factor= pre-treatment permeability/ post-treatment permeability

Gal- gallon volume

GLR- produced gas to liquid ratio

GOR- produced gas to oil ratio

H₂S - hydrogen sulfide, a dangerous toxic gas

HMW- high molecular weight of polymers

Impact- Impact Technologies LLC

Injectivity- measure of ease of injecting a fluid, or ease of flow, variously calculated

Inter-Well Capacity- measure of reservoir volume between wells, variously calculated

LPD- liter per minute rate

LPM- liter per minute rate

MMcf- million of cubic feet volume

MCFPD- thousand of cubic feet per day rate

PAM- polyacrylamide polymer

Ppm- parts per million concentration

PV- pore volume of sandpack

PI- Principal Investigator (me, the one writing this novel)

SPE - Society of Petroleum Engineers

SPI- Silicate Polymer Initiator solution

SPI1, SPI2, SPI3, SPI4, SPI5, SPI6, SPI7, SPI8, SPI9, SPI10, SPI11- new silicate treatments

WAG- water-alternating-gas, a cyclic CO₂ flooding injection method

WOR- water to oil ratio produced from production wells.