NEW TYPE SELECTIVE SEQUESTRANT FOR CROSS-LINKED FRACTURING FLUIDS CONTROLS IRON IN THE PERMIAN AND FORT WORTH BASINS

Tony Losacano
Javad Paktinat
Tom Watson
BJ-HUGHES SERVICES

ABSTRACT

A research project was undertaken to develop an iron sequestering agent which could be used to control the precipitation of iron in fracturing operations without affecting the rheological properties of the crosslinked gel. The control of iron in acidizing is well documented but it has only recently been recognized as a production problem in fracturing. Problems occur when oxygen in the fracturing fluid comes in contact with iron in solution in the formation water. The two components combine and if conditions permit an insoluble precipitant will form. This precipitate can cause severe permeability damage.

In acidizing, sequestrants have been widely used for years to control iron. However, when fracturing with crosslinked fluids these same sequestrants will complex with the gel crosslinker as well as with iron. This reaction will prevent the fracturing fluid from crosslinking. Recently, a new selective sequestrant was developed which reacts only with iron and therefore does not affect the rheology of the crosslinked gel.

This paper describes the problems associated with fracturing formations containing high amounts of in-situ iron and the manner in which this new selective sequestering agent can be used to prevent these problems. Rheology data will be presented to show the compatibility of the sequestering agent with the crosslinked gel system which was specifically designed to be used with the new sequestrant. Finally, its effectiveness as an iron control agent is demonstrated through lab flow tests and field case histories in which the compound was used.

INTRODUCTION

The presence of iron as a constituent of the formations of the Permian and Fort Worth Basin have long posed problems for oil and gas well operations there. Up until the late 70's the control of this iron was considered a major problem only in acidizing applications. However, it is now recognized that the precipitation of iron compounds due to the incompatibility of hydraulic fracturing fluids with formation waters can cause rapid post-frac production declines. In order to prevent this problem, iron control should be a major design factor in the treatment of formations containing high amounts of iron.

In acidizing treatments, the acid reacts with iron present in the acid storage tanks, the tubulars being pumped through and the treated zone. Initially, the acid puts iron in solution, but as the acid spends itself, the pH of the solution rises causing the solubility of the iron to be reduced. As a result the iron precipitates.

In contrast, hydraulic fracturing fluids typically being a pH of 3-9 will dissolve only a minimal amount of iron (<5 ppm). Therefore, oxygen entrained in the fracturing fluid reacts only with iron that is currently in solution in the formation.

This iron may have existed in the connate waters or have been put in solution during the breakdown acid treatment. The precipitate of iron hydroxides and other iron compounds can form along the entire length of the newly created fracture. During production, the precipitates migrate toward the wellbore causing severe permeability damage. As a direct result, high post-frac production rates may be shortlived causing the total production to fall far short of that initially projected.

In acidizing or linear gel treatments, sequestrants such as citric acid or EDTA are commonly used to minimize iron problems. However, when using crosslinked fracturing fluids, these sequestrants form a complex with the metal ion used to crosslink the polymer solution. This would essentially prevent the fluid from crosslinking.

This paper describes a sequestering agent that selectively reacts with iron found in formations without affecting the rheology of the crosslinked polymer solution. To prove the material's effectiveness, flow studies through sand packs were conducted. Included also are field results detailing cases of wells treated using this iron sequestering agent.

OXIDATION STATE OF IRON

Iron exists principally in one of two oxidation states, +2 or +3. Ferrous iron corresponds to the +2 state and ferric to the +3. The particular state in which the iron exists is critical to its control.

The oxidation state is highly dependent upon the solvent medium in which it exists. If oxygen is not present, or a reducing condition exists, then the ferrous state is more stable than the ferric. This is the normal environment in an untreated formation; therefore, the majority of iron in solution in a producing interval is typically in the ferrous state.

If however, oxygen is introduced into the system and an aerobic condition is formed, then the ferrous ion becomes unstable. When this happens the +2 ion will rapidly oxidize to the more stable ferric state. Such oxidation occurs when air entrained in a fracturing fluid is pumped into the formation.

IRON IN THE FORMATION

Iron is a constituent of the rock matrix in many of the producing formations of the Permian and Fort Worth Basins. It is of particular importance in the San Andreas, Clearfork and Marble Falls intervals. Table 1 shows the principle minerals in which iron is associated and the oxidation state in which it exists. As the table shows, in most cases iron will be found in the ferrous or +2 state.

Iron is also found in solution in the connate water of many of the formations in Texas and New Mexico. Table 2 displays the concentration of dissolved iron and the pH of the water in a number of different formations in Texas. The table demonstrates how drastically the iron content of one particular formation can change from county to county or well to well. For example, the water of the Upper Clearfork sampled in Yoakum county show 200 mg/l iron in solution. In Gaines county the same formation has almost 1000 mg/l dissolved iron. The pH of the different waters also varies significantly. Table 2 clearly reinforces the need to obtain representative water samples of the interval to be fractured in order to determine if the concentration of iron is great enough to cause post-frac production problems. If this is the case, then an iron control additive should be added to the fracturing fluid to prevent the precipitation of iron compounds.

IRON PRECIPITATION AND ITS PREVENTION

The pH of the water and the oxidation state of iron are the principal factors in determining the point at which iron will drop out of solution. At a pH of about 7.5 ferrous iron begins to precipitate. The major precipitate formed will be a white crystalline or gelatinous compound, ferrous hydroxide, $Fe(OH)_2$. The gelatinous form, by its very nature, will cause the most serious damage to production.

In most cases the pH of the fracturing fluid when mixed with formation water is below 7.5. Therefore, the precipitation of ferrous compounds is not likely to occur. Of greater concern in fracturing operations is the precipitation of ferric iron compounds. As mentioned previously, the vast majority of iron in solution downhole exists in the +2 oxidation state. This ferrous iron readily oxidizes to ferric when exposed to oxygen entrained in the fracturing fluid. Ferric iron starts to drop out of solution at a pH of about 2.5 and will be completely precipitated at 3.5. The prime precipitate is ferric hydroxide, $Fe(OH)_3$ a reddish-brown crystalline or gelatinous compound.

The exact pH values at which the different iron compounds will precipitate is somewhat effected by the concentration of other ions present. In addition, the exact form of the precipitate, whether gelatinous or crystalline, is dependent upon the concentration of anions in the solution.

The new sequestrant prevents iron precipitation by complexing with ferrous and ferric ions to form a compound that is both stable and water soluble. This newly formed water soluble iron complex can then be safely flowed back to the surface. In contrast to acidizing sequestrants, the iron control agent is selective in that it combines with dissolved iron but does not react with the metal ions being used to crosslink the polymer solution specifically designed for use with the sequestrant. As a direct result, the iron control agent can be used in the crosslinked fracturing fluid without adversely affecting the system's rheological properties.

Table 3 displays the rheological properties of the crosslinked fracturing fluid containing the new selective sequestrant. The table also shows the same system with EDTA in one test and citric acid in another replacing the new sequestrant in the fracturing fluid. The concentration of the three additives represent the quantity used to sequester approximately 1500 mg/l iron. A 30#/1000 gal crosslinked polymer solution with the new selective sequestrant has an apparent viscosity of 375 centipoise measured at 170 sec^{-1} after 1 hour at 80°F. This is compared to 12 and 11 centipoise for EDTA and citric acid, respectively.

The sequestrant also acts as a buffering agent to keep the pH of the crosslinked fracturing fluid between 3 and 4. By keeping the pH below 7.5 the precipitation of any ferrous iron which may not have been complexed by the sequestrant can be prevented.

In addition the system's iron control capacity may be enhanced by the addition of an oxygen scavenger. An oxygen scavenger will react with free oxygen and prevent the oxidation of ferrous iron to ferric. Some anti-oxidants also act as reducing agents and can be used to reduce any ferric iron in solution to ferrous. Once the iron is reduced it can be effectively controlled by the low pH maintained by the sequestering agent.

FLOW TESTS

The ultimate test of the effectiveness of an iron control agent is its capacity to prevent permeability damage in the formation in the presence of high amounts of iron. To gauge the sequestrant's ability to perform under these conditions flow tests through packed sand columns were performed.

Two identical flow tests were conducted. A new sand column was prepared for each one. In both tests an acrylic plastic tube was filled with 40-60 mesh Ottawa sand. The tube was 22 inches long and had a 15/16 inch inside diameter. A fluid reservoir was designed such that a constant hydrostatic pressure of 28 inches was maintained throughout the test. The sand packs were standardized using filtered 2% potassium chloride brine. Both columns had initial flow rates of approximately 100 milliliters of brine per 3 minutes.

The base fluid for all the tests was filtered distilled water containing 2% potassium chloride. For the first test all the oxygen was removed from a volume of 2% KCl brine. This was done by bubbling nitrogen gas through the brine. The pH of this fluid was then adjusted to 7.0. Finally, enough ferrous sulfate was introduced to bring the level of ferrous iron in the brine to 3000 mg/l. Next, an equivalent amount of brine was pH adjusted to 3.3. Finally, equal volumes of the two fluids were combined and flowed through the sand pack. The volume versus time of recovered filtrate as well as the final pH of the combined fluids were recorded.

For the second test all the oxygen was once again removed from a volume of brine by bubbling nitrogen gas through it. The pH of the fluid was then adjusted to 7.0. Sufficient quantities of ferrous sulfate were added to the brine to bring the level of ferrous iron in solution to 3000 mg/l. Next, the sequestrant was added to an equivalent volume of brine. The concentration of sequestrant was 15#/1000 gal of potassium chloride solution. This brought the pH of the mixture to 3.3. As in the first test, equal volumes of the two fluids were combined and flowed through the sand pack. The same data was recorded in this test as in the former sampling.

In both tests oxygen was taken out of the portion of brine receiving the ferrous sulfate. This was done to assure that both tests were initiated with only ferrous ions present in solution. However, no attempt was made to flush oxygen out of the second volume of brine before it was combined with the iron solution. Since pH is critical in the control of iron, care was also taken to assure that the pH of all the combined solutions were equivalent. By controlling the solution's pH, the iron control agent's sequestering and buffering capacity is highlighted.

Table 4 shows the results of the two flow tests. The first test, in which no iron control additive was used, 914 mls of solution flowed through the pack in the first 30 minutes. However, after 4 hours of continuous flow the rate had decreased to only 111 ml per 30 minutes. This is an 88% reduction in permeability.

In the flow test with the new iron sequestering agent the initial 30 minute flow rate was 951 mls. After 4 hours of continuous flow the rate was 945 mls per 30 minutes. Thus, the original permeability of the proppant pack was essentially unchanged. This test effectively demonstrates the iron sequestering capabilities of the compound.

The chemical also acts as a buffering agent. The pH of the filtrate in Test 1 was 5.6. In comparison the pH of the filtrate in the test utilizing the new sequestrant was 4.0. This demonstrates the compound's buffering capacity as it maintains a significantly lower pH than the untreated sample even when mixed in a 1:1 ratio.

FIELD APPLICATION

The sequestering agent is being used primarily in the Fort Worth Basin, in the Marble Falls Conglomerate and in the Applachian Basin in the Clinton formation. It is also being used in the San Andreas formation of West Texas and the Granite Wash and the Basal Pennsylvania Unconformity Sand in Oklahoma.

The following case histories involving wells in which the new iron sequestrant has been applied detail the chemical's ability to complex with high amounts of iron and safely flow them back to the surface. Information about the amount and concentration of proppant pumped during the treatment is also included to give an indication of the competence of the crosslinked fluid when combined with the sequestering agent.

In Eastland County, Texas, 16,000 gallons of 25#/1000 gal crosslinked system was pumped into the Marble Falls Conglomerate formation. 26,000 pounds of 20-40 and 12,000 of 10-20 sand was injected with the fluid. The returned fluid had 500 ppm of iron in solution. The initial production was 60 BOPD, 10 BWPD and 125 mcf/d. The stabilized production after six months was 45 BOPD, 30 BWPD and 75 mcf/d.

In Crane County, Texas, a 30#/1000 gal crosslinked system was pumped at 25 BPM. 60,000 pounds of 10-20 sand was pumped into the Sand Andreas formation using 20,000 gallons of fluid. The sand concentration was pumped at up to 8 pounds per gallon. The initial fluid flow back contained 660 ppm iron in solution.

In Hood County, Texas, 60,000 gallons of a 30#/1000 gal crosslinked system was pumped at 20 BPM into the Marble Falls Conglomerate. 31,000 pounds of 20-40 and 43,000 pounds of 10/20 sand along with 800 scf/bbl of nitrogen were also injected. The recovered fluid contained 600 ppm iron in solution.

In Garvin County, Oklahoma 57,000 gallons of 30#/1000 gal crosslinked fluid was pumped with 70,000 pounds of 20-40 sand. The formation being treated was the Basal Pennsylvania Unconformity Sand. The initial fluid returns had 850 ppm iron in solution.

In Eastland County, Texas, The Marble Falls Conglomerate was treated with a 30#/1000 gal crosslinked gel at 20 BPM. The treatment also contained 18,000 pounds of 20-40 and 7,000 pounds 10-20 sand. The well initially flowed 40 BOPD and stabilized to 30 BOPD for 9 months. This is considered excellent for that area. Initially, the well flowed back fluid containing 125 ppm iron in solution.

In Washington County, Ohio, 25,000 gallons of 30#/1000 gal crosslinked gel was pumped into the Medina formation. The fluid also contained 19 tons of CO_2 and 30,000 pounds of 20-40 sand. The initial flow back samples contained 750 ppm iron.

SUMMARY AND TREATMENT RECOMMENDATIONS

1. Water samples should be taken and analyzed for iron for each well that is to be fractured. If the sample contains over 100 ppm iron the use of an iron control agent should be considered.

2. The acid used for the pre-frac breakdown should contain an iron sequestering agent if an older well or iron-rich formation is being treated.

3. The formation should not be over treated with a greater concentration of acid than is needed to effectively break down the zone of interest. Excess acid can dissolve large amounts of iron in the formation and as the pH of the spent acid increases the solubility of the iron is reduced. As a result, the iron may form a gelatinous or crystalline precipitate.

4. When high amounts of iron are present in the formation of a well that is to be fractured, an iron sequestering agent should be used in the fracturing fluid. The sequestrant should be in the pre-pad, pad and slurry portion of the treating fluid. The sequestrant also acts as a buffer keeping the pH below 7.5. This will maintain any uncomplexed ferrous iron in solution.

5. An oxygen scavenger/reducing agent can also be used to enhance the iron control capacity of the system.

6. A selective sequestrant can be used which combines with iron,but does not react with the metal ion being used to crosslink the polymer solution specifically designed for use with the sequestrant. As a direct result, the rheology of the crosslinked treating fluid is unaffected by the sequestering agent.

7. The use of an iron sequestrant in fracturing can minimize the chances of an iron precipitation problem causing a rapid post-frac production decline. As a result, an expensive remedial clean-up treatment can be prevented.

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Table 1
Oxidation State of Iron in the Formation

Mineral	Composition	Oxidation State
Pyrite	FeS_2	Fe^{+2}
Pyrrhotite	FeS	Fe^{+2}
Hematite	Fe_2O_3	Fe^{+3}
Magnetite	Fe_3O_4	Fe^{+2}, Fe^{+3}
Siderite	$FeCO_3$	Fe^{+2}
Chlorite	$(Fe,MG)_5 Al(AlSi_3O_{10})(OH)_8$	Fe^{+2}

Table 2
Analysis of Texas Formation Water

Formation	County	Dissolved Iron mg/l	Depth, ft	pH
Brown Dolomite	Carson	215	3000	7.5
Wilcox	Colorado	395	9568	6.9
Wilcox	DeWitt	45	7756	6.4
San Andreas	Gaines	34	4900	7.2
Upper Clearfork	Gaines	999	6900	5.7
Clearfork	Gaines	200	6930	6.6
Clearfork	Gaines	360	7188	6.0
Wilcox	Hardin	295	8500	7.0
Edwards Lime	Karnes	197	10900	7.2
Sprayberry	Martin	430	8350	6.9
Wilcox	Polk	215	7790	5.3
Unknown	Reagan	475	5200	5.9
Clearfork	Reagan	112	6194	6.5
Sprayberry	Reagan	84	6194	6.4
Ellenberger	Reeves	620	14000	6.4
Ellenberger	Terrel	700	9000	5.7
Mississippi	Throckmorton	94	4800	7.5
San Andreas	Yoakum	136	4900	7.5
Clearfork	Yoakum	266	6700	7.0
Upper Clearfork	Yoakum	200	6900	6.8
Cisco	Young	79	900	6.7
Caddo	Young	50	3750	7.0

Table 3
Rheology Data

A. 30 #/Mgal polymer + buffer + crosslinker + 15 #/Mgal Sequestrant

B. 30 #/Mgal polymer + buffer + crosslinker + 90 #/Mgal EDTA

C. 30 #/Mgal polymer + buffer + crosslinker + 45 #/Mgal Citric Acid

Note: The concentration of the sequestrants was chosen based on their ability to complex approximately 1500 mg/l iron.

	Viscosity, Cps. @ 170 sec^{-1}	n'	k'
A	375	.51	.096
B	12	.71	.00095
C	11	.727	.0009

* Rheology measured on Fann 50, at 80°F after one hour

Table 4

The fluids in Test 1 and 2 were mixed in a 1:1 ratio.

Temperature	:	72^{o}F
Pressure	:	Hydrostatic (28 in.)
Packed Sand Column	:	22 in. long X 15/16 in. I.D.
Sand	:	40-60 Mesh Ottawa

Fluids for Test 1

A) Filtered and deoxygenated 2% KCl brine + 3000 mg/l ferrous iron + NH_4OH to a pH of 7.0

B) Filtered 2% KCl brine + HCl to a pH of 3.3

Fluids for Test 2

A) Filtered and deoxygenated 2% KCl brine + 3000 mg/l ferrous iron + NH_4OH to a pH of 7.0

B) Filtered 2% KCl brine + 15#/Mgal sequestrant - Addition of sequestrant will lower pH to 3.3.

	Test 1		Test 2	
Time, Hrs.	30 Minute Flow, Milliliters	Cumulative Volume, ml	30 Minute Flow, Milliliters	Cumulative Volume, ml
0	--	--	--	--
0.5	914	914	951	951
1.0	775	1689	941	1892
1.5	664	2353	947	2839
2.0	560	2913	941	3780
2.5	402	3315	947	4727
3.0	294	3609	935	5662
3.5	214	3823	940	6602
4.0	111	3934	945	7547

Final pH of Filtrate - 5.6

Final pH of Filtrate - 4.0