IRON CONTROL IN FRACTURING OPERATIONS

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ABSTRACT

Iron control studies over the last 30 years have dealt primarily with iron control in acidizing operations. In fracturing operations, iron control has received much less consideration.

Certain hydrocarbon producing zones contain iron compounds in both the rock composition and formation water.

Fluids used in fracturing operations may be incompatible with the formation water or rock itself, if iron is present in them. Special consideration should be given to the design of fracturing fluids and fracturing techniques so that iron problems will be minimized.

This paper presents: (1) data and treating information on 3 formations (Clinton Sandstone in Ohio, Granite Wash in Oklahoma, Limy Sand in Texas) that contain iron in the formation rock and formation water and were treated with an iron control fracturing procedure. (2) the new iron control fracturing procedure that helps maintain iron in solution and helps provide compatibility of the fracturing fluids with the formation. (3) treating techniques to control iron problems and (4) field results from jobs that utilized the modified fracturing fluid and procedure.

Sharp production decline curves have plagued operations in the formations listed. The Clinton Sandstone, Granite Wash, and Limy Sand formations have responded well to fracturing treatments; however, in many instances the production increases have not been sustained as long as desired. Iron, a constituent of the reservoir rock, may well be a primary factor in this problem.

Utilization of iron control additives and treating techniques as applied to the formations encountered in Pennsylvania, Michigan, Illinois, Indiana, Kentucky, West Virginia, Tennessee, Alabama, Texas, and Oklahoma should be considered for improving cleanup operations, production stimulation and rate of production decline in the same or similar formations in other areas.

INTRODUCTION

Iron problems have been recognized in oil field operations for about 30 years. Studies have dealt primarily with iron control in acidizing operations. Acid systems have been designed to dissolve iron scale or iron in the formation and maintain the iron in solution until the treating fluid is recovered.[1,2,3,4] Fracturing fluids are weakly acidic or basic and dissolve very little iron. Iron frequently has been overlooked as a factor in fracturing treatment design.

Investigation has shown that iron may present a significant and complex problem. This problem had previously been approached by using sequestering agents. Breakdown acid systems incorporated iron chelating agents or a combination of a chelating and a pH control agent to control iron precipitation.[1,2,3,4] In fracturing fluids, ammonium citrate has been used as an iron control additive. Reports from several producers in the Ohio area and flow test data presented in Table 3 indicate that it was successful to some extent.

However, research was initiated to obtain an iron control system that would help achieve satisfactory production and sustain production increases in the Appalachian Basin.

IRON COMPOUNDS IN SANDSTONE FORMATIONS

Iron is an important constituent of the Clinton, Granite Wash, and Limy Sand formations. Iron is found in the matrix structure of the formation as hematite, magnetite, siderite, pyrite, and as a component of Chlorite and mixed layer clays.

Iron is present as ferrous iron (+2 oxidation state) and ferric iron (+3 oxidation state). The oxidation state of the iron in the formation components is listed in Table 1.

A study of water samples from the Clinton formation shows that the iron content ranges from 50 to more than 1400 mpl and the pH ranges from 3.1 to 6.0. Analysis of water samples from the Granite Wash formation show an iron content of at least 128 mpl and a pH that ranges from 6.3 to 7.0. The water in the Limy Sand formation contains at least 84 mpl of iron and has a pH of 6.2. Data is shown in Table 2. Iron is usually in solution in formation water as ferrous iron. Ferrous iron will usually remain in solution if oxygen in a treating fluid does not oxidize it to ferric iron.

Iron in solution may precipitate and deposit in the formation or the fracture thereby reducing the production flow capacity of the fracture. These iron deposition problems are aggravated by acidic breakdown fluids and by the oxidation of divalent iron by entrained air in treatment fluids. Cleaning up a well after it is already plugged with precipitated iron may be difficult. Preventative measures appear easier and more effective.

MAINTAINING IRON IN SOLUTION

The oxidation state of iron is critical to iron control. This state determines the pH at which iron precipitation occurs. An increase of pH may occur due to the mixing of formation water and treating fluid or possibly the reaction of the treating fluid with the formation. Ferric iron starts to precipitate when the pH of the fluid increases to about 2.5 and is completely precipitated when the pH reaches about 3.5. Ferrous iron (+2 oxidation state) on the other hand remains in solution to a pH of about 7.5.

A New Iron Control Agent (NICA) was developed which may be used in breakdown acids in conjunction with other iron sequestering additives in the system. The NICA developed is an oxygen scavanger. It removes free oxygen from treating fluids and prevents the oxidation of ferrous iron to ferric iron. The additive also acts as a reducing agent and reduces dissolved ferric iron to ferrous iron.

NICA also is used in fracturing fluids to help provide compatibility of the fracturing fluid and the formation water. In a fracturing fluid, NICA removes free oxygen from the system and the divalent iron inherent to the formation is maintained in solution during the cleanup operation. Additionally, dissolved iron in the +3 oxidation state (ferric) is reduced to ferrous iron so that it is maintained in solution.

The pH of the fracturing fluid is also an important consideration. The pH should be kept below 7.5 so that ferrous iron remains in solution. Buffering agents are used in fracturing fluids to adjust the pH in a range of about 2.5 to 5.0.

When iron exists in solution it presents no blockage potential and production deliverability is at a maximum. The problem exists when iron precipitates as crystalline fines or a gelatinous mass. These precipitates, particularly the gelatinous mass, hinder flow capacity. The additives that remove oxygen from solution, reduce iron, and control pH should help maintain iron in solution and help sustain stimulated production.

FLOW TESTS USING IRON CONTROL ADDITIVE

Flow tests were conducted to determine and compare the flow rate of treating fluids through a 5/8 in. diameter column of sand that was 12 in. long and contained residual water. The residual water in the sand contained 2000 mpl of ferric iron in solution at a pH of 1.72.

Tests were conducted using a 2% potassium chloride solution without additives, 2% potassium chloride that contained ammoniated citric acid, and 2% potassium chloride that contained NICA. The (19.5 in.) hydrostatic pressure of the 2% potassium chloride solution was the driving force. Flow volumes were recorded at 2.0, 2.5, and 3.0 hrs. Data is shown in Table 3.

Results from the 3 hour flow measurement show that ammoniated citric acid improved the flow rate 123% while NICA improved the flow rate 300%.

In sandstone formations that contain iron, the beneficial effect of NICA is considered relative to the flow test data. Iron should be kept in solution, not hinder flowback and be recovered at the surface.

TREATMENT RECOMMENDATION

The factors previously discussed that may be detrimental to a fracturing operation in the presence of iron compounds indicate that an effective treatment recommendation should involve the following considerations.

I. Breakdown Acid
   A. Use the lowest concentration of hydrochloric acid that will achieve effective breakdown of the formation and thus minimize the amount of fines released by the acid reaction.
   B. Treat the breakdown acid with 10 gallons of acetic acid and 50 pounds of citric acid per 1000 gallons. These iron control additives will help maintain up to about 10,000 mpl of iron in solution to improve clean-up operation.
   C. A third iron control additive, NICA, which removes dissolved and entrained oxygen from the acid and reduces ferric iron in solution to ferrous iron should be considered. This additive may not be necessary in acid that is treated with adequate concentrations of iron chelating agents and pH control agents. However, it should enhance the previously described iron control systems to some extent.

II. Fracturing Fluids

A. Pre-pad

1. Treat with non-emulsifier, fluid loss additives, potassium chloride, clay stabilizers, etc.
2. Treat the pre-pad with NICA that removes dissolved and entrained oxygen and reduces ferric iron in solution to ferrous iron. This makes the pre-pad compatible with formation water that contains ferrous iron.
3. Adjust pH with buffering agent so that the pH is between 2.5 and 5.0. All iron contacted should be in solution as ferrous iron and should remain in solution at pH's up to about 7.5.

B. Viscous Sand Carrying Frac Fluid

1. Treat with NICA to remove dissolved and entrained oxygen and reduce dissolved ferric iron contacted to ferrous iron.
2. Adjust pH with buffering agent so that it is between 2.5 and 5.0. The pH is adjusted to shorten clean-up time, and to help maintain a pH below 7.5 so that ferrous iron remains in solution, and flow back is not effected.

JOB RESULTS

NICA, has become an integral part of many fracturing treatments in the iron rich Clinton formation of Ohio, West Virginia, Pennsylvania, and New York. Approximately 7000 fracturing jobs that utilized NICA have been conducted in this area.

NICA has also been recognized as an effective aid to iron control in fracturing operation in the Granite Wash formation in the Anadarko Basin in Oklahoma and the Limy Sand in the Wichita Falls Texas area.

Results indicate that systems utilizing NICA are superior to systems used previously. Following are some results from the treatments.

In Cattaraugus County, New York, flowback of fracturing fluids that contained NICA held up to 2000 mpl iron in solution.

In Crawford County, Pennsylvania, a flowback from a fracturing treatment without NICA was found to have about 200 mpl iron in solution. An offset well was fractured with a similar base fluid that was treated with NICA. The flowback carried 850 mpl iron.

In Holmes County, Ohio, operators noted clear flowbacks when using NICA. A colorless to dark fluid indicates iron is in solution as ferrous iron and will remain in solution if the pH remains below 7.5. Treating fluids without NICA flowed back an orange colored fluid. This indicates that ferric iron was present and had precipitated to some extent.

In Harrison County, Ohio, a gelled fracturing fluid that utilized NICA flowed back 900 mpl iron.

In Ashtabula County, Ohio, an operator that used NICA when stimulating the Clinton reported that cleanup time was decreased significantly in some cases.

In the Burns Flat Oklahoma area, the Granite Wash formation was broken down with acid and fractured. Initial production was high but the well plugged itself off. The job was re-run using NICA in the non-acid aqueous treating stages. The well tested at 900 MCF of gas and 20 barrels of condensate per day. Six months after the last job, the well is still producing at a high rate.

In the Wichita Falls Texas area, fracturing treatments in the Limy Sand formation that utilized NICA showed greater initial production and sustained production than off-set wells that were fractured with frac fluid that did not contain NICA. Two wells treated with NICA in the treating fluid were producing 10 and 4 bbls of oil per day, as last reported. Off-set wells fractured with frac fluid that did not contain NICA were producing 1 bbl of oil per day at last report.

CONCLUSIONS

1. Breakdown acid should have as low a concentration of acid as possible to effectively breakdown the formation for the fracturing operation.
2. Breakdown acid should contain iron control additives to maintain dissolved iron in solution and make the acid compatible with formation water.
3. The water base fracturing fluids should be treated with NICA, that removes free oxygen and reduces ferric iron that may be contacted to ferrous iron, to help provide the compatibility of the frac fluid with formation water contacted.
4. The fracturing fluid should contain a pH control additive that will maintain a pH that ranges from 2.5 to 5.0.
5. Laboratory data and treatment results indicate that the use of NICA and a pH control system can greatly improve the results of fracturing operations in the formations that contain iron.

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TABLE 1 — STATE OF OXIDATION OF IRON IN FORMATION COMPONENTS

Formation	Hematite	Magnetite	Siderite	Chlorite	Mixed Layer Clay
Clinton	Fe+++	Fe++ Fe+++	Fe++	Fe++	Fe++
Granite Wash	-	Fe++ Fe+++	Fe++	Fe++	Fe++
Limy Sand	Fe+++	-	-	Fe++	Fe++

TABLE 2 — IRON CONTENT AND pH OF FORMATION WATER

Formation	Iron in Solution	Precipitated Iron	pH
Clinton	57 to 1425 mpl	0-650 mpl	3.1 to 6.0
Granite Wash	128 mpl	-	6.3 to 7.0
Limy Sand	24 mpl	60 mpl	6.2

TABLE 3 — FLOW TESTS DATA

Treating Fluids: A - 2% KCl, pH 4.0
B - 2% KCl, 5 lbs. citric/M gal plus NH_4OH to pH 6.0
C - 2% KCl, 15 lbs. citric/M gal plus NH_4OH to pH 6.0
D - 2% KCl, 20 lbs. NICA/M gal., pH 4.0

Temperature: 74°F
Pressure: Hydrostatic (19.5 in.)
Horizontal Sand Column: 12 in. long x 5/8 in. diameter
Sand: Okla. No. 1 Saturated with 2000 mpl Fe^{+++} solution, pH 1.72

Flow (Milliters)

Time (hrs.)	A	B	C	D
2.0	149	165	175	410
2.5	180	195	207	517
3.0	203	245	256	602