IRON: MINIMIZING PROBLEMS AND MAXIMIZING TREATMENT EFFECTIVENESS

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ABSTRACT

The precipitation of iron compounds following well treatment is a common problem in most areas of Texas and New Mexico. This insoluble gelatinous precipitate is both an effective plugging agent and an emulsion stabilizing agent. Either condition damages permeability and greatly restricts production of oil and gas.

In order to effectively deal with the problem, the chemistry and physical characteristics of iron as an ion and its subsequent reactions must be understood. Sources of iron, well conditions, types of iron control agents and their properties will be discussed and evaluated.

INTRODUCTION

Most wells are acidized with the basic assumption that:

ACID + RESERVOIR will create Enhanced Production.

However, the result can also be:

ACID + RESERVOIR will create Damaged Permeability.

To accurately predict the result, one must understand in detail the composition of the reservoir, the fluid, and how they interact. All factors which present a problem must be eliminated or mitigated. Iron, in its various forms, can cause severe permeability damage, scaling problems and/or fines problems.

To effectively deal with the problems iron creates, its physical and chemical characteristics must be understood. Many techniques and agents for controlling various iron problems exist. The problem is a matter of choosing the proper agent and using the appropriate technique to minimize the particular problems possible in an individual treatment.

IRON IN SOLUTION

Acid easily dissolves iron wherever it is contacted. The dissolved iron stays in solution as an ion with one of two oxidation states, Fe(II) or Fe(III). In either state, it will remain in solution until its solubility index is exceeded. At that point it precipitates out of solution in the hydroxide form, which produces a gelatinous mass.. Solubility indexes are very pH sensitive. Fe(III) precipitates when the acid spends to pH 2.2 as ferric hydroxide. By pH 3.2 all of the ferric hydroxide is precipitated. Fe(II) precipitates out as ferrous hydroxide when the pH reaches 7.2. If hydrogen sulfide gas is present in the system, Fe(III) will reduce and a precipitate of elemental sulfur will form at a pH of 1.92. Once the acid is spent, any remaining FeS will precipitate out.

Most of the dissolved iron in treating fluid is of the Fe(II) oxidation state with an estimated ratio of 5 Fe(II):1 Fe(III). since the Fe(II) does not precipitate until pH 7.2 and most acid is completely spent at pH 5.3, it has been assumed that the ferrous hydroxide is not a problem. Please note that as the well conditions and treating conditions vary, so does the validity of this assumption. The ratio of Fe(II) to Fe(III) can be altered by well conditions. Rusts and scales in the tubular goods which have experienced oxygen corrosion are usually Fe(III). Rust from storage tanks and surface equipment is also Fe(III). When dissolved by the passage of acid these become a source of additional Fe(III). Oxygen dissolved in treating acid can also become a source by oxidizing the Fe(II) to Fe(III). Only a limited amount of oxygen is normally present in acid, so about 55 ppg (Fe(II) can be expected to be oxidized by 1000 gallons of acid. Oxygen carried into the reservoir during water injection can be another source of oxidation.

Contamination of acid by Fe(III) before injection into the well is another major concern. A recent field study showed only 180 ppg in treating acid mixed and delivered in service company equipment. However, more serious contamination can occur when the acid is stored or transferred to field storage tanks. Concentrations of 3000 ppm Fe(III) or more were observed in samples from such tanks.

Sour crude wells produce an environment where iron is reduced, which leads to greater corrosion problems and precipitation of both sulfur and iron (II) sulfides.

$$H_2S + 2Fe\ (III) \text{ -- } 1\ S^\circ + 2Fe(II) + 2\ H^+.$$

The free hydrogen can lead to a form of corrosion known as hydrogen embrittlement of sulfide stress cracking. This is believed to be the result of free hydrogen entry into the material followed by the combination of individual hydrogen atoms into molecular hydrogen H_2. This combining occurs in voids and along grain boundaries and the cracks occur because the molecular hydrogen occupies a larger volume than the atomic entity. Stress cracking leads to a loss of strength and to more surface area for further acid corrosion.

The precipitation of elemental sulfur occurs while the acid is spending between pH 1.92 and its final spent pH. Once the acid is spent any remaining Fe(II) and sulfur will precipitate as iron sulfide. These precipitations may occur in the formation, in the wellbore and on the surface.

In addition to these factors, which are independent of the rock composition, the reservoir mineralogy and morphology must be considered. Many of our new producing horizons in the area will be from dirty formations as most of the clean sandstones, pure limestones and dolomites have already been discovered. Rocks are not inert. All three types of formations can undergo changes. Reservoirs are not homogeneous either. Zones of lesser or greater permeability are common.

In limestones or dolomites, stringers of non-carbonate rock are often found. Intergranular porosity can be infilled with various materials including hematite (Fe_2O_3), iron oxide, and pyrites. In extreme cases, stringers of hematites, which release Fe(III) are present. Any core which exhibits a reddish color or staining can be suspected of containing Fe(III) compounds. Siderite is iron carbonate and generally contains both Fe(II) and some Fe(III) ions. The ratio of these ions will vary depending on the history of the reservoir.

The most commonly ignored problem is the effect of acid in a sandstone reservoir. Because live acid often returns to the wellhead, the assumption is made that iron will not be precipitated. This assumption is wrong. The acid immediately around the wellbore may remain unspent, but an area of spending or spent acid will be formed on the leading edge. Any iron carried into the reservoir or contacted within it will be dissolved and concentrated in the leading edge of the acid. This will also be the last acid recovered from the well. As it spends, Fe(III) will precipitate if an iron control agent is not used. If the acid is a spearhead in front of a fracturing job, the length of recovery time, degree of spending, and the likelihood of Fe(III) and Fe(II) precipitation all increase.

All of the diagenetic minerals described as existing in the carbonates can also be found in the sandstones. Often only clay minerals are considered a problem. This is also a dangerous assumption. This was illustrated well by the following in scenario originally cited by Dr. David K. Davies:

> "Engineers had designed a small acid job which used only 250 gallons of 15% acid for a hole opener. They then fractured the formation using an oil based treating fluid. From this it can be determined that they were worried about disturbing both calcite cementitious material and water sensitive clays.
>
> "After the stimulation the production was reduced from 100 bopd to 10 bopd. Because of this a core study was done which included Scanning Electron Microscopy and Energy Dispersive Xray analysis (SEM & EDX). The SEM showed the pore throats were lined with an iron rich chlorite, and that pore infills of pyrite, and iron oxide were present. The minor on Xray diffraction was calcite. EDX showed this to be heavily iron substituted. The acid had liberated large amounts of iron, spent and precipitated them as ferric hydroxide. With the reduced permeability and porosity of the clay filled reservoir the Fe(III) OH plugging caused dramatic production decreases. The well was retreated with weak acid and iron chelator and oxygen scavenger. Its productivity was returned."

The moral obviously is to study the composition of your reservoir carefully. You really do need to know what minerals are present, where they are in the reservoir, and what amounts of iron they contain.

Minerals containing iron in sandstones include the following:

Biotite; a form of mica which contains Fe(II). It is sheet silica similar in structure to clay minerals. It often shows XRD peaks in the same area as illite. The potassium ion is readily exchangable with sodium or calcium ion. This reaction can cause the edges to splay, break, and migrate.

Carbonates; calcite, dolomite and siderite each display slightly different problems, but under the right conditions all three can release Fe(III), release fines as cement binder breaks down, and can seal or restrict pores. Siderite can also cause density tools to falsely record low porosity.

Pyrite; the most common high density mineral in reservoirs. It can, because of its density cause a logging tool to show low porosity. It can, because the mineral is conductive, cause a logging tool to show low resistivity if a sufficient quantity is present. It is high in Fe(II) and is readily soluble in acids. The more stable form, Fe_2S, can be destabilized by acid and become a migratory fine.

Glauconite; is structurally like a clay but occurs in grain size particles. Its XRD peak is also at the same place as illite and is often reported as such. It holds water, shows low resistivity, can cause a logging tool to show low porosity. It reacts with HCl to release FE(III).

Chlorite; a clay mineral that occurs in 2 common forms, attached to grains and as a grain lining rim. Where chlorite lines the grains and pore throats, it makes the formation highly susceptible to damage. It disperses and migrates rapidly in high pH environments. It degrades in HCl to release Fe(II), aluminum and amorphous silica. It is not readily stabilized by clay control additives.

Changing to HF acid does not solve the need for iron control. This fact has been demonstrated in laboratory test by treating Berea sandstone with 1000 mls of 5% HCl and following this with 500 mls of Mud Acid containing 3% HF. During the second step, analysis of the effluent showed 3200 ppm Fe and 15,600 ppm Al. The effluent was spent with $CaCO_3$ to pH 5 and large quantities of Fe(III)OH precipitated. Analysis of the spent acid showed only 11 ppm iron in solution. The fluoride present forms preferentially with the aluminum, so did not complex the iron.

EMULSIONS AND FINES PROBLEMS

Wherever the iron in solution begins to form any of the three common precipitates, it is often still mixed with formation hydrocarbons. In order to precipitate from a solution, any particle has to reach a certain size. Unfortunately, before the iron hydroxides reach a sufficient size to precipitate, they have already reached a size large enough to serve as the nucleation point of an emulsion. Emulsions can be very thick, gelantinous, or stringy, but in all forms can effectively block permeability.

From several years of experience in field laboratories where emulsion breaking is routine it has been determined that there are iron stabilized emulsions. There are also emulsions stabilized by pyrite fines and mixtures of iron compounds and hydrocarbon particles. Those emulsions which are iron stabilized can be broken if a chelating agent is added with the normal non-emulsifiers tested. In some cases, the emulsion can be chemically broken only in the presence of the chelator. In many more cases, the addition of the chelator will greatly reduce the breakout time of the emulsion. Please note that to break an emulsion, the carrier fluid does not have to be acidic. The tendency to form iron stabilized emulsions appears to be greater in sour wells.

Fines released during acidizing, like pyrites and other iron sulfides, or those present as mobile fines naturally can become major production headaches. These fines carried out of the well in either the water or hydrocarbon phase of the produced fluids can stop up downhole pumps, increase corrosion rates, and play havoc with a variety of surface equipment. They also play an important role in the formation of scales in tubulars. In areas where the reservoir is known to have large amounts of pyrite surrounded by calcite or other carbonate cementitious material should not be candidates for large acid jobs. While chelators do help somewhat in bringing these fines out of the well in the acid treatment there is a definite limit to their influence. For pyrites entrained in the hydrocarbon phase, the usual procedure is to change their wetabilities and precipitate them out on the surface. Sometimes changing out the bottomhole pump for a different type which is designed to handle produced fines will help alleviate the problem downhole.

In high corrosion rate wells, ie. H_2S or CO_2 producing, production of fines accelerates the corrosion process by erosion. There is a highly synergistic effect which can increase the corrosion rate 100 times or more. Particles are especially effective in stripping off corrosion inhibitor films. Therefore, completion designs should be based on continuous replacement of corrosion inhibitor and erosion velocity should be determined before tubulars are chosen. Once the corrosion velocity is determined, the tubing ID's can be chosen to mitigate its effects.

IRON CONTROL AGENTS

Precipitation control is achieved by adding stabilizers to the treating systems. The two types of stabilizers in use are reducing agents and chelators.

Reducing agents are best represented by erythorbic acid. It is very effective, inexpensive, and nontoxic . Because it can reduce ferric to ferrous iron at a nine to one ratio over complexation by citric acid, it is considered the most efficient iron stabilizer. It is stable at temperatures up to 400° F and does not form any complexes which can precipitate. It can be used in the newer gelled acid systems where compatibility problems with other treating chemicals can be a problem. Its limitation is that it works only on ferric ion in solution, so is not effective as an emulsion breaking aid or scale remover.

Chelating agents include such chemicals as nitriloacetic acid (NTA), ethylene diaminetetracetic acid (EDTA), citric acid and acetic acid. Mixtures of acetic and citric acids are also used. All of the chelators will preferentially complex Fe(III) over calcium because there are large differences in the stability indexes of the compounds formed.

Major differences in their behavior and abilities exist for each chelator. Just knowing that a sequestering agent is present is not a guarantee of protection. Acetic acid is a very good chelator at low temperatures, but becomes essentially ineffective between 125° F and 150° F. For this reason, it is often mixed with citric acid at elevated temperatures. In such a mixture, above 150° F you are getting the effect of the citric acid only.

Citric acid is a good stabilizer for all temperatures. However, the lack of solubility of its calcium salt has, through the years, led to papers which talk of the formation damage caused by iron sequestering agents. Once it has chelated the FE(III) present, any excess will complex the next most stable ion present, which in a carbonate reservoir is usually Ca(II). It should not be used when it is known that the Fe(III) content is 2000 ppm.

EDTA is the most versatile of the chelators. It is temperature stable, has a soluble Ca complex, and is effective in dealing with iron solids. It is a very good emulsion breaker for iron stabilized emulsions. By substituting the dissociation points with various cations, the chelator can be tailored for various uses. Figure 1 gives the normal metallic displacement series for EDTA. As can be seen, the more stable complexes are formed by the trivalent cations. Fe(III) is the most common trivalent ion in the reservoir so it is chelated first. Any ions on the displacement list above it will also be chelated before calcium. This list can be changed somewhat by altering the EDTA. When two of the four sodium ions were replaced by hydrogens, the resultant EDTA chelated Ca before Fe(II). This process allowed for the dissolution of a specific scale in Prudhoe Bay wells without disturbing the siderite cementitious material present in the pay. In these wells the natural cements were in decreasing order of abundance; silica, siderite, pyrite, and feroran calcite. The wells had developed near wellbore damage that was found to be a $CaCO_3$ scale. Small acid washes were only temporarily successful with the wells returning to rapid decline rates. EDTA was shown to be capable of dissolving the scale and effective in preventing its reoccurrence for a year or more. It was found that Na_2H_2EDTA dissolves $CaCO_3$ 47 times faster than does $FeCO_3$. Any excess present would both dissolve the siderite and chelate the Fe(II) to prevent precipitation.

DESIGNING TREATMENTS

The first question to ask one's self is, 'Why am I acidizing?'. Is it to: open perfs? remove scale? or place acid deep in the reservoir? Each of these jobs represents different amounts of acid, types of acid, additives and techniques. For example: Opening perf tunnels requires a small amount of acid with few additives and a short recovery time. The amount of iron in the returning acid will depend on 1) surface contamination, 2) that picked up from the tubulars, 3) that from dissolving casing fragments and powdered cement from perforation, and 4) that leached from the perf tunnel walls. Here a reducing agent may work very well. For a larger stimulation job, the number of variables increases. 1) Surface contamination could be larger. 2) Iron extracted from the tubulars may be less or the same. 3) Fines in the perf tunnels should not be a problem. 4) Some leaching from the tunnel walls is still possible. 5) Iron from formation minerals may now be very important. 6) Acid, both live and spent, may reach BHST. 7) Recovery time will be longer. 8) Acid will mix with both formation hydrocarbons and connate waters. In this case, one of the chelators may be a better choice than the reducing agent.

CONCLUSIONS

1) When designing a treatment, all available facts and the common assumptions must be considered. Table I gives a list of questionable, commonly accepted assumptions. Table II summarizes basic considerations for treatment design.

2) By careful examination of these factors, one can design a successful treatment or process which will mitigate any iron problems. Treating suggestions are given in Table III.

3) Achieving an understanding of all important conditions present may require a careful complete analysis of the reservoir. Table IV gives a summary of reservoir analyses available.

4) Iron precipitation is not the only problem which must be considered.

5) If someone else is designing the treatment, both they and you must understand the conditions present, and the techniques and agents used to control or mitigate problems.

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Table I
Questionable Assumptions

1) RESERVOIRS ARE HOMOGENEOUS.
2) ONLY CARBONATES ARE REACTIVE.
3) SANDSTONE RESERVOIRS ARE CLEAN OR INERT.
4) ALL IRON FROM FORMATION MINERALS IS Fe(II).
5) THERE IS ALWAYS MORE Fe(II) THAN Fe(III).
6) UNLIMITED AMOUNTS OF IRON CAN BE CHELATED OR REDUCED.
7) REDUCED IRON STAYS REDUCED.
8) IRON CONTROL IS NEEDED ONLY IN HCL SYSTEMS.
9) SCALE REMOVAL HAS TO BE DONE WITH ACIDIC SYSTEMS.

Table II
Summary of Considerations for Choosing Iron Control Agents

1) BHST or BHCT

2) Fe(III) CONCENTRATION EXPECTED
   a. Old or New Pipe
   b. Field Storage Tanks
   c. Producing or Injecting Well
   d. Formation Minerals Present and Their Concentration

3) Fe(II) CONCENTRATION EXPECTED
   a. Surface Contamination
   b. Tubular Conditions
   c. Formation Minerals Present and Their Concentrations

4) WELL ENVIRONMENT
   a. H_2S
   b. CO_2

5) EXPECTED LENGTH OF RECOVERY TIME

6) SOLUBILITY OF COMPLEXES FORMED (ESP. Ca)

7) ADDITIVE COMPATIBILITY

8) HYDROCARBON AND/OR CONNATE WATER COMPATIBILITY

9) COST EFFECTIVENESS

Table III
Treatment Suggestions for Maximum Effectiveness

1) USE ACETIC ACID ONLY BELOW 125° F.

2) USE ACETIC / CITRIC ACID BLENDS ONLY BELOW 150° F.

3) QUICK RECOVERY OF SPENT ACID IS HELPFUL IN ANY WELL.

4) CIRCULATE ONE OR TWO TUBING VOLUMES OF ACID OUT OF WELL BEFORE PUMPING INTO THE FORMATION. (Especially helpful for workovers or injectors)

5) USE THE MAXIMUM AMOUNT OF IRON CONTROL IN LEADING EDGE OF TREATMENTS.

6) USE IRON CONTROL IN TREATMENTS OF SANDSTONES.

7) USE INCREASED AMOUNTS OF IRON CONTROL IN OLDER WELLS, INJECTORS AND SOUR WELLS.

8) USE CHELATORS IN SOUR WELLS TO PREVENT SULFUR PRECIPITATION.

9) USE CITRIC ACID ONLY WHEN Fe(III) CONCENTRATION EXCEEDS 2,000 PPM.

10) USE IRON CONTROL IN HF SYSTEMS.

11) CONDUCT EMULSION STUDIES WITH SPENT ACID AND HYDROCARBONS FROM THE WELL BEFORE ACIDIZING. (Especially in high iron sulfide, or sour, or high formation iron environments)

12) DESIGN BOTH PRODUCTION SYSTEMS AND TREATING PROCESSES TO MITIGATE SOLIDS PROBLEMS.

13) LEARN THE CHEMISTRY AND CAPABILITIES OF IRON CONTROL COMMONLY USED.

14) USE CHELATORS IN EMULSION BREAKING FLUID.

15) USE CHELATION IN SCALE REMOVAL.

Table IV
Application of Geological Analyses to the Petroleum Industry

RELIABILITY OF AVERAGE ANALYSIS	TS	SEM	XRD	X-RAD	ASA	CORE	LOG/RE-CORDS
	SQ	QL	SQ	QL	QL	QL	SQ/QL
GEOLOGICAL APPLICATIONS							
● Bulk Mineralogy	●		●				
● Clay Mineralogy		●	●				
● Pore Distribution/Geometry	●	●					
● Texture/Fabric	●	●					
● Depositional Environment	●			●	●	●	●
● Diagenetic History	●	●	●				
ENGINEERING APPLICATIONS							
● Identification of Formation Damage	●	●	●			●	●
● Reservoir Description	●			●	●	●	●
● Identification of Permeability Barriers	●			●		●	●
● Directional Permeability	●			●		●	●
PETROPHYSICAL APPLICATIONS							
● Model Identification	●	●		●		●	
● Refinement of Computation	●	●	●		●		
● Log Calibration					●	●	
● Cation Exchange Capacity		●	●				

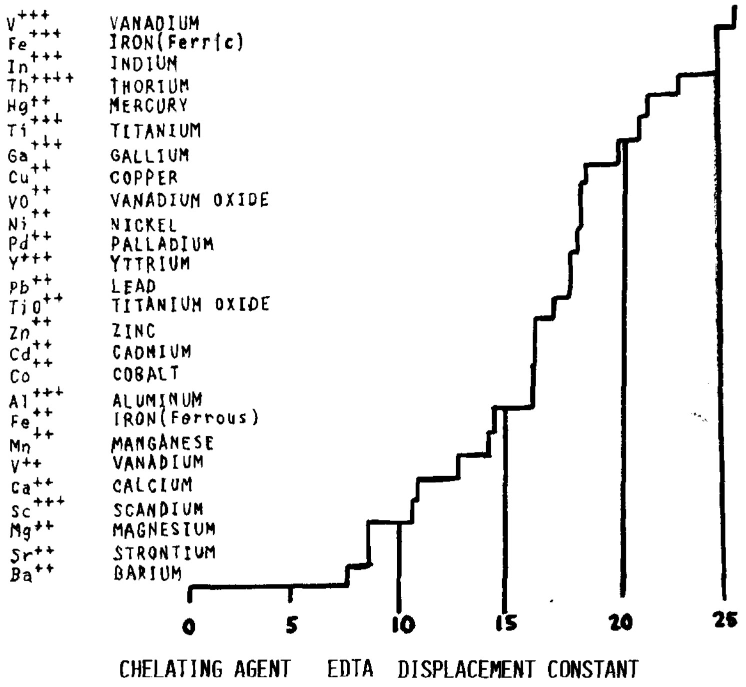

Figure 1—Metal chelate displacement series for EDTA