GUIDELINES FOR SELECTING IRON STABILIZERS FOR USE IN ACIDIZING TREATMENTS

C. W. CROWE
Dowell Division of Dow Chemical USA

ABSTRACT

During the course of any acidizing treatment, a certain amount of iron is dissolved by action of the acid upon treating lines, equipment, downhole tubular goods and iron containing minerals present within the formation. Upon spending of the acid, this iron may precipitate as insoluble gelatinous ferric hydroxide. This precipitate is an effective plugging agent which damages permeability and restricts oil and gas production.

In order to prevent iron precipitation, stabilizers are routinely added to the treating acid. These stabilizers form soluble chelates or complexes with iron and prevent precipitation of ferric hydroxide. This paper describes the advantages and limitations of the various commonly used iron stabilizing agents. Guidelines are presented for selecting the proper additive and determining the concentration needed for iron control. Well conditions, as they relate to the need for iron stabilizing agents, are also discussed.

INTRODUCTION

Formation damage from ferric hydroxide precipitation is a potential problem in any acidizing treatment. Acid readily dissolves iron scales in pipe and attacks iron containing minerals in the formation under treatment. This dissolved iron will remain in solution until the acid spends. As the pH of the spent acid rises, the iron will lose its solubility and precipitate as a gelatinous residue. This precipitated ferric hydroxide causes formation damage and can greatly reduce the productivity of the well.

Ferric hydroxide precipitation can be controlled by adding iron stabilizers, usually complexing or chelating agents, to the acid. These stabilizers combine with the dissolved iron to keep it in solution. Care should be taken in the selection of iron stabilizers since some commonly used agents are ineffective at elevated temperatures or may form insoluble precipitates upon spending of the acid.

OXIDATION STATE OF DISSOLVED IRON

Dissolved iron may exist in acid in either the ferric (Fe^{+++}) or ferrous (Fe^{++}) oxidation state. This is an important fact since only the ferric iron will normally present a precipitation problem. During spending of the acid, initial precipitation of ferric hydroxide will occur when the pH rises to about 2.2(1). Upon reaching a pH of 3.2, essentially all of the dissolved ferric iron will have precipitated as ferric hydroxide. None of the ferrous iron will precipitate, however, since ferrous hydroxide precipitation only begins once a pH of 7.7 is reached. Since the maximum pH of spent acid is usually about 5.3, precipitation of ferrous hydroxide is rarely a problem. Consequently, it is only necessary to use enough iron stabilizer to prevent precipitation of the ferric iron dissolved by the acid.

Fortunately, most iron dissolved by the treating acid is in the ferrous oxidation state. It has been estimated that, on the average, the Fe^{+++} to Fe^{++} ratio present in spent acid is about 5:1. This will vary, however, depending upon well conditions and the type of formation being treated.

WELL CONDITIONS AFFECTING IRON PRECIPITATION

Unless the formation being treated is sufficiently reactive with acid to produce complete acid spending, there is little danger of iron precipitation. When acidizing sandstones, live acid returns are often observed following the treatment. Unless a pH of 2-3 is reached, ferric hydroxide precipitation can not occur downhole.

Other well conditions can also affect the precipitation of ferric hydroxide by shifting the ratio of ferric to ferrous iron. For example, rust or scale formed by oxygen corrosion will be largely of the ferric type and when dissolved by acid will present a potentially more serious precipitation problem. As a result, it is advisable to employ higher concentrations of iron stabilizer when treating through rusty pipe or when treating water injection wells where oxygen corrosion may have occurred. Producing wells usually present less of a problem since most iron scales formed in the pipe are of the ferrous type. Corrosion of the pipe metal by acid will always produce ferrous iron.

Concern is often expressed about dissolution, of iron containing minerals such as siderite and chlorite from the formation and subsequent precipitation of the dissolved iron. The iron in these minerals usually occurs in the ferrous oxidation state, and does not present a precipitation problem(2). Exceptions to this rule do exist when streaks of pure hematite (Fe_2O_3) are sometimes observed in some formations. Cores containing ferric iron can often be distinguished by the reddish color which the iron imparts. When this condition is observed, larger amounts of iron stabilizing agents are needed to control ferric hydroxide precipitation.

Oxygen dissolved in the treating acid can also contribute to the problem by converting a certain amount of dissolved ferrous iron to the potentially damaging ferric condition. The amount of oxidation is limited, however, since acid exposed to air contains a maximum of less than 8 ppm dissolved oxygen(3). Consequently, only about 55 ppm ferrous iron can be oxidized by the dissolved oxygen.

A factor which is usually overlooked when considering possible precipitation of ferric hydroxide is the presence of hydrogen sulfide. Hydrogen sulfide will reduce any ferric iron present to the ferrous state according to the following chemical reaction.

$$H_2S + 2\,Fe^{+++} \rightarrow S^\circ + 2\,Fe^{++} + 2\,H^+$$

Consequently, it is doubtful if ferric iron can exist, either in corrosion scale or formation minerals, in a sour environment. Some precipitation of sulfur may occur, however, as the result of H_2S reaction with ferric iron.

IRON IN RECOVERED SPENT ACID

The iron concentration in spent acid is often in excess of 10,000 ppm, thus, causing concern about possible precipitation downhole. Upon standing, the spent acid samples usually precipitate a large amount of red ferric hydroxide as a result of air oxidation of the ferrous iron. We must keep in mind, however, that this is not a problem downhole in the absence of oxygen. We should only suspect iron precipitation if freshly recovered samples of spent acid contain reddish suspended material. This usually indicates that iron precipitation has occurred downhole. More often acid samples are greenish in color and only form a red precipitate after exposure to air.

IRON SEQUESTERING AGENTS

Sequestering agents have been used for many years to prevent the reprecipitation of iron from spent acid solutions. Those most commonly used include citric acid, acetic acid, mixtures of citric and acetic acids, lactic acid and ethylene diamine tetracetic acid (EDTA). Of these various materials, all have certain advantages as well as limitations. Before selecting a particular additive, well conditions should be carefully considered since no single additive is superior under all treating conditions. The downhole conditions of each individual well must be taken into consideration if the most effective and economical additive is to be selected.

Conditions which influence the choice of sequestering agent include:

1. Expected amount of ferric iron in spent acid.

2. Bottom-hole temperature.

3. Shut-in time following treatment.

4. Possibility of oxygen corrosion in treating lines and downhole tubular goods.

5. Presence of H_2S in producing reservoir.

6. Cost of sequestering agent required to control iron present under expected treating conditions.

7. Possibility of precipitating the sequestering agent as its calcium salt if excessive quantities are used.

When choosing an iron sequestering agent, an additive should be selected which will keep the dissolved iron in solution at the anticipated well temperature. The time required to recover the spent acid should also be considered since some agents are effective for only a limited period of time. In general, the more stable the iron complex formed, the longer the working time and higher the temperature before iron hydroxide will begin to precipitate.

Table I contains conditional stability values for several complexes of iron as calculated at a pH of 6(4). The larger numbers represent the more stable complexes. As is seen, EDTA and citric acid form the most stable complexes and are the most suitable for high temperature applications. Complexing agents such as acetic acid and lactic acid are ineffective at temperatures above 150°F but are usually adequate at lower temperatures, especially when only short working times are needed. Table II shows a comparison of the relative effectiveness of various commonly used iron sequestering agents as determined in laboratory tests in which 15% hydrochloric acid, containing various amounts of ferric iron and sequestering agent, was spent on marble chips (1). These tests were designed to determine the minimum amount of sequestering agent required to prevent precipitation of ferric hydroxide at the test temperature indicated. These tests show that only EDTA and citric acid should be considered for use at temperatures above 150°F. Both of these materials are effective up to 350°F, the maximum temperature tested. Mixtures of citric and acetic acids, have limited effectiveness above 150°F although they are highly efficient at lower temperatures.

Another consideration in the selection of iron sequestering agents is the solubility of its calcium salt. Unless sufficient iron is present to be complexed by the agent used, the sequestering agent itself may precipitate. This is a problem when using citric acid since the solubility of calcium citrate in water is only 0.22 gm per 100 mL at 86°F. Its solubility in spent acid is further reduced by the common ion effect of dissolved calcium. A comparison of the solubilities of calcium salts of several commonly used iron sequestering agents is found in Table III (5).

As is seen, care must be exercised in selecting sequestering agents for use in preventing iron precipitation from spent acid. Factors such as reservoir conditions, sequestering agent advantages, limitations and economics, play an important part in choosing the proper agent for a particular application. Table IV contains a summary of advantages and limitations of the various iron sequestering agents. This table may be used as a guide in selecting the best additive for a particular well application.

CONCLUSIONS

1. Iron dissolved during an acidizing treatment may reprecipitate as insoluble ferric hydroxide, causing extensive formation damage.

2. Under normal conditions, only the iron which is in the ferric oxidation state will precipitate upon spending of the acid.

3. Ferric hydroxide precipitation is usually a greater problem when treating injection and disposal wells since iron scales, dissolved by the acid, usually occur in the ferric form.

4. Producing wells, especially those producing H_2S, present less of an iron precipitation problem since most of the iron dissolved by the acid is of the nonprecipitating ferrous form.

5. Bottom-hole temperature as well as the time the spent acid will remain in the formation should be considered in selecting an iron sequestering agent.

6. Of the sequestering agents in common use, only citric acid or EDTA is effective when treating wells having bottom-hole temperatures above 150°F. Citric acid should be used with caution, however, due to the limited solubility of its calcium salt.

REFERENCES

1. Smith, C. F., Crowe, C. W., Noland, T. J.: "Secondary Deposition of Iron Compounds Following Acidizing Treatments", Jour. Pet. Tech. (Sept. 1969) 1121-1129.

2. Dana, E. S.: "A Textbook of Mineralogy," John Wiley & Sons, Inc., New York, 1932.

3. "International Critical Tables," Vol. III, P. 271, McGraw-Hill Book Co., Inc., 1928.

4. Ringbom, A. J.: "Complexation of Analytical Chemistry," Interscience Publishers, 1963.

5. Linke, W. F.: "Solubilities of Organic and Inorganic Metal Compounds," American Chemical Society, Washington, D.C., 1958.

TABLE 1—STABILITY OF IRON COMPLEXES

Complexing Agent	Stability Value at pH 6 (log $^{\alpha}$M)
EDTA	18.3
Citrate	13.6
Acetate	6.0

TABLE 2—EFFECTIVENESS OF VARIOUS IRON SEQUESTERING AGENTS IN SPENT ACID

Sequestering Agent	Quantity Agent Used (lbs/1000 gal Acid)	Temp. (°F)	ppm Fe^{+++} Stabilized	Time
Citric Acid	35	>350	1,000	> 2 days
Mixture of Citric Acid, Acetic Acid	50	75	10,000	2 days
	87	75	5,000	7 days
		150	10,000	24 hrs.
		150	5,000	7 days
		200	10,000	15 min.
		200	5,000	30 min.
Lactic Acid	65	75	1,700	24 hrs.
		150	1,700	2 hrs.
		200	1,700	10 min.
Acetic Acid	174	75	10,000	24 hrs.
		150	5,000	2 hrs.
		200	5,000	10 min.
		200	1,000	20 min.
Gluconic Acid	103	150	1,500	20 hrs.
Tetrasodium salt of EDTA	225	>350	4,300	> 2 days

TABLE 3—SOLUBILITY IN WATER OF THE CALCIUM SALT OF VARIOUS SEQUESTERING AGENTS

Sequestering Agent	Solubility (gms/100 mLs.)	Temp. (°F)
Calcium Citrate	0.22	86
Calcium Lactate	7.9	86
Calcium Acetate	33.8	86
Calcium disodium salt of EDTA	3.74	86

TABLE 4—COMPARISON OF VARIOUS IRON SEQUESTERING AGENTS

Sequestering Agent	Advantages	Disadvantages	Amount Required in 1000 gal. of 15% Hydrochloric Acid to Sequester 5000 ppm Fe(III) for Minimum of 2 days at 150°F.
Citric Acid	Effective at temperatures of up to at least 350°f.	Will precipitate as calcium citrate when excess quantities are used.	175 lbs
Citric Acid-Acetic Acid Mixture	Very effective at lower temperatures	When indicated amount is used, calcium citrate will precipitate unless at least 2000 ppm Fe(III) is present in spent acid. Efficiency decreases rapidly at temperatures above 150°F.	50 lbs. (citric acid) 87 lbs. (acetic acid) @ 150°F
Lactic Acid	Little chance of calcium lactate precipitation if excessive quantities are used.	Not very effective above 100°F.	190 lbs. @ 75°F.
Acetic Acid	No problem from possible precipitation as calcium acetate.	Effective only to about 160°F.	435 lbs
Tetrasodium Salt of Ethylenediamine Tetracetic Acid	Large excesses may be used without precipitation of calcium salt. Effective at temperatures up to at least 350°F.	More expensive to use than many of the other agents.	296 lbs