PROPER TREATMENT OF TUBULARS
KEY TO IRON CONTROL

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ABSTRACT

Proper cleanout of millscale and other iron oxides from new tubular goods prior to their use reduces production damage by deposition (in the producing formation) of iron solids and iron in solution.

Iron removed from new tubulars by stimulation fluids has caused formation damage and reduced production for many decades. This iron is available for removal from the walls of the casing and tubing by the action of stimulation acids and erosive proppants being pumped to stimulate the well. The sources of this iron are listed below.

1. Millscale (magnetite) is a thin layer of iron oxide found on the surface of tubulars. Millscale is deposited as a result of cooling the tubular steel after heating and extruding processes are done.

2. Iron oxides have many forms, but are basically rust. Although numerous iron scales are encountered in oilfield operations, and many are contacted by stimulation fluids, they are by-products of oil and gas production. Millscale and rust arrive on location with tubing and casing, and there is little doubt that the problem exists on most locations.

This paper presents a method to "pickle" tubulars to help eliminate the source of many iron deposition problems.

INTRODUCTION

Precipitation of iron and iron sulfides in producing formations has accompanied acidizing operations since the beginning of acid-stimulation in oil and gas wells. Oil industry literature contains many examples of successful treatments that help prevent precipitation and reprecipitation of iron, and the subsequent production decreases that usually follow deposition of iron sludge into producing formations.

Hall and Dill[1] presented methods to sequester iron in the presence of sulfides and compared effectiveness of various iron-sequestering additives. They identified sources of formation iron as hematite, magnetite, pyrite, siderite, chlorite clay, and mixed-layer clay. They also reported that tubulars were a significant source of iron.

Dill and Fredette[2] reported three major problems caused by iron compounds.
1. Relatively insoluble iron compounds may be released by acidizing fluids and have a plugging effect when they migrate.
2. Acid-soluble iron compounds may reprecipitate when the acid spends.
3. Aerated fracturing fluids may be incompatible with formation waters that contain ferrous iron.

Coulter and Gougler[3] described a field study conducted to identify the source and magnitude of the iron problem in West Texas oil operations. The study indicated that the primary source of iron in most cases was the tubing in the well.

Walker, Dill, and Besler[4] reported their finding that the major source of damage to sour-gas wells after acidizing was reprecipitation of iron from spent acid fluid. The source of this compound was redissolution, by stimulation acid, of existing iron-containing sulfides on the tubulars. Iron-containing sulfides were found to exist on production tubulars as a result of corrosion of tubulars by produced fluids which contain hydrogen sulfide.

The scope of this paper is limited to a study of iron control in new tubular goods. Well returns from six northwestern Texas wells have been analyzed to determine iron content, and to establish guidelines for designing the optimum acid treatment to effectively remove available iron (millscale, etc.) from tubulars. This process is commonly called "pickling."

NEW TUBULARS AS IRON SOURCE

In a 1984 investigation, Broaddus[5] found that oilfield tubulars are not pickled at the factory, so they contain millscale that totals about 0.010 in. thickness. Millscale thickness varies with cooling rate and manipulation during manufacture. Millscale is in two distinct layers, with a hard, dense layer (0.003 in. thick) next to the pipe, and a softer, flaky layer (0.007 in. thick) on top of the hard layer. Most of the soft layer pops off the pipe during the straightening procedure. Equations and example calculations in Appendix A show how to calculate the volume of scale to expect in new tubular goods.

PROCEDURE

This section describes the conduct of a typical pickling operation performed in northwestern Texas, and presents an analysis of well returns from an example well for which new tubing was pickled before acidizing.

1. Go in the hole with new tubing string. If perforated, set a retrievable bridge plug just above the top perforation. If not perforated, set end of tubing below expected perforated interval.

2. Establish circulation in the hole with produced water or 2% KCl water. (In this case the well was 6600 ft.)

3. Pump 750 gal 15% HCl containing corrosion inhibitor and 1 gal/Mgal microemulsion penetrating agent down the tubing at 1 bbl/min.

4. With water, displace the acid about 10 bbl out into the annulus.

5. Pump displacement fluid down the backside and reverse acid out to pit at 0.5 to 1 bbl/min.

Table 1 shows data collected from six tubing cleanout jobs performed on new tubing installed in 6700 ft wells. Values were summarized from the six wells to create this table. The treatments consisted of pumping 750 gal 15% HCl and reversing out. Sampling technique used on the returned fluid was such that Sample 1 from each of the six wells had spent the shortest time exposed to the tubing walls, and Sample 6 in all cases had spent the most time of exposure. Examination of the data shows that the leading edge of the acid (the one exposed longest) removed most of the iron deposits from the tubing. Sample 1 had spent the least time of exposure and removed the least iron.

Figure 1 illustrates amount of iron removed versus time of exposure. Figure 2 contrasts iron removed to acid spending rate. Figure 3 shows that ferric iron removed is approximately double the amount of ferrous iron removed.

CONCLUSIONS

1. Walls of new tubular goods carry enough loose iron deposits to damage formation permeability when the deposits are loosened by stimulation treatments and enter the formation in stimulation fluids.

2. These deposits can and should be removed by an acid treatment prior to conducting the primary stimulation treatment.

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3. Coulter, A.W. Jr. and Gougler, P.D.: "Field tests indicate tubing is main source of iron precipitation in the wellbore," Oil and Gas Journal, Sept. 4, 1984.

4. Walker, M.S., Dill, W.R., and Besler, M.R.: "Iron Control in Sour Wells Provides Sustained Production Increase," paper CIM 89-40-41, presented at the 40th Annual Technical Meeting of Petroleum Society of CIM, Banff, May 28-31, 1989.

5. Broaddus, G.C., private communication, July 30, 1984.

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APPENDIX A^5

$V = 0.0218\ t\ (D-t)$ (A-1)

where V = volume of scale in ft^3/linear ft

t = thickness of scale in inches

D = pipe ID in inches

To determine the volume of soft millscale on 2 7/8 in., 6.5 lb/ft tubing, substitute the following into Eq. A-1.

D_1 = pipe ID = 2.441

D_2 = pipe ID with hard millscale on pipe (2.441- 0.003) = 2.438

t = thickness of flaky scale = 0.007

$V_1 = 0.0218t\ (D_2 - t)$

$= 0.0218 \times 0.007\ (2.438 - 0.007)$

$=0.00037$ ft^3/linear ft of pipe

To determine the volume of hard millscale on 2 7/8 in., 6.5 lb/ft tubing, substitute the following into Eq. A-1.

$D_1 = 2.441$

t_1 = scale thickness of hard scale = 0.003 in.

$V_2 = 0.0218 \times 0.003\ (2.441 - 0.003)$

$= 0.00016$ ft^3/linear ft of pipe

Specific gravity is approximately 4.0 for the soft scale and 5.0 for the hard scale. The weight of soft scale per linear foot would be

Specific gravity of scale x weight of 1 cu ft water x cu ft scale (A-2)

Substituting,

$4 \times 62.4 \times 0.00037 = 0.0923$ lb/linear ft

Assume that three-fourths of the scale pops off during straightening. Soft scale left on the pipe is

$0.0923 \times 0.25 = 0.023$ lb/linear ft

Hard scale left on the pipe is

$5 \times 62.4 \times 0.00016 = 0.050$ lb/linear ft

The following illustrates computation of acid volume needed to remove millscale from tubing. First, a balanced chemical equation is needed.

$$8\mathrm{HCl} + \underset{\text{(millscale)}}{\mathrm{FeO.Fe_2O_3}} \dashrightarrow \mathrm{FeCl_2} + 2\mathrm{FeCl_3} + 4\mathrm{H_2O} \qquad \text{(A-3)}$$

Equation A-4 provides the means to calculate the amount (in pounds) of HCl needed to dissolve 1 lb of millscale.

To calculate the volume of acid required to dissolve 1 lb of millscale substitute into eq. A-4.

$$\frac{X}{\begin{array}{l}\text{Mol. wt. of HCl}\\ \text{x number of}\\ \text{mole of HCl}\end{array}} = \frac{\text{1 lb millscale}}{\begin{array}{l}\text{Mol. wt. of magnetite}\\ \text{x number of mole}\\ \text{of magnetite}\end{array}} \qquad \text{(A-4)}$$

Molecular weight of HCl = 36.5
Molecular weight of Fe_3O_4 = 231.5
X = lb of HCl necessary to dissolve 1 lb of millscale

$$\frac{X}{36.5 \times 8} = \frac{1\ \text{lb}}{231.5 \times 1}$$

$$X = \frac{36.5 \times 8 \times 1}{231.5 \times 1} = 1.26\ \text{lb of HCl gas.}$$

One gallon of 15% HCl contains 1.342 lb of HCl gas per gallon of acid.

Therefore $\frac{1.26}{1.342}$ = 0.94 gal 15% HCl required per lb of millscale.

The volume of 15% HCl required to dissolve millscale from new 2 7/8 in., 6.5 lb/ft tubulars equals

0.073 lb millscale/linear ft x 0.94 gal 15% HCl/lb millscale
= 0.069 gal 15% HCl/linear ft of pipe.

For 2 7/8 in. 7.9 lb/ft tubular,

0.069 lb millscale/linear ft x 0.94 gal 15% HCl/lb of millscale = 0.065 gal 15% HCl/linear ft of pipe.

For example, to acidize a 10,000 ft well through new 2 7/8 in., 6.5 lb/ft tubing, the acid required to remove the millscale would be 0.069 x 10,000 ft, or 690 gal 15% HCl. This means that in addition to the volume of acid required to acidize the well, 690 gal HCl is added.

Some of the leading edge of the acid could be spent before it reaches the perforations. Volume of the acid spent would depend on the contact time. The slower the injection rate and the higher the temperature of the acid, the more acid will be spent.

When 15% HCl spends on magnetite it will dissolve 1.064 lb magnetite per gallon of 15% HCl. Magnetite is 72.4% iron, so 1 gal spent 15% HCl will contain 1.06 x 0.724 = 0.770 lb of total iron (both Fe^{++} and Fe^{+++}).

This would be $\frac{1{,}000{,}000 \text{ lb}}{8.96 \text{ lb/gal of } 15\% \text{ HCl}} \times 0.770 \text{ lb} = 85{,}938$ ppm total iron. Of this 2/3 of the iron is ferric iron so 85,938 x 2/3 = 57,292 ppm ferric iron.

Ferric iron will start to precipitate as ferric hydroxide at a pH of 2.0 and will be completely precipitated at a pH of 3.5. The ferrous iron will not begin to precipitate until the pH reaches 7.5, which will seldom be reached in acidizing.

If the acid does spend on magnetite special additives are required to prevent the precipitation of ferric hydroxide.

Table 1
Summary of Treatments from Six Tubing Cleanouts*

Sample	1	2	3	4	5	6
Total Iron (Fe)	2250	2550	3600	7000	17,700	37,850
Ferrous Fe^{++}	1800	2100	2800	4000	6200	12,500
Ferric Fe^{+++}	450	450	800	3000	11,500	25,350
Color	Light Yellow	Light Brown	Dark Yellow	Limey Yellow	Brownish Lime	Deep Lime Green
Percent Acid	16	16	16	15.81	13.35	9.47
Fines	Some	Some	Many	Most	Many	Some

*Six samples were taken from acid reversed out of six wells in which new tubulars had been installed. Sample 6 in each case had the longest exposure, and Sample 1 had the shortest time of exposure to the tubing walls.

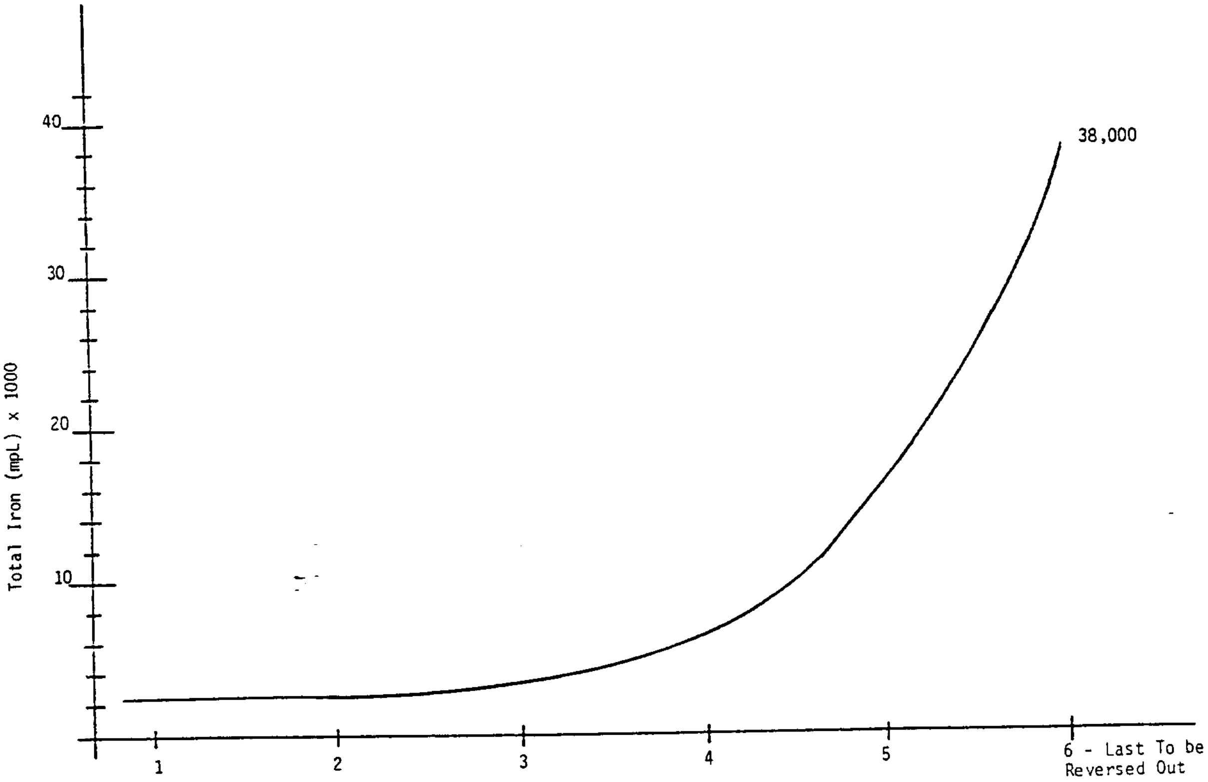

Figure 1

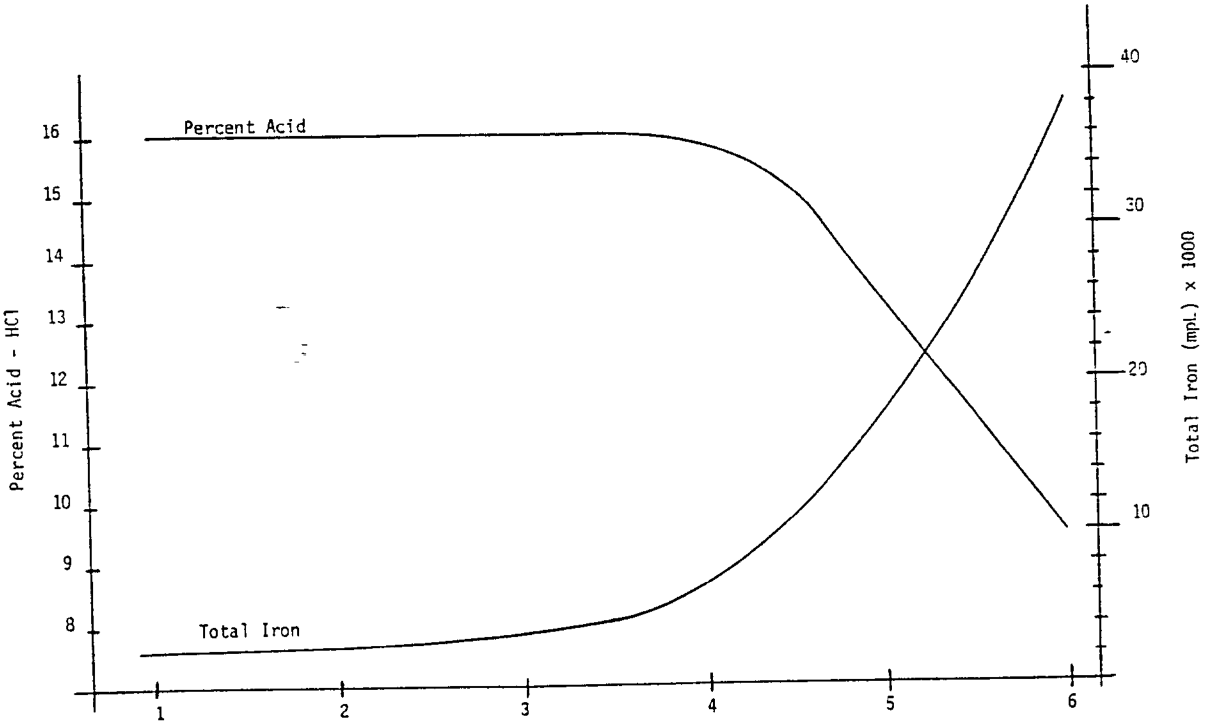

Figure 2

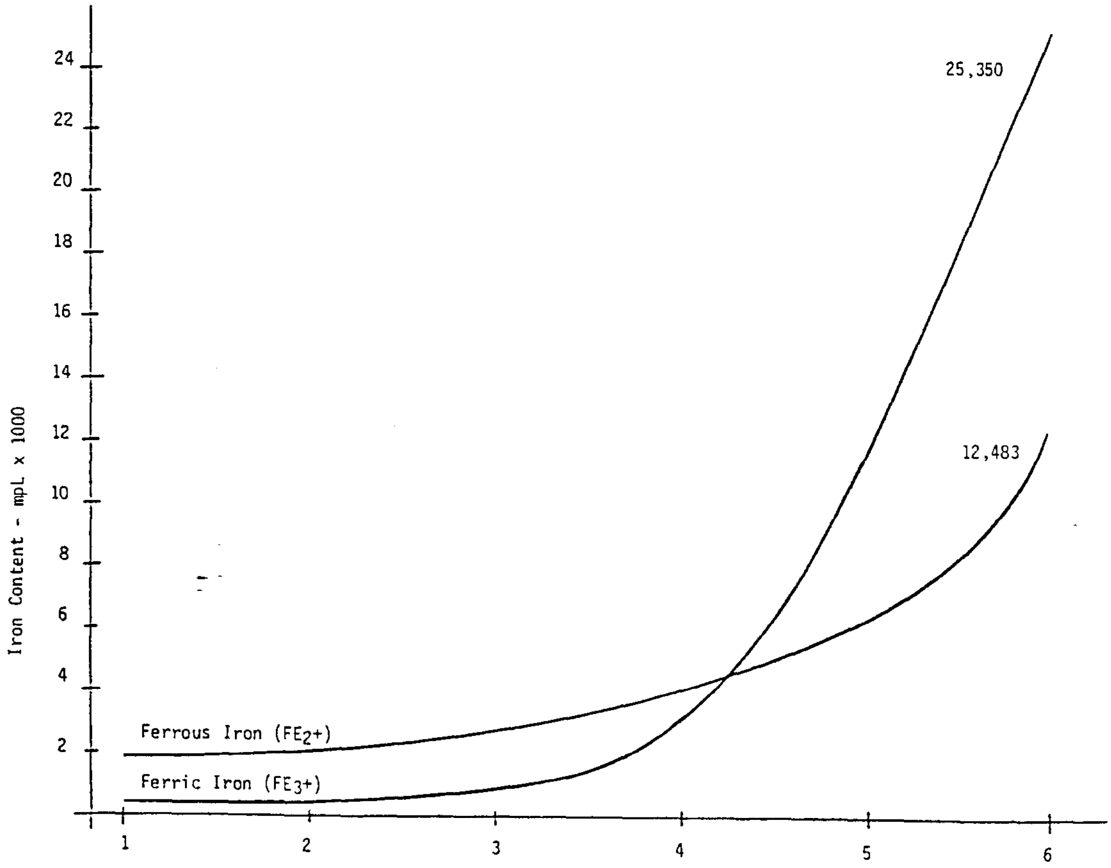
Iron Content - mpL x 1000
24
22
20
18
16
14
12
10
8
6
4
2
1
2
3
4
5
6
25,350
12,483
Ferrous Iron (FE2+)
Ferric Iron (FE3+)

Figure 3