Removing a Typical Iron Sulfide Scale – The Scientific Approach

Daniel G. Brawley, Brawley Petroleum Corp.
Robert G. Fulton, D.L. Parkey, William G.F. Ford,
Martin Halterman, and Michael Walker Halliburton Services

Abstract

Iron sulfide scales vary in composition; this paper, in three parts, describes how a thorough analysis of the scale is necessary to optimize the chemical treatment and successfully remove the damage.

The first part describes the different types and compositions of iron sulfide scale and the need for a tubing cleanout prior to an acidizing treatment. The second part describes the detailed analysis of the scale through the use of quantitative X-ray diffraction analysis and elemental analysis by energy dispersive X-ray. The third part of this paper presents scale removal treatment case histories.

Introduction

Several methods that have been successfully used to control iron reprecipitation in sweet wells do not work as well in the presence of hydrogen sulfide. This is because the buffering systems, some chelating agents, and reducing agents fail to prevent reprecipitation of iron with H_2S to form iron sulfide and, in some cases elemental sulfur.[1]

Iron sulfide reprecipitation in the formation (from spent-acid solution) is the most probable reason that acid jobs fail to achieve sustained production in sour wells. The primary source of the reprecipitated iron sulfide is iron-containing sulfide scales dissolved from the tubing by the acidizing fluid.[1]

Scale Composition and Types

Wells that produce or inject sulfide-containing fluids will usually contain iron sulfide scales or iron sulfide corrosion products. The type of iron sulfide deposited depends on a number of considerations, including temperature, brine salinity, and the presence of other gases such as CO_2. Some of the common iron sulfides are mackinawite (Fe_9S_8), troilite (FeS), pyrrhotite (Fe_7S_8), pyrite (FeS_2), and marcasite (FeS_2). To effectively design an efficient acidizing treatment, detailed knowledge of scale compositions and types need to be known.

One thing that complicates developing an effective acidizing system is that one or more types of iron sulfide will often precipitate and undergo further reaction with either H_2S or the iron surface to create layers of different compositions of iron sulfide.

Each compound has its own specific solubility. The general trend is that compounds with approximately one-to-one stoichiometry will be readily soluble and have rapid reaction rates with HCl, while compounds with higher sulfur stoichiometries will have lower solubility and much slower reaction rates **(Table 1)**.[1]

Wells with moderate to small amounts of H_2S will not necessarily form less scale or corrosion product on the tubing than wells with higher H_2S concentrations. To a large extent, it is the source of iron and not the

SPE 24327, "Removing a Typical Iron Sulfide Scale: The Scientific Approach" was presented at the SPE Rocky Mountain Regional Meeting in Casper, WY, May 18-21, 1992.

amount of hydrogen sulfide in the produced fluids that determines the amount of scale. The presence of iron is the result of a corrosion process, and the precipitation or formation of FeS is more dependent upon the pH and salinity of the water than on H_2S control.

Most of these sulfide scales are soluble to some degree in acidic stimulation fluids. Damage occurs when these scales or corrosion products are redeposited in the formation.

Iron sulfide scales can react with the HCl treatment acid to an extent that effectively reduces the acid concentration to less than 1% HCl content. These fluids, which are high in ferrous iron and H_2S content, will further spend when contacted with the formation containing calcium carbonate or other acid-consuming species. When the acid content is reduced to the point where sulfide ion content, rather than H_2S or HS-, exceeds the capacity of the solution to hold iron sulfide, precipitation occurs.

The amount of iron sulfide present on the tubing and dissolved by the acid determines the amount of damaging iron sulfide that is reprecipitated. Relatively thin scales can cause significant damage because iron sulfide is contacted by the acid as it passes through the tubing to the formation **(Table 2)**.[1] Scale as thin as 1/64 in. [0.040 cm] can contain 0.58 ft^3 [0.016 m^3] of iron sulfide in 2.38-in. [6.045 cm] nominal wall tubing/1000 linear ft [304.8 m]. Thus, a 5,000 ft [1,524 m] well can require up to 666 gal [2,521.08 L] of 15% HCl just to remove the 1/64-in. [0.040 cm] thick scale, and if scale of 1/4-in. [0.635 cm] or more is encountered, then the lead acid will be completely spent on the scale.

Contact with the iron sulfide will reduce the acid strength of the stimulation fluid. This fluid, the first to contact the formation, will have decreased calcite rock-dissolving capacity and reaction rate on the rock. As a result, operators often try to inject a fluid or to break down a formation with applied acid of considerably lower acid strength than expected **(Table 3)**.[1] It is anticipated that the first fluid to reach the formation usually will contain more than 0.417 lbs/gal [50,000 mg/L] (in some cases, more than 0.835 lb/gal [100,000 mg/L]) of iron in solution.

Cleanout of Tubing

Tubing cleanout procedures use acid to remove products that have precipitated on the tubing surface. In normal acidizing procedures, the fluids that first contact the pipe and acid-soluble materials are injected into the formation. When tubing cleanout is used, the initial acid is not injected into the formation, but is returned to the surface with the damaging ions in solution. This means the most soluble and damaging materials are removed from the wellbore and are not placed in the formation where possible impairment can occur.

Cleanout-acid compositions vary in makeup, usage, and volumes. The acid system typically is based on 15% HCl, although higher acid concentrations are often used. Furthermore, solvents or surfactants are used to aid removal of hydrocarbons or other materials adhering to the acid soluble precipitates, which may retard the dissolution of the iron scales.

Iron-sequestering agents often are added to tubing-cleanout acid systems. This is necessary only if the tubing-cleanout fluid is expected to be lost to the formation. It is recommended, however, that in cleanout procedures used to remove iron sulfide, a sulfide-control agent be added to help prevent damage caused by excessive corrosion resulting from the interaction of H_2S and the corrosion inhibitor.[1]

If a proper tubing cleanout is performed, then most of the accessible and soluble scale will be removed by the tubing-cleanout fluid and returned to the surface for disposal. Iron sulfide-control agents can perform effectively at these lower concentrations, preventing damage in subsequent acid volumes pumped into the formation.[1]

Compositional and Analytical Tests of Scale from British Columbia Well

Several wells in a field in northeast British Columbia had heavy scale buildup in the tubing. To obtain optimum stimulation results from these wells, a detailed plan was desired for the scale treatment. Before such plan was made, the composition of the scale was analyzed. Tests included X-ray diffraction analysis, acid solubility, and elemental analysis mapping.

Quantitative X-Ray Diffraction Analysis.

As previously discussed, iron sulfide will often precipitate and undergo further reaction with either H_2S or the iron surface to create layers of different compositions of iron sulfide. To determine how the composition varies in this British Columbia well, quantitative analysis of the iron sulfide scale was accomplished with X-ray diffraction techniques.

Experimental Procedure. Several field samples of tubing containing iron sulfide scale were obtained. One tubing section, marked 'C', was selected for detailed analysis and was further divided into sections, marked C-1, C-2, and C-3 (Figure 1).

The thickness of the scale at location C-2 (approximately 0.75 in. [1.905 cm]) allowed investigation of compositional changes within the scale as a function of distance from the pipe wall. This investigation was accomplished by cutting sample C-2 with a Buehler Isomet trim saw equipped with a 0.0125 in. [0.032 cm] thick diamond blade, lubricated with deionized water. Sample C-2 was glued to a standard petrographic slide and cut into nine slabs starting from the center of the pipe (Cut 1) and ending next to the pipe (Cut 9), each about 0.05 in. [0.127 cm] thick.

After drying, the slabs were ground using a mortar and pestle to pass a 200 mesh screen. Minus 250 mesh ground silica was mixed with each sample at approximately 5% of the total weight as an internal standard. The powdered samples were then backpacked into standard Phillips sample holders and scanned from 10 to 50° two-theta on an automated Phillips APD 3600 diffractometer. Instrumental conditions were as follows: tube voltage of 45 kV and tube current of 40 mA. Step size was 0.02° with a count time of 4 seconds per step. Previous qualitative scans indicated that the following peaks could be used for quantitative analysis:

- 11.95° for akaganeite
- 17.6° for mackinawite
- 21.2° for goethite
- 23.0° for sulfur
- 25.9° for barite
- 26.65° for quartz
- 31.95° for siderite
- 33.0° for pyrite
- 43.7° for pyrrhotite

Reference Intensity Ratios (RIR) to quartz, based on peak areas, were used to quantify the various phases.[2] An RIR for pyrrhotite was determined from one of the scale samples in which RIR values for all other phases were known. An RIR for mackinawite was determined from an unrelated scale sample containing mackinawite and pyrite after selectively removing the mackinawite with acid. RIR values for the other minerals had previously been determined. The weight fraction of each phase in a sample was calculated by multiplying the measured area by the respective RIR and the weight ratio of sample to quartz. The component weights were then normalized to 100%.

Analysis. The analysis of the scales is given in **Table 4**. The composition of the scale at location C-2 changes from predominantly pyrrhotite (Fe_7S_8) at the scale surface (flow side) to a mixture of pyrrhotite and mackinawite (Fe_9S_8), a more iron-rich phase, towards the pipe wall. **Figure 2** graphically represents the percentages of minerals from a representative slab taken from the middle of the sample. Elemental sulfur was detected in trace quantities towards the exposed surface. Akaganeite and goethite, both iron (III) oxide hydroxides, were found adjacent to the pipe surface. Siderite ($FeCO_3$) is more or less constant as a minor component at all locations. Barite and pyrite are present in the sample from C-1 and in three other tubing samples from other locations in this well, marked D, E, and G **(Table 5)**.

Acid Solubility of Scales.

The gravimetric solubility of samples C-1, D, and E were determined in 100 ml of 15% HCl after 1 hour at 150°F [65.56°C] (**Table 6**). The scale samples and their respective acid solubilities are C-1, 84.8%; D, 80.1%; and E, 83.6%. In this procedure, approximately 1 g of sample was used, and temperature was maintained in a covered water bath. The test does not necessarily indicate absolute solubility of the scale, but rather the amount dissolved under static conditions for 1 hour of contact time.

Elemental Analysis Mapping.

Sample C-3 was analyzed with an elemental mapping technique on a Tracor Northern 5500 energy dispersive X-ray unit on a JEOL 35CF scanning electron microscope. Tracor's XPHASE software allows individual 256 x 256 pixel grid elemental maps to be combined and calculates relative percents of the components. Iron and sulfur were mapped and the color photographs show areas in which iron, sulfur, iron sulfide, or neither of the elements were detected. Operating voltage was 15 kV at a magnification of 20x.

The cross section surface was analyzed radially between the scale area next to the pipe wall and the exposed surface of the scale towards the center of the pipe. Three areas were studied as listed in **Table 7**, and as can be seen, there is a concentration of sulfur at the inner and outer surfaces of the scale although some sulfur is found throughout the sample. Locations in which only iron is detected are interpreted to be primarily siderite ($FeCO_3$), although diffraction analysis found iron (III) oxide hydroxides in the scale layer adjacent to the pipe wall.

Scale Problems in Panhandle Wells

The British Columbia well was not acidized at this time because of unfavorable economic situations. The data from the scale analysis of the British Columbia well, however, can be applied to other areas. Iron sulfide scaling problems in the panhandle areas of Texas and Oklahoma are similar to the problem in the British Columbia wells. Qualitative X-ray diffraction analysis of scales from wells completed in the Dolomite formation in the Texas Hugoton Field show a large amount of mackinawite, a moderate amount of pyrrhotite, small to moderate amounts of sulfur and trace to small amounts of pyrite and akaganeite (Table 8). From this analysis, an effective, economical acidizing recommendation was made. (See Cases 1 and 2.)

Case Histories

The case histories presented here used treatments designed after extensive analysis of typical scale.

Case 1. A gas well completed in 1974 in the Dolomite formation in the Texas Hugoton field at a depth of approximately 3,000 ft [914.6 m] was acidized with 3,000 gal [11,356 L] of 15% HCl iron control acid. The well had a measured potential of 776 Mcf/D [21,974 m^3/D] in November 1974. Well was shut in from November 1974 to March 1977 waiting on a pipeline. The first six months' production averaged 272 Mcf/D [7,702 m^3/D]. Production fell to 114 Mcf/D [3,228 m^3/D] in 1989 before treatment. The well was acidized with 400 gal [1.514 m^3] of energized 15% HCl containing sour well iron control additives in October 1989. One month later, the well produced at 220 Mcf/D [6,230 m^3/D]. Six months later, the well averaged 238 Mcf/D [6,739 m^3/D]. Two years after the acid treatment, the well produced 206 Mcf/D [5,833 m^3/D]. Tubing cleanout was not performed prior to acidizing. Production history from February 1988 to October 1991 is represented in Figure 3.

Case 2. A gas well completed in 1968 in the Dolomite formation in the Texas Hugoton field at a depth of approximately 3,100 ft [945 m] was initially acidized and had a measured potential of 470 Mcf/D [13,309 m^3/D]. Production had steadily declined over the years. The six-month average from January to June 1988 was 94 Mcf/D [2,662 m^3/D]. The well was acidized with 1,500 gal [5.678 m^3] of 15% HCl containing conventional iron control additives. The six-month average production from August 1988 to January 1989 was 171 Mcf/D [4,842 m^3/D]. From July 1989 to January 1990, production averaged 133 Mcf/D [3,766 m^3/D]. The production for January 1990 was 107 Mcf/D [3,030 m^3/D]. From August 1988 to January 1990, we saw a 23.3% decline rate for the eighteen-month period.

The well was acidized in February 1990 with 500 gal [1.89 m^3] of energized 15% HCl containing sour well iron control additives. One month later, the well was producing at 145 Mcf/D [4,106 m^3/D]. From March to August 1990, the well averaged 142 Mcf/D [4,021 m^3/D]. The well was producing at 136 Mcf/D [3,851 m^3/D] in October 1991. For the twenty-month period from March 1990 to October 1991, we only saw a 2.4% decline rate. Tubing cleanout was not performed prior to acidizing. Production history from January 1987 to October 1991 is shown in Figure 4.

Case 3. A newly completed well in the Edson area of Alberta was treated to improve production. Before treatment, the well was producing 4,001 Mcf/D [$113.3 \times 10^{+3}$ m^3] gas per day. Three weeks after a 1,849 gal [7 m^3], 28% HCl sour well iron control acid treatment was performed, the well has had a sustained production of 15,998 Mcf/D [$453 \times 10^{+3}$ m^3] gas per day. Tubing cleanout was not performed prior to acidizing.[3]

Conclusions

1. Iron sulfide is not a single compound that deposits in a well.
2. The iron sulfides will vary in composition, nature, and reactivity.
3. Taking into account these variables, designs can be used to advantageously remove these scales.
4. Performing scale analysis provides a better understanding of what minerals are present in the scales that we are trying to remove.
5. The presence of elemental sulfur interspersed within the scale necessitates the use of a sulfur solvent to prevent further damage.

Acknowledgements

The authors thank the management of our sponsoring companies for permission to present this paper. The contributions of Kathy Black and LaVonna F. Funkhouser, Halliburton Services, are gratefully acknowledged.

References

1. Walker, Michael L., et al.: "Iron control in West Texas Sour-Gas Wells Provides Sustained Production Increases," JPT (May 1991) 603-607.
2. Bayliss, Peter: "Quantitative Analysis of Sedimentary Minerals by Powder X-Ray Diffraction," Powder Diffraction, vol. 1, no. 2 (1986) 37-39.
3. Walker, Michael L., Dill, Walter R., and Besler, Monte R.: "Iron Control Provides Sustained Production Increase in Wells Containing Sour Gas," J. Cdn. Pet. Tech. (Nov. 1990 sup.) 46-50.

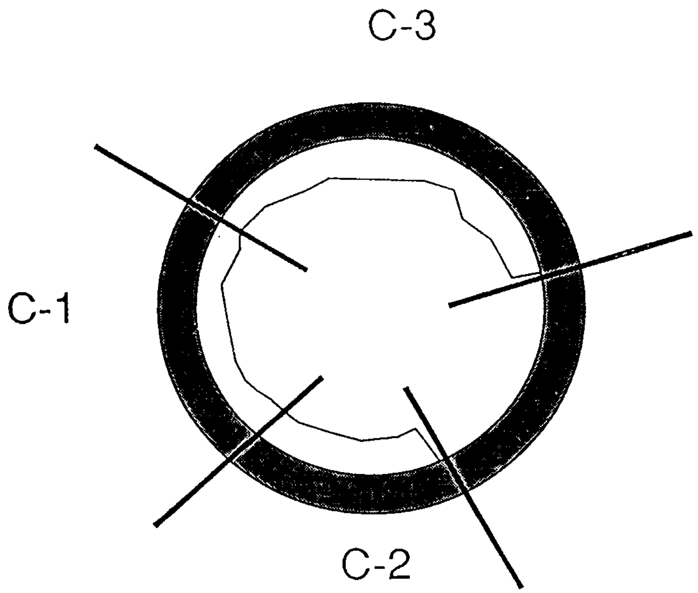

Figure 1 - Sections of Sample C from the NE British Columbia well

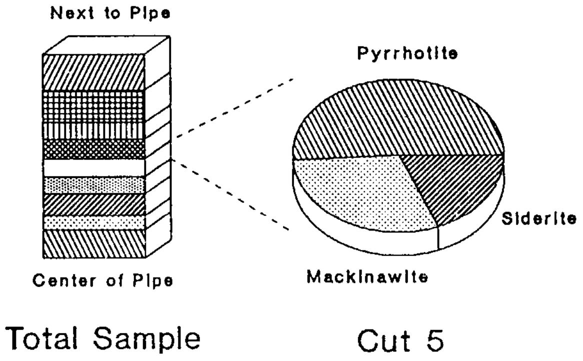

Figure 2 - This chart graphically depicts the mineral composition of a representative slab (Cut 5) from Sample C-2.

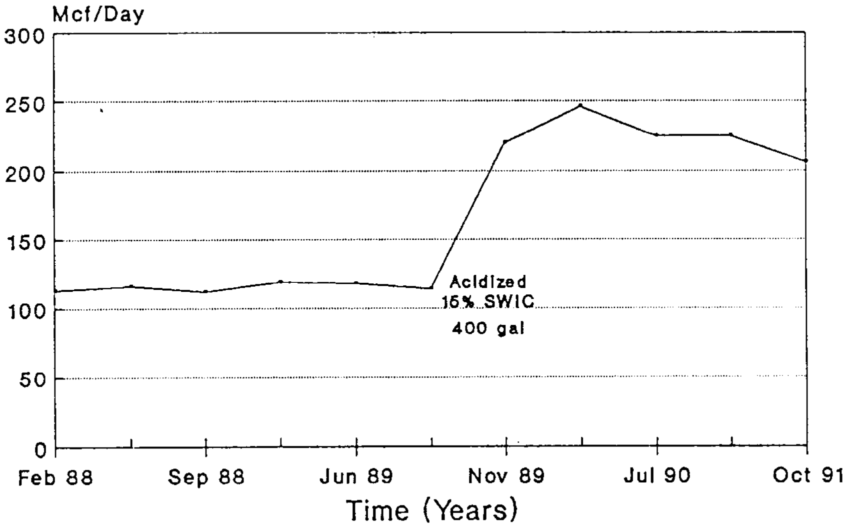

Figure 3 - Production history of Case 1 well February 1988 - October 1991

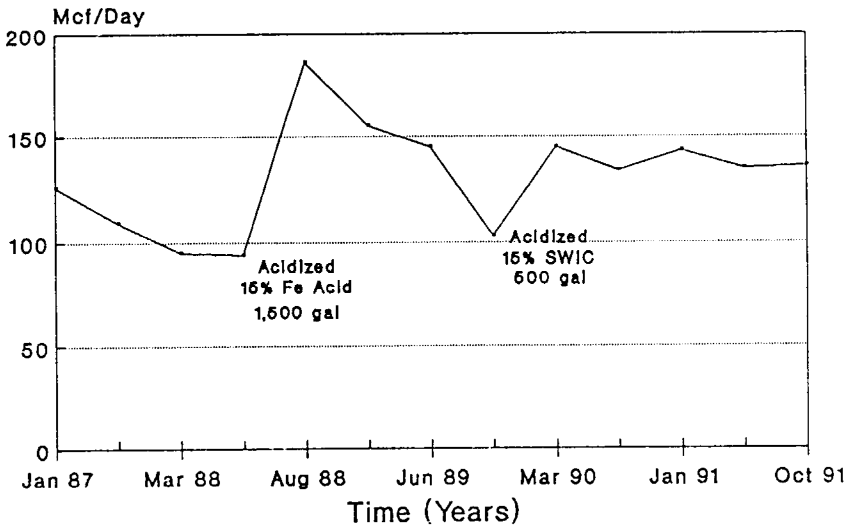

Figure 4 - Production history of Case 2 well January 1987 - October 1991