

New Insight into the Mechanisms of Iron Carbonate Formation in Sweet Gas Carbonate Reservoirs during Acid Stimulation

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ABSTRACT

Acid stimulation is a frequently used technology to enhance the production rate of hydrocarbons from a reservoir. Severe iron carbonate deposition has been observed recently during acid stimulation in sweet carbonate gas wells, especially for high-temperature high-pressure (HTHP) wells. It offsets the performance of acid stimulation, causes severe flow assurance issues, such as formation damage and tubing blockage.

To study iron carbonate formation during acid stimulation, corrosion coupon tests were conducted to collect data of the corrosion rate and iron released from tubing during the acid injection stage of acidizing treatment. To simulate iron carbonate depositing in the near-wellbore region, scale prediction software (ScaleSoftPitzer) was applied to simulate the scaling tendency and potential mass deposition. This allows an insight into the iron carbonate precipitation.

Results show iron carbonate deposition during acid stimulation is a corrosion induced scale issue. A high concentration of iron can release from tubular due to severe corrosion during acid injection, especially for the high-temperature reservoir. Minor iron carbonate could deposit at the initial stage of acid injection due to low the pH of spent acid. However, severe iron carbonate can precipitate when spent acid with pH ~3.8 mixes with formation water. A large amount of iron carbonate could deposit in the near-wellbore region or tubing, which potentially causes severe flow assurance issues and offsets the performance of acid stimulation.

This paper presents a fundamental study to understand the mechanisms of iron carbonate deposition during acid stimulation in sweet carbonate reservoirs. It will benefit defining a proper strategy to control iron carbonate deposition in downhole tubing and near-wellbore matrix. Appropriate mitigation strategies are recommended.

Key words: Iron carbonate, acid stimulation, mechanism

INTRODUCTION

The formation of mineral scale is a flow assurance problem during oil and gas production. Scale deposition on the surface facilities, downhole tubing and near wellbore region in the reservoirs may create many problems including pipe or valve blockage, unscheduled equipment shutdown, and even more importantly production reduction.¹⁻⁵ Over the past few decades, great efforts have been made to understand the conventional oilfield scale formation and inhibition, such as CaCO_3 , BaSO_4 and CaSO_4 . Compared to these conventional mineral scale deposits, iron carbonate, an exotic scale, has received fewer attentions.

The carbon steels are commonly used for well completion, pipelines and production tubular in the oil and gas industry. Under sweet conditions, iron carbonate film/layers can form on steel surfaces when the supersaturation of iron carbonate in the bulk is high enough.⁶ The reaction of iron carbonate formation in sweet gas wells is shown in Equation 1.



Iron carbonate films formed on mild steel surface in the oil and gas industry generally offer satisfactory protection from potentially destructive acts of internal pipeline corrosion during production.^{7,8} The thin-film of iron carbonate scale deposited during production stage works as a protective layer to mitigate the further interactions between the metal surface and the produced gas/fluid media. It significantly reduces the further corrosion and deposition of iron carbonate scale. A thin layer of iron carbonate scale is expected due to the formation of a protective iron carbonate film. However, a thick layer of iron carbonate dominant scale was observed and deposited in the carbon steel downhole tubing in the sweet carbonate gas wells. It caused tubing blockage, interfered with well intervention, and reduced hydrocarbon production. Other mechanisms of the formation of thick layers of iron carbonate in downhole tubing of sweet carbonate gas wells should be further investigated.

In order to understand the mechanisms of iron carbonate formation in the sweet carbonate gas wells, it is essential to understand the source of Fe^{2+} ion, which is one of the major reaction compounds for iron carbonate formation. The three major sources of the iron are: 1) sweet corrosion by-product of carbon steel during production; 2) Iron released from carbon steel tubing during acid stimulation; 3) other sources of iron, like iron from the reservoir dissolution if Fe-bearing minerals existed in carbonate formation or iron introduced during drilling.⁹

The iron released due to sweet corrosion during production contributes to iron carbonate film formation or formation of a thin layer of iron carbonate, but not a thick layer of iron carbonate formation.⁸ The iron released from the iron-bearing minerals in carbonate reservoir is minimal due to low solubility of iron carbonate under the well conditions. The iron could be introduced during drilling, less than 100 ppm. This contamination could give iron carbonate deposition in a short-term only and with a very limited amount of iron carbonate deposition. They may not be the major contribution of the source of iron for a thick layer of iron carbonate deposited in the downhole tubing in the sweet carbonate wells.

According to Chen's study,¹⁰ a large amount of iron can be generated and introduced in the production system during acid stimulation. A high concentration of iron could release from tubular due to acid attack, despite the corrosion inhibitor is used in the stimulation fluid package.

This paper presents a fundamental study to understand the mechanisms of iron carbonate surface deposition in the sweet carbonate gas wells during acidizing treatment by combining scale modeling and laboratory tests. Such an effort will contribute for understanding the mechanisms of iron carbonate formation and developing suitable strategy to manage the iron carbonate deposition in downhole tubular and near-wellbore matrix.

METHODOLOGIES

To study iron carbonate formation during acid stimulation in the sweet carbonate wells, a typical three-stage bullhead matrix acidizing treatment is applied. The chemical pumping stages and volumes are shown in Table 1. The organic solvent is applied to remove the hydrocarbon on the surface of carbonate formation and make the surface of carbonate formation available for acid reaction. 26 wt% HCl, a very high concentration of HCl, is pumped into formation to react with carbonate formation, increase the permeability of carbonate formation, and further increase the gas production rate. The last stage is to pump treated water as an overflush to push the acid into formation.

Table 1
Chemical Pumping Stages of Bullhead Matrix Acidizing Treatment

<i>Fluid type</i>	<i>Volume (bbls)</i>	<i>Average pumping rate (bpm)</i>	<i>Acid and tubing contact time (minute)</i>
Organic solvent	200	~10	--
Corrosion inhibited 26 wt% HCl	1000	~10	~30
Treated water overflush	200	10	--

Corrosion coupon tests

Laboratory corrosion coupon tests, one of the simplest and longest-established methods of estimating corrosion losses in the industry, were conducted to collect data of the corrosion rate and iron released from tubing during the acid injection stage of acidizing treatment. T-95 carbon steel test coupons were polished and pre-weighed prior to soaking into 30 ml corrosion inhibited 26 wt% HCl. The ratio of the surface area of test coupon and volume of the 26 wt% HCl applied in lab test is calculated and equivalent to the ratio of the surface of 4.5-inch downhole tubing and volume of the acid applied in the field application. The tests were performed at 125 °C over 30 minutes. After 30 minutes soaking, the coupons were pulled out, washed, and then dried for final weight measurement. The corrosion rate and iron released from tubing can be calculated.

To calculate the corrosion rate from metal loss is given in Equation 2:

$$\text{Corrosion rate (mm /y)} = 87.6 \times (W / \text{DAT}) \quad (2)$$

where:

W=weight loss in milligrams

D = metal density in g /cm³

A = surface area of sample in cm²

T = time of exposure of the metal sample in hours

Iron carbonate scale prediction

To simulate iron carbonate depositing in near wellbore region and downhole tubing, scale prediction software (ScaleSoftPitzer)⁺ was applied to simulate the scaling tendency and mass deposition. Thermodynamic calculations were performed to predict iron carbonate deposition in sour gases well. The calculations were based on a software developed by Rice University⁺ for simulating the thermodynamic equilibrium states of common scale minerals, such as calcite, barite, calcium sulphates, iron and zinc carbonate, calcium fluoride, iron carbonate, strontium sulphate, and sodium chloride. The program uses the Pitzer theory of electrolytes to determine the effect of high T, P, TDS and composition on activity coefficients.

The scale prediction calculations give values for the saturation ratio (SR) or saturation index (SI), where $SI = \log_{10} (SR)$, which represent the thermodynamic driving force for scale formation. The formula for saturation ratio is given in Equation 3.

$$\text{Where} \quad SR = (a_1 \times a_2) / K_{(P,T)} \quad (3)$$

$$a = \gamma \times C$$

a_1 and a_2 are the activity of scaling cation and anion in the solution. $K_{(P,T)}$ is the solubility product which is a function of pressure (P) and the temperature (T). C is the concentration of the ions in the solution and γ is the ionic activity coefficient.

Thermodynamic equilibrium is represented by $SR = 1$. At $SR > 1$, supersaturation is generated and scale formation is thermodynamically favored. Scaling tendency increases with SR. One of the guidelines for the interpretation of SR values is given in Table 2.

Table 2
Interpretation of Scale Prediction Results

SR	Interpretation
< 1	Under-saturated, non-scaling system.
=1	Equilibrium state, no scale formation.
1 - 10	Scaling likely, but should not severe.
10 – 100	Scaling almost certain to occur.
> 100	Severe scaling expected.

In this study, the thermodynamic scale prediction model was carried out with the input of acid, spent acid and a typical formation water chemistry, reservoir conditions and production rates of a sour gases well. The typical formation water chemistries, reservoir pressure and temperature, and gas/water production rates, as shown in Table 3.

+ ScaleSoftPitzer designed by Rice University