

Development of Novel Iron Sulfide Control Model and Understanding of Iron Sulfide Dispersant Mechanism

Xin Wang

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Saebom Ko

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Zhaoyi Dai

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Yue Zhao

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Chong Dai

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Samridhdi Paudyal

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Yuan Liu

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Xuanzhu Yao

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Amy T. Kan

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

Mason B. Tomson

Rice University-Brine Chemistry Consortium
6100 Main Street,
Houston, Texas, 77005
United State

ABSTRACT

In this study, a strictly anoxic bottle test setup has been built for FeS scale nucleation and growth kinetic at various temperatures, pH and ionic strength conditions. The FeS was generated by in-situ mixing of ferrous ion (Fe(II)), sulfide ion (S(-II)), dispersant and pH buffer (PIPEs or acetic acid), respectively. The

glass vial reactors were then placed into the heating block to reach the designated reaction temperature for 2 hours, and then set at room temperature for another 20 h. The ferrous ion and total sulfide remained in the aqueous phases were filtered and measured to evaluate the control efficiency. Under experimental condition, the iron sulfide scale was effectively controlled by CMC dispersant. The dispersant mechanism was studied combined lab observation and nucleation-diffusion theory. According to our study, iron sulfide particle would go through a very fast nucleation, which is hard to do inhibition control like barite or calcite. While the dispersant like CMC can effectively stop iron sulfide scale formation by crystal growth inhibition. A new numerical theory has been proposed to predict the required amount of CMC to effectively disperse iron sulfide particle and control the size under 1 μm for 22 hours under temperature 23 to 90 $^{\circ}\text{C}$, pH 4.4 to 6.7 and ionic strength 0.1 to 5M conditions.

Keywords: iron sulfide, kinetics, chemical control, precipitation model

INTRODUCTION

Increasing drilling and production activities in sour environment with equipment and piping made of low corrosion-resistant carbon steel resulted in significant iron sulfides (FeS) corrosion and scaling problems.¹⁻³ When hydrogen sulfide is evolved from sulfate reducing bacteria, dissolving of sulfide minerals or other thermal decomposition of sulfate, iron sulfide forms easily due to its low solubility and fast precipitation kinetics, especially at high temperature and high pH conditions.⁴⁻⁵ The accumulation of iron sulfide scale can cause many severe problems in oil field operations, including reducing oil production efficiency, interfering with the pumping system, leading to further corrosion, and significant health and environmental risk.⁶ Also, Iron sulfide particles are known to be oleophilic, and usually partition to oil phase and form a thick pad at the oil-water interface, causing separation issues and severely impairing oil quality.⁷

Iron sulfide has many crystalline phases with different solubility and other chemical properties, many of them have been reported in oil and gas production, such as amorphous FeS, mackinawite (FeS), and pyrite (FeS₂).^{2,5} It is expected that different phases of iron sulfide might have dramatically different precipitation, dissolution, and phase transfer kinetics, although little study has been done on the kinetic of iron sulfide. Most of these phases are dissolvable in hydrochloric acid (HCl), but pyrite is not dissolvable even in 15% HCl.⁸ These complicated phase transitions add additional difficulties to the iron sulfide management.

Unlike the threshold inhibitors, well-known for other common scales such as calcite or barite, very few chemicals have been reported for effective FeS scale control.⁸ Effective chemical treatment for FeS scale are still desired by field engineers, but to our knowledge, reliable FeS scale control method have not been established yet. Our previous studies have tested over 60 chemicals for FeS scale inhibition or dispersion, including commercial scale inhibitors, chelating agents, and polymer dispersants, but none of them showed threshold inhibition of FeS scale.⁹⁻¹⁴ Instead, we have found that carboxymethyl cellulose (CMC) polymer compound or its derivative functionalities as a promising FeS scale treatment chemical by dispersing nano-particulates for an extended period of time, which could significantly influence the particle-growth and deposition behavior of FeS scale.⁹ These polymers also demonstrated satisfactory thermal stability and their ability to effectively prevent FeS particle partitioning into the oil phase.

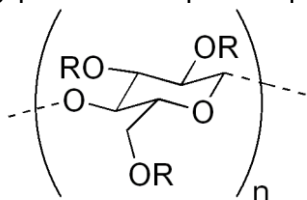


Figure 1. Chemical structure of carboxymethyl cellulose (CMC)

In this study, the CMC dispersion efficiency was evaluated at various temperatures, ionic strengths, pH and different CMC molecular weights. The dispersant mechanism of CMC polymer was studied by

combining lab observation and classic nucleation theory. It was found that iron sulfide particle formation rate could be described by a crystal growth processes, and the CMC polymer impacts through combining with the growing FeS particle and prevent for further growth. A novel numerical model has been developed to predict the required CMC dosage to effectively control FeS particle size under 1 μm and prevent FeS precipitation up to 5 M ionic strength and 90°C, respectively. This study successfully bridged the experimental observations with theoretical assumptions and illustrated a new way to understand the iron sulfide precipitation kinetics and the control strategy.

EXPERIMENTAL PROCEDURE

Anoxic conditions

A strictly anoxic bottle test setup has been developed for the FeS scale nucleation and growth inhibition.^{13,14} The key components of the experimental apparatus are shown in **Figure 2**. Several procedures were applied to avoid oxidation. Ultra-high purity argon gas (99.999%) was used to sparge dissolved oxygen from solution and remove air in the apparatus for at least 2 hours, and two oxygen traps were used in downstream of the argon cylinder to further reduce the oxygen concentration below 1 ppb. All connection lines between bottle, pump and connection tee are made of low oxygen permeable polyether ether ketone (PEEK) tubing. The argon gas was pre-saturated with the solution with the same background within the stock solution before they purge the stock solution.

The FeS particles were generated in a 33 mL glass reaction vial by in-situ mixing of four stock solutions that contain ferrous ion (Fe^{2+}), buffer, dispersant chemical, and sulfide ion (S^{2-}), respectively. The solutions were transferred by using four different gas-tight syringes. The glass vial reactors and the gas-tight syringes were prefilled with argon gas within a glove bag. In the glove bag, the vacuum and ultra-high purity argon blowing cycles were repeated seven to ten times to ensure the oxygen level less than 10 ppb. The glass vial reactors were capped with a polytetrafluoroethylene(PTFE)/silicon liner screw thread closure inside the glass bag.

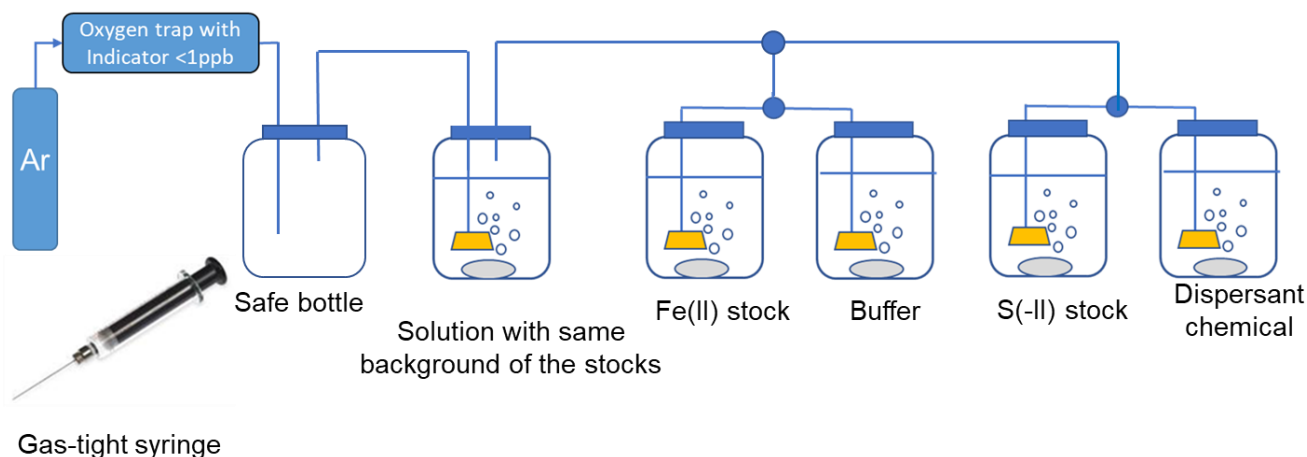


Figure 2. Key components of the anoxic bottle test setup for iron sulfide study

FeS disperse study

The iron stock solution was prepared at pH 4.0, and the sulfide solution was prepared at pH 10.0, to prevent hydrogen sulfide evaporation during the argon sparging. The reaction pHs were set at 6.7 or 5.0, maintained through piperazine-N,N'-bis(2-ethanesulfonic acid) sodium salt (adjusted PIPES) or sodium acetate/acetic acid buffer, respectively. To ensure the formation of FeS particles was at the desired temperature, the ferrous ion solution, buffer solution, and the dispersant chemical were initially mixed, the total volume was about 14 mL. Then the reaction vial was heated to the target temperature. Then, 1 mL of concentrated sulfide solution was added to generate the FeS particles –this 1 mL had little influence on the solution temperature. The reaction temperature was maintained via a temperature-controlled

aluminum heating plate while samples were stirred for 2 hours. After that, the glass vial reactors were set at room temperature without stirring for another 20 hours to allow the FeS particles to precipitate.

For each designated condition, the total sulfide ion(-II) concentration was five times higher than the ferrous ion concentration, and the solution saturation index was calculated using ScaleSoftPitzer2020. Typical reaction conditions are summarized in **Table 1**.

Table 1. Typical reaction conditions.

Parameters	Conditions
Temperature	25°C/ 50°C/70°C/ 90°C
Total solution volume	15 mL
Pressure	1.7 atm
pH	6.7/ 5.0 ± 0.10
Reaction time	2 hr heating + 20 hr room temperature
Fe(II) : S(-II)	1: 5
Fe(II) concentration range	Around 2 – 300 ppm
S(-II) concentration range	Around 10 – 900 ppm
Range of SI	0.59 – 1.81
NaCl	0.01 – 5.00 m
PIPES / Acetic buffer	0.010 m
CaCl ₂ ·2H ₂ O	0.025 m (1000 ppm Ca ²⁺)
Molecular weight of CMC	90,000 / 250,000

Post-test analysis and dispersant evaluation

After each experiment, photos were taken of the reaction vials to visually evaluate the performance of the FeS control. For experiments wherein solid particles formed, the supernatant was withdrawn from the vial and filtered with 1 µm pore size syringe filter, the solution was then analyzed using a Hach colorimetric spectrometer, the ferrous ion was analyzed by the 1,10-phenanthroline method, and the total sulfide was analyzed using the methylene blue method. The performance of the chemicals was also evaluated in terms of the percentage of ferrous ion (Fe(II)) in the filtered sample as shown in equation (1).

$$Dispersion\ Efficiency(\%) = \frac{Fe\ conc.\ in\ filtrated\ solution}{Initial\ Fe(II)\ conc.} \times 100\% \quad (1)$$

Typical results are shown in **Figure 3**. For each condition, 5 different concentrations of CMC were tested to get the minimum required CMC concentration for complete dispersion. If over 90% of the Fe(II) were retained in the filtered solution, the corresponding dispersant concentration was deemed successful for chemical control and was used in model calculations. As shown in **Figure 3**, as little as 90 ppm CMC can partially disperse the FeS particles. This 90 ppm is difficult to identified by visual observation, but 120 ppm CMC solution is easily identified as dispersed and would be classified as “effective dispersion of iron sulfide (see below).”

For each experimental pH condition, one sample without dispersant was collected, and the FeS solid particles were filtered by a vacuum filtration system with 0.45 µm pore size filter paper. The solid particles on the filter paper were then dried and analyzed by scanning electron microscopy energy dispersive spectroscopy (SEM/EDS) or X-ray diffraction (XRD). The experimental generated FeS was always identified as Mackinawite.

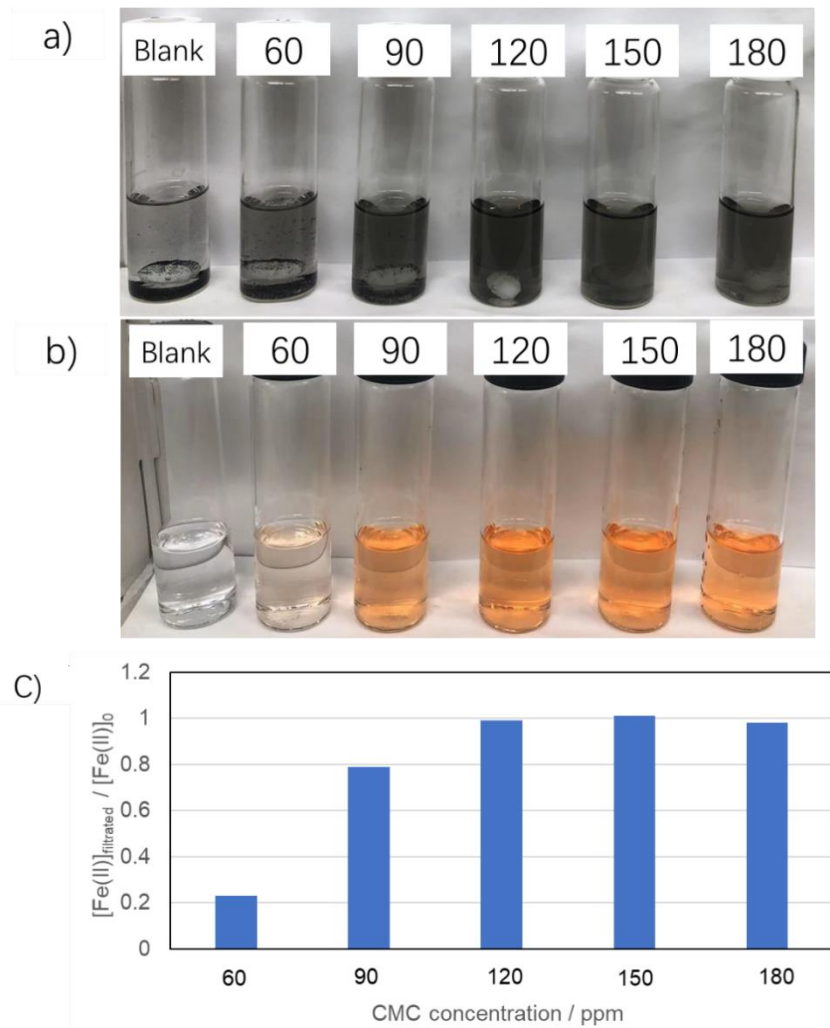


Figure 3. a) Image of the relative dispersion of FeS at various concentrations of CMC, in 1M NaCl, 1000 ppm Ca^{2+} , SI 1.46, pH 6.7 and temperature 70°C, with CMC molecular weight 250kDa, the number above the bottle is the CMC concentration in ppm. b) 1,10-phenanthroline colorimetric analysis of the ferrous ion concentration in filtered solution. c) CMC dispersion efficiency of the solution.

Model development

The formation of FeS scale can be expressed as follows:



The saturation index (SI) of the iron sulfide is defined as follows:

$$SI \equiv \log_{10} \frac{\gamma_{Fe^{2+}} [Fe^{2+}] \gamma_{HS^{-}} [HS^{-}]}{a_{H^{+}} K_{sp, FeS}} \quad (3)$$

Where $[•]$ and γ stand for molal concentration (mol/kg water), and activity coefficients of different species, respectively; K_{sp} is the solubility product of iron sulfide. Theoretically, SI should be equal to zero when solution is at equilibrium with the iron sulfide solid. The SI of iron sulfide in this study was calculated by using ScaleSoftPitzer2020.¹⁵⁻¹⁷