

Iron sulfide scale control using a dispersant of carboxymethylcellulose (CMC) in sour environment

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ABSTRACT

When hydrogen sulfide gas is evolved in the presence of iron from various corrosion processes in downhole, iron sulfide can quickly precipitate. In the recent year, sulfide scale issues have been drawing lots of attention. Firstly, iron sulfide is one of the most or significantly unsolved deposition problem in oil and gas production. Secondly, iron sulfide has oleophilic nature so that it can be difficult to separate iron sulfide from oil phase during production processes. Polymeric dispersants have exhibited their feasibility to prevent the deposition of iron sulfide scales, but dispersants have not been widely validated to control FeS scale problems and limited numbers of trials and reports have been available. The goals of this study were (1) to develop efficient and effective technology preventing iron sulfide particle deposition on the surface as well as maintaining iron sulfide in the water phase; and (2) to understand FeS scale controlling reaction mechanism. Our studies indicate that carboxymethylcellulose (CMC) displays the excellent performance of iron sulfide dispersion in pH 4.3 – 6.7, temperature 70 – 90 °C, and FeS saturation index (SI) 0.13 – 1.27. At pH 5.2, the required minimum CMC concentration to disperse FeS particles (C_{crit}) was 20 mg/L at 70 °C and $SI(FeS_m) = 0.54$ and 40 mg/L at 90 °C and $SI(FeS_m) = 0.59$. As pH increased to 6.7 at 70 °C, C_{crit} was reduced to 5 mg/L at $SI(FeS_m) = 1.27$. On the other hand, C_{crit} significantly increased to 100 mg/L at $SI(FeS_m) = 0.13$ and 400 mg/L at $SI(FeS_m) = 0.44$ at pH 4.3 and 70 °C. Hydrodynamic

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particle sizes remained in nano-size in different CMC concentrations in ranges of 300 to 530 nm at pH 4.3 and 170 to 335 nm at pH 5.0. The combination of DTPMP and CMC displayed synergistic effect. The greater portion of FeS particles were dispersed and kept their size smaller in the combination of DTPMP and CMC than CMC by itself. But it became less effective at 90 °C to inhibit or disperse iron sulfide solid formation than at 70 °C. FeS particles remained in water phase in the presence of CMC, while they stayed in oil phase in the absence of CMC.

INTRODUCTION

Mineral scales frequently occur in tanks, pipelines, cooling and heating system, production wells of oil and gas, external and internal membrane, and other equipment during industrial processes, causing the reduction of process efficacy and millions of dollars on dealing with the scale issues. As oil and gas are produced increasingly in more unconventional reservoirs, such as deeper and tighter zones, with new technologies, more challenges are encountered to mitigate scale problems ¹.

In recent years, many reports have been made regarding iron sulfide scales which tend to be formed in sour wells producing H₂S gas to a great extent. It could be related to transferring to the practices that are more aggressive technologies and unconventional fields, such as high pressure, high temperature, and high salinity ². Iron sulfide scales are often precipitated with organic deposits and adhered to the oil and water interface and stabilize emulsions due to their oleophilic property, causing other issues during oil and gas operational activities ^{3, 4}. Furthermore, the iron sulfide solubility product is uncertain, and sulfide chemistry is extremely complex ⁵. There exist numerous phases of iron sulfides that have different crystal structures and chemical properties. It is a challenge to know what phases form and how much they will be formed under certain conditions ⁶. With these complexities, the prediction of iron sulfide formation tendency is challenging, leading to poor management of scale mitigation, for example, insufficient inhibitor dosage, sometimes due to wrong calculation of iron sulfide saturation index ^{1, 7, 8}.

Another challenge associated with iron sulfide scale mitigation is stable ion pairs and their fast precipitation. To inhibit mineral scale formation and growth, it is estimated for the threshold inhibitors to cover surface area by 15 – 20% ⁹ or increase molar volume by about 20% ¹⁰ of scales. Threshold inhibition is a kinetic process in that the solution remains supersaturated but without precipitation ¹¹. Conventional threshold inhibition does not work for iron sulfide because the activation energy of iron sulfide precipitation ($E_a = 7.13$ kJ/mol) ⁸ is much lower than other minerals, such as barite ($E_a = 30.6$ kJ/mol) ¹². Upon the first formation of iron sulfide precipitates, they quickly grow along the c-axis ⁵.

Dispersion of mineral scale practices has gained attentions as an alternative mineral scale control method of threshold inhibition for crystal formation and growth, especially for sulfide scales which are difficult to be inhibited otherwise ¹³⁻²². Polymeric dispersants have been shown to prevent the deposition of iron sulfide scales, but dispersants have not been widely validated to control FeS scale problems and limited numbers of trials and reports are available. Our previous study showed that polymeric dispersants, especially carboxymethylcellulose (CMC), were effective to control difficult scale issues, such as sulfide scales (i.e., FeS, PbS, and ZnS) ^{20, 22, 23}. CMC is a derivative of cellulose in which carboxymethyl groups are bound to hydroxyl groups on the cellulose backbone, shown in Figure 1. CMC is a green chemical, used as a viscosity modifier and emulsion stabilizer in various applications from ice cream, toothpaste, eye drops to drilling mud and water shut-off agents ^{24, 25}. The goals of this study are to investigate CMC's performance as a dispersant of FeS scale in sour environment and the role of the conventional scale inhibitors on the dispersion process. Diethylenetriamine penta(methylene phosphonic) acid (DTPMP) as a representative phosphonate inhibitor and phosphino-polycarboxylic acid (PPCA) as a polymeric inhibitor were chosen due to their common applications as conventional threshold scale inhibitors.

EXPERIMENTAL PROCEDURE

Anoxic environment

All solutions were prepared in air-tight apparatus while sparging at least 1 hour with ultra-high purity argon (Ar) gas that was connected to oxygen trap, minimizing oxygen level of water to 5 ppb. Reactions were carried out in temperature-controlled glass reactors. Apparatus was connected through polyether ether ketone tubes to minimize the permeability of oxygen. All solutions were prepared daily under well controlled anoxic environment. Glass reactors, where mineral scale particles would be produced, were purged with Ar gas in a glove bag, and then the reactors were capped with a polytetrafluoroethylene/silicon liner screw thread closure. An aliquot of solution was transferred to the Ar gas purged glass reactors using a gas-tight syringe. A more detailed anoxic setup for this experiment can be found in Ko, et al.²².

FeS scale dispersion

Dispersion tests of FeS scale were performed at different conditions of ion concentrations in the background brine solution of 1M NaCl and 25 mM Ca²⁺. The reaction temperatures were 70 and 90 °C in pH 4.3 – 6.7. Total iron concentrations tested ranged from 30 to 200 mg/L and total sulfide concentrations from 90 to 600 mg/L. Solution pH was maintained through sodium acetate/acetic acid buffer at pH 5.2 and sodium acetate/acetic acid buffer and added HCl to pH 4.3. Water soluble polymer of carboxymethylcellulose (CMC, molecular weight of 250,000 g/mol, degree of carboxymethyl substitution of 0.7) was applied as a FeS particle dispersant. Phosphonate inhibitors of diethylenetriamine penta (methylene phosphonic acid) (DTPMP) and phosphino-polycarboxylic acid (PPCA) were amended in the combination with CMC to examine the synergistic effect on FeS particle dispersion and inhibition. A summary of experiment conditions is presented in Table 1.

The total volume of a 40 mL glass vial (headspace volume: ~ 20 mL) was used for experiments at pH 5.2 and a 28 mL thick wall glass tube (headspace volume: ~5 mL) for experiments at pH 4.3. The order of chemical additions was iron solution followed by phosphonate inhibitor, polymeric dispersant, and sulfide solution last.

Wettability test of FeS scale

In Exp. #3 condition, wettability of FeS scale was evaluated during dispersion experiment with 400 mg/L CMC. The volume of 9 mL ISOPAR-L oil was first added to a reactor, followed by stock solutions of iron, CMC and sulfide at last. The mixtures were reacted at 70 °C for 2 hours.

Analysis

After 2-hour reaction time was over, an aliquot of samples was withdrawn for Fe analysis and particle size measurement using disposable syringe needle without opening a cap. The remaining solution in a glass reactor was kept overnight at room temperature and then images were taken for the record of visual observation of dispersed and settled FeS particles.

HACH FerroVer spectrophotometric method was used to determine total iron concentrations in solution after 2-hour reactions. FerroVer powder pillow was made of 1,10-phenanthroline as an indicator that forms the complex with Fe²⁺, developing orange color complex, and sodium sulfite as a reducing agent. The absorbance was measured at the wavelength of 510 nm. Before Fe analysis, samples were filtrated using 5, 1.2, and 0.22 µm nitrocellulose membrane filters and then filtrates were diluted in 0.1 mM HCl, providing the range of solution pH of 3 – 5, at which 1,10-phenanthroline and ferrous iron form a stable orange-red complex.

Hydrodynamic sizes of FeS particles dispersed in CMC solution were measured using dynamic laser scattering (DLS). FeS particle-containing solution was diluted with DI water to get optimum ranges of scattering light intensity.

Table 1
Summary of FeS scale control experiment conditions

Experiment No.	Exp. #1	Exp. #2	Exp. #3	Exp. #4	Exp. #5	Exp. #6	Exp. #7
Brine composition							
Na (mg/L)	23,129	23,129	23,863	23,829	23,043	23,129	23,129
Ca (mg/L)	1,000	1,000	1,000	1,000	100	1,000	1,000
Fe (mg/L)	30	30	200	100	10	30	30
S (mg/L)	90	90	600	577	30	90	90
Cl (mg/L)	37,275	37,275	37,275	37,275	37,275	37,275	37,275
Active concentrations of additives							
Dispersant (mg/L)	20 – 80	20 – 80	100 – 400	100 – 200	5 – 20	20	20 – 80
Inhibitor (mg/L)	0	0	0	0	0	10 – 20	10 – 20
Reaction condition							
Reaction time (hr)	2	2	2	2	2	2	2
Temperature (°C)	70	90	70	70	70	70	90
pH	5.2	5.2	4.3	4.3	6.7	5.2	5.2
Saturation index (SI)	0.54	0.59	0.44	0.13	1.27	0.54	0.59

H₂S gas partial pressure (P_{H_2S}) in Exp. #1 and #6 is 0.0451 atm; 0.049 atm in Exp. #2 and #7; 0.342 atm in Exp. #3; and 0.327 atm in Exp. #4. The ratio of H₂S concentration in aqueous phase ($[H_2S]_{aq}$) to total S concentration in Exp. #1 and #6 is 0.65; 0.57 in Exp. #2 and #7; 0.73 in Exp. #3; and 0.74 in Exp. #4 (SI , P_{H_2S} , and $[H_2S]_{aq}$ are calculated by *ScaleSoftPitzer* (SSP) 2021 developed by Brine Chemistry Consortium (BCC) at Rice University.

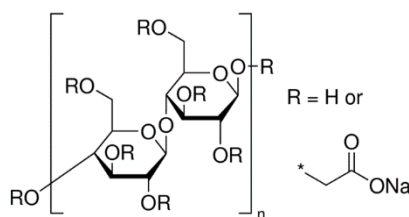


Figure 1: Carboxymethylcellulose (CMC) structure

RESULTS AND DISCUSSION

FeS dispersion in the presence of CMC

The performances of CMC on FeS particle dispersion were evaluated in different temperatures (70 and 90 °C) and pHs (4.3 – 6.7). The CMC performance was evaluated by the required minimum CMC concentration to disperse FeS particles, hereafter referred to as critical concentration (C_{crit}).

Temperature effect

Figure 2 and **3** show the temperature effect on FeS dispersion with CMC at 70 °C and $SI(FeS)$ 0.54 (Exp. #1) and 90 °C and $SI(FeS)$ 0.59 (Exp. #3). To disperse FeS particles for at least 2 hours, C_{crit} were 20 mg/L at 70 °C and 40 mg/L at 90 °C as shown in **Figure 2A** and **3A**, respectively. At C_{crit} in Exp. #1 (20 mg/L) and #2 (40 mg/L), 50% of initial Fe were recovered in filtrate passing through 1.2 μm pore size membrane and 100% of initial Fe in filtrate, respectively. In Exp. #2, at 20 mg/L CMC, the fractions of recovered Fe concentrations in filtrate passing through 1.2 and 0.22 μm pore size membranes were almost as same as ones in the blank sample to which CMC was not added.

As temperature increased, the greater concentration of CMC was also required to disperse the majority of FeS particles. The greater concentration could be related to the acceleration of FeS precipitation kinetics, requiring the greater amount of CMC to prevent FeS particle growth. The observation of temperature effect in this study was consistent with the dispersion model developed by Wang et al.²⁶ which predicts required dispersant concentration (Eqn (1)). According to the model, the required dispersant concentration is inversely proportional to the square root of temperature, as follow:

$$C_{dis.} = \frac{M_{dis.}}{A_{dis} * N_A * (\frac{k_b T}{3\pi\mu R_e} * t_{ind})^{1/2}} \quad (1)$$

Where, $C_{dis.}$ = the concentration of dispersant CMC (mg/L); $M_{dis.}$ = the molecular weight of the dispersant (g/mol); $A_{dis.}$ = the projected area of the dispersant, calculated by $A_{dis} = 4\pi R^2$, where R is the CMC molecule radius (m); N_A = the Avogadro constant; k_b = Boltzmann constant; T = the temperature (K); μ = the dynamic viscosity of the solution (N s/m²); R_e = the effective radius of the polymer molecule; t_{ind} = the induction time (sec) defined as the time when the new solid phase is visibly detected and can be expressed as the sum of the time of nucleation and crystal growth²⁷.

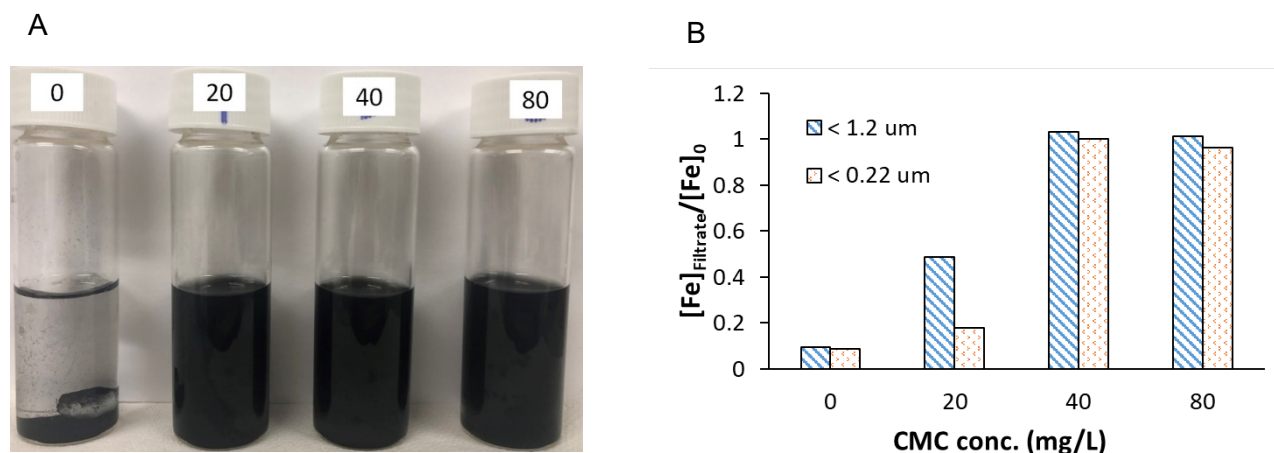


Figure 2: A) Visual observation of dispersed FeS particles in the presence of CMC in Exp. #1. A number in the text box indicates an active concentration of CMC. B) Comparison of the fraction of recovered Fe in filtrates in different CMC concentrations from 0 to 80 mg/L in Exp. #1.