



Performance of dithiocarbamate-type flocculant in treating simulated polymer flooding produced water

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Abstract

Produced water from polymer flooding is difficult to treat due to its high polymer concentration, high viscosity, and emulsified characteristics. The dithiocarbamate flocculant, DTC (T403), was prepared by the amine-terminated polyoxypropylene-ether compound known as Jeffamine-T403. The product was characterized by IR spectra and elemental analysis. The DTC agent chelating with Fe^{2+} produced a network polymer matrix, which captured and removed oil droplets efficiently. Oil removal by the flocculant on simulated produced water with 0, 200, 500, 900 mg/L of partially hydrolyzed polyacrylamide (HPAM) was investigated for aspects of effectiveness of DTC (T403) dosage and concentrations of HPAM and Fe^{2+} ions in the wastewater. Results showed that HPAM had a negative influence on oil removal efficiency when DTC (T403) dosage was lower than 20 mg/L. However, residual oil concentrations in tested samples with different concentrations of HPAM all decreased below 10 mg/L when DTC (T403) dosage reached 30 mg/L. The concentration of Fe^{2+} in the initial wastewater had a slight effect on oil removal at the range of 2–12 mg/L. Results showed that Fe^{3+} could not be used in place of Fe^{2+} as Fe^{3+} could not react with DTC under flocculated conditions. The effects of mineral salts ions were also investigated.

Key words: dithiocarbamate; flocculation; hydrolyzed polyacrylamide; oil removal

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Introduction

During crude oil extraction, water containing polymer (partially hydrolyzed polyacrylamide, HPAM) is usually injected into the stratum to expel oil from the ground. This polymer flooding process can enhance oil recovery by 12% compared with water (polymerless) flooding (Bartelds et al., 1997; Han et al., 1999). In recent years, polymer flooding has been widely used in major oilfields of China, such as Daqing and Shengli. As a result, a significant quantity of wastewater contains high concentrations of produced HPAM. Research has shown that residual HPAM increases wastewater viscosity and water film strength, which inhibits coalescence and oil droplet floatation (Deng et al., 2002a, 2002b; Cao et al., 2004) and the ability to treat wastewater. Traditional treating processes used in oilfields, including gravitational settling and floatation and filtration, are ineffective in treating produced water from polymer flooding compared to treating water flooding (Deng et al., 2002b). Installing new equipment and implementing new treating processes would be, however,

very expensive. At present, the most applicable method is the addition of effective flocculants that help small oil droplets join together in the presence of HPAM and separate from the polymer solution. If cationic flocculants such as polyaluminium chloride (PAC) and cationic polyacrylamide (CPAM) are used to treat produced water, they react with anionic HPAM by charge neutralization, which results in a significant increase in cationic flocculants dosage (Zhao et al., 2008) and the cost of treatment. It is hoped that HPAM can exist in treated water, which benefits crude oil extraction when the treated water is injected into the stratum.

Dithiocarbamate (DTC) is a type of negatively charged compound synthesized by the reaction of primary/secondary amines and carbon disulfide in alkaline solution. Dithiocarbamate ligands ($-\text{CSS}^-$) contain double sulfur atoms and can coordinate with most heavy metal cations, such as Fe^{2+} , Zn^{2+} , Pb^{2+} , and Cd^{2+} , to form chelates with high stability constants (Yang et al., 1996; Singhal et al., 2004; de Vries et al., 1973; Cheremisina and Larionov, 1971). Research has suggested that DTC compounds with more than two dithiocarbamate groups ($-\text{CSS}^-$) can chelate with polyvalent metal cations to form

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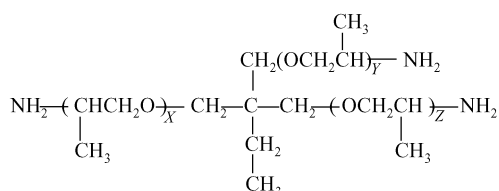
insoluble polymer matrices with a cross-linked network structure, and suspended particles are net captured and swept from the wastewater (Bellos and Louis, 2000; Jia, et al., 2009). Since the 1990s, DTC-type flocculants have been developed and applied to oilfield wastewater treatment in America (McClure et al., 1998) and some DTC compounds are efficient in clarifying O/W emulsions in combination with heavy metal cations (Thompson and Asperger, 1989; Evain et al., 1993; McClure et al., 1998). To date, however, few reports on DTC's flocculation performance on produced water from polymer flooding have been presented.

In this study, DTC was prepared by the amine-terminated polyoxypropylene-ether compound known as Jeffamine-T403. The product was then characterized by IR spectra and elemental analysis. Finally, oil removal effect of DTC on simulated produced water was investigated in regards to effectiveness of DTC's dosage and concentrations of HPAM and Fe^{2+} ions in the wastewater.

1 Materials and methods

1.1 Materials

Crude oil was obtained from the Tuoyi Station of Shengli Oilfield in China. The HPAM used was characterized by molecular weight ranging from 3×10^6 to 5×10^6 , hydrolysis degree of 20%–30%, and solid content above 90%. Jeffamine-T403, an amine-terminated polyether compound with an average molecular weight of 403 obtained from the Huntsman Company (USA), was used as raw material to synthesize the flocculant DTC. Its molecular structure is as follows:



Structure of Jeffamine-T403 ($X + Y + Z \approx 5.6$).

1.2 Preparation of flocculant

Molar content of the Jeffamine-T403 amino-group ($-\text{NH}_2$) was determined by hydrochloric acid-ethanol titration before DTC was prepared. Results showed that 1 mol of amine ($-\text{NH}_2$) was obtained from 157 g of Jeffamine-T403.

The synthesis of DTC was as follows: add 20 g deionized water and 1.57 g Jeffamine-T403 (containing 0.01 mol $-\text{NH}_2$) into a 100 mL flask with a magnetic stirrer, and put 0.40 g NaOH (0.01 mol) in the dropping funnel. Cool the mixture in an ice bath to 10–15°C and then add 0.76 g CS_2 dropwise to maintain the reaction temperature. Heat the reaction mixture to 25°C and continue to stir for 3 hr. The final product is DTC (T403).

1.3 Preparation of stock solution

According to the actual quality of produced water from polymer flooding in Shengli Oilfield, the brine was prepared with (mg/L) NaCl 7208, NaHCO_3 1607, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ 321, and CaCl_2 283. The HPAM was dissolved into the brine to obtain the stock solution.

1.4 Preparation of simulated produced water

One hundred milliliters of surfactant OP-10 solution with a concentration of 200 mg/L and 5.00 g of crude oil were added to a 150-mL jar. The mixture was heated to 50°C and then emulsified for 10 min at 15,000 r/min with a FM200 emulsifier (Fluko Company, Germany) to obtain the O/W emulsion.

The prepared emulsion was mixed with 3 L of stock solution, and settled for 4 hr. The floating oil was then scrapped out. The median size of the oil droplets was about 5 μm , measured by Mastersizer 2000 (Malvern Company, England). Oil concentrations of simulated wastewater were also determined as 250–300 mg/L.

1.5 Flocculation test procedures

All flocculation experiments were conducted using conventional Jar-test apparatus, the DC-506 Laboratory Stirrer. A simulated wastewater sample of 500 mL was added to 1,000 mL breakers. For the formation of flocs by coordinating reaction between DTC (T403) and metal cations, Fe^{2+} ions were provided by adding FeSO_4 into the samples. The emulsion was stirred rapidly at 200 r/min for 2 min after DTC (T403) was dosed, followed by slow stirring at 40 r/min for 10 min and then settling for 10 min. The supernatant samples were taken from a point 3 cm below the surface for analysis.

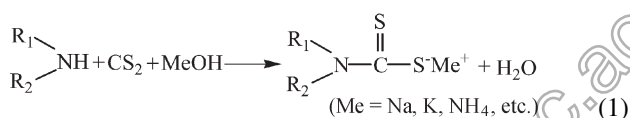
1.6 Analytical methods

Infrared spectra in the range of 4000–400 cm^{-1} were recorded in KBr medium on a 20SX, FT-IR spectrophotometer (Nicolet Corp., USA). Oil concentrations of the test water samples were determined by measuring the absorbance of benzene extract (boiling range from 90–120°C) at a wavelength of 430 nm using a JH752 UV/Vis spectrophotometer (Jinghua Ltd., China). The residual total iron concentrations in samples were measured by phenanthroline spectrophotometry and HPAM concentrations were measured by starch-cadmium iodine (Taylor, 1994).

2 Results and discussion

2.1 Molecular structure of the synthesized product

Dithiocarbamates can be synthesized by the reaction of nucleophilic addition between primary/secondary amines and carbon disulfide under strong alkaline conditions, as shown in the following Reaction (1).



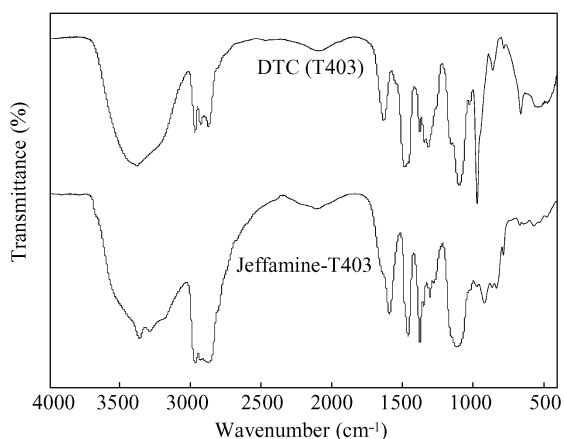


Fig. 1 IR spectra of Jeffamine-T403 and DTC (T403).

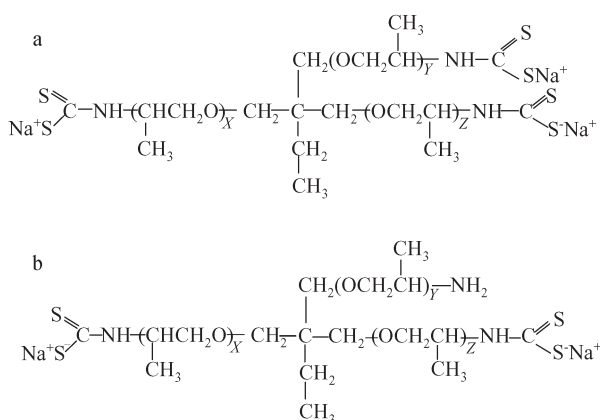


Fig. 2 Molecular structures of DTC (T403). (a) tri-dithiocarbamic structure; (b) bis-dithiocarbamic structure.

As mentioned above, DTC (T403) was prepared by the reaction of nucleophilic addition between Jeffamine-T403 and carbon disulfide under strong alkaline conditions.

Figure 1 presents the IR spectra of Jeffamine-T403 and DTC (T403), which shows N-CSS⁻ stretching vibration at 1485 cm⁻¹ between C-N stretching mode (1250–1350 cm⁻¹) and C=N stretching mode (1640–1690 cm⁻¹), indicating considerable double bond characteristics (Cocouvanis and Fackler, 1967). Singhal et al. (2004) reported a C-S band in the region 962–989 cm⁻¹. A strong band was also observed at 969 cm⁻¹, while another C=S stretching mode at about 1360 cm⁻¹ was in accordance with previous studies (Nakanishi and Solomon, 1977).

Elemental composition of DTC (T403) was determined by a PerkinElmer 240c Elemental Analyzer (USA) after vacuum drying and abstersion with ether. The molar ratio of S and N should be 2:1 if all amine groups (-NH₂) have proceeded with the reaction. Results showed, however, that the contents (weight) of S and N were 19.22 and 4.791, respectively, and the molar ratio was 1.755:1, which suggests that part of the -NH₂ groups had not reacted with CS₂. This may be due to the volatilization of CS₂ (boiling point at 46°C). Therefore, the two primary molecular structures in DTC (T403), displayed in Fig. 2a and b, had a tri-dithiocarbamic structure and a bis-dithiocarbamic structure, respectively.

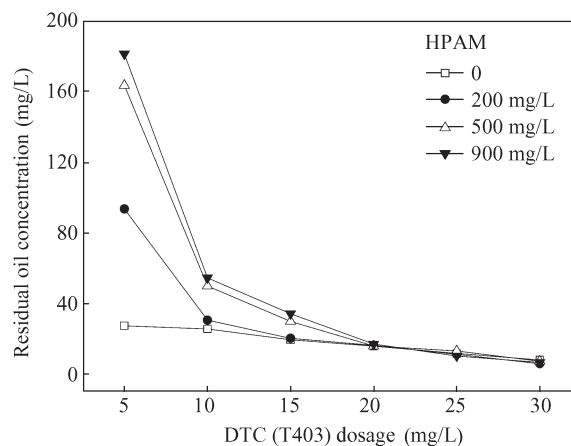


Fig. 3 Relationship between residual oil concentrations and DTC (T403) dosages at different concentrations of HPAM.

We calculated that 87.7% of -NH₂ groups reacted with CS₂, therefore more than 64% of molecules belonged to tri-dithiocarbamic (Fig. 2a).

2.2 Effect of DTC (T403) dosage on oil removal

Simulated produced water samples with 0, 200, 500, 900 mg/L of HPAM were prepared to investigate the effect of DTC (T403) dosage on oil removal. Given that metal ions must coordinate with DTC to form flocs (Bellos and Louis, 2000), FeSO₄ was added to provide water samples with 10 mg/L of Fe²⁺ before DTC (T403) dosage. Selection of Fe²⁺ as ferrous ions are often found in oilfield produced water.

The relationship between residual oil concentrations in the supernatant samples and the changes in DTC (T403) dosages are shown in Fig. 3. As shown, DTC (T403) provides high oil removal efficiency at the 5 mg/L dosage for simulated wastewater without HPAM, which resulted in a significant decrease in oil content from approximately 300 mg/L to 27 mg/L. Even though the effect of HPAM on oil removal was more noticeable at lower dosages, all residual oil concentrations decreased to about 16 mg/L to 20 mg/L when dosage increased, and at 30 mg/L the oil concentration decreased to less than 10 mg/L, which reached the standard of the re-injected water quality.

In dithiocarbamate compounds, the ligand -CSS⁻ easily coordinates to metal cations in a bidentate chelating form. Since DTC (T403) had two or three ligands in its molecular (Fig. 2), a polymer matrix network structure (Fig. 4) was formed by the coordination reaction between the DTC agent and Fe²⁺. Consequently, flocs developed by the matrix filter out oil droplets as they migrate to the interface. The net capturing and sweeping behaviors of the flocs were the main flocculation mechanism. In addition, DTC (T403) took hydrophobic polyoxypropylene ether as the molecular skeleton, which is one of the properties of surfactants, and was able to facilitate oil droplet approach and coalescence. The flocs formed by DTC agents also showed stronger lipophilicity. These factors could play a positive role on flocculation effect.

2.3 Effect of HPAM on oil removal

The results shown in Fig. 3 indicate that flocculation effectiveness decreased significantly as HPAM concentrations increased when the dosages were below 20 mg/L. This suggests that high concentrations of HPAM had a negative effect on the treatment.

High concentrations of HPAM increased water viscosity greatly, with the apparent viscosity of the test samples containing different concentrations of HPAM (0, 200, 500, and 900 mg/L) determined as 1.05, 1.68, 2.45 and 3.30 mPa·sec, respectively. Based on coagulation kinetics, there are two types of particle collision and aggregation: perikinetic flocculation and orthokinetic flocculation. The former is induced by Brownian diffusion and the latter is forced by hydrodynamic shear gradients. The two collision mechanisms can be expressed as (Fukasawa and Adachi, 2006; Sato et al., 2004; Xiao et al., 2008; Bridgeman et al., 2008) Eqs. (2) and (3):

$$\left(\frac{dn}{dt}\right)_p = \frac{-4a_p k T n^2}{3\mu} \quad (2)$$

$$\left(\frac{dn}{dt}\right)_o = \frac{-2a_o G d^3 n^2}{3} = \frac{-2a_o d^3 n^2}{3} \times \sqrt{\frac{P}{\mu V}} \quad (3)$$

where, a_p is the collision efficiencies of perikinetic collision, a_o is that of orthokinetic collision at T , μ is the water viscosity, n is the particle number concentration, d is the particle size, k is the Boltzmann's constant, G is velocity gradient, P is power dissipated on stirring, and V is fluid volume.

As shown in Eqs. (2) and (3), perikinetic and orthokinetic collision efficiencies are both reversely related to water viscosity. Perikinetic collision primarily dominates dynamics of particles smaller than 1 μm , which showed

that increasing viscosity lowered collision and reaction rates between DTC and Fe^{2+} , leading to the formation of fewer polymer matrices. The orthokinetic mechanism mainly controls the collision rate of particles larger than 1 μm . Under the same stirring conditions, therefore, oil droplet capture and sweeping by the flocs weakened with water viscosity increase.

Increasing water film strength and negative zeta potential due to HPAM adsorption on oil droplets probably influenced the flocculation effect. Unlike cationic flocculants, however, the DTC agent could not produce an electric charge neutralization reaction with HPAM. Variations in HPAM concentration after flocculation with the increase of DTC (T403) are shown in Fig. 5. No significant reduction in polymer concentrations with DTC (T403) increase was observed. As the dosage increased, therefore, flocs formation was sufficient and HPAM was no longer a critical flocculation treatment factor. Figure 3 shows that residual oil concentrations in the different samples tended to be the same with dosage increase. Oil content decreased to less than 10 mg/L at the DTC (T403) dosage of 30 mg/L.

2.4 Effect of Fe^{2+} concentrations on oil removal

Simulated produced water with different Fe^{2+} concentrations were used to investigate the influence of metal cation concentrations on oil removal efficiency, under the condition of 25 mg/L DTC dosage (Fig. 6).

As shown in Fig. 6, residual oil concentrations decreased as Fe^{2+} ion dosage increased. When Fe^{2+} ion dosage was higher than 10 mg/L, the concentration of residual oil increased with continuous Fe^{2+} addition. It is possible that more ferrous ions chelating with DTC produced more polymeric matrices, which would have sunk down due to their larger density while residual oil captured in the matrix

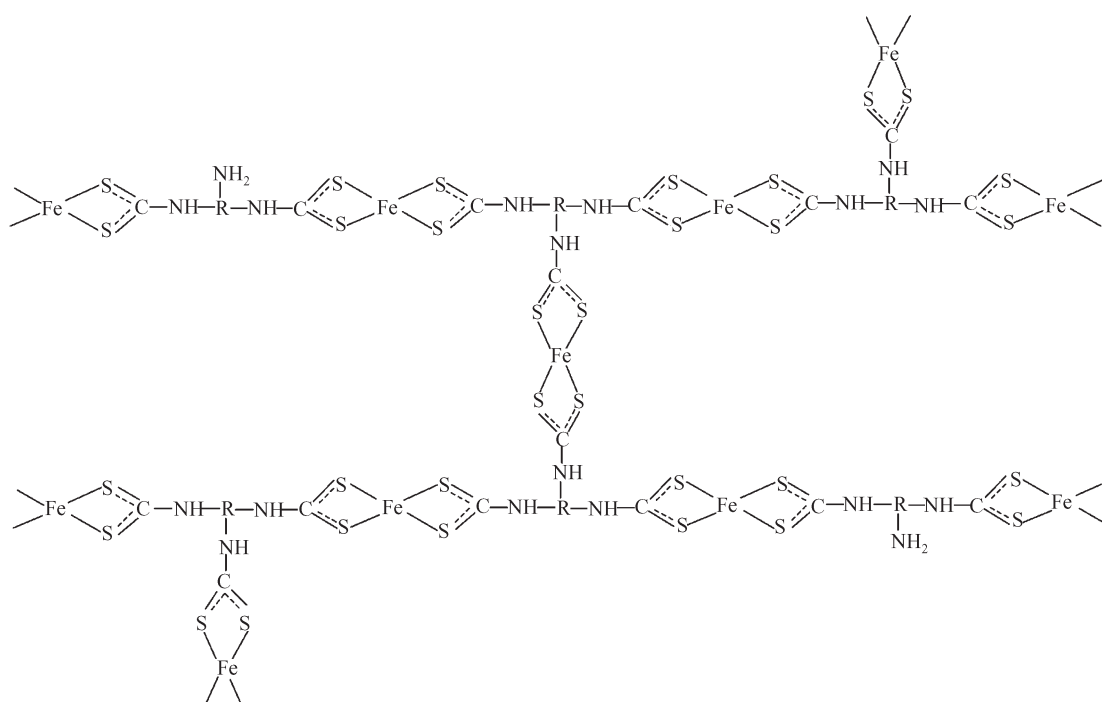


Fig. 4 Network structures of coordinated polymer matrix.

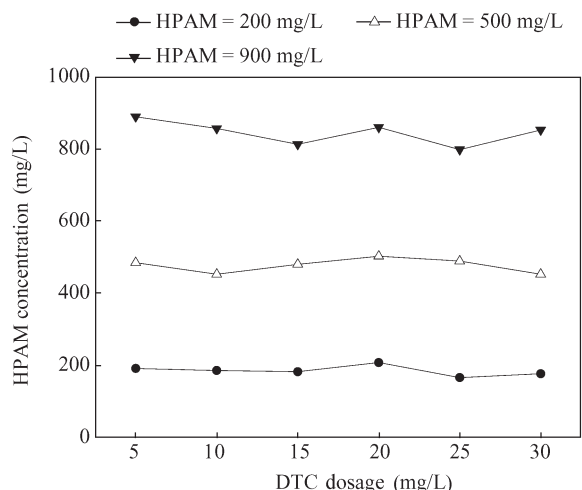


Fig. 5 Variations of HPAM concentration after flocculation with DTC (T403) increase.

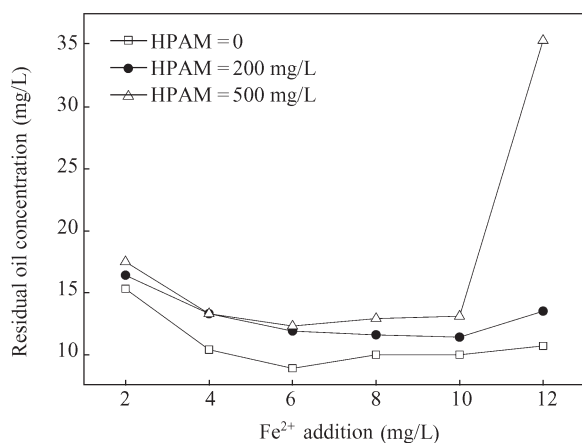


Fig. 6 Relationship of oil removal effect with the initial concentrations of Fe^{2+} .

would cause it to float up. As a result, trashy flocs, which failed to capture enough oil droplets and aggregate with other flocs, may be suspended in the water and cause the decline in supernatant quality. The more Fe^{2+} added, the more flocs were suspended in the water. At 25 mg/L DTC (T403) dosage, the optimal concentration of Fe^{2+} ions was 6 mg/L.

Figure 7 shows the variations of ferrous consumption with different Fe^{2+} addition and HPAM concentrations. Ferrous consumption was caused by the coordination reaction of DTC agent and formed flocs. Greater Fe^{2+} consumption suggested greater flocs formation. It should be noted that ferrous consumption in the test samples without HPAM was greater than the other samples, which strongly indicated that HPAM inhibited reaction rates between DTC and Fe^{2+} .

2.5 Effect of Fe^{3+} acting as the coordinated ion on oil removal

Fe^{2+} ions are easily oxidized to be tri-valence in water. We investigated whether Fe^{3+} could be taken as the center cations coordinated with DTC and used for clarifying wastewater. The results are shown in Fig. 8.

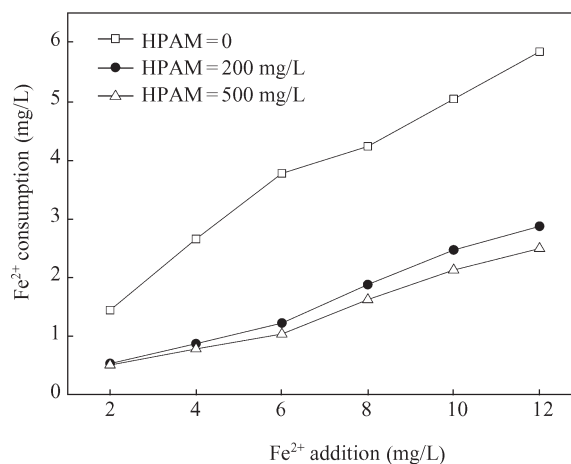


Fig. 7 Fe^{2+} consumption at different HPAM concentrations.

Although residual oil concentrations showed a continuous decrease with increasing Fe^{3+} dosage in the water samples containing no HPAM, brown flocs were formed instead of the expected black of chelates formed by DTC and Fe^{3+} . Tri-valence iron does not exist as simple metal ions (Fe^{3+}) in solution as it can easily coordinate with oxygen atoms. Instead, it usually appears as hydrated $Fe(H_2O)_6^{3+}$ in acidic solutions and as polyhydric ions through a series of hydrolytic and complex reactions when pH increases. Furthermore, based on the hard-soft acid-base principle, Fe^{3+} ions coordinate with oxygen atoms more easily than with sulfur atoms. In this case, the decrease in residual oil concentration in water samples without HPAM was attributed to the coagulation behavior of Fe^{3+} salts.

In addition, there was little oil removal effect on the water samples containing HPAM (Fig. 8) because the carboxylic groups on HPAM coordinated with Fe^{3+} and made the cations lose their coagulative performance.

2.6 Effect of mineral salts

Because mineral salts are dissolved in the injected water during the oil exploitation process, produced water contains a large amount of mineral ions, mainly Na^+ , Ca^{2+} ,

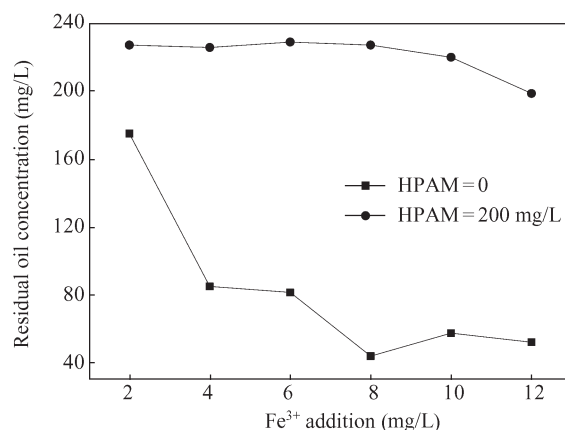


Fig. 8 Effect of Fe^{3+} acting as coordinated ions instead of Fe^{2+} on oil removal.

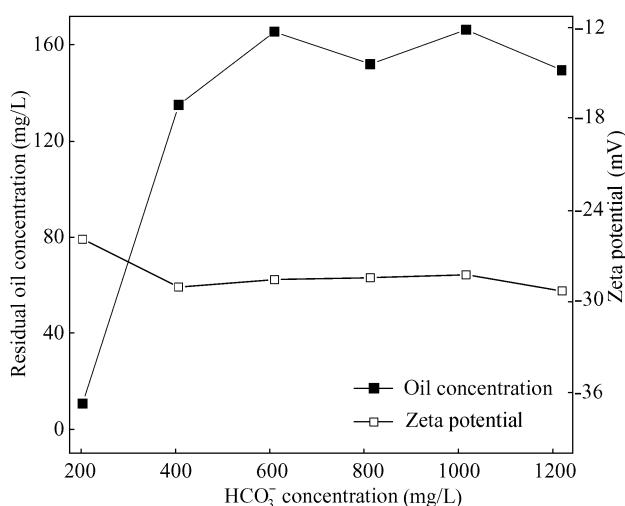
Table 1 Relationship of residual oil concentration with mineral salt ions

Sample	Mineral salt	Corresponding ion concentration (mg/L)					Residual oil concentration (mg/L)
		Na ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	HCO ₃ ⁻	
1	–	–	–	–	–	–	7.14
2	NaCl	2834	–	–	4374	–	6.43
3	CaCl ₂ + MgCl ₂ ·6H ₂ O	–	102	38	293	–	8.21
4	NaHCO ₃	440	–	–	–	1167	157.14
5	NaHCO ₃ + CaCl ₂	440	102	–	181	1167	11.07
6	NaHCO ₃ + MgCl ₂ ·6H ₂ O	440	–	38	112	1167	150.35
7	NaHCO ₃ + NaCl	3274	–	–	4374	1167	152.14

Mg²⁺, HCO₃⁻ and Cl⁻. To study the effect of each mineral ion type on flocculation, one or two of the following mineral salts, NaCl, NaHCO₃, MgCl₂·6H₂O and CaCl₂, were added according to the content of each mineral ion type in wastewater from the Tuoyi Station of the Shengli Oilfield. Preparation methods of mineral salts solution are displayed in Table 1. In this experiment, HPAM was not added. The Fe²⁺ and DTC (T403) dosages were 10 mg/L and 25 mg/L, respectively.

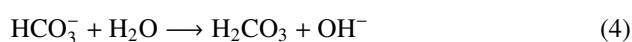
As shown in Table 1, sample #1 (without mineral salts) and sample #2 (containing NaCl only) both showed excellent oil removal efficiency, which indicated that Na⁺ and Cl⁻ had no adverse impact on flocculating performance. Sample #3, CaCl₂ and MgCl₂·6H₂O, also showed no negative influence on oil removal. A poor flocculation parameter was obtained from sample #4 (NaHCO₃ only), indicating that HCO₃⁻ had a negative effect on flocculating treatment. Sample #5 showed, however, that the negative effect produced by the addition of HCO₃⁻ appeared diminished when NaHCO₃ was added together with CaCl₂. We concluded that Ca²⁺ inhibited the influence of HCO₃⁻. When NaCl or MgCl₂·6H₂O was added with NaHCO₃ (samples #6 and #7), however, such inhibition was not observed.

We also investigated the effect of Ca²⁺ and HCO₃⁻ on residual oil removal in terms of their concentrations and the theory behind it. Figure 9 suggests that oil removal became poor when HCO₃⁻ exceeded 400 mg/L. Zeta potentials, however, showed no significant difference at different HCO₃⁻ concentrations, which indicates that Zeta

**Fig. 9** Effect of HCO₃⁻ on oil removal and zeta potential.

did not play a dominant role in removing oil. Figure 10 suggests that when HCO₃⁻ concentration was 1167 mg/L, 80 mg/L of Ca²⁺ already inhibited the influence of HCO₃⁻ with flocculation performance.

Based on inorganic chemical theories, HCO₃⁻ ions have two hydrolysis pathways (Reactions (4) and (5)):



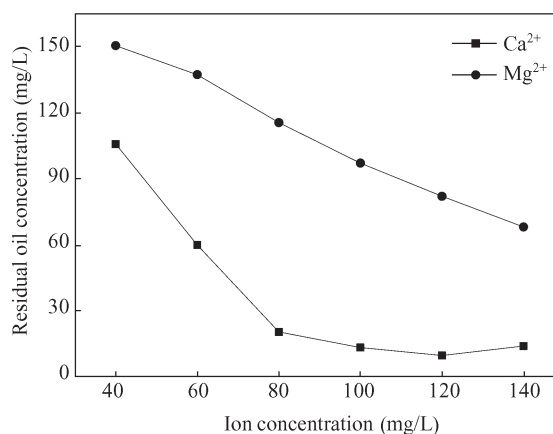
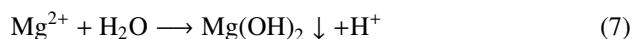
When NaHCO₃ exists alone in the solution, Reaction (4) is the major pathway and produces a basic solution. As a result, Fe²⁺ in the test samples with HCO₃⁻ was oxidized much more rapidly than without HCO₃⁻ as OH⁻ promoted the following Reaction (6):



Consequently, the presence of HCO₃⁻ leads to a rapid decrease in oil removal efficiency (Fig. 9), due to a lack in metal cation and DTC (T403) coordination.

The precipitation reaction between Ca²⁺ and CO₃²⁻, however, promoted Reaction (5) and restrains Reaction (4) and Reaction (6). Therefore, the addition of Ca²⁺ inhibited the negative effect of HCO₃⁻ and improved oil removal performance.

As shown in Fig. 10, Mg²⁺ ions were similar but relatively less effective compared with Ca²⁺ on inhibiting the negative effect of HCO₃⁻, which may be related to the fact that Mg²⁺ ions can hydrolyze easily in the solution:

**Fig. 10** Effect of Ca²⁺ or Mg²⁺ on oil removal. Samples were added with 1167 mg/L of HCO₃⁻.

Reactions (4) and (7) promoted each to proceed. As a result, HCO_3^- ions were transformed to H_2CO_3 . Residual oil concentration therefore descended and oil removal efficiency increased with the increase of Mg^{2+} ions (Fig. 10).

3 Conclusions

(1) The flocculant DTC (T403) synthesized by Jeffamine-T403 and CS_2 in the basic solution had three dithiocarbamic ligands as terminated groups and could coordinate with Fe^{2+} ions to form network polymer matrices (flocs). The capturing and sweeping behavior of the flocs network structure on oil droplets was identified as the main flocculation mechanism.

(2) High concentrations of HPAM increased viscosity, which not only decreased reaction rates between DTC (T403) and Fe^{2+} and the formation of flocs, but also influenced the ability of flocs on capturing and sweeping oil droplets. At DTC (T403) dosages lower than 20 mg/L, oil removal rates decreased with HPAM increase. As the dosage increased, enough flocs formed and HPAM was no longer a significant factor influencing oil removal efficiency. The residual oil content was less than 10 mg/L at DTC (T403) dosages of 30 mg/L and 10 mg/L of Fe^{2+} ions.

(3) The flocs capturing and sweeping enough oil droplets would float up. At the same DTC (T403) dosage, the more Fe^{2+} ions that existed in the wastewater, the more flocs were formed by the reaction between DTC (T403) and Fe^{2+} . Flocs that had not captured enough oil droplets, however, were suspended in the water and influenced supernatant quality. At 25 mg/L DTC(T403) dosage, the optimal concentration of Fe^{2+} ions was 6 mg/L. Fe^{3+} could not be used as center ions to coordinate with DTC (T403) and form effective flocs.

(4) HCO_3^- had a negative effect on oil removal due to its hydrolysis producing OH^- , which promoted the oxidation of Fe^{2+} , but Ca^{2+} and Mg^{2+} inhibited hydrolysis of HCO_3^- and improved flocculation effect.

Acknowledgments

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