Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23538

142 (2019) 185–192
February

Emulsifying and demulsifying chemistry for enhancing the ClO_2-oxidative separation pilot of ultrastable oil-water emulsions

Dandan Yuan, Shihao Liu, Yuli Zhang, Xin Sui, Chunhong Nie, Hong Jiang, Baohui Wang*

College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing, China, Tel. +86 13359509696; Fax: +86 459-6503170; email: wangbh@nepu.edu.cn (B. Wang), Tel. +86 459-6503331; email: yuandandan@nepu.edu.cn (D. Yuan), Tel. +86 459-6504498; email: shliu@stu.nepu.edu.cn (S. Liu), Tel. +86 13836999275; email: zyl@nepu.edu.cn (Y. Zhang), Tel. +86 459-6504368; email: suixin@nepu.edu.cn (X. Sui), Tel. +86 18804595357; email: chunhongnie@126.com (C. Nie), Tel. +86 13836709203; email: jianghong@nepu.edu.cn (H. Jiang)

Received 10 July 2018; Accepted 27 November 2018

ABSTRACT

Due to the difficult task of demulsification of ultrastable oil-water emulsions during the middle and later stages of oil production, many technologies have been developed for the realization of this goal. An alternative and facile strategy of efficient oil/water separation, namely, the ClO_2-oxidative demulsification, had emerged and been piloted for the treatment of ultrastable oil-water emulsified layers in Chinese oil fields. For an in-depth understanding of the mechanistic chemistry of the ClO_2-oxidative demulsification and enhancement of the technical route, the chemistry and mechanism were studied in this paper. We started with an analysis of the pilot technical route and formation/structure of oil-water emulsifying layer stabilized by specific interfacial-active substances, exemplified by the ultrastable oil-water separation/demulsification in the settling tank of the oil field. Experimental tests were employed for proving the technical pathway and chemistry of the ClO_2 demulsification, including the oxidation reaction and thermodynamics, as well as kinetics and process conditions. Combining the theoretical and experimental results, the pathways and mechanisms were schematically presented to provide insight into the ClO_2-oxidative demulsification. The obvious chemistry totally provided a valuable knowledge of its reactivity for insight into the demulsification of ClO_2 oxidation. The data can be recognized for understanding and instructing the pilot operation of the ClO_2 oxidative demulsification in oil fields.

Keywords: Oil field; Demulsification; Chlorine dioxide; Oxidation; Oil-water emulsifying layer

---

1. Introduction

Crude oil production has recently encountered a significant challenge in the form of low recovery rates. Many technologies designed to enhance oil recovery have ubiquitously been applied in Chinese oil fields, such as the polymer flooding and alkali/surfactant/polymer (ASP) flooding methods [1–4]. The relevant problem of demulsification of ultrastable oil-water emulsions has arisen with the system's production of waste [5,6]. The water layer usually contains a high residual concentration of polymer, alkaline material, and surfactants containing a high viscosity and oil content. So the demulsification process is becoming a critical issue because it affects the environmental and economic aspects of oil production. Considerable technologies have also been developed to promote an efficient demulsification in oil fields such as chemical demulsification [7–12], physical demulsification [13–18], and biological demulsification [19,20]. Although they have been proven to be effective, most of these methods involve heating and electrical techniques, which make them expensive due to the intensive energy consumption [21,22]. Thus, it is essential to develop an alternative for this specific demulsification [23].

---

* Corresponding author.

1944-3994/1944-3986

Currently, the strategies for demulsification are focused on the chemical oxidation processes due to a high effectiveness and smooth operation.

Based on the advantages of this technique for the treatment of organic pollutants in wastewater, chemical oxidation is the best choice for the demulsification. The promising application of chlorine dioxide has been shown to be the best option for the oil-water demulsification in the laboratory and pilot-scale studies. As an alternative, chlorine dioxide is suitable due to a high oxidation potential and easy manipulation. Hence, an application of chlorine dioxide could achieve both oxidative elimination of various organic compounds and reduced materials, which could dominate the composition of the emulsifying layer and consequently breakup the oil/water interfacial structure. Until now, chlorine dioxide has been suggested and investigated for this novel application with a great effectiveness and high efficiency as a pilot operation in the Chinese oil fields [24]. For an in-depth understanding of the technical route and mechanistic chemistry of demulsification promoted by ClO_2 oxidation, the chemical fundamentals and mechanisms were studied herein. By the exemplification of the oil-water separation/demulsification in the settling tank of the oil field, the theoretical and experimental results were schematically presented for an insightful demonstration of the chemistry and mechanisms.

2. Experimental sections

2.1. Chemicals and preparation of the emulsion

All the chemicals, such as ClO_2 (0.6% aqueous solution, Tianjin Chemicals, Tianjin, China) and H_2SO_4 (98%, AR, Damao Chemicals, Tianjin, China) were used as received. The emulsion of the ultrastable oil-water emulsifying layer was sampled and separated freshly from the settling tank of the transportation system in the Chinese Daqing oil field [25,26].

2.2. Analysis of the chemical composition of the emulsifying layer

After the ultrastable oil-water emulsifying layer was freshly sampled and separated, the oil and water contents were determined by conventional heating dehydration. The physical structure of the oil-water emulsifying layer was divided via the analysis of phases including the water phase, the oil phase, and the solid phase (suspended solid) from the breaking emulsion. The chemical compositions (except for the water and oil), such as the FeS, FeO, Fe_2O_3 (corrosion products), natural surfactant (parasitic), PAM (polyacrylamide), and surfactant (foreign from the ASP), were analyzed by a combination of chemical and instrumental methods. The particular compositions were studied by a complex way, which first used a titration method to analyze the carbonates and then used acidic dissolution to determine the insoluble residue. Finally, a colorimetric method and atomic absorption spectrometry were utilized for the analysis.

2.3. Demulsification test of oil-water emulsion (emulsifying layer)

The rate/degree of the demulsification was evaluated by a quiescent gravitational settling technique at different temperatures [27]. The schematic diagram of the demulsification method is shown in Fig. 1. The received emulsions were allowed to cream and settle down for several minutes for stability. The volume of the emulsion and water was recorded as the initial value. The chemicals (ClO_2, H_2SO_4) were added to the emulsion for the full mixture at constant temperature. Then, it was settled in a still stand such that the aqueous phase, oil phase, and emulsion were separated by gravitational settling. The volume of the water layer was recorded by measuring phase separation of quiescent settling at intervals.

Dehydration rate was calculated to estimate the effectiveness of the demulsification on the oil-water emulsions. Accordingly, the dehydration rate was calculated by

$$\text{Dehydration rate } \eta_{\text{dewater}}(\%) = \left(\frac{V}{V_0}\right) \times 100\% \tag{1}$$

and the rate of residual water in the emulsion is given by

$$\eta_{\text{water}}(\%) = 1 - \eta_{\text{dewater}} = \frac{(V_0 - V)}{V_0} \times 100\% \tag{2}$$

where V is the volume of the separated water during the demulsification and V_0 is the initial water content in the emulsion (the emulsifying layer). The initial content (V_0) in the emulsion was determined by the conventional thermal dehydration method.

3. Results and discussion

3.1. Practical analysis of technical route of the demulsification via ClO_2 oxidation

The Daqing oil field, one of the biggest oil outputs in China, has entered the late stages of production and has incorporated many applications for enhanced oil recovery. Many operating systems have been deteriorated by the conventional techniques and facilities at this point.

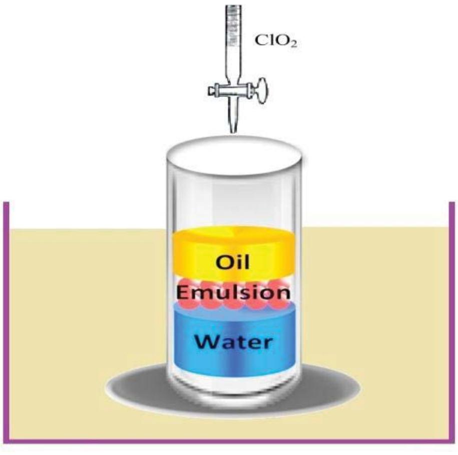

Fig. 1. Setup of the ClO_2-oxidative demulsification in the laboratory test.

Alternatives have urgently been needed. For the transportation of settling tank, a huge layer of oil-water emulsion, commonly known as the sludge, is aggregated in the middle of the tank. The emulsion has a long-term stability ranging from 1 to 5 d. The typical treatment such as the addition of demulsifying agents (nonoxidative chemicals) has failed in promoting a fast and efficient separation. So, the chemical oxidation via demulsification was first studied in the laboratory. The pilot field test of the demulsification by ClO$_2$ oxidation has been successfully applied in the transportation settling tank with a real effectiveness and smooth operation in the Daqing oil field, China. The technical route is schematically displayed in Fig. 2. Primary equipment in the system is a tanked chemical reactor with a heating unit, chemical injection pump, stirring device, and control box. The emulsion (transition layer) collected from the settling tank was pumped, and the chemicals were injected and mixed in the reactor. The separation occurred by keeping a constant retention time. Then, the water and oil were pumped to the next tank. The rate/degree of the demulsification can be controlled by the ClO$_2$ dosage, reaction temperature, and retention time according to the degree and stability of the emulsifying layer.

3.2. Analysis of the formation/structure of oil-water emulsion stabilized by the specific interfacial-active substances

Based on the fundamentals of emulsion chemistry, there are three major proposed mechanisms that possibly rule the stability of emulsions against demulsification. (1) The surfactant stabilization due to the orderly arrangement of the interfacial film between water and oil, which is essential for the formation of emulsion, and the parasitic and foreign surfactant for the oil; (2) depletion stabilization due to the surface-charged film, which is set by the oil-water environments such as the ions and wcompounds; and (3) structural stabilization due to the aggregation and viscosity of interfacial substances, which is supported by the specific substances such as the parasitic asphalts, foreign polymers, and particle colloids. In general, the interfacial film is a key factor to control the stability of emulsions. Thus, the strategies for the demulsification undoubtedly are to destroy the substance and structure of the interfacial film between water and oil, consequently breaking the film. Commonly, the interfacial film consists of orderly arrangement of emulsifiers (e.g., surfactants, sometimes fine particles, and other interface-active substances). Replacement or removal of the emulsifiers is an important route to demulsification. The emulsifying layers from the Daqing oil fields commonly exist in the form of O/W or W/O emulsions as shown in Fig. 3.

The presence of native surface-active fractions, such as organic acids (fatty acid and naphthenic acid), asphaltenes, and resin and porphyrin materials, can be adsorbed onto the interface and form a film at the oil-water interface, resulting in high stability of emulsions. As most of the foreign PAM and surfactant reside in the produced water from the polymer/ASP flooding, the viscosity of wastewater is rather high and the oil or water droplets in it are tiny with an even distribution [28]. The PAM and other surfactants, when in contact with both the oil and water phases, often result in the formation of highly stabilized emulsions. It has been found that the long-chain PAM adsorbs and surrounds the droplet surface, thus acting as a barrier preventing the droplets from coalescence. Viscoelastic PAM molecules in the wastewater, by forming a viscoelastic interface, influence on the interfacial rheological properties. According to Bancroft [29], the stability of any emulsion is mainly due to the nature of the finished interfacial film. The stability of the film is strongly dependent on its interfacial rheological properties. The interfacial viscoelasticity blocks the aggregation and flocculation of emulsified droplets. Therefore, the small size of the oil droplets and the high viscosity of the produced water are expected to make the oil-water separation difficult for the produced water. During the oil droplet coalescence, an increase of the strength of oil/water films results in the difficulty for oil droplets to break the interfacial film and coalesce into bigger ones. The PAM in the produced water also increases the produced water viscosity, which decreases the lifted velocity of oil droplets. The PAM surely plays a significant role in emulsion stability.

The typical data of the analysis for the interface-active substances in the Daqing oil fields are revealed in Table 1.

On the basis of the above descriptions and analytical results plus our previous studies [30,31], a schematic diagram is proposed for illustrating the microstructure and interface-active compositions of the emulsions from the oil field as shown in Fig. 4. The native and foreign surface-active substances, PAM molecules, and particle colloids are orderly set on the interface to stabilize the oil-water emulsions.

So, it is evident that the interfacial film contains the native and foreign surfactants, active asphaltenes, PAM, FeS, FeO, Fe$_2$O$_3$, and soluble silica colloids. Surely, most of those are

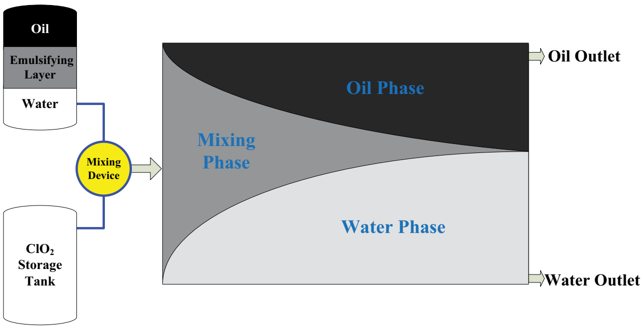

Fig. 2. Practical technical route of the ClO$_2$-oxidative demulsification in the pilot operation.

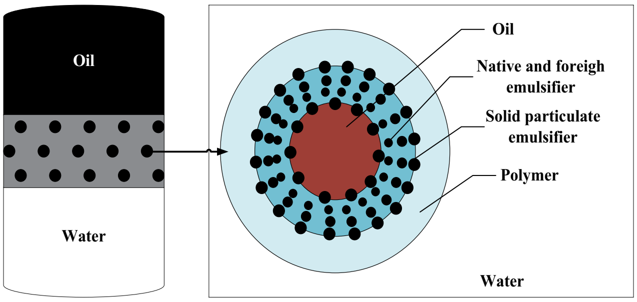

Fig. 3. Formation and structure of the ultrastable oil-water emulsifying layer in the settling tank.

Table 1
Typical data of the analysis for the interface-active substances in the Daqing oil fields

Interface-active substance	Native surfactants (denoted by long-chain organic acids)	Active asphaltenes	Foreign surfactants (denoted by sodium dodecyl benzenesulfonate)	PAM	FeS	FeO	Fe_2O_3	Soluble silica colloids (denoted by SiO_2)
Concentration (ppm)	3,800	8,500	360	550	65	36	72	260

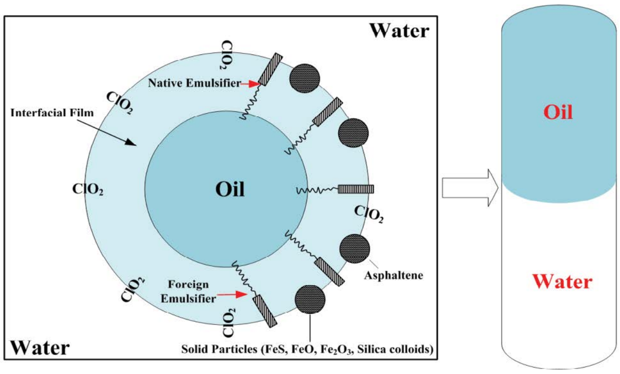

Fig. 4. Interface film structure, composition, and ClO_2 demulsification of the ultrastable oil-water emulsifying layer (emulsion) in oil fields.

chemically reduced substances. A key strategy for the interfacial film destruction is to oxidate the substances by using suitable oxidants with high oxidation potential, as they have low operational and economical cost and are harmless after chemical oxidation.

3.3. Fundamentals and chemistry of the demulsification of ClO_2 oxidation

The current study on the demulsification was switched to focus on the chemical oxidation. Regarding chemical oxidation techniques, some strong oxidants, such as chlorine, chlorine dioxide, $KMnO_4$, and hydroxyl radicals, have been widely applied for disinfection of potable waters and wastewaters and often for the transformation/elimination of undesired organic pollutants from drinking water [32]. Chlorine is one of the most widely used disinfectants for drinking water and wastewater treatment. Chlorine dioxide has been often used as an alternative disinfectant for chlorine, often to minimize the formation of chlorine-based disinfection by-products [33]. The hydroxyl radical is a primary oxidant in advanced oxidation processes such as UV/H_2O_2 and O_3/H_2O_2, and their applications have been considered for transforming various pollutants in potable waters as well as wastewaters for water reuse [34]. The hydroxyl radical is quite different from other oxidants because of its high reactivity and thus low selectivity [35]. Due to reaction velocity and nonselectivity, it can cause an uncontrollable reaction that limits application in the oil field sector.

Chlorine dioxide is a useful oxidizing agent that is widely used in water treatment. Its redox potential (1.511 V) is greater in comparison with similar oxidizing agents such as $KMnO_4$ (1.51 V), Cl_2 (1.36 V), ClO^- (0.89 V), and ClO_2^- (0.77 V). It has a strong reaction activity and oxidation capacity. If the oxidation capacity of chlorine is defined to be 100%, then the order of the oxidation capacity for several substances will be ClO_2 (263), H_2O_2 (209), $NaClO_2$ (157), $KMnO_4$ (111), Cl_2 (100), NaClO (93), Na_2O_2 (91), trichloroisocyanuric acid (89.7), $Ca(OCl)_2 \cdot 3H_2O$ (83), and sodium dichloroisocyanurate (60–64). The sequence of redox potential (V) in water is ClO_2 (1.511), $KMnO_4$ (1.51), Cl_2 (1.36), OCl^- (0.89), and ClO_2^-(0.77) . From these data, it is not difficult to see that chlorine dioxide as an oxidant has obvious advantages.

Chlorine dioxide has the half reaction and redox potential given by the following equation:

$$ClO_2 + 4H^+ + 5e^- = Cl^- + 2H_2O \phi^0 = 1.511V \tag{3}$$

As indicated in the aforementioned table and figures, there are many reducing substances contained in the interfacial film such as the native and foreign surfactants, active asphaltenes, PAM, FeS, FeO, and soluble reduced colloids.

The half reactions and redox potentials of the major substances are listed as follows:

- For Fe^{2+}: $Fe^3 + e^- = Fe^{2+}$ ($\phi^0 = 0.771$ V, 25°);
- For S^{2-}: $S + 2e^- = S^{2-}$ ($\phi^0 = -0.476$ V, 25°); $SO_3^{2-} + 4e^- = S$ ($\phi^0 = 0.449$ V, 25°); and $SO_4^{2-} + H_2O + 2e^- = SO_3^{2-} + 2OH^-$ ($\phi^0 = 0.172$ V, 25°).

The reduction potentials of the reducing substances are less than the oxidation potential of chlorine dioxide (1.511 V). It has been clearly understood that all the substances can be oxidized under standard conditions. It can be predicted that the oxidation reaction will be enhanced by lifting the temperature. Also, there are a lot of oil fractions inside and outside the interfacial film. According to the related potentials and data, the fractions, such as alkanes and aromatic hydrocarbons, cannot be oxidized.

For a clear exhibition of the substances, chemical compositions, and oxidative products, the process of the ClO_2 oxidation in the interfacial film is shown in Fig. 5.

The chemical mechanism of the reactions (in H_2SO_4 for acidification):

- with Fe^{2+} (typically in the case of $FeSO_4$),

$$3ClO_2 + 15FeSO_4 + 6H_2SO_4 = 7Fe_2(SO_4)_3 + FeCl_3 + 6H_2O \tag{4}$$

- with single and poly-sulfur (typically in case of S),

$$5S + 6ClO_2 + 8H_2O = 6HCl + 5H_2SO_4 \tag{5}$$

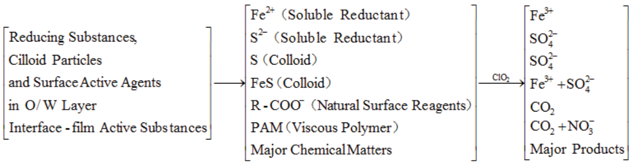

Fig. 5. Reactions of ClO_2 oxidation of substances in the interfacial film

- with S^{2-}(typically in case of Na_2S),

$$8ClO_2 + 5Na_2S + 4H_2O = 5Na_2SO_4 + 8HCl \tag{6}$$

- with FeS particles,

$$5FeS + 9ClO_2 + 2H_2O = Fe_2\left(SO_4\right)_3 + 3FeCl_3 + 2H_2SO_4 \tag{7}$$

- with FeO particles,

$$10FeO + 2ClO_2 + 15H_2SO_4 = 5Fe_2\left(SO_4\right)_3 + 2HCl + 14H_2O \tag{8}$$

- with organic interface-active agents (typically in the case of sodium dodecyl benzene sulfonate),

$$5C_{18}H_{29}NaSO_3 + 102ClO_2 = 90CO_2 + 19H_2O + 102HCl + 5NaHSO_4 \tag{9}$$

- with PAM (typically in case of acrylamide, monomer),

$$C_3H_5NO + 4ClO_2 = 3CO_2 + 4HCl + HNO_3 \tag{10}$$

The above results display that chlorine dioxide is feasible for the oxidation of the interface-active substances with a high redox potential. This clear chemistry offers valuable knowledge on the reactivity, thus providing insight into the demulsification of the ClO_2 oxidation.

3.4. Experimental tests for the enhancement of demulsification rate of ClO_2 oxidation

In typical chemical oxidation, the process will be dominated by temperature, oxidant, and pH value. So, three major reaction conditions are needed to be studied for enhancing the demulsification promoted by ClO_2.

The dehydration rate verified at the reaction temperature was performed under different temperatures by the emulsion from the ultrastable emulsifying layer acidified by the proper H_2SO_4.

Fig. 6 shows the changes in dehydration rate as a function of the reaction temperature. It could be concluded that the dehydration rate has a high dependence on the temperature of the reaction. The rate of the residual water decreased exponentially with the temperature increase. The oxidation reaction was enhanced at high temperature, reaching 85.23% at 55°C (0.1% acid weight in the emulsion).

The strong effect of temperature suggests that the oxidation of ClO_2 is an endothermic reaction. Also, it is likely due to the variation of the molecular mobility at different temperatures. At low temperature, the molecules move slowly and the water/oil separation is difficult. At high temperature, the fast molecular mobility enhances the reaction and separation which dramatically reduces the interfacial tension of the layer. As a consequence, the oil/water emulsion is easily segregated, which results in the increase of the dehydration rate.

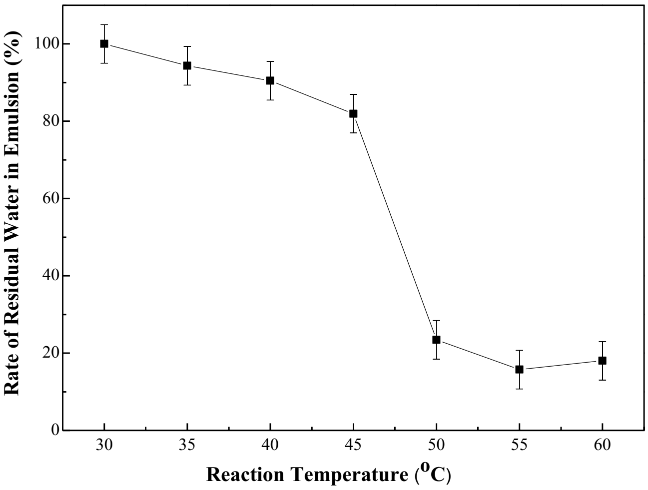

Fig. 6. Dependence of dehydration rate of the ultrastable emulsion on temperature.

The aqueous ClO_2 solution is easily decomposed. However, it is more stable under acidic condition due to its disproportionate reaction. Therefore, the ClO_2 solution can be stabilized by lowering pH to make the ClO_2 stable. Simultaneously, the oxidation effect of ClO_2 is strengthened in such a condition, which is conducive to the oxidation of the demulsification. Paying attention to the acidic effect is important.

Based on the dependence of the ClO_2 oxidation reaction (ϕ^0) on pH value, $\phi^0 = 1.511 - 0.0473\,\mathrm{pH} + 0.0118\lg[ClO_2]/[Cl^-]$; pH value surely affects the dehydration rate promoted by the chemical oxidation. So, finding the proper pH value is a key factor to perform the dehydration successfully.

The addition of acid makes the ClO_2 chemically stable as ClO_2 undergoes disproportionation reaction in an acidic environment. Therefore, we studied the acid volume and its influence on the dehydration rate of the transition of water layer shown in Fig. 7. The figure indicates the dependence of dehydration rate of the emulsion on acidification (acid weight in the emulsion) under a temperature of 30°C by adding a concentration of 3,500 ppm of ClO_2. It reveals that by increasing the acid volume from 0.1% to 1%, there is a significant increase in the dehydration. The largest dehydration rate was promoted by 0.5% (v/v) of acidic volume. Beyond this, the dehydration rate tends to decrease with the increase of acid volume.

Similarly, as demonstrated in Fig. 8, the dehydration rate is significantly reduced when the ClO_2 concentration is less than 1.05%. With an increase of the ClO_2 concentration, the dehydration rate increases sharply, reaching 82.49% and remaining stable when the concentration is beyond 3.5%.

It has been reported that the acidity can enhance the oxidation effect of ClO_2 so that the dehydration rate is higher in acidic solutions. However, when the acid volume is saturated, the charge effect increases on the surface of

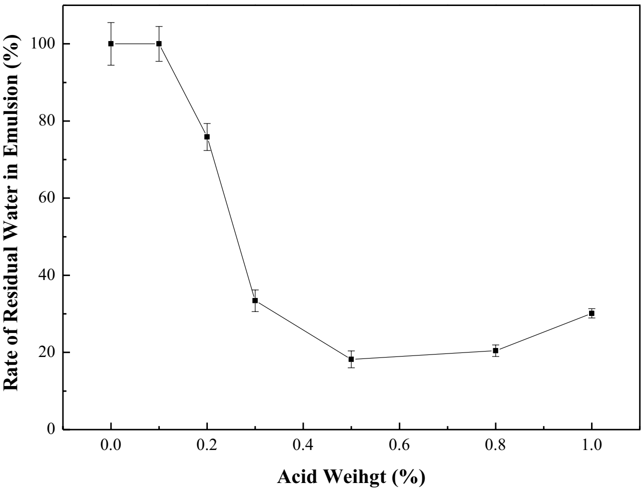

Fig. 7. Dependence of dehydration rate of the ultrastable emulsion on acidification (acid weight in the emulsion).

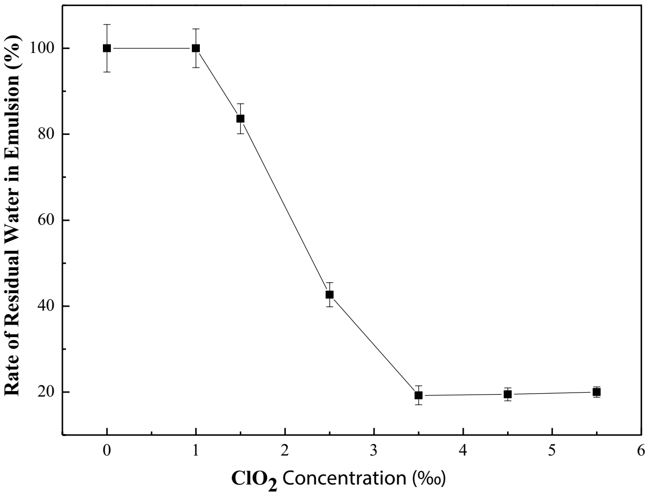

Fig. 8. Dependence of dehydration rate on ClO_2 concentrations.

dispersed droplets, leading to a thicker diffusion layer and decreased dehydration rate.

The optimized conditions for the demulsification promoted by ClO_2 oxidation can be provided by an operation that considers the above results. Based on the results, we can choose the reaction temperature, reaction time, ClO_2 concentration, and acid weight to obtain an optimized operation. Thus, the optimized reaction time is 4 h (compared with more than 48 h of the quiescent settling demulsification); the reaction temperature is 55°C (the reservoir temperature of 45°C–55°C in the Daqing oil field); ClO_2 concentration is 3.5‰; and the acid volume is 0.5%. A dehydration rate of 86.11% was achieved under these optimal conditions.

3.5. Kinetic rate of demulsification promoted by ClO_2 oxidation

Fig. 9 shows the changes of dehydration rate for an ultrastable emulsion as a function of reaction time. It is illustrated that the dehydration rate is extremely inefficient during the initial 1 h of the reaction. The dehydration was improved with the increase of the reaction time. It reached 84.18% and remained unchanged after 4 h. One speculates that the reaction of the oxidation takes place throughout the extended reaction time, thus raising the dehydration rate. Compared with the quiescent settling method, the demulsification promoted by ClO_2 oxidation is faster and more efficient.

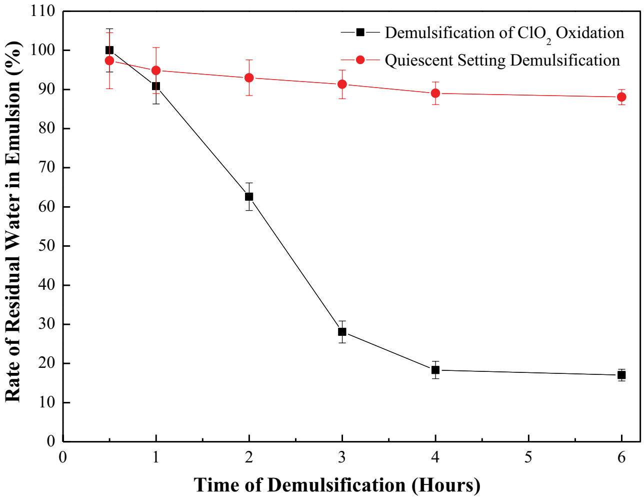

Fig. 9. Dependence of dehydration rate of the ultrastable emulsion on reaction time.

For the emulsion breaking, the kinetic equation can be expressed generally as

$$\left[\text{Emulsion}\right]_{\text{initial time}} = \left[\text{Emulsion}\right]_{\text{time}} + \text{ free water} \tag{11}$$

Denoted by the concentration of water, it will yield

$$\left[C_{\text{water}}\right]_{\text{initial time}} = \left[C_{\text{water}}\right]_{\text{time}} + \text{free water} \tag{12}$$

where the $[C_{\text{water}}]_{\text{initial time}}$ is the water content in the emulsion at the initial time, being identical to one reactant, and the $[C_{\text{water}}]_{\text{time}}$ is the water in the emulsion at some other time, being identical to one product. So, we describe the rate of the reaction regarding the rate of disappearance of water in the emulsion,

$$\text{Rate} = -\frac{dC_{\text{water}}}{dt} = k^{\alpha}_{\text{water}} C^{\alpha}_{\text{water}} \tag{13}$$

In Eq. (13), k_{water} is called the rate constant and the exponent α is called the order.

For a reaction of first order ($\alpha = 1$),

$$-\frac{dC_{\text{water}}}{dt} = k_{\text{water}} C_{\text{water}} \tag{14}$$

After the integration, one obtains an equation for k_{water}:

$$k_{\text{water}} = \frac{1}{t} \ln \frac{C_{0\,\text{water}}}{C_{\text{water}}} \tag{15}$$

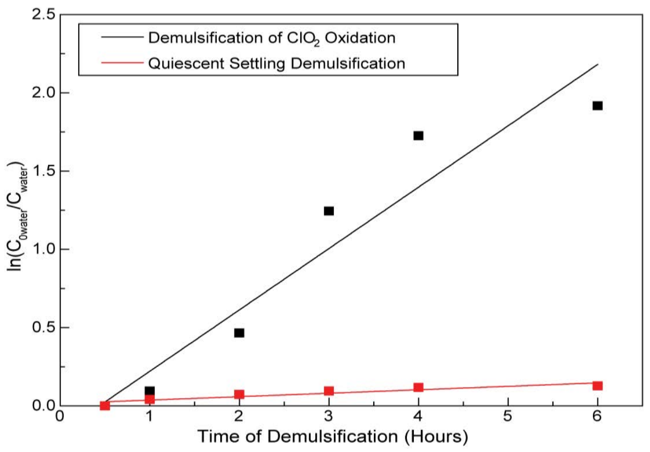

Fig. 10. Kinetic rate of the demulsification of ClO_2 oxidation.

where the C_{0water} is the water concentration in the emulsion at the initial time and C_{water} is the concentration of water in the emulsion at some other time.

The dehydration rate dependence on reaction time (shown in Fig. 9) was used to calculate the kinetic rate by fitting Eq. (15) with the data curves illustrated in Fig. 10.

Apparently, a large enhancement in kinetic rate is driven by the demulsification of ClO_2 oxidation. The kinetic rate constants are 0.392 for $K_{dewater\text{-}ClO_2}$ (the demulsification promoted by ClO_2 oxidation) and 0.022 for $K_{dewater\text{-}settling}$ (quiescent settling demulsification) at 55°C. For comparison, the ClO_2 oxidation surpasses 17.8 times the quiescent settling demulsification. Thus, the oxidation strategy stands as a fast and efficient process.

4. Conclusions

As a strategy to face the substantial challenge of tough demulsification during the latter stages of oil production, a novel technique of ClO_2-oxidative demulsification has been successfully applied in a pilot test for treatment of the ultrastable oil-water emulsifying layer in the Chinese oil fields. The mechanistic chemistry of the demulsification promoted by ClO_2 oxidation was studied for an in-depth understanding and enhancement of the technical route and chemical pathway. The conclusions are summarized as (1) the analysis of the practical technical route and formation/structure of the emulsion schematically demonstrates that the interfacial film contains native and foreign surfactants, such as active asphaltenes, PAM, FeS, FeO, Fe_2O_3, and soluble silica colloids. Most of these are reduced substances and a key strategy for the demulsification is to promote an oxidation of the substances; (2) a study of chlorine dioxide chemistry, which is a suitable oxidant with high oxidation potential, easy usage, low cost, and no post-use harm, compared with the other chemicals in common usage at the oil field; (3) the chemistry for the oxidation of the interface-active substances by chlorine dioxide displays that chlorine dioxide is efficient and feasible for the oxidation; (4) the kinetic rate reveals a huge enhancement in the rate of the ClO_2 oxidation demulsification; and (5) the tests of the demulsification provide the optimized conditions as follows: the reaction temperature of 55°C (45°C–55°C of the Reservoir in the Daqing oil field), reaction time of 4 h, ClO_2 concentration of 3.5% (w/w), and acid weight of 0.5% (w/w) to achieve the dehydration rate of 86.11% for the emulsion treatment from the specific oil-water emulsion in the Daqing oil field. The data can be applied effectively for directing the practical demulsification of the ClO_2 oxidation.

Acknowledgements

This research is financially supported by the National Science Foundation of Heilongjiang Province (Grant No. E2018014) and Science Foundation of Northeast Petroleum University(Grant No. 2018018). We are grateful to Daqing Oilfield, PetroChina, for their assistance.

References

[1] J.J. Sheng, A comprehensive review of alkaline–surfactant–polymer (ASP) flooding, Asia-Pac. J. Chem. Eng., 9 (2014) 471–489.
[2] H. Saboorian-Jooybari, M. Dejam, Z. Chen, Heavy oil polymer flooding from laboratory core floods to pilot tests and field applications: half-century studies, J. Petrol. Sci. Eng., 142 (2016) 85–100.
[3] H. Ma, B. Wang, Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection, J. Hazard. Mater., 132 (2006) 237–243.
[4] H. Wang, J. Liu, H. Xu, Z. Ma, W. Jia, S. Ren, Demulsification of heavy oil-in-water emulsions by reduced graphene oxide nanosheets, RSC Adv., 6 (2016) 106297–106307.
[5] Z.L. Kiss, I. Kovács, G. Veréb, C. Hodúr, Z. László, Treatment of model oily produced water by combined pre-ozonation–microfiltration process, Desal. Wat. Treat., 57 (2016) 23225–23231.
[6] M. Ebrahimi, Z. Kovacs, M. Schneider, P. Mund, P. Bolduan, P. Czermak, Multistage filtration process for efficient treatment of oil-field produced water using ceramic membranes, Desal. Wat. Treat., 42 (2012) 17–23.
[7] T. Ichikawa, Electrical demulsification of oil-in-water emulsion, Colloids Surf. A Physicochem. Eng. Asp., 302 (2007) 581–586.
[8] L. Fu, G. Zhang, J. Ge, K. Liao, H. Pei, P. Jiang, X. Li, Study on organic alkali-surfactant-polymer flooding for enhanced ordinary heavy oil recovery, Colloids Surf. A Physicochem. Eng. Asp., 508 (2016) 230–239.
[9] M. Nikkhah, T. Tohidian, M.R. Rahimpour, A. Jahanmiri, Efficient demulsification of water-in-oil emulsion by a novel nano-titania modified chemical demulsifier, Chem. Eng. Res. Des., 94 (2015) 164–172.
[10] S.A. Issaka, A.H. Nour, R.M. Yunus, Review on the fundamental aspects of petroleum oil emulsions and techniques of demulsification, J. Petrol. Environ. Biotechnol., 6 (2015) 1.
[11] C. Hou, Q. Jiang, Z. Song, G. Tan, Z. Shi, Combined heating and chemical treatment for oil recovery from aging crude oil, Waste Manage. Res., 34 (2016) 686–690.
[12] Z. Wang, X. Le, Y. Feng, Z. Hu, Dehydration of aging oil by an electrochemical method, Chem. Technol. Fuels Oils, 50 (2014) 262–268.
[13] Y. Chen, X. Lin, N. Liu, Y. Cao, F. Lu, L. Xu, L. Feng, Magnetically recoverable efficient demulsifier for water-in-oil emulsions, Chem. Phys. Chem., 16 (2015) 595–600.
[14] S. Li, N. Li, S. Yang, F. Liu, J. Zhou, The synthesis of a novel magnetic demulsifier and its application for the demulsification of oil-charged industrial wastewaters, J. Mater. Chem. A, 2 (2014) 94–99.
[15] Y. Kagawa, T. Ishigami, K. Hayashi, H. Fuse, Y. Mino, H. Matsuyama, Permeation of concentrated oil-in-water emulsions through a membrane pore: numerical simulation using a coupled level set and the volume-of-fluid method, Soft Matter, 10 (2014) 7985.

[16] T. Roques-Carmes, H. Monnier, J.F. Portha, P. Marchal, L. Falk, Influence of the plate-type continuous micro-separator dimensions on the efficiency of demulsification of oil-in-water emulsion, Chem. Eng. Res. Des., 92 (2014) 2758–2769.
[17] W. Wang, Z. Ye, F. Li, Removal of oil from simulated oilfield wastewater using modified coal fly ashes, Desal. Wat. Treat., 57 (2016) 9644–9650.
[18] M. Ebrahimi, O. Schmitz, S. Kerker, F. Liebermann, P. Czermak, Dynamic cross-flow filtration of oilfield produced water by rotating ceramic filter discs, Desal. Wat. Treat., 51 (2013) 1762–1768.
[19] X. Huang, J. Liu, L. Lu, Y. Wen, J. Xu, D. Yang, Q. Zhou, Evaluation of screening methods for demulsifying bacteria and characterization of lipopeptide bio-demulsifier produced by *Alcaligenes* sp, Bioresour. Technol., 99 (2009) 1358–1365.
[20] H. Salehizadeh, A. Ranjbar, K. Kennedy, Demulsification capabilities of a Microbacterium species for breaking water-in-crude oil emulsions, Afr. J. Biotechnol., 12 (2013) 2019–2026.
[21] A.A. Peña, G.J. Hirasaki, C.A. Miller, Chemically induced destabilization of water-in-crude oil emulsions, Ind. Eng. Chem. Res., 44 (2004) 1139–1149.
[22] S.S. Wang, C.J. Lee, C.C. Chan, Demulsification of water-in-oil emulsions by use of a high voltage AC field, Sep. Sci. Technol., 29 (1994) 159–170.
[23] C. Yan, J. Han, C. Huang, T. Mu, Demulsification of water-in-oil emulsions for the petroleum industry by using alternating copolymers, Energy Technol., 2 (2014) 618–624.
[24] J. Romaine, T. Strawser, M. Knippers, Application of chlorine dioxide as an oilfield facilities treatment fluid, SPE Prod. Facil., 11 (1996) 18–21.
[25] X. Liu, J. Li, Q. Zhu, J. Feng, Y. Li, J. Sun, The analysis and prediction of scale accumulation for water-injection pipelines in the Daqing Oilfield, J. Petrol. Sci. Eng., 66 (2009) 161–164.
[26] S. Deng, G. Yu, Z. Chen, D. Wu, F. Xia, N. Jiang, Characterization of suspended solids in produced water in Daqing oilfield, Colloids Surf. A Physicochem. Eng. Asp., 332 (2009) 63–69.
[27] P. Becher, Encyclopedia of Emulsion Technology, Basic Theory, Vol. 1, Marcel Dekker, Paul Becher Associates Ltd., Wilmington, Delaware, 1983.
[28] B. Su, M. Dou, Y. Wang, X. Gao, C. Gao, Study on seawater nanofiltration softening technology for offshore oilfield polymer solution preparation, Desal. Wat. Treat., 51(25–27) (2013) 5064–5073.
[29] S.F. Tam, Stability and Chemical Demulsification of Water-in-Crude Oil Emulsions (Chemical Method), in: Universiti Malaysia Pahang, Kuantan, Pekan, 2009.
[30] B. Wang, D. Gu, L. Ji, H. Wu, Photocatalysis: a novel approach to efficient demulsification, Catal. Commun., 75 (2016) 83–86.
[31] B. Wang, Y. Chen, S. Liu, H. Wu, H. Song, Photocatalytical visbreaking of wastewater produced from polymer flooding in oilfields, Colloids Surf. A Physicochem. Eng. Asp., 287 (2006) 170–174.
[32] T. Ammar, K. Abid, A. El-Bindary, A. El-Sonbati, Chlorine dioxide bulk decay prediction in desalinated drinking water, Desalination, 352 (2014) 45–51.
[33] D.J. Gates, Chlorine Dioxide Handbook, AWWA, Denver, 1998.
[34] A.D. Benetti, Water reuse: issues, technologies, and applications, Eng. Sanit. Ambient., 13 (2008) 247–248.
[35] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (OH/O^-) in aqueous solution, J. Phys. Chem. Ref. Data, 17 (1988) 513–886.