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Theoretical and experimental study on the safety chemistry of separation of oil/water transition layer by oxidation of chlorine dioxide

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The safety chemistry of ClO_2 oxidative treatment of an oil/water transition layer was studied and evaluated by theoretical calculation and experiments. The theoretical analysis indicated that the unsafe factors were recognized as the difference of overpressure during the oxidation process, which originates from the decomposition of ClO_2 and the release of gas from the oxidation of the reduced substances in the layer. The experimental results showed that the process pressure increased to a quite high value with the highly concentrated ClO_2, and the overpressure caused an increase in the reactive temperature. Based on these data, some suggestions were presented for the safe production. The latter should ensure that the decomposed gas from chlorine dioxide leaves the atmosphere smoothly if the reaction process is an open system. ClO_2 should be used at temperatures as low as possible, and the pressure control should be as stable as possible. This study provides safety control of the oxidation performance of chlorine dioxide, and efficient resolution of the settling tank oil/water transition layer with thickening, low-quality crude oil and high water quality.

Key words: Chlorine dioxide, Transition layer, Safety, Oxidation, Overpressure.

INTRODUCTION

The existence of oil/water transition layer in the middle and late stages of crude oil exploitation leads to a significant reduction of dehydration efficiency of crude oil, which seriously affects its quality. In order to solve the problem of separation of oil/water transition layer in a settling tank, the oil/water layer was treated by initial chlorine dioxide oxidation and consequent demulsification. The pilot operation of the ClO_2 oxidative treatment was applied to the oil/water transition layer in oil fields. As the gas chlorine dioxide itself has flammable and explosive characteristics, both production and application of chlorine dioxide bring a lot of danger and inconvenience. At present, the safety of chlorine dioxide oxidation treatment of oil/water transition layer is a relatively new topic. The specifically related to it literature is scarce [1-3]. The oil/water transition layer has a large thickness, and seriously bumps the oil and water separation in the settling tank, overflow tank, electric dehydrator and so on. The layer holds an emulsion of oil and water with black particles which deteriorates the dehydration equipment and downstream water treatment equipment [4-6]. The smooth operation is one of the important issues in the oil field. In order to solve the problem of separation of oil/water transition layer in the settling tank, the layer has been treated by initial chlorine dioxide oxidation and consequent demulsification [4]. The pilot operation of the ClO_2 oxidative treatment has been applied to the oil/water transition layer in oil fields [4]. However, due to the flammable and explosive characteristics of chlorine dioxide, the production and application of the solution encounter a lot of dangers and safety issues which are essential for the safe and stable production of oil fields [7, 8]. In this paper, theoretical and experimental studies on the safety chemistry of separation of the oil/water transition layer by oxidation of chlorine dioxide were performed, which offer supporting data for safe operation.

EXPERIMENTAL

Analytical methods

The experimental setup of the safety chemistry of the ClO_2 oxidation of the oil/water transition layer is illustrated in Fig. 1.

Fig. 1. Experimental setup of the safety chemistry of the ClO_2 oxidation of the oil/water transition layer

The closed cylinder is equipped with a pressure meter. The samples, from the Daqing oil fields (China), were mixed with ClO_2 and acid, and then

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injected to the cylinder. On heating the system to the given temperatures, the pressure was recorded.

The experimental conditions were set as follows: adding chlorine dioxide of max. 40% to the oil/water emulsions from the transition layer, heating the cylinder to a temperature in the range of 50-90 ℃, and recording the changing pressure with temperature after 30 min reaction duration.

RESULTS AND DISCUSSION

Theoretical study of process analysis and safety chemistry

The principle and operation of ClO_2 oxidative demulsification and separation of oil/water transition layer was described in our previous paper [4].

ClO_2 is a powerful oxidizing reagent that is widely applied in water treatment [9]. It has a potential of 1.511V, higher than that of some oxidizing agents such as $KMnO_4$ (1.51V), Cl_2 (1.36V), OCl^- (0.89V) and ClO^{2-} (0.77V). The data indicate that many reducing substances, such as colloid particles, polymers and natural surface active agents in the oil/water transition layer, which dominate the demulsification process, can be oxidized by ClO_2. As a strong oxidizing reagent, ClO_2 is capable of oxidizing the emulsifying materials, as illustrated in Fig. 2.

According to the process of ClO_2-oxidation treatment, the safety chemistry was focused on the reactive change of the process pressure, which originates from the decomposition of ClO_2 and the release of gas from the oxidation of the reduced substances in the layer.

For determination of the limit release, the amount of the released gas can be calculated, that is, assuming that the consumed part of chlorine dioxide contributed to the oxidation of the reduced substances in the layer such as ferrous sulfide, all the gas was released by the decomposition of the residual of ClO_2 plus the evolution of CO_2 and H_2S products of the oxidative process. If the tank keeps chlorine dioxide concentration in the remaining gas space below the explosion limit of 10%, the system safety could be ensured [10-13].

The safety chemistry is displayed by two chemical factors, which lead to an increase in the pressure.

For the decomposition of ClO_2, the chemistry follows:

$ClO_2 = 1/2Cl_2 (g) + O_2 (g)$ (1)

For the oxidation of the interfacial reduced substances in the transition layer with ClO_2, the chemical scheme is illustrated in Scheme 1.

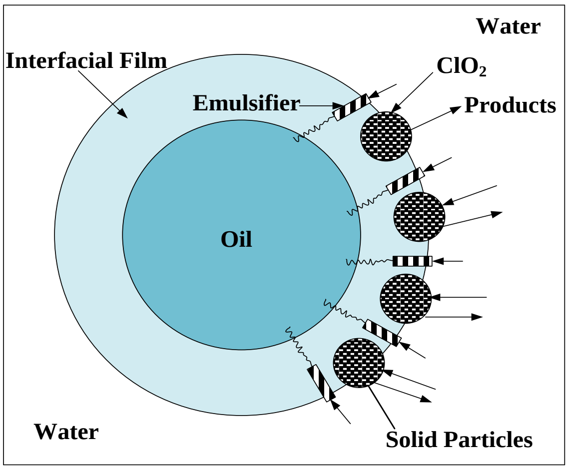

Fig. 2. Dependence of the pressure on temperature for the no-adding and adding processes

$$\begin{bmatrix}\text{Reducing Substances,}\\ \text{Colloid Particles}\\ \text{and Surface Active Agents}\\ \text{in O/W Layer}\end{bmatrix} \rightarrow \begin{bmatrix}Fe^{2+}\text{ (Soluble Reductant)}\\ S^{2-}\text{ (Soluble Reductant)}\\ S\text{ (Colloid)}\\ FeS\text{ (Colloid)}\\ R-COO^-\text{ (Natural Surface Reagents)}\\ \text{PAM (Viscous Polymer)}\end{bmatrix} \xrightarrow{ClO_2} \begin{bmatrix}Fe^{3+}\\ SO_4^{2-}\\ SO_4^{2-}\\ Fe^{3+}+SO_4^{2-}\\ CO_2\\ CO_2+NO_3^-\end{bmatrix}$$

Scheme. 1. Safety chemistry of the oxidation of interfacial reduced substances in the transition layer with ClO_2

It is seen that the gas is released in the chemical process, which results in a pressure change.

Acidic media such as H_2SO_4 and HCl were added to the system. The safety chemistry was varied in different modes by taking the reaction of an oil/water transition layer as an example.

(1) Safety chemistry of ClO_2-H_2SO_4 treated to the oil/water transition layer:

$FeS+H_2SO_4 \rightarrow FeSO_4+H_2S(g)$ （2）

$10FeSO_4+ClO_2+5H_2SO_4 \rightarrow 5Fe_2(SO_4)_3+2HCl+4H_2O$ （3）

$5H_2S + 8ClO_2 + 4H_2O \rightarrow 5H_2SO_4 + 8HCl$ （4）

Combining（2),（3）and （4）to the overall reaction one obtains：

$10FeS + 18ClO_2 + 5H_2SO_4 + 4H_2O \rightarrow 5Fe_2(SO4)_3 + 18HCl$ （5）

(2) Safety chemistry of ClO_2-HCl treated to the oil/water transition layer:

$FeS+HCl \rightarrow FeCl_2+H_2S(g)$ （6）

$5FeCl_2+ClO_2+4HCl \rightarrow 5FeCl_3+2H_2O$ （7）

$5H_2S+8ClO_2+4H_2O \rightarrow 5H_2SO_4+8HCl$ （8）

Combining（6）,（7）and (8）to the overall reaction one obtains：

$5FeS+9ClO_2+6HCl+2H_2O \rightarrow 5FeCl_3+5H_2SO_4$ （9）

In general, the safety of the chlorine dioxide treatment needs the following three points to be taken into account in the practical application. Firstly, chlorine dioxide itself has a heat instability, easy to produce chlorine and oxygen, leading to an explosion in a closed tank; secondly, the mixture of chlorine dioxide with a high concentration of reduced organic substances produces more than 40

KPa of pressure, which is prone to explode; thirdly, chlorine dioxide in water exists in the form of dissolved gas with a low stable concentration. The after-reaction residue of chlorine dioxide is easily volatilized into the air to increase the instantaneous concentration. An explosion will happen when the concentration of chlorine dioxide in the air is higher than 10% (wt/v). Therefore, in the practical application, attention should be paid to choose a reasonable reaction process and to control conditions in order to avoid overpressure or operational errors caused by the loss of the safety.

The safety evaluation of the treatment process was carried out on the basis of the limit of volatilization and comparative standard. The amounts of chlorine dioxide in the gas phase and the liquid phase were calculated by assuming that all the gas was released by decomposition of the residue of ClO_2 and the oxidation of the reduced substances in the layer. It is considered to be a safe limit by controlling that it remains below the 10% safe standard.

Chlorine dioxide is a highly explosive oxidizing gas. When chlorine dioxide in the steam reaches ≥ 40KPa, it will explode. At a concentration of chlorine dioxide solution higher than 10% (w/v) or 10% (v/v) in the air, it is prone to a low level of explosion. If there is organic steam present, the explosion may become strong. Because of its explosion, chlorine dioxide must be manufactured at the point of use. Chlorine dioxide gas is soluble in water with a balance of 23 times higher concentration in the liquid phase than in the gas phase at 25 ℃. If stored in a cool place, strictly sealed and dark, the aqueous solution is very stable. Chlorine dioxide solution is slightly acidic (pH=6), which can enhance its stability due to its disproportionation. So, these points the safe application should be known.

In the case of ClO_2-H_2SO_4 treated oil/water transition layer, the analytical data show that a FeS content of 1.97 mg was determined in 1 m^3 transition layer, and 2.73 g of chlorine dioxide was added for the full oxidation. If 0.33 m^3 of a 15% (wt/v) chlorine dioxide solution is injected into the transition layer per m^3, the system contains 49.5 g of chlorine dioxide. The remaining chlorine dioxide was 46.8 g and the concentration was 3.52% (wt/v), which was less than 10% of the explosion limit. If the remaining chlorine dioxide is fully released, and the gas space is less than 0.155 m^3, its concentration in the air is higher than 10%, prone to explosion, with the $\text{volume}_{\text{liquid phase}} : \text{volume}_{\text{gas phase}} = 1.33 : 0.155 \approx 8.57 : 1$.

In the case of ClO_2-HCl treated oil/water transition layer, both the determined FeS content and consumed ClO_2 amount are the same as the above data. If 0.33 m^3 of a 4% (wt/v) chlorine dioxide solution was injected into the transition layer per m^3, the system contains 13.2 g of chlorine dioxide. The remaining chlorine dioxide was 10.5 g, and the concentration was 0.79% (wt/v), which was less than 10% of the explosion limit. If the remaining chlorine dioxide is fully released, and the gas space is less than 0.035 m^3, the concentration in the air is higher than 10%, prone to explosion, with the $\text{volume}_{\text{liquid phase}} : \text{volume}_{\text{gas phase}} = 1.33 : 0.035 \approx 38.26 : 1$.

Temperature effect on process pressure variation

The temperature-dependent pressure data and curves are shown in Table 1 and Fig. 3.

Table. 1. Variation of the pressure on temperature for the no-adding and adding processes

Temperature (℃)	No adding of ClO_2 (MPa)	Adding of 40% ClO_2 (MPa)	Pressure difference (MPa)
50	0.010	0.020	0.010
60	0.029	0.046	0.017
70	0.040	0.059	0.019
90	0.073	0.100	0.027

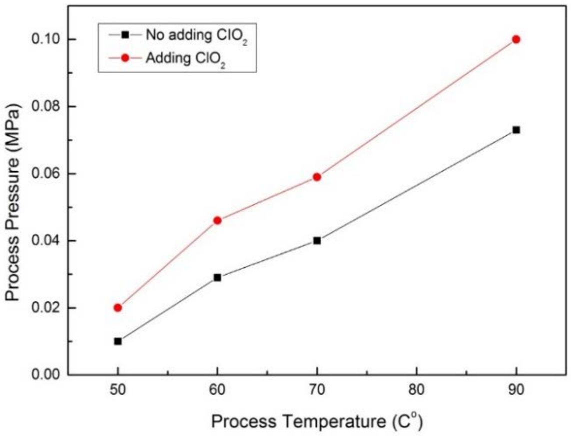

Fig. 3. Dependence of the pressure on the temperature for the no-adding and adding processes

From Table 1 and Fig. 3, it can be seen that the pressure increases with the increase in reaction temperature. When the reaction temperature rises to 90 ℃, the pressure reaches 0.1 MPa and 0.073 MPa for no-adding or adding process, respectively. The pressure difference is 0.010 - 0.027 MP in the range between 50 - 90 ℃. Compared with the no-adding process, the addition of chlorine dioxide significantly increases the pressure, which indicates that the addition of chlorine dioxide more easily causes overpressure, but as regards the explosion limit, the results could indicate that the pressure after adding chlorine dioxide is far from the explosion point, indicating that in practice a certain amount of chlorine dioxide can be present with a small risk. When the temperature was 50 °C, the results of the pressure changed with time as shown in Table 2 and Fig. 4.

Table. 2. Variation of the pressure on temperatures for the no-adding and adding processes

Reaction time (min)	Process pressure (MPa)
0	0
10	0.022
20	0.024
40	0.026
50	0.026
60	0.026
80	0.026
120	0.026

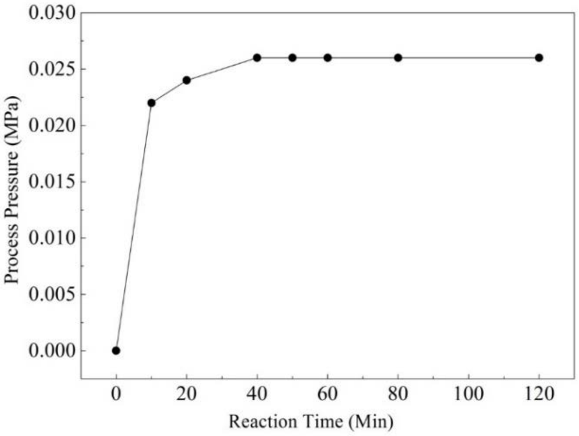

Fig. 4. Dependence of the pressure on temperatures for the no-adding and adding processes

Effect of reaction time on process pressure variation

It can be seen from Table 2 and Fig. 3 that the pressure increases with the reaction time. When the reaction time is 40 min, the pressure reaches the maximum value of 0.026MPa with no further increase. It is demonstrated that the pressure in the reaction tank increases during the initial period after the addition of the appropriate concentration of chlorine dioxide in the actual operation, but the pressure value will not change after a period of time.

Therefore, it will keep a constant value by one measured concentration of chlorine dioxide, in which, the appropriate pressure will eliminate possible explosion hazard.

From the theoretical and experimental study, the following safety suggestions are proposed: (1) in an open reaction system, the decomposed gas of chlorine dioxide should smoothly release the atmosphere; (2) the system should be operated at temperatures as low as possible; (3) the pressure control should be as stable as possible.

CONCLUSIONS

A theoretical and experimental study of the safety chemistry of separation of oil/water transition layer by oxidation using chlorine dioxide was carried out. In summary, chlorine dioxide has flammable and explosive characteristics leading to a lot of danger and inconvenience issues during its production and application. The theoretical analysis indicates that the unsafe factors were recognized as the difference in overpressure during the oxidation process.

The chemistry of the ClO_2 oxidative treatment reveals that the safety is dominated by the released gas which originates from the decomposition of ClO_2 and the evolved gas from the oxidation of the reduced substances in the layer. The experimental results showed that the process pressure increased to a quite high value with the highly concentrated ClO_2, and the overpressure increased at higher reaction temperatures. In the light of the related standards, the change is compliant and adaptive to PetroChina and in-service status of the equipment for the application. For the open reaction system, the decomposed gas of chlorine dioxide is ensured to smoothly release the atmosphere; the system is operated at temperatures as low as possible; the pressure control is kept as stable as possible. This study can provide a safety control of the oxidation performance of chlorine dioxide, and efficient resolution of the settling tank oil/water transition layer with thickening, low-quality crude oil and high water quality and other problems.

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