INTRODUCTION

A lot of oily sludge can be generated from the petroleum industry during the oil exploration, production, transportation, storage, and refining process.\(^1,2\) It is recognized as hazardous waste because it can pose serious threats to the environment and human health.\(^3,4\) Up to now, many oily sludge treatment methods have been developed, including incineration, solidification, solvent extraction, ultrasonic treatment, chemical treatment, and biodegradation.\(^5,8\) Polymer flooding for the enhanced oil recovery has been widely used in Bohai oilfield in China and the partially hydrolyzed polyacrylamide (HPAM) is the most used polymer.\(^9,10\) During the polymer flooding, many oil sludge produced from polymer flooding (OSPPF) were produced. The oil sludge studied in many reports\(^5,6,11-13\) contained a lot of inorganic solid and oil and no polymer. Different from these oil sludges, there were many polymers and a little inorganic clay in the OSPPF. Therefore, the regular oily sludge treatment methods were not suitable for the OSPPF. Usually, the OSPPF in offshore platform was firstly removed from the equipment by hands, then was transported to land by ship and at last was treated by incineration. The process is time-consuming and the economic cost is high. In this paper, the composition and formation of OSPPF produced from an offshore oilfield was analyzed firstly. Then, chemical degradation was proposed according to the formation mechanism. Mixture of \(\text{H}_2\text{O}_2\) and diethylene triamine pentacetic acid (DTPA) was chosen for the chemical degradation of OSPPF. The effects of different factors on degradation rate were studied and the national condition was obtained as follows: 3 g OSPPF, 3 g kerosene, and 9 g aqueous solutions containing 5 wt\% \(\text{H}_2\text{O}_2\)+ DTPA (\(\text{H}_2\text{O}_2\):DTPA was 1:1) were mixed at 65°C for 12 hour. After the degradation, the oil in the OSPPF can be recovered and polymer gel in the OSPPF can be destroyed completely. This chemical degradation is a good choice for treatment of OSPPF in situ.

KEYWORDS
causation analysis, chemical degradation, component analysis, oily sludge
2 | EXPERIMENTAL SECTION

2.1 | Materials

The OSPPF and HPAM which was used for the polymer flooding were supplied by CNOOC Energy Technology Drilling & Production Co (688 Bohai Oil Road, Binhai New Area, Tianjin, China). OSPPF was collected from the wellhead of a polymer injection well. It was stored in a sample bucket and was kept at room temperature. K$_2$S$_2$O$_8$, H$_2$O$_2$, diethylene triamine pentacetic acid (DTPA), disodium ethylenediamine tetraacetic acid (EDTA2Na), and citric acid were chemical pure and were obtained from Kelong-reagent Corporation (68 Longzhou Road, Chengdu, Sichuan, China).

2.2 | Measurement of the water content of OSPPF

The water content of OSPPF is obtained by oven drying method. The sample which is not less than 10 g was placed in a glass-surface vessel and then was put in an oven at 100°C until achieved a constant weight.

$$\text{Water content} = \frac{m_1 - m_2}{m} \times 100\%$$  \hspace{1cm} (1)

In which, $m$ is the mass of OSPPF (before dried); $m_1$ is the total mass of OSPPF (before dried), and glass-surface vessel; $m_2$ is the total mass of OSPPF (after dried) and glass-surface vessel.

2.3 | Measurement of the oil content of OSPPF

The oil content was extracted by Soxhlet extraction from the dried OSPPF which had been water-free. The dried OSPPF was washed by petroleum ether, benzene, ethanol, and chloroform in turn. After extraction, the solvent was removed by means of a rotary evaporator and the oil was yielded.

$$\text{Oil content} = \frac{m_3}{m} \times 100\%$$  \hspace{1cm} (2)

In which, $m_3$ is the mass of the oil.

2.4 | Measurement of the solid content of OSPPF

The solid content contains inorganics and polymer. The material which had been left in the chamber after Soxhlet extraction is the solid content. After incandesce in Muffle furnace at 550°C for 4 hour to remove the organics, the left material is the inorganics ($m_4$).

$$\text{Inorganics content} = \frac{m_4}{m} \times 100\%$$  \hspace{1cm} (3)

In which, $m_4$ is the mass of the left material after incandesce.

In addition, polymer content = 100% − water content − oil content − inorganics content.

2.5 | The degradation of the OSPPF

First, 3 g OSPPF, 3 g kerosene, and aqueous solution containing oxidant and chelating agent were mixed at a certain temperature for a certain time. Then, the mixture was filtered and the residue was dried. Degradation rate was calculated as follows: degradation rate = dried residue/(weight of OSPPF × solid content).

2.6 | Characterization

After drying and oil removal, SEM images and EDS of the OSPPF were performed on Quanta 450 Environmental Scanning Electron Microscope. And its Fourier transform infrared (FT-IR) spectra were obtained from the Thermo Fisher Nicolet6700 FT-IR spectrometer with a KBr pellet.

![The IR spectra of the solid and hydrolyzed polyacrylamide (HPAM)](image)
After drying, oil removal and incandesce at 550°C, XRD patterns of the OSPPF were recorded using Pert Pro X-ray diffractometer with a copper target at 40 kV and 40 mA.

### RESULTS AND DISCUSSION

#### 3.1 Composition and formation analysis of the OSPPF

Table 1 shows the composition analysis results of the OSPPF. It can be found that the solid part in the OSPPF was 71.9 wt% and the most solid in the OSPPF is the organics. The solid is elastic and likes as the gel. The IR spectrum of the solid is shown in the Figure 1. Both HPAM and the solid have the similar IR spectrum. It presented that the organics in the OSPPF is the HPAM.

The SEM results of the solid are shown in Figure 2. It showed that the inorganics particles were wrapped in the organics gels. The EDS results (Figure 3A) also confirmed that the most of the solid was organics because the C element has the highest content. As shown in the Figure 3A, there also some metal elements such as Na, K, Mg, Ca, Al, Fe, and so on. These metal elements had high content in the inorganics in the solid (Figure 3B) and the XRD (Figure 4) confirmed that the inorganics were sodium salt, calcium salt, and ferric salt.
The formation of the OSPPF may have a great relationship with the high valence metal ions (such as Ca$^{2+}$, Mg$^{2+}$, Al$^{3+}$, and Fe$^{3+}$). The organics gels in the solid may formed by the chelation action between metal ions and HPAM as shown in the Figure 5. During the formation of the organics gel, the oil droplet was adsorbed and the water was bound. Then, the OSPPF was formed.

3.2 Degradation of the OSPPF

In our study, according to the formation of organic gel shown in the Figure 5, two types of chemical agents including oxidant and chelating agent were selected for the degradation of OSPPF. The assumed degradation mechanism is shown in the Figure 6. Oxidant can destroy the main C-C chain and chelating agent can destroy the chelation.

 Peroxide compound is the most used oxidant. H$_2$O$_2$ and K$_2$S$_2$O$_8$ were compared. Multi-acid compound is the most used chelating agent. DTPA, EDTA-2Na, and citric acid were compared. When 3 g OSPPF, 3 g kerosene, and 9 g aqueous solutions containing different oxidants and chelating agents were mixed at 65°C for 24 hour, the results are listed in the Table 2. It can be found that H$_2$O$_2$ had better performance than that of K$_2$S$_2$O$_8$. At the same of addition of 1 wt%, H$_2$O$_2$ has more hydroxyl radical than that of K$_2$S$_2$O$_8$. That is why the H$_2$O$_2$ had better performance. DTPA had better performance than that of EDTA-2Na and citric acid because one DTPA molecular has five carboxyl groups, which is more than that of EDTA-2Na and citric acid. Therefore, H$_2$O$_2$ and DTPA were chosen to do the next experiments.

When the total concentration of H$_2$O$_2$ and DTPA was 5 wt% in the aqueous solution and the mixture were mixed at 65°C for 24 hour, the effect of mass ratio of H$_2$O$_2$ to DTPA on the degradation rate is shown in Figure 7. It indicated that the degradation rate had the highest value of 98.9% when the mass ratio of H$_2$O$_2$ to DTPA was 1:1. The results mean that there is a suitable ratio of H$_2$O$_2$ to DTPA for destroy of main C-C chain and destroy of the chelation.

When H$_2$O$_2$:DTPA was 1:1 in the aqueous solution and the mixtures were mixed at 65°C for 24 hour, the effect of their total concentration on the degradation rate is shown in the Figure 8A. In can be see that the degradation rate increased with their total concentration and when the total concentration was 5 wt%, the degradation had the degradation rate of almost 100%. When the chemical agent concentration was 5 wt% (H$_2$O$_2$:DTPA was 1:1) in the aqueous solution and the mixtures were mixed at 65°C, the effect of degradation time on the degradation rate is shown in the Figure 8B. We can find that the degradation rate had no great change after 12 hour. In addition, When the chemical agent concentration was 5 wt% (H$_2$O$_2$:DTPA was 1:1) in the aqueous solution and the mixtures were mixed for 12 hour, the effect of degradation temperature on the degradation rate was studied (Figure 8C). The degradation rate increased with temperature, when the

| No | Chemical agent type | Chemical agent | Degradation result |
|----|---------------------|----------------|--------------------|
| 1  | Oxidant             | 1%wt K$_2$S$_2$O$_8$, pH = 2 | No degradation     |
| 2  |                     | 1%wt H$_2$O$_2$, pH = 2 | The OSPPF had no elasticity |
| 3  | Chelating agent     | 5wt% DTPA, pH = 2 | The OSPPF had no elasticity |
| 4  |                     | 5wt% EDTA-2Na, pH = 2 | No degradation     |
| 5  |                     | 5wt% citric acid, pH = 2 | No degradation     |
temperature was reached 60°C the degradation rate was more than 95%. The OSPPF degradation is a chemical reaction, the reaction degree would increase with time and temperature. Therefore, the increasing time and increasing temperature are helpful for the degradation.

In a word, the national condition for the OSPPF degradation was follows: 3 g OSPPF, 3 g kerosene, and 9 g aqueous solutions containing 5wt% H₂O₂ + DTPA (H₂O₂:DTPA was 1:1) were mixed at 65°C for 12 hour. After the degradation, there was no solid in the mixture and the solid OSPPF can be flowing (as shown in Figure 9). There were three layers after the degradation, the top layer was oil, the middle layer was light yellow solution and the bottom layer was dark brown solution. In addition, both the viscosities of the middle solution and bottom solution were very low and were about 2-3 mPa.s. For investigating the substance after the degradation, the middle solution was dried by rotary evaporator and the bottom solution was dried by freeze drying to obtain the substance in the solution. The IR spectra of middle substance and bottom substance are listed in Figure 10. It can be found that they had the similar spectra. Peak at 3429 cm⁻¹ corresponded to the –NH₂ vibration from the degraded HPAM. Peaks at 2910

FIGURE 7  The effect of H₂O₂:DTPA on the degradation rate

FIGURE 8  The effects of different factors on the degradation rate (A) weight mass of H₂O₂ + DTPA; (B) degradation time; (C) degradation temperature
and 2846 cm\(^{-1}\) corresponded to the –CH\(_2\)-groups of DTPA. The peaks at 1659, 1558, 1443, and 1394 cm\(^{-1}\) corresponding to COO\(^-\) were also observed. These results indicated there were acrylamide and DTPA salt in the solution after the degradation. However, there was still a question. What is the difference between the middle substance and bottom substance? The results of their EDSs showed their difference (Table 3). Most of middle substance could be DTPA-Mg and most of bottom substance could be DTPA-Fe. Their densities were different and that it why they stayed at different layers.

### Table 3 The EDS results of the middle substance and bottom substance

| Metal element | Mg, %   | Al, % | Ca, % | Fe, % |
|---------------|---------|-------|-------|-------|
| Middle substance | 40.32   | 3.38  | 29.34 | 26.96 |
| Bottom substance | 18.14   | 3.23  | 31.95 | 46.68 |

4 | CONCLUSIONS

The formation of the OSPPF in the offshore oilfield was caused by the chelation action between the high valence metal ions and HPAM. It can be broken down by H\(_2\)O\(_2\)+ DTPA and national condition was follows: 3 g OSPPF, 3 g DTPA, and 9 g aqueous solutions containing 5wt% H\(_2\)O\(_2\)+ DTPA (H\(_2\)O\(_2\):DTPA was 1:1) were mixed at 65°C for 12 hour. After the degradation, no solid OSPPF was found and there were three layers: the top layer was oil, the middle layer, and bottom layer were DTPA slat solution.

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