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Process for the Reduction of High Water Content from Oily Sludge and Scum by Hot Washing

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ABSTRACT

The reduction of oily sludge and scum with high water content by hot washing and analysis of the main factors that affect the reduction and oil recovery rate of oily sludge and scum in hot washing were investigated. Best process conditions for the reduction of tank bottom sludge, refining sludge, and oily scum were carried out, which can make the oil recovery rate and reduction rate of tank bottom sludge after reduction reach 96.30% and 93.00%, respectively, the oil recovery rate and reduction rate of refining sludge after reduction reach 95.36% and 92.60% respectively, and the oil recovery rate and reduction rate of oily scum after reduction reach 95.92% and 93.60% respectively. After treatment, the oil content of the residue is reduced to below 5.1%, and the water content is reduced to below 59.0%. Oil content in the separated water is lower than 200 mg.L^{-1}, and the water content in the separated oil is lower than 0.2%, far below the requirement of 0.5% in the oilfield's crude oil gathering and transportation standard.

INTRODUCTION

Oily sludge occurs in oilfield exploitation, gathering, transportation, storage, refining, etc. (Tahhan & Abu-Ateih 2009). According to the specific location, it is mainly composed of four parts. First, oil sludge falls from drilling, operation, and pipeline perforation (Johnson & Affam 2018, Rocha et al. 2010). Second, the bottom mud of oil tanks, settling tanks, sewage tanks, and oil separators in transfer and combined stations (Egazaryants et al. 2015, Inguanzo et al. 2012). When the oil is stored in the tank, the oil sludge at the bottom is formed due to the oil's heavy, oily components deposited at the bottom (Murungi & Sulaimon 2022). Third, oil sludge is removed from oil-bearing water treatment facilities, light hydrocarbon processing plants, and natural gas purification devices in refineries (Chen et al. 2019, Hochberg et al. 2022). Oily sludge is generally a stable suspension emulsion system composed of oil in water (o/w), water in oil (w/o), and suspended solids, with poor dewatering effect (Long et al. 2013). The composition and physical properties of sludge are affected by factors such as sewage quality, treatment process, and dosing agent, which have large differences, high treatment difficulty, and large differences in oil content. Some of them have recycling value, and oily sludge contains PAHs, heavy metals, and other harmful substances, which also cause radioactive pollution to the environment (Puasa et al. 2019). The volume of oily sludge is huge. If it is directly discharged without treatment, it will not only occupy a large amount of cultivated land but also pollute the surrounding soil, water, and air, accompanied by the generation of malodorous gas (Hayhurst 2013, Anna et al. 2015, Ramirez & Collins 2018). Sludge contains a large number of pathogenic bacteria, parasites (eggs), copper, zinc, chromium, mercury, and other heavy metals, salts, polychlorinated biphenyls, dioxins, radionuclides, and other toxic and harmful substances that are difficult to degrade, such as shown in Fig.1 (Crelier & Dweck 2009). The arbitrary landfill will lead to serious pollution of groundwater and the destruction of the original ecology of food crops (Wu et al. 2019).

A large amount of oily sewage is usually produced in oil exploitation and refining. For the treatment of such oily

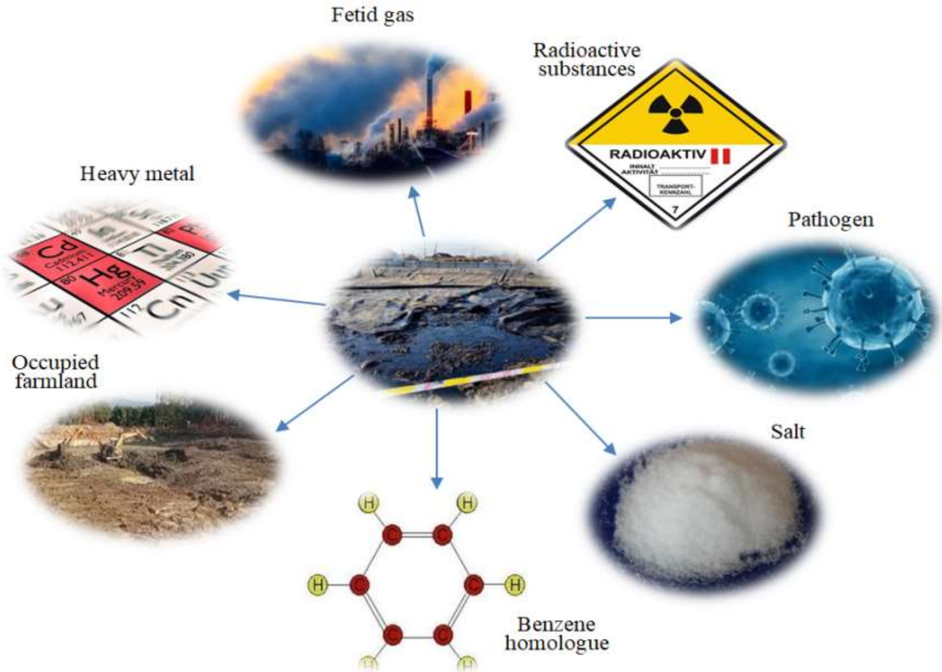

Fig. 1: Hazards of oily sludge.

sewage, the old three processes of "oil separation air flotation biochemical treatment" are generally adopted (Suganthi et al. 2018, Muneeswari et al. 2022). A large amount of oily scum will be produced by removing emulsified oil in the air flotation unit (Motlagh et al. 2019). The composition of oily scum is extremely complex, containing a large amount of aged crude oil, wax, asphaltene, colloid, solid suspension, etc., as well as various chemical agents such as coagulant and corrosion inhibitors added in the production process (Hu et al. 2013, Amudha et al. 2016). Oily sludge and scum have been included in the National Catalogue of Hazardous Wastes in China, and they are hazardous wastes (Wang et al. 2019). The amount of oily sludge and scum is large, and the moisture content is high, so direct refining or incineration will inevitably consume a lot of heat, leading to high energy consumption for enterprises (Skinner et al. 2015). Therefore, oily sludge and scum must be dewatered and reduced before harmless or resourceful disposal (Duan et al. 2018). Many domestic enterprises have adopted the mechanical conditioning three-phase separation process for dehydration treatment (Cheng et al. 2017, Shperber et al. 2011). Although certain results have been achieved, there are still some defects, mainly as follows: it is difficult to separate oil and water from oily sludge and scum, the oil recovery rate is low, the overall reduction rate of sludge is low, and the equipment cannot operate stably for a long period (Liu et al. 2022). Therefore, it is necessary to screen and analyze all the influencing factors in the process of sludge reduction, determine which are the main influencing factors, and determine the best process parameters to provide technical support for the reduction, recycling, and harmless treatment of oily sludge in the future (Mowla et al. 2013, Barneto et al. 2014, Gourdet et al. 2017).

TREATMENT PROCESS AND APPLICATION STATUS

There are many industrial application processes for the thermal washing reduction treatment of oily sludge and scum at home and abroad, but the principles are basically the same (Mahmoud et al. 2018). They all use pH adjustment, heating, stirring, demulsifier, flocculant, mechanical dehydration, and other means and methods to finally achieve the reduction treatment of oily sludge and scum (Bao et al. 2022). Through a large number of field investigations and actual operations, the author of this paper summarizes the treatment of oily sludge and scum at some oily sludge stations in China, as shown in Table 1. The reduction process of some sludge stations is shown in Fig. 2.

It can be seen from Table 1, and the technical status of development that the sludge reduction rate and oil recovery rate of most technologies and stations are lower than 85%, and the oil content of sludge after final treatment is higher than 6%. Most technologies and processes only reduce the

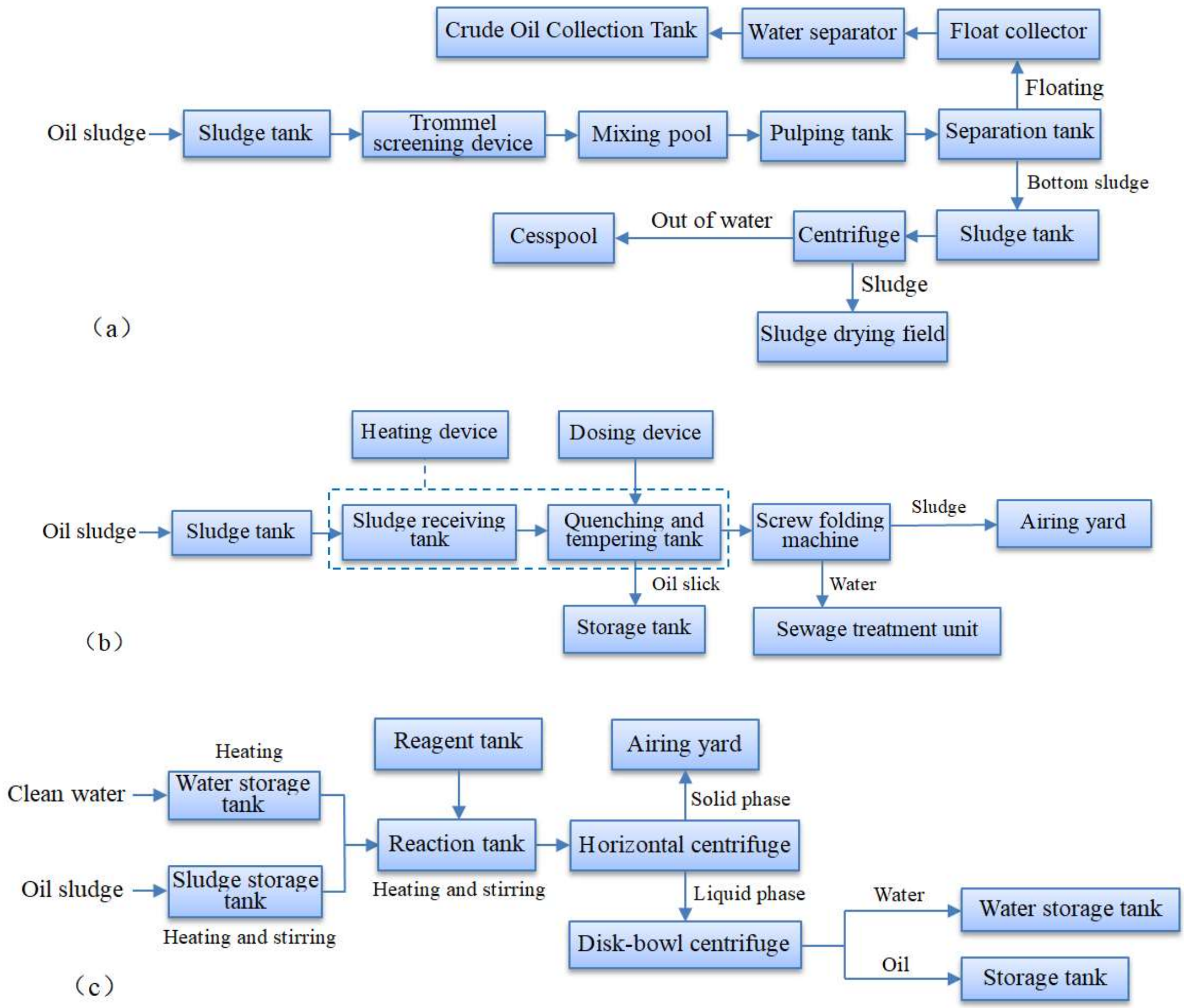

Fig. 2: Sludge reduction treatment process of (a) Oil Sludge Station in Tuha Oilfield; (b) Wuqi Oil Sludge Station in Changqing Oilfield; (c) Yumen Refineryfield.

sludge and do not achieve the best treatment effect. In this paper, the problems of unsatisfactory oily sludge and its reduction treatment effect and high oil content of sludge after treatment are studied in depth, the optimal operating conditions for oily sludge treatment and scum treatment are selected, and the importance of the influencing factors in the oily sludge and scum treatment process is ranked. The key factors affecting the oily sludge treatment are finally obtained.

MATERIALS AND METHODS

Materials

Analytical grade Sodium hydroxide (NaOH), hydrochloric acid (HCl), and demulsifier were used in the experiment. Industrial grade Poly Aluminum Chloride (PAC), poly aluminum sulfate (PAS), Polymerization Ferric Chloride (PFC), Polymeric Ferric Sulfate (PFS), and polyacrylamide (PAM) were used in this experiment.

Oil sludge samples were obtained from Yanchang Oilfield Shimian United Station, Yongping Refinery of Yanchang Oilfield, and Yan'an Petrochemical Plant of Yanchang Oilfield in Shaanxi Province, China. These samples were stored in a refrigerator at 4℃ to minimize biological and chemical reactions as much as possible. The general characteristics of the oil sludge samples from the workplace are shown in Table 2.

Experimental Procedure

Heat the sludge system temperature to the set temperature at the set heating rate. Adjust the pH of the system to the best experimental conditions. Adding a certain amount of demulsifier and adopting the best mixing method to stir for a certain time at a certain rate. After mixing, stand for a certain period of time. After standing, take out the upper clean water and oil to the oil-water separation device, and record the volume of oil and water, respectively. Adding

Table 1: Current situation of sludge reduction treatment in China.

Site name	Major equipment	Process parameters	Treatment effect
Tuha Oilfield Sludge Station	Drum screening device Mixing tank Slurry tank Sludge separation tank Sludge tank Centrifuge	Alternate operation of two pulping tanks Processing capacity: 100 $m^3.d^{-1}$ Add demulsifier and flocculant Heating method: steam-heat transfer oil Heating temperature: 70°C Vertical mixing shaft mixing mode Mixing time: 40 min Standing time: 30 min Rotating speed of centrifuge: 2600 $r.min^{-1}$ Centrifuge time: 30 min	The reduction rate can reach 85% The oil recovery rate can reach 80% The minimum oil content of the reduced sludge can be reduced to 7%
Dongrengou Oil Sludge Station of Yanchang Oilfield	Slag remover Conditioning tank Centrifuge Oil-water separator Heat exchanger Centrifuge	The three conditioning tanks operate alternately Processing capacity: 200 $m^3.d^{-1}$ Add demulsifier and flocculant Heating mode: steam. Vertical mixing shaft mixing mode Heating temperature: 60°C The mixing time: 30 min The standing time: 20 min Rotating speed of centrifuge: 2400 $r.min^{-1}$ Centrifuge time: 20 min	The reduction rate can reach 80%. The oil recovery rate can reach 83%. The minimum oil content of the reduced sludge can be reduced to 10%. The oil content in the treated water is less than 1%.
Yanchang Oilfield Fengchuan Youni Station	Sand setting device Reaction tank Screw stacking machine	Two reaction tanks operate alternately Processing capacity: 120 $m^3.d^{-1}$ Add regulator, demulsifier, and flocculant Heating mode: steam Vertical mixing shaft mixing mode Heating temperature 55°C The mixing time: 20 min The standing time: 40 min Sludge treatment time: 10 min	The reduction rate can reach 75%. The oil recovery rate can reach 81%. The minimum oil content of the reduced sludge can be reduced to 7%.
Changqing Oilfield Wuqi Oil Mud Station	Reaction tank Centrifuge Oil-water separation tank	Two reaction tanks operate alternately Processing capacity: 150 $m^3.d^{-1}$ Add regulator, demulsifier, cleaning agent, and flocculant Heating mode: steam Vertical mixing shaft mixing mode Heating temperature: 60°C The mixing time: 40 min The standing time: 30 min Rotating speed of centrifuge: 2400 $r.min^{-1}$ Centrifuge time: 15 min	The reduction rate can reach 70%. The oil recovery rate can reach 75%. The minimum oil content of the reduced sludge can be reduced to 10%.
Oil-bearing scum treatment workshop of Changqing Petrochemical	Homogenizing tank Reaction tank Centrifuge	Four reaction tanks operate alternately. Processing capacity: 300 $m^3.d^{-1}$. Add demulsifier and flocculant Heating mode: steam Inclined 45 ° mixing mode Heating temperature 50°C The mixing time: 20 min The standing time: 30 min Rotating speed of centrifuge: 2800 $r.min^{-1}$ Centrifuge time: 40 min	The reduction rate can reach 85%. The oil recovery rate can reach 78%. The minimum oil content of the reduced sludge can be reduced to 6%.

Table Cont....

Site name	Major equipment	Process parameters	Treatment effect
Oil sludge workshop of Yumen Refinery	Settling tank Reaction tank Centrifuge	The three reaction tanks operate alternately Processing capacity: 200 $m^3.d^{-1}$ Add demulsifier and flocculant Heating mode: steam - heat transfer oil Vertical mixing shaft mixing mode Heating temperature: 50℃ The mixing time: 40 min The standing time: 30 min Rotating speed of centrifuge: 2600 $r.min^{-1}$ Centrifuge time: 25 min	The reduction rate can reach 80%. The oil recovery rate can reach 78%. The minimum oil content of the reduced sludge can be reduced to 6%.
Nanyang Oilfield Sludge Station	Prefabrication tank Reaction tank Centrifuge Oil-water separation tank	The three reaction tanks operate alternately Processing capacity 150 $m^3.d^{-1}$ Add demulsifier and flocculant Heating mode: steam Vertical mixing shaft mixing mode Heating temperature 70℃ The mixing time: 30 min The standing time: 50 min Rotating speed of centrifuge: 2400 $r.min^{-1}$ Centrifuge time: 40 min	The reduction rate can reach 84%. The oil recovery rate can reach 83%. The minimum oil content of the reduced sludge can be reduced to 9%.

Table 2: Characteristics of the oil sludge samples.

Sludge type	Oil content [%]	Water content [%]	Solid content [%]
Bottom mud of combined station tank	17.86	80.53	1.61
Refining sludge	24.33	75.32	0.35
Oily scum	9.80	86.75	3.45

PAM of a certain concentration to the bottom sludge after standing before entering the centrifuge and stirring it evenly. Centrifuge it for a certain time at a certain speed in the centrifuge. Take out the centrifuged sludge, then take out the upper clean water and oil to the oil-water separation device, and record the volumes of oil and water, respectively. Take out the centrifuged bottom sludge to measure the water and oil content.

The single-factor experimental method was used to screen the best process. The final experimental effect was based on the overall sludge reduction rate, oil recovery rate, and the bottom sludge's water content and oil content after centrifugation.

Analytical Methods

The initial pH was measured using a pH meter (PHS-3C, Shanghai INESA & Scientific Instrument Co., Ltd.).

The determination method of water content in oil shall be in accordance with the method specified in the Determination of Water Content in Crude Oil Distillation Method (GB/T 8929-2006). Oil content in water shall be determined according to the method specified in Water Quality Determination of Petroleum, Animal, and Vegetable Oils Infrared Spectrophotometry (HJ 637-2012). The oil content of the bottom sludge shall be tested according to the method specified in the Control Limits for Disposal and Utilization of Oily Sludge (DB61/T 1025-2016).

The oil recovery rate was calculated by using the following equation:

$$\text{Oil recovery rate}: \mu = \frac{m}{n} \times 100\%$$

where μ is the oil recovery rate (%), m is the volume of reduced separated oil (mL), and n is the volume of oil in crude mud (mL).

The reduction rate was calculated by using the following equation:

$$\text{Reduction rate}: \rho = \frac{x}{y} \times 100\%$$

where ρ is the reduction rate (%), x is the final residual solid sludge volume after centrifugation (mL), and y is the volume of crude oil sludge (mL).

RESULTS AND DISCUSSION

Many factors affect the reduction process and the effect of oily sludge and scum. For example, the pH value of the system, the type, and dosage of agents can affect the aggregation degree of sludge particles, the temperature can affect the oil recovery rate in the reduction process of oily sludge and scum, and the mixing time, speed and method can affect the size, existing state and particle grading of sludge particles (Zhang et al. 2021, Liang et al. 2017). Therefore, the effect of operating conditions on the reduction process and oily sludge and scum was investigated.

Effects of Operating Parameters on the Reduction Process and Oily Sludge and Scum

Initial pH

It can be seen from Fig. 3 that when the pH is acidic, the oil recovery rate of the three samples is lower than 70%, and the reduction rate is lower than 80%. When pH becomes alkaline, oil recovery and decrement increase gradually, and when pH=8.5, oil recovery and decrement reach the highest. When the pH exceeds 8.5, the oil recovery and decrement rates decline slightly. The reason for this phenomenon is that when the system's pH is weakly alkaline, it is helpful for the demulsification of oily sludge and scum. It can also react with the colloid and asphaltene in the sludge to generate salts, increase its water solubility, saponify with naphthenic acids, and improve the separation performance of chemical agents on oily sludge and scum. The oil recovery rate and the reduction effect worsen with the continuous pH increase. That is because some chemicals added have higher requirements for pH, and their effects will be weakened when they exceed a certain value.

Through the screening of this group of experiments, the optimal pH value of the three samples in the reduction process is 8.5. At this time, the oil recovery and reduction rates of the tank bottom mud of the combined station are 69.43%, and 71.40%, respectively. The oil recovery and reduction rates of refinery sludge were 75.63% and 73.60%, respectively. The oil recovery and reduction rate of oily scum is 71.43% and 81.20%, respectively.

System Temperature

It can be seen from Fig. 4 that when the temperature rises from 40°C to 80°C, the oil recovery and decrement rate of the three samples show a trend of gradual increase. That is because the viscosity of the oil film is closely related to the temperature. The increase in temperature reduces the viscosity and surface tension, and the thermal expansion weakens the adhesion of the oil film, making it easier to separate the oil during the mixing process. However, when the temperature exceeds a certain value, the increasing trend of oil recovery and decrement rate is no longer obvious. This may be because the performance of the system in the system will gradually decline when the temperature exceeds a certain value.

Through the screening of this group of experiments, the optimal temperature for treating tank bottom sludge and refining sludge is 70℃, and the oil recovery rate and sludge reduction rate of tank bottom sludge are 77.27% and 76.60%, respectively. The oil recovery and reduction rates of refinery sludge were 82.20% and 79.40%, respectively. The optimum temperature for the treatment of oily scum is 60℃, and the oil recovery and reduction rates are 77.55% and 84.00%, respectively.

Heating Rate

It can be seen from Fig. 5 that the optimal heating rate in the process of the three samples' reduction is different, but the changing trend of the treatment effect of the three samples is the same. With the acceleration of the heating rate, the effect becomes better first and then worse. The reason may be that the time for the sludge to reach the experimental temperature is too short due to a too-fast heating rate,

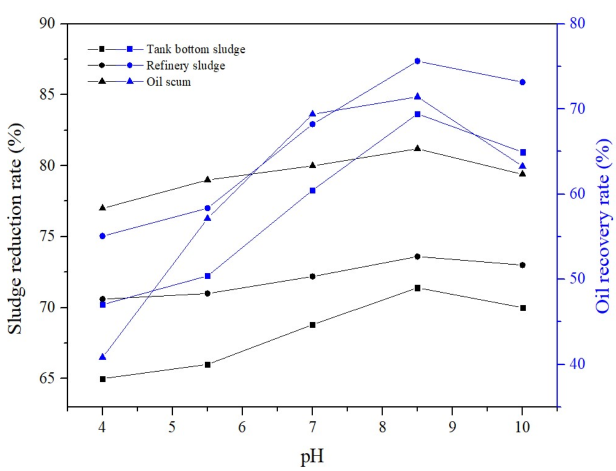

Fig. 3: The black line and blue line represent the sludge reduction rate and oil recovery rate at different pH, respectively.

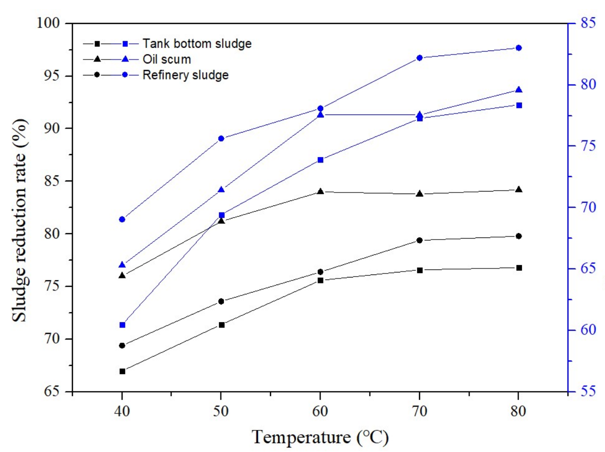

Fig. 4: The black line and blue line represent the sludge reduction rate and oil recovery rate at different temperatures, respectively.

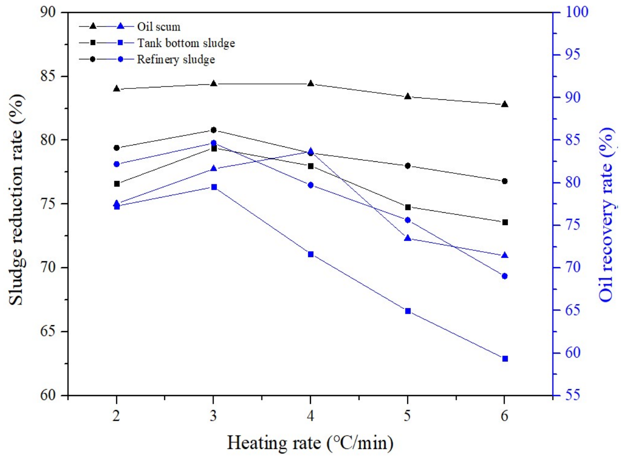

Fig. 5: The black line and blue line represent the sludge reduction rate and oil recovery rate at different heating rates, respectively.

which leads to uneven heating of the sludge, especially for the sludge in contact with the wall of the reaction vessel. The temperature rise of some sludge in the middle of the reactor that increases the temperature by heat transfer will be relatively slow, resulting in a relatively large temperature difference in the sludge system, which cannot completely separate the emulsion to the maximum extent, resulting in a trend of increasing first and then decreasing.

Through this group of experiments, the optimal heating rate of tank bottom sludge and refining sludge during treatment is 3°C. min^{-1}. The oil recovery rate of tank bottom sludge and refining sludge is 79.51% and 84.67%, respectively, and the reduction rate is 79.40% and 80.80%, respectively. The optimum heating rate of oily scum is 4°C. min^{-1}, and the oil recovery and reduction rates are 83.67% and 84.40%, respectively.

Type and an Additional Amount of Demulsifier

It can be seen from Fig. 6 (a) that the best demulsifiers in the reduction process of the three samples are different because different types of sludge have certain differences in properties, and different demulsifiers have different demulsifying capacities for the organic phase, with a certain degree of specificity. The demulsifying performance directly affects the effect of oil-water separation; therefore, it is a key factor in selecting appropriate emulsifiers for this high-emulsified oil cement system. It can be seen from Fig. 6 (b) that the optimum dosage of the three samples in the process of decrement is different. With the dosage increase, the oil recovery and the decrement rates increase first and then decrease. This may be because the demulsifier acts as an emulsion after exceeding a certain amount in the system, decreasing dehydration efficiency.

Through the screening of this group of experiments, the best demulsifier for treating tank bottom mud in the multi-purpose station is 1 # demulsifier. When the dosage is 220 $mg.L^{-1}$, the oil recovery and reduction rates reach 85.11% and 81.00%, respectively. The best demulsifier for refining sludge treatment is a 2 # demulsifier. When the dosage is 200 $mg.L^{-1}$, the oil recovery and reduction rates reach 84.67% and 80.80%, respectively. The best demulsifier for oily scum treatment is a 4 # demulsifier. When the dosage is 200 $mg.L^{-1}$, the oil recovery and reduction rate reach 85.71% and 86.00%, respectively.

Mixing Speed and Mixing Time

It can be seen from Fig. 7 (a) that the reduction treatment effects of the three kinds of sludge show a trend of increasing and then decreasing with the increase of mixing speed. That is because proper mixing intensity can improve the combination of agent and oil sludge, enhance the flocculation of sludge

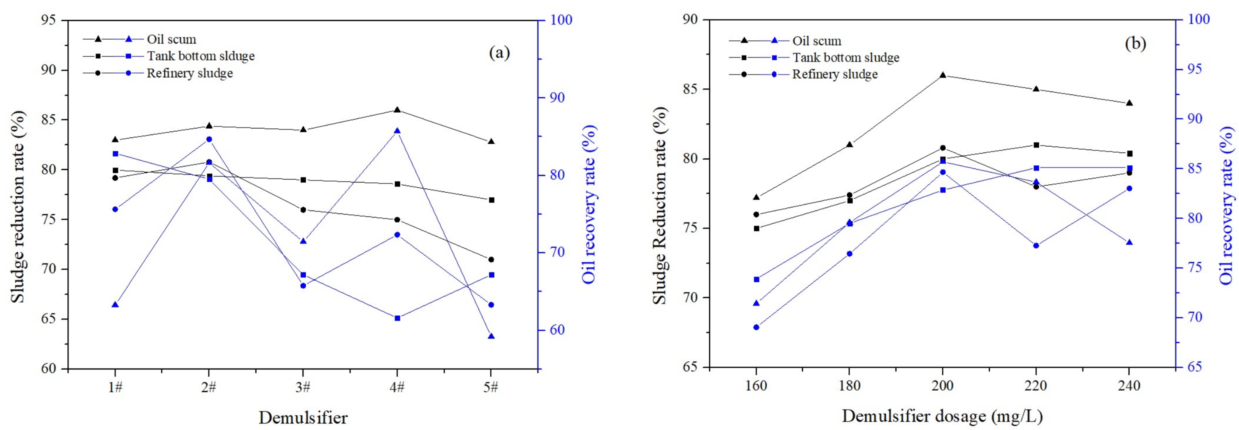

Fig. 6: (a) Sludge reduction and oil recovery rates at different demulsifiers. (b) Sludge reduction rate and oil recovery rate at different demulsifier dosage.

particles, and accelerate the falling off of surface sand, which is conducive to separating oil sludge water. However, when the mixing speed exceeds a certain value, the emulsification of oily sludge and scum will become more serious, so the oil recovery and reduction rates will decline. It can be seen from Fig. 7 (b) that the reduction treatment effects of the three kinds of sludge show a trend of first increasing and then stabilizing with the extension of mixing time. Because with the extension of the mixing time, the oil sludge and the agent will be mixed more fully, and the temperature of the oil sludge will be more uniform. However, when the mixing time exceeds a certain value, the oil sludge and the agent will be fully mixed, and the oil sludge will be heated uniformly, so the overall treatment effect will not change too much.

Through this group of experiments, when the mixing speed is 200 r.min^{-1} and the mixing time is 30 min, the oil recovery and reduction rate can reach 89.58% and 82.00%, respectively. When the stirring speed is 180 r.min^{-1} and the stirring time is 30min, the oil recovery and reduction rates can reach 87.96% and 81.20%, respectively. When the stirring speed is 160 r.min^{-1} and the stirring time is 30min, the oil recovery and reduction rate can reach 89.79% and 86.60%, respectively.

Type of Flocculant

It can be seen from Fig. 8 that PAM has the best effect on reducing three kinds of sludge. The oil recovery and tank bottom sludge reduction rates are 90.71% and 82.60%, respectively. The oil recovery and reduction rates of refinery sludge were 90.42% and 81.00%, respectively. The oil recovery and reduction rate of oily scum is 91.84% and 86.80%, respectively. For five agents, the trend of treatment effect is the same when treating three types of sludge, and the order of effect from good to bad is PAM>PAS>PFS>PAC>PFC.

Molecular Weight and Dosage of PAM

It can be seen from Fig. 9 (a) that the influence of PAM molecular weight on the three kinds of sludge during the

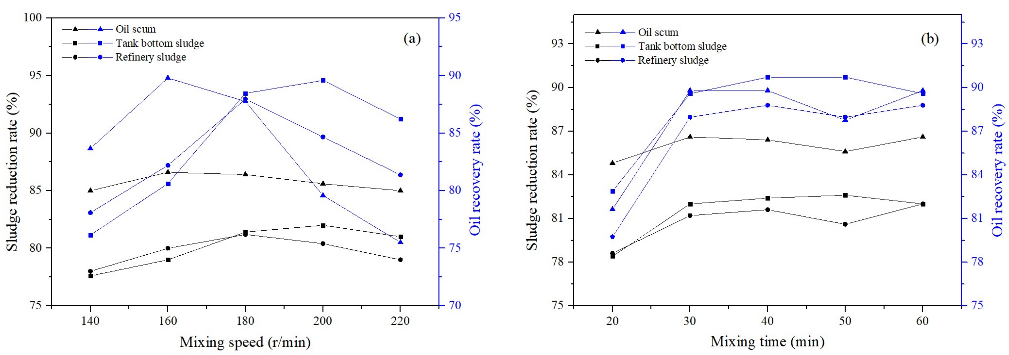

Fig. 7: (a) Sludge reduction and oil recovery rates at different mixing speeds. (b) Sludge reduction rate and oil recovery rate at different mixing times.

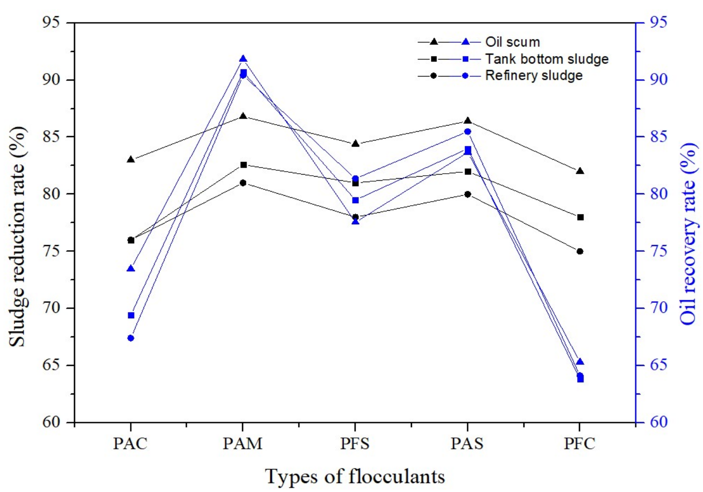

Fig. 8: The black line and blue line represent the sludge reduction rate and oil recovery rate at different types of flocculants, respectively.

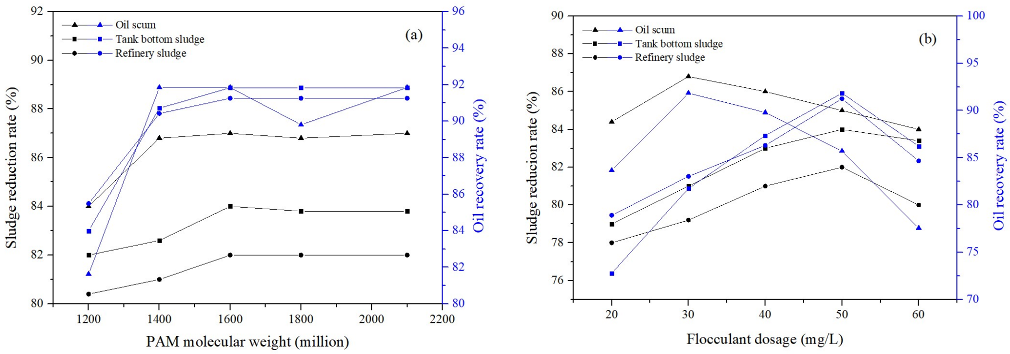

Fig. 9: (a) Sludge reduction and oil recovery rates at different PAM molecular weights. (b) Sludge reduction rate and oil recovery rate at different flocculant dosage.

reduction treatment process is the same. With the gradual increase of molecular weight, the oil recovery rate and the reduction rate show a gradual increase trend because, with the increase of molecular weight, the chain of PAM is longer, the more impurities or suspended solids can be attached, and the larger the flocs are formed, the better the dehydration effect will be. However, when the molecular weight reaches a certain level, the treatment effect will no longer be significantly improved, or even partially decreased, because in the same experimental time, the higher the molecular weight of PAM is, the worse its solubility will be, and the treatment effect will become worse. It can be seen from Fig. 9 (b) that with the gradual increase of flocculant dosage, the oil recovery rate and reduction rate show an upward trend because flocculant is a strong electrolyte with charge, which is added to the sludge to break the imbalance of an original colloid or emulsion, to achieve sludge destabilization. The treatment effect becomes better with the increase of flocculant dosage. It shows that the added flocculation dose is insufficient to make the system's positive and negative charges reach equilibrium. However, when the amount of flocculant continues to increase, and the positive and negative charges in the system reach the equivalent state, the sludge treatment effect is the best at this time. If the amount of flocculant continues to increase, the excess negative charges will repel each other in the sludge, leading to a decline in the treatment effect.

Through this group of experiments, the PAM with a molecular weight of 16 million is better when treating tank bottom sludge and refining sludge. When the dosage is 50 mg.L^{-1}, the oil recovery rate can reach 91.83% and 91.25%, respectively, and the sludge reduction rate can reach 84.00% and 82.00%, respectively. When treating oily scum, the PAM with 14 million molecular weight is better. When the dosage is 30 mg.L^{-1}, the oil recovery and sludge reduction rates reach 91.84% and 86.80%, respectively.

Centrifuge Speed and Centrifuge Time

It can be seen from Fig. 10 (a) that the influence trend of different centrifuge speeds on the three kinds of sludge in the process of reduction treatment is the same. With the increase in centrifuge speed, the oil recovery and reduction rates are also increasing. That is because the higher the speed is, the greater the centrifugal force is, and the easier the solid and liquid phases are separated. However, when the rotating speed of the centrifuge exceeds a certain value, the centrifugal effect will no longer change significantly because the best separation state of the centrifuge has been reached. This experiment's rotating speed has not increased because the best separation state has been reached. However, if the rotating speed increases, the centrifugal force and the mechanical force on the gauze in the centrifuge increase. When the rotating speed exceeds a certain value, the gauze will be damaged, the density of the gauze will become smaller, so some small particles of sludge will flow out with the water phase, resulting in a decline in the effect. It can be seen from Fig.10 (b) that with the increase of centrifuge speed, the oil recovery rate and decrement rate also increase because the longer the centrifugation time is, the longer the solid-liquid phase has enough time to separate, making the separation more thorough. However, when the centrifuge time reaches a certain value, the centrifuge effect will no longer change significantly because the best separation state of the centrifuge has been reached. It can be seen from the comparison between the oil recovery rate and the decrement rate that, with the increase of centrifugation time, the decrement rate is still rising when the oil recovery rate is no longer changing within the same time. Therefore, the optimal centrifugation time under this phenomenon should be the time corresponding to the maximum decrement rate.

Through this group of experiments, when the rotating speed of the centrifuge for treating tank bottom sludge is 2800 r.min^{-1} and the centrifuge time is 15 min, the oil recovery rate and sludge reduction rate can reach 96.30% and

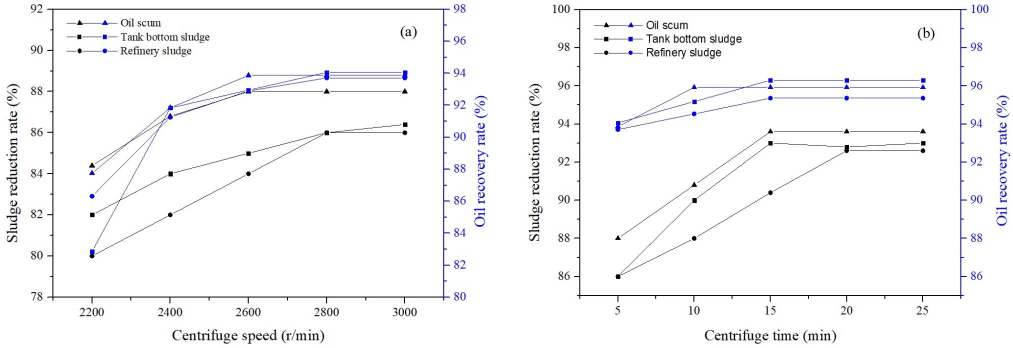

Fig.10: (a) Sludge reduction and oil recovery rates at different centrifuge speeds. (b) Sludge reduction rate and oil recovery rate at different centrifuge time.

93.00%, respectively. When treating refinery sludge, when the rotating speed of the centrifuge is 2800 r.min^{-1} and the centrifuge time is 20 min, the oil recovery rate and sludge reduction rate can reach 95.36% and 92.60%, respectively. When dealing with oily scum, the oil recovery rate and sludge reduction rate can reach 95.92% and 93.60%, respectively, when the rotating speed of the centrifuge is 2600 r.min^{-1} and the centrifugation time is 15 min.

Process Optimization

All the above experimental conditions are summarized, and the best process for each of the three kinds of sludge is shown in Table 3.

Determine the oil content, water content, and solid content of the residues of the three kinds of sludge after treatment according to the best process, the oil content of the separated water, and the water content of the separated oil. The test results are shown in Table 4.

It can be seen from Table 4 that the determination results of the three kinds of sludge after being treated by the best process show that the oil content of the residue can be reduced to below 5.1%. The water content can be reduced

Table 3: The best process for reducing different types of sludge.

Sludge type	Optimum process conditions
Tank bottom sludge	The pH value of the system is 8.5. Temperature 70°C. The heating rate is 3°C.min^{-1}. Add 220 mg.L^{-1} 1 # demulsifier. Mixing speed 200 r.min^{-1}. The mixing time is 30 min. Before centrifugation, add 50 mg.L^{-1} PAM with a molecular weight of 16 million into the sludge and stir it evenly. Centrifuge at 2800 r.min^{-1} for 15 min in a centrifuge. Under the above experimental conditions, the oil recovery rate and reduction rate of tank bottom sludge in the process of reduction treatment can reach 96.30% and 93.00%, respectively.
Refining sludge	The pH value of the system is 8.5. Temperature 70°C. The heating rate is 3°C.min^{-1}. Add 200 mg.L^{-1} of 2 # demulsifier. Mixing speed 180 r.min^{-1}. The mixing time is 30 min. Before centrifugation, add 50 mg.L^{-1} PAM with a molecular weight of 16 million into the sludge and stir it evenly. Centrifuge in a centrifuge at 2800 r.min^{-1} for 20 min. Under the above experimental conditions, the oil recovery rate and reduction rate of refinery sludge in the process of reduction treatment can reach 95.36% and 92.60%, respectively.
Oily sludge	The pH value of the system is 8.5. Temperature 60°C. The heating rate is 4°C.min^{-1}. Add 200 mg.L^{-1} of 4 # demulsifier. Mixing speed 160 r.min^{-1}. The mixing time is 30 min. Before centrifugation, add 30 mg.L^{-1} PAM with a molecular weight of 14 million into the sludge and stir it evenly. Centrifuge at 2600 r.min^{-1} for 15 min in a centrifuge. Under the above experimental conditions, the oil recovery and reduction rate of oily scum in the process of reduction treatment can reach 95.92% and 93.60%, respectively.

Table 4: Analysis of residue, water, and oil after sludge reduction.

After sludge reduction treatment		Processing results		
		Tank bottom sludge	Refinery sludge	Oil scum
Residue after sludge reduction	Oil content [%]	4.5~5.0	4.3~5.1	3.5~4.5
	Water content [%]	53.2~55.7	52.4~56.5	55.5~59.0
	Solid content [%]	39.3~42.3	38.4~43.3	36.5~41.0
Oil content in water after sludge centrifugation [mg.L^{-1}]		175~190	180~200	150~180
Water content in oil after sludge centrifugation [%]		≤0.2	≤0.2	≤0.15

to below 59.0%, and the treatment effect has exceeded the technical level at home and abroad. The oil content of the separated water is less than 200 $mg.L^{-1}$, which can be directly sent to the sewage treatment system of the oilfield combined station for advanced treatment. The water content of the separated oil is lower than 0.2%, which is lower than the requirement of 0.5% in the oilfield's crude oil gathering and transportation standard.

Morphological Changes of Oily Sludge and Scum Before and After Treatment

To more intuitively explain the effect of oily sludge reduction, the morphology of oily sludge and scum before and after treatment was analyzed and studied by scanning electron microscope, as shown in Fig. 11.

It can be seen from Fig. 11 that the oily sludge and scum present a certain spatial network structure before treatment, with a certain cross-linking structure. The volume of the oily sludge and scum is swollen and wrapped with oil droplets, which leads to the enhanced stability of the oily sludge and scum, and the oil is wrapped and difficult to remove. After the reduction treatment, the oily sludge and scum have obvious differences in structure, which split into small pieces of blocky material. The spatial network structure is broken, and

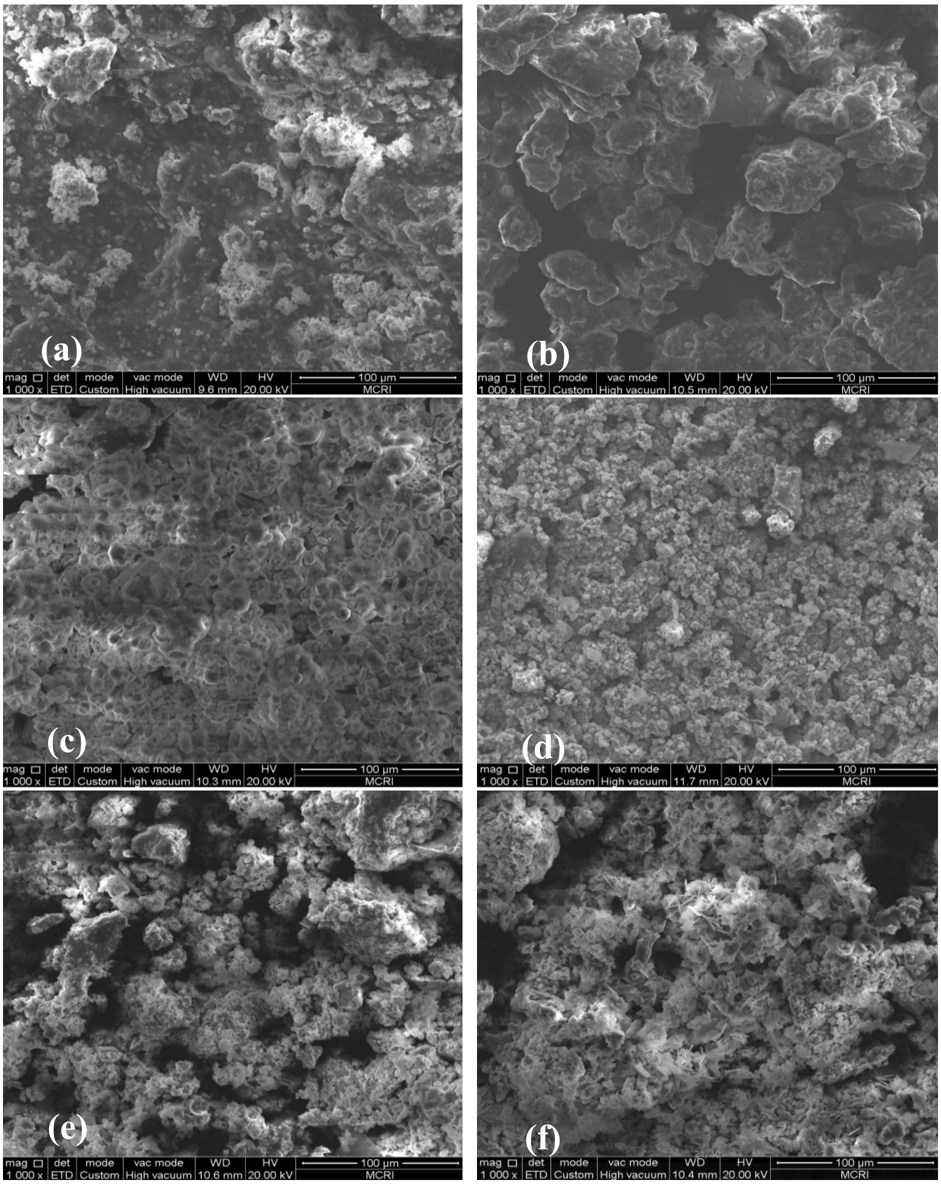

Fig. 11: Morphological comparison of (a,b) tank bottom mud (c,d) refinery sludge (e,f) oily scum before and after treatment.

the oil droplets wrapped in them can be released to remove the oil in the oily sludge and scum.

CONCLUSION

(1) Under the conditions of the best experimental parameters, the oil recovery rate and reduction rate of the tank bottom sludge after the reduction could reach 96.30% and 93.00%, respectively, and the oil recovery rate and reduction rate of the refining sludge after the reduction treatment could reach 95.36% and 92.60% respectively, the oil recovery rate and reduction rate of oily scum after reduction treatment reached 95.92% and 93.60% respectively.

(2) Oil content of the residue can be as low as 5.1% and the water content as low as 59% after three types of sludge are treated under the best process conditions.

(3) Oil content in the water separated from the three types of sludge is less than 200 mg.L^{-1}, which can be directly sent to the sewage treatment system of the oilfield combined station for advanced treatment. The water content in the separated oil is lower than 0.2%, far lower than the requirement of 0.5% in the oilfield's crude oil gathering and transportation standard.

(4) Based on the morphology of sludge, oily sludge, and scum had obvious differences in structure. They split into small pieces of blocky material, the spatial network structure was broken, and the oil droplets wrapped in them could be released so that the oil in the oily sludge and scum could be removed.

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