Review on oily sludge treatment technology

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Abstract. Oily sludge is one of the most important solid pollutants produced by petroleum industry. Due to the serious pollution and the increasing production of oily sludge year by year, how to effectively treat oily sludge is the focus of worldwide attention. This paper mainly introduces the source, characteristics, environmental impact, as well as traditional and newly developed oily sludge treatment technologies. With the improvement of national environmental protection requirements, oily sludge quality reduction, recyclable and harmless treatment technology will become the most potential technologies in the future.

1. Introduction
The petroleum production includes such procedures as exploration-installing derrick - drilling-cementing-logging-seepage-drilling-gathering-refining-transportation-storage of refined oil. Oily sludge is one of the main pollution generated during these processes. The contained oil in oily sludge may be thought as the recovery resource; otherwise it is harmful to the environment. With the continuous exploitation of petroleum resources, and the accompanying excessive environmental contamination, the task of environmental protection is becoming more and more crucial [1]. Thus, the treatment and reuse of oily sludge in oilfield industry has become a research hotspot in recent years[2].In this paper, the characteristics and environmental impact of oily sludge, as well as the traditional and newly developed oily sludge treatment technologies are discussed, and their application status are analyzed.

2. The characteristics of oily sludge
Oily sludge is a stable emulsifying dispersion system composed of water, solid, petroleum hydrocarbons (PHCs) and metal[3]. Total petroleum hydrocarbon (TPH)content in oily sludge is 15-50% (percentage of mass), while water and solid contents are 30-85% and 5-46%respectively[4]. The composition of oily sludge is very complex. It usually contains a large amount of crude oil, asphaltene, wax, gum, solid suspended matter, heavy metal salts, benzene series, phenols, anthracene, pyrene and other toxic and harmful substances [5]. The pH value of oily sludge is usually between 6.5 and 7.5. Generally, oily sludge is composed of (percentage of mass) 28-33% aromatics, 40-55% alkanes, 8-12% asphaltene and 10-22.4% resin[6].
3. The environmental impact of oily sludge
Oily sludge is a hazardous waste. It will bring serious negative effects if it is not properly treated and disposed. The negative effects can be manifested in three aspects. (1) The volatilization of petroleum components in oily sludge will lead to excessive concentration of total hydrocarbons in the air of surrounding areas; (2) The improperly treated oily sludge will pollute the surface water, even the groundwater, and make the concentration of COD and petroleum substances in the water seriously exceed the standard; (3) Oily sludge contains a large number of toxic and harmful organic compounds, such as hydrocarbons, phenols, anthracene and benzene ring compounds. Some substances have carcinogenic, teratogenic and mutagenic effects to the environment [7]. Therefore, oily sludge has been listed in the National Hazardous Waste List.

4. Reduction, recyclable and harmless treatment of oily sludge
Three strategies adopted for treatment and management of oily sludge are quality reduction, recyclable and harmless [8]. (1) Promote the improvement of production technology of petroleum industry, thus reduce the amount of oily sludge produced by petroleum and petrochemical enterprises from the headstream. (2) Extract and recycle the reusable petroleum energy from the existing oily sludge. (3) Apply different technologies to treat non-recoverable oily sludge residue or the oily sludge itself, in order to prevent the environment pollution caused by oily sludge [9].

This paper mainly focused on the different treatment technologies which meet the purpose of the above strategies (2) and (3). Traditional oily sludge treatment technologies include solvent extraction technology, chemical cleaning technology and pyrolysis technology. Newly developed treatment technologies include supercritical water oxidation (SCWO) technology, ultrasound treatment technology and microwave radiation technology.

4.1. Traditional oily sludge treatment technology

4.1.1. Solvent extraction technology. Solution extraction is based on the principle of "similar miscibility"[10]. Organic solvents with similar properties to crude oil are selected to extract petroleum substances from oily sludge, thus realizing the purpose of crude oil recovery. The oily sludge extraction is a typical liquid-solid extraction, which is the process of choosing the appropriate extraction solution and mixing it with the sludge adequately, then distilling the solvent/oil mixture and separating the oil from the solvent [11]. The solvent can be recycled after condensation. Commonly used extractants are trichloromethane, propane triethylamine, reforming oil, etc.

Solvent extraction is a simple and effective recyclable treatment method, which can effectively separate oily sludge into recyclable hydrocarbons, smaller solid and semi-solid residues. Solvent extraction method has the potential to treat a large number of oily sludge. At present, one of the major obstacles to the large-scale application of oily sludge treatment method is that the consumption of the organic extractants is too large, and a large amount of used organic solvents can easily cause secondary pollution [12]. Supercritical fluid extraction method can effectively reduce the dosage of extractants and shorten the extraction time. However, it is not suitable for large-scale application because of its harsh operation conditions [13]. Therefore, the focus of future research is to find high-efficiency, wide-source and low-cost extractants or to develop new alternative methods and processes to improve the solvent extraction ability.

4.1.2. Chemical cleaning technology. The main purpose of chemical cleaning technology is to realize oil, sludge and water three-phase separation. The process is as follow: add an appropriate amount of hot water and chemical reagents into oily sludge, and change the properties of oil-liquid phase and oil-mud interface in oily sludge by the roll-up, emulsification, dissolution and solubilisation function of chemical reagents. As a result, crude oil is washed off from the surface of sludge, and the viscosity of oily sludge is reduced. Finally, the separation of oil, sludge and water is realized by the following settling and swirling processes [14].
The advantages of chemical cleaning method are simple, low cost, high reliability and high oil recovery rate. However, the chemical cleaning agent is easy to cause secondary pollution, and it has strong specificity. The separation efficiency of chemical cleaning method is affected by the type and dosage of reagent, washing temperature, liquid-solid ratio, stirring intensity, stirring time and pH value [15].

4.1.3. Pyrolysis technology. Pyrolysis technology refers to the method of heating oily sludge under the condition of micro-positive pressure without oxygen, in order to separate out oil and organic matter, and segregate oily sludge into pyrolysis residue, pyrolysis liquid, and pyrolysis gas to achieve the purpose of resource utilization [16]. The thermal transformation process of oily sludge can be divided into two stages: the first stage is called evaporation. When the temperature is below 350℃, light hydrocarbons with a low boiling point will evaporate from the oily sludge. The second stage is called parallel-sequential reaction. The pyrolysis reaction will happen on the heavy oil when the temperature exceeds 350℃, and hydrocarbons will generate free radicals due to thermal activation at about 400℃[17]. At the same time, a series of free radical reactions will occur. On the one hand, they are directed towards the pyrolysis process of generating small molecular hydrocarbons, and on the other hand, they are directed towards the condensation process of coking carbon generation [18]. Finally, oil, water, non-condensable gas and hard coke are produced. However, the proportion of things varies slightly when the reaction conditions changed.

Compared with the incineration method, the NOx and SOx discharged by the oily sludge pyrolysis process are far lower than the incineration process [19]. Heavy metals and other pollutants in oily sludge can be enriched and fixed in solid residue, which greatly reduces the environmental pollution degree. The liquid product produced by pyrolysis process has good capacity reduction effect and is convenient for storage and transportation; the recovered oil can be directly applied to diesel engines; the carbon-containing solid residue can also be reused as adsorbent, flocculent, soil improver and so on. Thus, the pyrolysis method really realizes "turning waste into treasure" and recovers and utilizes the resources effectively [20]. However, oily sludge usually contains a large amount of water and the cost of the dehydration process before pyrolysis is high. In addition, the temperature of pyrolysis reaction and the energy consumption are high, and the requirements for equipment are strict. At present, the technology is still in the laboratory testing stage, and the related technology needs to be further improved [21].

4.2. Newly developed oily sludge treatment technology

4.2.1. Supercritical water oxidation (SCWO) technology. Supercritical water oxidation (SCWO) method is a technology that uses supercritical water as reaction medium and uses air, oxygen and hydrogen peroxide as catalysts to initiate free radical reaction under high temperature and high pressure to degrade organic matter, so as to achieve oily sludge harmless treatment purpose[22]. The advantages of supercritical water oxidation method are fast and efficient. It can degrade pollutants thoroughly and is less interference by the external environment. However, the disadvantages of this technology are that its operation cost is quite high and it cannot eliminate the harm caused by heavy metals.

The factors affecting the efficiency of supercritical water oxidation technology are reaction temperature, pressure, time, the ratio of actual dosage of hydrogen peroxide to theoretical requirement, the concentration of alkali and the pH of the solution [23].

4.2.2. Ultrasound treatment technology. Ultrasound treatment technology is mainly realized by the acoustic cavitation effect, mechanical effect and thermal effect of the sound field [24]. Under the irradiation of ultrasonic, the temperature of the oily sludge emulsification system increases and the viscosity of the emulsification system decreases, which significantly reduces the stability of the oily sludge emulsification system. This process promotes the desorption of waste oil from the surface of
solid particles [25]. The micro-jet velocity generated by acoustic cavitation can reach 400 km/h. Under this shock wave the movement speed of small droplets in the oil-bearing sludge emulsion system increases, and their collision frequency also increases. These make the condensation and coalescence of droplets easier to occur and promoting the separation of water and oil phases[26]. The oil removal effect of oily sludge is better under weak acoustic cavitation condition than strong acoustic cavitation condition. The influence of various factors on oil removal effect in ultrasonic treatment technology was also studied. It was found that the order of influencing factors was ultrasonic frequency > ultrasonic power > Treatment temperature > treatment time [27].

Ultrasound treatment technology has the advantages of high efficiency, fast speed and no secondary pollution. It is a "green" method which can treat oily sludge in a relatively short time. However, the treatment of oily sludge by ultrasonic radiation technology is mostly in the experimental stage [28]. There are few reports on the large-scale application of oilfield. In the future, it is necessary to further study the specific oily sludge system, optimize the equipment and improve the reactor structure.

4.2.3. Microwave radiation technology. Microwave radiation technology has thermal, electrical, magnetic and chemical effects [29]. Microwave radiation can destroy the Zeta potential of the oil-water interface in oily sludge. The magnetic field formed by microwave can also magnetize non-polar oil molecules and demulsify and dehydrate oily sludge [30]. The principle of microwave heating is to use polar molecules in substances to vibrate and rub in the high-speed electromagnetic field to produce a large amount of heat, so that substances can be heated. Microwave can directly penetrate the material and start heating from the inside of the material [31].

The effect of microwave heating is characterized as fast and uniform, sensitive, high efficiency and good selectivity [32]. Using this microwave radiation technology, the oily sludge can be dried and dewatered, and the oil-water emulsion in the sludge can be demulsified and separated. Thus the oil, water and residue can be separated and recycled [33].

5. Conclusions
The production of oily sludge is an unavoidable problem in the process of petroleum development, and the harm of oily sludge to the environment is extremely serious. Therefore, it is urgent to treat oily sludge properly. The solvent extraction technology, chemical cleaning technology, pyrolysis technology, supercritical water oxidation (SCWO) technology, ultrasound treatment technology and microwave radiation technology introduced in this paper have good treatment effect on oily sludge treatment and can be applied in the petroleum industry.

In the practical application of oily sludge disposal project, petrochemical companies should select comprehensive oily sludge disposal methods according to the characteristics of various disposal methods, combined with their own geographical location, crude oil types, process features, characteristics of oily sludge and enterprise demand. Single treatment technology cannot meet the requirements of environmental protection, while combined treatment technologies can meet the requirements efficiently. In the application of oily sludge treatment technology, attention should also be paid to the combination of traditional technology and newly developed technology, with comprehensive consideration to the cost and the feasibility of the technology. In a word, according to the characteristics of oily sludge, selecting efficient advanced treatment technology is the focus of future research.

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