Toxic Rational Analysis of Oily Sludge and Its Treatment Residues

Wanjing Li¹, Tao Yu¹, Chengtun Qu¹,²*, Hao Zheng¹ and Yanfei Wang¹

¹ College of Chemistry & Chemical Engineering, Shaanxi Province Key Laboratory of Environmental Pollution Control and Reservoir Protection Technology of Oil fields, Xi’an Shiyou University, Xi’an, China
² State Key Laboratory of Petroleum Pollution Control, CNPC Research Institute of Safety and Environmental Technology, Beijing 102206, China
Email: xianquct@xsyu.edu.cn

Abstract. In view of the present situation of oily sludge pollution, the different treatment methods for oily sludge in different uses were briefly described. The composition and structure of oily sludge are affected by sludge type, source, pyrolysis conditions and subsequent treatment conditions, which lead to different treatment methods and treatment effects. At present, there is no unified standard for the treatment of oily sludge at home and abroad, which brings difficulties to the unified management of oily sludge treatment. Through the toxicity analysis of oily sludge and its residues, it is helpful to judge the harmfulness of oily sludge and its treatment residues, according to the harmfulness of oily sludge, effectively choose different follow-up treatment methods, it is beneficial to establish the scientific standard of oily sludge treatment. In this paper, the present post-treatment indexes of petroleum hydrocarbon content, heavy metal ion content, water content, Polycyclic aromatic hydrocarbon content and sulfur content in oily sludge are summarized.

Keywords. Oily sludge; treatment residue; toxicological study; treatment standard.

1. Introduction
Oily sludge is a kind of solid waste formed by the adhesion and penetration of petroleum substances in the process of petroleum exploitation, refining, storage and use. At present, the treatment methods of oily sludge mainly include: landfill method, incineration method, biological method, thermochemical cleaning method, solvent extraction method, heat treatment method and the like. At present, there is no unified standard for the treatment and disposal standards of oily sludge in China. Therefore, each major oilfield has established corresponding standards, such as Liaohe Oilfield and Shengli Oilfield. The control index of the treatment process of the oily sludge cleaning station is the oil in the sludge after treatment. The amount is ≤3%. The Environmental Protection Bureau of Heilongjiang Province issued the “Control Standard for Comprehensive Utilization of Oil-Containing Sludge in Oil Fields”, which established 11 pollution control indicators for oily sludge in the oilfields used in the wells, wells and agricultural fields. The petroleum content is ≤ 2% [1].

As the intensity of oil exploitation increases year by year, the amount of oily sludge continues to rise, but how to effectively dispose of the treated residue and safely use it is still a problem faced by many oil fields. These residues contain a variety of toxic and hazardous substances, which are harmful to the environment. For example, in the pyrolysis products of oily sludge, the pyrolysis residue accounts for a large part, and contain oil resources that are not completely recovered and residual...
heavy metals. Elements, etc., have been included in the “National Hazardous Waste List” and will cause secondary pollution if not handled properly. Therefore, the research on the disposal of oily sludge residues has gradually attracted the attention of scholars at home and abroad.

2. Toxicological Study of Oily Sludge and Its Residues
The treatment of oily sludge and its residue after treatment and its final destination will have different effects on the environment directly or indirectly. Therefore, it is particularly important to study the toxicological properties of oily sludge and its residue.

2.1. Petroleum Hydrocarbon Content
If the oily sludge is not treated properly, the recovered oil is not thorough enough, and the petroleum substances in the residue are very harmful to the environment. The volatile components enter the atmosphere, causing the total hydrocarbon concentration in the atmosphere to exceed the standard, and the crude oil in the residue will enter the soil. Harm to microbial and soil plant ecosystems, ecosystems are severely affected. According to different disposal methods, foreign countries have different control indicators for petroleum hydrocarbons in hazardous solid waste such as oily sludge. For example, the index used for landfill in the United States and France is ≤ 2%, the road construction is ≤ 5%; the indicator used for landfill in Canada is also ≤ 2% [2].

Wang [3] made inference calculations for the identification of hazardous waste using petroleum hydrocarbon indicators. The results show that the petroleum hydrocarbon content of solid waste such as oily sludge and its treatment residue is ≤0.25%, which is not hazardous waste. When the petroleum hydrocarbon content is between 0.25% and 1.7%, whether it is hazardous waste, the final identification of hazardous waste is required. It is determined that petroleum hydrocarbon content >1.7% is classified as hazardous waste.

2.2. Heavy Metal Ion Content
The oily sludge also contains heavy metal ions such as copper, zinc, chromium, cadmium, mercury, lead, etc., in order to avoid the adverse effects of landfill residue on the soil, the heavy metal content of landfill, road construction and agricultural sludge residues in various countries. Strict requirements have also been raised. Due to the different nature of the soil, the regulations on the content of heavy metals in landfill residues are not the same at home and abroad.

Juli [4] and other research and research on the treatment and comprehensive utilization of oily sludge in oil fields have formulated pollution control standards for comprehensive utilization of oily sludge in oil fields. The pollution control indicators are shown in Table 1.

Ren [5] and others made the residue of the oil-free sludge harmless treatment into roadbed materials, and detected pollutants such as As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, DDT, and BHC. The results show that the oily sludge is made into roadbed material after harmless treatment (oil content ≤ 2%), and the detection values of 10 indicators of heavy metals and pesticides specified in GB15618-1995 Soil Environmental Quality Standard are required. Within the limits, there is no excess.

2.3. Moisture Content
The oily sludge has a relatively high water content. If the pyrolysis treatment is directly carried out, the energy consumption is too large. Therefore, it is necessary to carry out dry pretreatment of the oily sludge.

Zhu [6] et al. conducted a study on the pyrolysis residue of pyrolysis treated oil sludge after pyrolysis treatment, and found that the pyrolysis residue was dried and followed. After treatment, it can be used to remove SO$_2$ from flue gas, and has good adsorption and desulfurization ability, and has potential for further improvement and improvement.

2.4. Polycyclic Aromatic Hydrocarbon Content
Polycyclic aromatic hydrocarbons (PAHs) are mainly carcinogenic compounds produced by pyrolysis
and incomplete combustion of coal, petroleum, wood, etc. They have strong hydrophobicity and are easily adsorbed on the surface of soil particles after entering the soil environment. Degradation can be absorbed into the organism through the roots of plants and enriched through the food chain, which is teratogenic, carcinogenic and mutagenic to the human body. Therefore, polycyclic aromatic hydrocarbons have been listed on the priority list by many countries, and China has listed 7 polycyclic aromatic hydrocarbons in the blacklist of environmental pollutants [7].

Table 1. Pollution control indicators for comprehensive utilization of oily sludge in oil fields.

| Serial number | Project | Pollution control indicator | Agricultural use (mg/kg Dry sludge) |
|---------------|---------|-----------------------------|-----------------------------------|
|               |         | Drilling field              | Soil pH<6.5 | Soil pH≥6.5 |
| 1             | Petro   | ≤20000                      | ≤3000      | ≤3000       |
| 2             | As      | ≤75                         | ≤75        | ≤75         |
| 3             | Hg      | ≤5                          | ≤15        | ≤15         |
| 4             | Cr      | ≤0.8                        | ≤600       | ≤1000       |
| 5             | Cu      | ≤150                        | ≤250       | ≤500        |
| 6             | Zn      | ≤600                        | ≤500       | ≤1000       |
| 7             | Ni      | ≤150                        | ≤100       | ≤200        |
| 8             | Pb      | ≤375                        | ≤300       | ≤1000       |
| 9             | Cd      | ≤3                          | ≤5         | ≤20         |
| 10            | pH      | ≥6                          | -          | -           |
| 11            | Moisture content | ≤40%               | -          | -           |

He [8] and others studied the repair effect of soil-contaminated soil under the combined action of plant microorganisms. The test proved that the phytoremediation treatment of soil, the degradation rate of polycyclic aromatic hydrocarbons reached 60%, the benzopyrene content also decreased significantly, and its content degradation reached 57.2%.

Liu [9] et al. analyzed the content, source and total toxic equivalent concentration (TEQ) of polycyclic aromatic hydrocarbons (PAHs) in oily sludge from five different sources, and determined the acute biotoxicity of different organic solvent extracts and analyzed the PAHs and acute biotoxicity of sludge contaminated water samples. The study found that the content of PAHs in different oily sludge was 496.10-4233.25 μg·g⁻¹, and the total toxicity equivalent (TEQ) of PAHs was 8.41-231.56 μg·g⁻¹. The content of PAHs in the contaminated water samples was 9.68-385.16 ng·mL⁻¹. Except for the water samples contaminated by the clear sludge, the benzo (a) pyrene (BaP) in other sludge contaminated water samples did not exceed the standard, but all the tested water The samples all have high acute toxicity, and the relative luminescence inhibition rate is up to 87.46%, which greatly exceeds the inhibition rate of Zn²⁺ of the toxic reference substance 100 mg·L⁻¹.

Wu [10] and other research conducted supercritical fluid extraction and solid phase extraction column purification pretreatment combined with gas chromatography-mass spectrometry to treat oily sludge in Xinjiang oilfield. The experimental results show that when extracting 16 common polycyclic aromatic hydrocarbons in sludge, the pressure is 25-35 MPa, the temperature is 40-50 °C is the extraction efficiency is better. A method for simultaneously detecting 16 polycyclic aromatic hydrocarbons in oily sludge was established with high accuracy and precision.

2.5. Sulfur Content
Sulfur content is one of the important factors to be considered in the process of oil sludge treatment or resource utilization. For oily sludge with high sulfur content, acidity or alkalinity, attention should be paid to the influence of corrosion on equipment and process, corrosion-resistant equipment and pipelines should be selected, equipment should be protected by reasonable anti-corrosion method, and harmless in oily sludge. In the treatment, the key rule of sulfur transfer law is studied to prevent secondary pollution of oily sludge treatment.
Zhao [11] and other reference sulphur classification methods in coal, the sulfur content of the sludge is divided into 5 grades, it is found that the formation of oily sludge and sulfate-reducing bacteria formed after heavy oil treatment will increase the sulfur content in the oily sludge.

In the process of oily sludge treatment or resource utilization, the impact of corrosion on equipment and process should be considered for oily sludge with high sulfur content, acidity or alkalinity. It should be selected from equipment and pipeline materials and anti-corrosion methods. Consider equipment protection, and focus on the transfer law of sulfur elements to prevent secondary pollution of oily sludge treatment.

3. Conclusion
The treatment standards for petroleum hydrocarbon content, heavy metal ion content and water content in oily sludge and its treatment residues have been proposed for different purposes, but the treatment standards for polycyclic aromatic hydrocarbons, sulfides and other substances have not been pointed out.

There is no uniform standard for the treatment and disposal of oily sludge in various regions. The safe disposal of oily sludge depends mainly on local policies. The research on the treatment of oily sludge in developed countries such as Europe and the United States started earlier. At present, relatively mature treatment and disposal technologies and supporting control standards have been formed. However, there is no quantitative indicator for the disposal of oily sludge in China. Through the toxicological analysis of oily sludge and its residue, it can help to judge the dangerous properties of oily sludge and its residue after treatment; establish a scientific oil sludge treatment standard and follow the harmless and resource treatment of oily sludge Provide evidence.

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