Application Status and Prospect of Combined Treatment Technology for Oily Sludge in Domestic Oil Fields

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Abstract. The oily sludge has a wide range of sources and complex composition, the corresponding treatment technology and equipment also show a diversified trend, after the combined treatment of oily sludge, the oily sludge can meet the technical requirements of resource utilization and harmless treatment. Through the actual and literature research, the principle, scope, characteristics and development of the commonly used oily sludge treatment methods at home and abroad are summarized, the application status of several new oily sludge combined treatment technologies in China's petrochemical enterprises is introduced, including sieving fluidization-tempering-mechanical dehydration technology, electrochemical bio-coupling advanced treatment technology, sludge centrifugal dewatering-superheated steam injection treatment technology, hot-washing coupling treatment technology and microbial-plant combined treatment technology, summarized whether the oil content of the residue after treatment by the existing treatment method meets the standard requirements of HJ 607-2011 "Technical Specifications for Pollution Control of Used Mineral Oil Recovery, Recycle and Reuse" and the resource utilization of the residue goes. The problems and treatment effects of the integrated oil sludge treatment technology in application have not yet been treated in a satisfactory manner to completely treat all oily sludge, and further research is needed.

Keywords: Oily sludge; non-biological methods; biological methods; combined treatment; process comparison.

1. Introduction
Oily sludge is generally a stable system of suspended emulsions composed of oil in water (O/W), water in oil(W/O) and suspended solids, difficult dewatering. The composition and physical properties of sludge are affected by factors such as the wastewater quality, treatment processes, type of chemical agents and dosage, big difference and difficult for handling. The oil content of oily sludge varies greatly, and part of it has recycling value. Oily sludge contains a large number of pathogenic bacteria, parasite (egg), heavy metals such as copper, zinc, chromium and mercury, and a large number of malodorous poisonous substance such as benzene series, phenols, polychlorinated biphenyl, dioxin, anthracene, pyrene, and hard biodegradation poisonous and harmful substance such as Radionuclide. It is also
radioactive to the environment, If not treated and direct discharge, it will cause pollution to soil, water and air, it was listed in the National Hazardous Wastes Catalogue [1].

Table 1. Biological treatment and effects

| handling methods                  | treatment degree                                      | secondary pollution                       | Technology level     |
|-----------------------------------|-------------------------------------------------------|------------------------------------------|---------------------|
| Land farming and composting       | All the TPH in the sludge is degraded                 | Soil and Groundwater Pollution           | Simple, mature      |
| Bioaugmentation technique         | Total degradation of organic matter                   | malodorous gas                           | Complexex, immaturity|
| Bioreactor treatment prepared bed | Limit pollutant diffusion and migration                | Destruction of the original ecosystem    | Simple, immature    |
| Biological flotation treatment    | Oil removal efficiency \( \geq 95\% \)               | malodorous gas                           | More complex, more mature |

Table 2. Abiotic treatment and effects

| handling methods                  | treatment degree                                      | secondary pollution                       | Technology level     |
|-----------------------------------|-------------------------------------------------------|------------------------------------------|---------------------|
| Coking process                    | Oil content of waste residue \(<0.3\%\)                | Dust, odorous gas produced               | More complex, mature |
| Direct landfill                   | whole processors                                       | Direct pollution of the environment      | Simple, mature      |
| incineration disposal             | Organic matter all treatment, recovery of heat        | dust, \( \text{SO}_2 \), etc              | More complex, more mature |
| Curing stable treatment           | Complete treatment of organic matter                   | Leakage causes environmental pollution   | Simple, mature      |
| Solvent extraction treatment      | Handle more thoroughly                                  | solvent pollution problem                | Simple, prematuration|
| ultrasonication                   | Recovered oil thoroughly                               | Residues such as heavy metals            | More complex, immaturity |
| pyrolysis treatment               | Organics are all treated, gas recovery                 | smoke pollution                          | More complex, prema |
| chemico - heating wash            | Recovery of oil is not complete                        | Chemical contamination                    | Simple, mature      |
| Injection formation treatment     | Handle complete                                         | stratum, groundwater pollution           | Simple, more mature |
| Tempering separation treatment    | Not thoroughly degreased                                 | chemicals pollute the water              | More simple, more mature |
| Profile control technology        | Handle complete                                         | Seepage causes soil contamination         | Simple, mature      |

At present, there are many typical combined remediation technologies for oily sludge at home and abroad, including screen fluidization-hardening and tempering - Mechanical dewatering technology, electrochemical biological coupling processing technology, sludge centrifugal dewatering - superheated
steam injection treatment technology, heat wash coupling treatment technology, microbial - plant combined remediation technology and so on. Through the use of these combined treatment technologies, the annual generation of a large part of the oil sludge harmless treatment resources, reduce air pollution caused by the oil in the oily sludge evaporation and volatile substances, reduce the soil and water pollution caused by the accumulation of oily sludge infiltration.

2. Joint repair technology introduction

2.1. Screen fluidization-hardening and tempering - Mechanical dewatering technique

Cause the source and moisture content of oily sludge are different, in order to ensure the normal operation of the follow-up equipment and achieve the expected effect, oily sludge should be carried out screen fluidization-hardening and tempering, then appropriate additives are added to different oily sludges, the oil can be desorbed more easily from the solid particle surface. Through experiment, additives include surfactant thinners, diluent (decane), electrolyte (sodium chloride solution), demulsifier (Anion and non-ion), ph controlling agent and so on, and supplemented by conditioning means, such as, heating to reduce viscosity (Generally more than 50⁰C, less than 80⁰C).

Chen Zhongxi et al.[2]. through model analysis of screen fluidization-hardening and tempering - Mechanical dewatering technique by the sample of mixed oily sludge from settling tank sludge and settling tank sludge in Daqing Oilfield. search for the best screen fluidization processor as the operating parameters, cleaning agent applicable conditions, among the structure of demulsifier, the tempering temperature of sludge with different oil content, centrifuges spinning, dosage of flocculant, operating parameters of oil-water separator, then the corresponding optimal industrial operation parameters are obtained, the oil content of sludge after treatment is less than 2%.

2.2. Electrochemical biological coupling processing technology

Electrochemical biological coupling processing technology a new treatment method for oily sludge after laboratory and field experiments, it is a treatment technique of electric field coupling and biodegradation simultaneously, there are three types: electrochemical-biological leaching technology, Electrochemical injection of nutrient substrates or degradative bacteria, electrochemical methods stimulated and enhanced the metabolism of degrading bacteria[3]. Maini et al. [4] proposed the method combining bioleaching with electrodynamics to remediate land contaminated by metal ions.

Wei li et al. [3] studied deep processing technology of electrochemical biological coupling in laboratory and field after sampling at a plant in Daqing, five technological methods were used, electricity before bacterium, bacterium before electricity, electricity and bacterium at the same time, pure electric processing and pure microbial treatment. The crude oil removal rate of sludge inside different process device is shown in table 3.

| process unit                  | surface layer | bottom layer |
|-------------------------------|---------------|--------------|
| electricity before bacterium  | 66.22         | 72.86        |
| bacterium before electricity  | 67.11         | 83.20        |
| electricity and bacterium at the same time | 59.74 | 88.89 |
| pure electric processing      | 54.85         | 77.27        |
| pure microbial treatment      | 71.43         | 87.50        |

2.3. Sludge centrifugal dewatering - superheated steam injection treatment technology

Sludge centrifugal dewatering - superheated steam injection treatment technology is oily sludge raised to a homogeneous tank and stirred evenly, then to heat exchanger by the lift pump or directly into the centrifuge, the oil sludge dehydrated by the centrifuge is transported to the high-temperature treatment
tank, it was crushed under high temperature and high speed steam jet, at the same time the oil and water are evaporated, the crushed particles enter the cyclone chamber together with the steam, the separation of steam and solid particles is realized under the action of cyclone, the solids then enter the recovery tank and the steam enters the oil-water separation tank, oil and water are separated after cooling. Principle diagram is shown in figure 1.

![Principle diagram](image)

**Fig.1 Sludge centrifugal dewatering - superheated steam injection treatment working principle diagram**

Lin Haibo et al. through sludge centrifugal dewatering, and Gasification separation under superheated steam above 600℃, the water content of the recovered oil after treatment is less than 0.5%. The oil content of the residue can be controlled to a minimum of 0.3%, the moisture content is less than 10%, so as to achieve the reduction and harmless of oily sludge. Li Ying et al. carried out an energy saving optimization design for the disadvantage of high energy consumption of superheated steam injection treatment technology, by adding remaining heat exchanger and heat exchange process make waste heat recovery efficiency is 12.7%, expected to save 70400RMB/a, the payback period is just over 2 months, and it is feasible. This kind of process adopts airtight process to improve safety and cleanliness, short process, low energy consumption, automatic control and strong practicality, it can deal with all kinds of sludge such as the ground oily sludge, tank oily sludge and flotation scum.

2.4. Heat wash coupling treatment technology
Heat washing technology is also called thermal desorption, it is a process in which a certain proportion of hot water and chemical agents are added to the oily sludge for repeated washing to make the oil desorption or aggregation and separation from the solid surface. The commonly used hot washing agents are warm buck and surfactant. However, the oily sludge residue after hot washing treatment can not meet the national emission standards, the recovery of crude oil is not complete, and can not treat seriously emulsified oily sludge. Therefore, many professionals transform the hot wash technology and introduce the hot wash coupling processing technology.

Lv Ronghu et al. proposed hot wash - air flotation separation technology is transfer the cleaned oily sludge mixture to the air flotation device. Under the optimal process condition, the removal rate of oil can reach 92.5%~93.5%, Residual oil content in soil was 0.9%~1.0 %, The concentration of pollutants in oily sludge residue is basically satisfied HJ 607-2011 “Technical Specifications for PollutionControl of Used Mineral Oil Recovery, Recycle and Reuse”

2.5. Microbial - plant combined remediation technology
Microbial - plant combined remediation technology is often studied and used in two types: plant-fungal joint repair and plant - obligate degrading bacteria combined repair[5]. Mycorrhiza of plant-fungal joint repair is a combination of fungi and plant roots, its necessary carbohydrates can be extracted from the roots, meanwhile, mycorrhiza can also provide nutrients and water to plant roots, when treated heavy metal contained soil, mycorrhiza can improve plant growth environment, reduce heavy metal toxicity and promote plant growth. Plant - obligate degrading bacteria combined repair is microorganisms...
convert heavy metals into non-toxic or low-toxic compounds through a series of chemical reactions, adding obligate degrading bacteria with strong degradation ability can more efficiently treat soils contaminated with oily sludge when using plants to repair the soil[6].

Although the microbial strains and plants were greatly affected by the environment during the combined restoration, and further affected the restoration, therefore, it is difficult to construct an effective combination of microbial and phytoremediation of oil-contaminated soil, however, because this method is economically feasible, it is favored by most oilfields.

3. Comparison of combined remediation technology

Through the comparison with screen fluidization-hardening and tempering - mechanical dewatering technology, electrochemical biological coupling processing technology, sludge centrifugal dewatering - superheated steam injection treatment technology, heat wash coupling treatment technology and microbial - plant combined remediation technology on repair time of processing mode, facilities spend, in-situ and ex-situ, and practical investigation, we can find that It is difficult for a single treatment to achieve the requirements of reduction, harmless and resource, it is necessary to use combined sludge treatment method according to the characteristics of sludge producing area and form a complete treatment system. it can realize harmless and resource treatment of the oily sludge. See table 4 for details.

| Table 4. Comparison of oily sludge treatment methods |

| treating technology | repair time | infrastructure investment | in-situ / ex-situ | target | Repair purpose | Oily sludge can be treated | Application point |
|---------------------|------------|---------------------------|------------------|--------|---------------|---------------------------|------------------|
| screen fluidization-hardening and tempering - mechanical dewatering technology | About 107 d | high | ex-situ | the oil content of sludge after treatment is less than 2%, and meet the technical standards required by Pollution control standards for the comprehensive utilization of oil-bearing sludge in oil fields(DB 23/T1413-2010). Meet the requirements of landfill paving | realize resourceful utilization | All kinds of oily sludge | Daqing Oilfield |
| electrochemical biological coupling processing technology | About 75 d | low | ex-situ | oil content≤3‰, reach the maximum permissible limit in the soil standards required by Technical Specifications for Pollution Control of Used Mineral Oil Recovery, Recycle and Reuse(HJ 607-2011), meet the heavy metal and other indicators to achieve emission standards | Realize the deep treatment of oily sludge | refinery oily sludge | Daqing Oilfield |
| sludge centrifugal dewatering - superheated steam injection treatment technology, | About 150 d | low | ex-situ | The oil content in the solid residue is less than 0.3%, heavy metal content in accordance with the corresponding national standards, the recovery rate of crude oil is more than 99%, and the recovered oil is pure, no second pollution, solid residue can be used for building materials, build roads or for landscaping | Realize the double benefit of resource recovery and environmental protection | All kinds of oily sludge | Jilin Oilfield |
| heat wash coupling treatment technology | about 40 d | medium (About 20.5 million RMB | ex-situ | removal rate of oil in oily sludge reached 92.5%~93.5%, residual oil content in soil was less than 1.0%, contaminant content in oily sludge residue meet the technical specification of Technical Specifications for Pollution Control of Used Mineral Oil Recovery, Recycle and Reuse(HJ 607-2011). | oil sludge sand has basically realized harmless, recycling and reduction, which brings positive environmental benefits | All kinds of oily sludge | Shengli Oilfield, Daqing Oilfield, Liaohe Oilfield, Jilin Oilfield, Xinyang Oilfield |
| microbial - plant combined remediation technology | 150 d | low | in-situ | The highest degradation rate was achieved 85.67% | Maximizes deficiencies in a single microbial repair, Through the multi-scale three-dimensional remediation technology, the remediation of oil-contaminated soil is strengthened, and the oily sludge after treated TPH<0.1% | can meet the applicable field environmental conditions of microbial - plant combined remediation technology | Most Oilfield |
4. Conclusion and forecast

(1) The oil content of sludge treated by screen fluidization-hardening and tempering - mechanical dewatering technology was all less than 2%, meet the industry standards for landfill paving requirements, but not up to agricultural standards, and with the oil sludge treatment technology more and more mature, requirements for landfills are getting higher and higher, therefore, screen fluidization-hardening and tempering - mechanical dewatering technology can only be used as the pretreatment technology of oily sludge, and need further research before it can be widely used.

(2) Electrochemical biological coupling processing technology improved degradation rate and cost-effectiveness of electrochemical treatment, however, it is affected by temperature, humidity, pH and other factors in field application, therefore, the technology is still in the laboratory experiment stage, it needs further improvement and further research If the technology is to be popularized in oil fields.

(3) The effect of microbial - plant combined remediation technology is obviously better than that of single microbial repair and phytoremediation, but there are still many problems to be solved: ① combined remediation studies remain largely in the laboratory, large-scale projects are rare, however, the environmental conditions in the field are much more complicated than those in the laboratory, and laboratory results may not be fully applicable to field applications. ② native plant and microorganism in most oil-polluted areas have low tolerance to petroleum hydrocarbons, low degradation capacity and can not meet the needs of remediation of petroleum pollution. At this point, it is need introduce the foreign organisms to achieve the desired effect. Imported alien organisms will compete with native organisms for living space and threaten the survival of native organisms. ③ Optimize microbial strains and plant varieties as well as effective combinations between plants and microorganisms.

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