Application of chemical hot washing method for oily solid waste treatment

LI Ying1, a, CHEN Xi1,b, WANG Yihan1, LI Xiumin1, WANG Zhansheng2,c, YANG Zhongping3, LI Chunxiao1, YUN Jian3,

1 Room 523, block A12, CNPC science and technology center, changping district, Beijing, China
2 Room 518, block A12, CNPC science and technology center, changping district, Beijing, China
3 Room 513, block A12, CNPC science and technology center, changping district, Beijing, China

aliying1416@cnpc.com.cn, bchen-xi@cnpc.com.cn, cwangzc@cnpc.com.cn

Abstract. In this study, five types of chemical hot cleaning agent were screened to evaluate the oil removal efficiency, which was based on the component analysis of an oily solid waste from an oilfield in western China. The best experimental conditions were determined through single-variable and orthogonal tests. The results indicate that pharmacy AST-01 has the best removal efficiency. The optimum treatment conditions were as follows: AST-01 concentration, 20.0 g/L; temperature, 60 °C; stirring speed, 125 rpm; and stirring time 30 min. The oil content decreased to 1.91% under these conditions. The influence order of different factors decreased in the following order: the dosage of pharmacy, stirring speed, and temperature. The results of a combined experiment show that the removal efficiency was improved. The optimum proportion of pharmacies AST-01 and AST-02 was 10:1. The oil content decreased to 0.82%. The field engineering tests showed that the oil content of the residue was less than 2% when the optimum proportion was used. In general, this method decreases the oil content in an oily solid waste significantly and thus reduces the harmfulness of oily solid wastes.

1. Introduction
During oilfield development and production, oily solid wastes such as oily sludge, oil-bearing drilling mud, and waste-oil-based drilling mud produced during oil and natural gas exploration are not disposed effectively due to various reasons. They are deposited on the construction site for a long time, which affects the environment severely. Petroleum products are rich in benzene, toluene, ethylbenzene, and xylene and polycyclic aromatic hydrocarbons that are carcinogenic, teratogenic, and mutagenic [1]. They can cause severe damage to human health in direct or indirect ways. Therefore, the disposal of oily solid wastes is one of the most important problems that need to be urgently solved for petrochemical enterprises by developing proper oily solid waste treatment methods.

Oily solid wastes have a complex composition except for insoluble large-particle debris; they are usually composed of oil-in-water, water-in-oil, and suspended solids [2-5]. It is a relatively stable suspension emulsion system. At present, commonly used treatment methods for oily solid wastes
include incineration, biological treatment, chemical hot washing, solvent extraction, solidification, coking, ultrasonic treatment, tempering, demulsification, and complete utilization of oily sludge [6-13]. Because of different geological structures, such as mud systems, crude oil properties, and methods, times, and locations of solid wastes, the nature of solid waste is very different. The treatment effects of different methods are significantly different.

In this study, the oily sludge in an oilfield was taken as a sample for treatment. The optimum chemical hot cleaning agent was screened through experiments. The effects of concentration, temperature, stirring speed, and time of hot cleaning were evaluated. A combined chemical experiment was carried out to determine the optimum processing conditions for oily solid waste treatment and to provide guidance for other engineering applications.

2. Analysis of Sludge Characteristics

The experimental sludge was taken from a project site of an oil field in western China. Before the screening and evaluation of hot cleaning chemical agents, the oil, mud, and moisture contents of the sludge were analyzed following the relevant test methods. The results are shown in Table 1. By following the standard SY/T5119-2008 “Composition Analysis of Soluble Organic Matter and Crude Oil in Rocks,” the composition of key oil components in the oily sludge was analyzed. The results are shown in Table 2.

![Table 1](attachment:table1.png)

![Table 2](attachment:table2.png)

3. Results and discussion

3.1. Screening of chemical hot washing agents for oily sludge treatment

Five types of hot washing chemicals AST-01–AST-05 were formulated into 2, 3, 4, 5, and 6 g/L, respectively. When the agent/sludge ratio is 5:1, the temperature was 60 °C and the stirring speed was 75 rpm. This was followed by stirring and standing for 30 min and then stratification. The upper oil slick was removed, and the lower sludge aqueous solution was transferred to a centrifugal test tube. The solution was centrifuged at a speed of 2000 rpm for 20 min, and the upper layer aqueous solution was decanted. The remaining oil was extracted with 50 mL of petroleum ether, and the extracted sludge and aqueous solution were poured into a separating funnel and shaken thoroughly. After the standing stratification, the extract was collected in a 50 mL colorimetric tube, diluted with petroleum ether to the mark, and shaken. Using petroleum ether as the blank sample, the absorbance of the sample was measured using a spectrophotometer (wavelength 430 nm). The oil content was calculated by measuring the amount of residual oil using the standard curve. The experimental results are shown in Figure 1. As shown in Figure 1, the organic surface-active hot washing agent is better than the inorganic hot washing
agent, especially the hot washing agent AST-01 was the most effective. With an increase in the concentration, the amount of residual oil in the sludge continued to decrease. For the other four types of agents, when the concentration exceeded a certain value, the residual oil in the sludge showed a rising trend.

![Figure 1](image1.png)

**Figure 1.** Removal effect of various hot washing chemicals

### 3.2. Effect of pharmacy concentration on hot washing

About 20 g of oily sludge was weighed, and 5, 10, 15, 20, and 25 g/L of AST-01 were added. At the agent/sludge ratio 5:1, the temperature was 60 °C, the stirring speed was 75 rpm, and the mixture was stirred and was allowed to stand for 30 min. The oil content was measured by centrifugation for 20 min at a speed of 2000 rpm. The experimental results are shown in Figure 2.

![Figure 2](image2.png)

**Figure 2.** Effect of AST-01 concentration on treatment

As shown in Figure 2, at a certain ratio of agent and sludge, the best concentration of AST-01 was 20 g/L, and the oil content significantly increased when the concentration exceeded 20 g/L. This is mainly because AST-01 is a surface-active agent. At a certain agent/sludge ratio, when the concentration is too high, the content of hot washing agent and sludge mixture surfactant AST-01 is higher. This not only did not afford separation but also caused emulsification, resulting in reduced separation efficiency.

### 3.3. Effect of agent/sludge ratio on hot washing

About 20 g of the oily sludge 1 and 20 g/L of AST-01 were weighed. The agent/sludge ratios were 2:1, 3:1, 4:1, 5:1, and 6:1. The temperature was 60 °C and the stirring speed was 75 rpm. The mixture was stirred and was allowed to stand for 30 min, and centrifuged at a speed of 2000 rpm for 20 min. Then, the oil content was measured after collecting the sludge. The experimental results are shown in Figure 3. As shown in Figure 3, with an increase in the amount of added solution, the effect of oily sludge separation gradually increased. The trend of the line shows that a better separation effect was obtained when the agent/sludge ratio was about 5:1. The addition of a sufficient amount of solution can better make the agent fully contact with the oily sludge, whereas the addition of a very small amount of the solution does not favor the separation of oily sludge. However, if too much solution is added, it leads to a large
increase in subsequent oily wastewater and operating costs such as an increase in the dosage. Thus, a suitable agent/sludge ratio is about 4:1–5:1.

3.4. Effect of temperature on hot washing
About 20 g of oily sludge 1 was weighed and 20 g/L of AST-01 was added. The agent/sludge ratio was 5:1. The temperature was 40 °C, 50 °C, 60 °C, 70 °C, and 80 °C. The stirring speed was 75 rpm. The mixture was stirred and was allowed to stand for 30 min and centrifuged at a rate of 2000 rpm for 20 min. The oil content was measured after collecting the sludge. The experimental results are shown in Figure 4. As shown in Figure 4, the oil content significantly decreased when the temperature was increased from 40 °C to 60 °C. On one hand, the viscosity of the sludge decreased, improving the oil separation efficiency of the oily sludge; whereas, on the other hand, an increase in the temperature enhances the Brownian motion of impurity particles in water and thus increases the number of collisions between the particles, increasing the chances of colloidal aggregation. When the temperature exceeded 60 °C, the residual oil efficiency increased. This is probably because of the partial decomposition of AST-01 caused by overtemperature, reducing the effect of agent on the separation of oily sludge. Thus, the suitable temperature was 60 °C.

3.5. Effect of stirring speed on hot washing
About 20 g of oily sludge 1 was weighed, and 20 g/L of AST-01 was added. The agent/sludge ratio was 5:1 and the temperature was 60 °C. The stirring speed was 50, 75, 100, 125, and 150 rpm. The mixture was stirred and was allowed to stand for 30 min each. The centrifugation speed was 2000 rpm and the mixture was centrifuged for 20 min. Then, the oil content was measured after collecting the sludge. The experimental results are shown in Figure 5.
As shown in Figure 5, with an increase in stirring speed, the oil content of oily sludge first decreased and then increased. The data show that a change in the stirring speed significantly affects the oil content, mainly because a moderate stirring speed can completely mix the sludge and agent. A too strong stirring speed leads to sludge emulsification. The mixer smashes the sludge, making the sludge smaller and making it difficult to settle the sludge. The figure shows that a stirring speed of 125 rpm achieved a better oily sludge separation.

3.6. Effect of stirring time on hot washing

About 20 g of oily sludge 1 was weighed and 20 g/L of AST-01 was added. The agent/sludge ratio was 5:1. The temperature was 60 °C and the stirring speed was 75 rpm. The stirring time was 10, 20, 30, 40, and 50 min. The mixture was allowed to stand for 30 min and centrifuged at a speed of 2000 rpm for 20 min for measure the oil content. The experimental results are shown in Figure 6. As shown in Figure 6, the oil content of the oily sludge gradually decreased with an increase in the stirring time, mainly because of the higher viscosity and poor fluidity of the oily sludge. If the stirring time is not sufficient, it is difficult to make complete contact with the surface-active agent to achieve the separation effect. When the time reaches about 30 min, the sludge and surfactant were mixed evenly. The surfactant plays a better role in separation. When the stirring time exceeds 30 min, with the longer stirring time, the larger the energy loss, the worse the separation effect. Thus, the suitable stirring time is about 30 min.

3.7. Effect of standing time on hot washing
About 20 g of oily sludge 1 was weighed and 20 g/L of AST-01 was added. The agent/sludge ratio was 5:1. The temperature was 60 °C. The stirring speed was 75 rpm and the stirring time was 30 min. The standing time was 10, 20, 30, 40, and 50 min. The centrifugal speed was 2000 rpm. The mixture was centrifuged for 20 min, and then the oil content was measured. The experimental results are shown in Figure 7. As shown in Figure 7, with an increase in the standing time, the oil content of oily sludge gradually decreased. When the settling time was 50 min, the oily sludge has the best separation effect. However, if the standing time is too long, it does not favor the actual production on-site needs. Thus, the suitable standing time is 30 min.

![Figure 7. Effect of standing time on extraction efficiency](image)

3.8. Optimum conditions for the separation of oily sludge by hot washing

To achieve the complete effect of various factors on oily sludge separation, the optimal conditions for sludge separation were obtained. The oily sludge 1 was taken as an example. Hot cleaning agent AST-01 was selected as the sample. The concentration of agent, stirring speed, and temperature were considered as the factors. At the agent/sludge ratio 5:1, L9 (3^3) orthogonal test table was used to carry out an orthogonal test. The level of factors is shown in Table 3 and the test results are shown in Table 4.

| Leve l | Factors         | Factors         | Factors         |
|-------|-----------------|-----------------|-----------------|
| A AST-01 concentration (g/L) | B Stirring Speed (rpm) | C Temperature (°C) |
| 1     | 15.0            | 100             | 50              |
| 2     | 20.0            | 125             | 60              |
| 3     | 25.0            | 150             | 70              |

Table 4 shows that the optimum dehydration condition in the orthogonal test is No. 4. Through analysis and discussion, combined with the actual conditions, it can be concluded that the optimum working conditions for oily sludge separation are as follows: a concentration of AST-01 is 20 g/L, a stirring speed of 125 rpm, and a temperature of 60 °C. The oil content was 1.91%. The size of the extreme difference R in Table 4 shows that the various working conditions affecting the sludge separation effect are as follows: AST-01 dosage > stirring speed > temperature.
Table 4. Orthogonal test results

| Test Number | 1(A) | 2(B) | 3(C) | Oil Content (%) |
|-------------|------|------|------|-----------------|
| 1           | 1    | 1    | 1    | 7.28            |
| 2           | 1    | 2    | 2    | 7.02            |
| 3           | 1    | 3    | 3    | 8.55            |
| 4           | 2    | 1    | 2    | 1.91            |
| 5           | 2    | 2    | 3    | 5.28            |
| 6           | 2    | 3    | 1    | 7.96            |
| 7           | 3    | 1    | 2    | 7.34            |
| 8           | 3    | 2    | 1    | 8.91            |
| 9           | 3    | 3    | 3    | 8.12            |
| T1          | 22.85| 16.53| 24.15|                 |
| T2          | 15.15| 21.21| 16.27|                 |
| T3          | 24.37| 24.63| 21.95|                 |
| t1          | 7.62 | 5.51 | 8.05 |                 |
| t2          | 5.05 | 7.07 | 5.42 |                 |
| t3          | 8.12 | 8.21 | 7.32 |                 |
| Extreme difference R | 3.07 | 2.70 | 2.63 |                 |
| Order of primary and secondary | A>B>C |     |     |                 |
| Excellent level | A2   | B2   | C2   |                 |
| Optimal combination | A2B1C2 | | | |

3.9. Pharmacy compound experiment

An agent compound experiment of oily sludge hot washing was carried out to further improve the efficiency of oily sludge treatment. First, 20 g/L of AST-01 solution was taken and 1.0, 2.0, 3.0, 4.0, and 5.0 g/L of AST-02 was added and mixed evenly. About 20 g of oily sludge 1 and 2 was weighed. The agent/sludge ratio was 5:1. The temperature was 60 °C. The stirring speed was 100 rpm and stirring time was 30 min. The mixture was allowed to stand for 30 min, centrifuged at a speed of 2000 rpm for 20 min to carry out sludge treatment experiments. The oil content of the sludge was measured after separation. The experimental results are shown in Table 5. Table 5 shows that the oil content of the oily sludge 1 decreased from 1.91% to 0.82% and the oil content of oily sludge 2 was 1.67% in comparison with the results obtained using a single agent. This is mainly because of the synergistic effect produced by the
mixing of the surfactants, which improves the separation effect of the oily sludge. The separation effect was the best when the concentration of AST-02 was 2.0 g/L. In this study, the mixture of a hot cleaning agent and AST-02 (2.0g / L) at a mass ratio of 10:1 was named AST-07, i.e., the hot washing agent contains 20.0 g/L of AST-01 and 2.0 g/L of AST-02.

The practical project uses the mixture AST-07. When the agent/sludge ratio was 5:1, the treatment temperature was 70–80 °C, the total stirring time was 30 min, and the mixture was allowed to stand for 20–30 min, and the sludge residue after the treatment was as low as 0.9%.

Table 5. Effect of mixed agent on the separation of oily sludge

| AST-02 Concentration (g/L) | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
|----------------------------|-----|-----|-----|-----|-----|
| Sludge 1                   | 3.82| 0.82| 1.21| 3.35| 6.46|
| Sludge 2                   | 4.45| 1.67| 2.67| 3.84| 5.77|

4. Conclusions
In this study, an oilfield sludge in western China was used as an object and treated using the chemical hot cleaning method. The following results were obtained:

1. The removal effects of a single sludge hot cleaning pharmacy AST-01 are best for the oily sludge in the oilfield, followed by AST-02.

2. The optimum treatment conditions are as follows: When the ratio of agent/sludge is 5:1, the concentration of AST-01 is about 15.0–20.0 g/L. The temperature was 60 °C. The stirring speed was about 100–125 rpm and the stirring time was about 20–30 min. When the static settling separation time was 30 min, the effect of oily sludge treatment was good, and the oil content decreased to 3.76%.

3. When the agent/sludge ratio was 5:1 and the static settling separation time was 30 min, the optimum conditions for oily sludge treatment obtained by the orthogonal test were as follows: an AST-01 concentration of 20.0 g/L, temperature T = 60 °C, stirring speed r = 125 rpm, and stirring time t = 30 min. The effects of various factors on the oily sludge separation effect decreased in the following order: JHHG-01 dosage > stirring speed > temperature. Under the optimal conditions, the oil content in the sludge after the separation was 1.91%.

4. The suitable mixed agent mass ratio of AST-01 and AST-02 was 10:1. It was named as AST-07 after mixing and the oil content in the sludge after AST-07 treatment was 0.82%.

5. The field application verified that by using AST-07 agent, the agent/sludge ratio was 5:1, the treatment temperature was 70–80 °C, the total stirring time was 30 min, the mixture was allowed to stand for 20–30 min and the residue of oily sludge after the treatment was as low as 0.9%.

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