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1 **Thermal treatment of heavy oily sludge: resources recovery**
2 **and potential utilization of residual asphalt-like emulsion as**
3 **a stabilization/solidification material**

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6 **Abstract**

7 An innovative application of oily sludge via distillation modification treatment has
8 been proposed. Particular attention was paid to key parameters of recovered light oil
9 and residual emulsion, including the separation ratio of light oil, the change of
10 chemical composition, values of penetration and softening point of the residual
11 emulsion. In addition, leaching tests were conducted to investigate the effect of
12 modified oily sludge as a material to solidify other hazardous waste on controlling the
13 release of heavy metals. Results showed that the separated light oil was higher than
14 29.2% of original dewatered oily sludge, such as 33.4% at 493 K and 39.2% at 573 K
15 for 180 min. In appropriate range of thermal treatment parameters (distillation
16 temperature 493-533 K and time 2-3 h), the research achieved more desirable results
17 for residual emulsion. For example, the content of resin and asphaltene in residual
18 emulsion was increased from 29.1% to 47.5% at 493 K for 180 min. Furthermore, it
19 was found that the values of penetration and softening point of the residual emulsion
20 were 88 and 48.5 °C, respectively. And this modification enhanced its bond capacity.
21 When this asphalt-like emulsion was used as solidifying or embedding materials, an
22 ideal ratio was achieved at 0.5 (m/m) for controlling the release of heavy metals in the

1 study. The results contribute to the development of new technologies relating to the
2 utilization of oily sludge.

3 **Keywords:** oily sludge; distillation; asphalt-like emulsion; toxicity characteristic
4 leaching procedure (TCLP); heavy metals

5

1 **1. Introduction**

2 Oily sludge is co-produced during the process of petroleum
3 exploration and production, and is considered as a special type of hazardous waste
4 from the flotation cell or settling tank in oilfields, in terms of continuing to pose
5 significant risks to human health.^{1, 2} Incineration or landfill is usually adopted after
6 recycling the light oil, but some valuable uses of oily sludge are often neglected.
7 Generally, oily sludge contains different concentrations of water (40–70 wt.%),
8 petroleum hydrocarbon (15–25 wt.%), and mineral particles (10–20 wt.%).^{3, 4} If the
9 oily sludge is dewatered, a valuable substance remains that contains approximately
10 70% hydrocarbons (mostly paraffins and asphaltenes), together with clay, sand,
11 inorganic matter and heavy metals. Perhaps the most effective approach is to utilize
12 the sludge intact, for example in building or embedding materials, as this can
13 completely avoid the technical problems otherwise experienced during hydrocarbon
14 extraction processes, such as demulsification, desorption and separation.^{5, 6} Hassan et
15 al.^{7, 8} investigated the potential uses of petroleum-contaminated soil (PCS) in highway
16 construction. The results indicated that the use of PCS in an asphalt–concrete mixture
17 application would pose no immediate or long-term threat to the environment; the
18 concentrations of metals and organic compounds did not exceed the maximum
19 contaminant levels set for TCLP (toxicity characteristic leaching procedure) extracts.
20 Therefore, the benefits of recovering and reusing oily sludge include not only a saving
21 of vast quantities of petroleum, but also an absolute decrease in hydrocarbon and
22 heavy metal pollution.

1 Some studies have suggested that the oily sludge can be treated by low temperature
2 distillation. Producing a residue of greater value in an alternative fuels program or a
3 asphalt-like emulsion reuse were well-documented and oft-repeated.^{9, 10} Ayen and
4 Swanstrom evaluated low temperature thermal treatment of filter cakes using
5 laboratory and pilot-scale equipment. Considering the content of cyanides within the
6 acceptable limit and combined with stabilization of heavy metals in the treatment
7 residues, the process was successfully designed and commercialized. In addition, the
8 paper reported the sludge stream carries the same waste codes as the original waste
9 feed, and it can be filtered. The most likely use of this stream would be as fuel to a
10 cement kiln. However, it did not mention the detailed steps for removal the clay
11 minerals. Obviously, single mechanical filtration can not achieve desired separation
12 effect for viscous sludge with lots of minerals. Kuriakose et al.¹¹ reported that the
13 waste sludge from a refiner plant can be converted into different grades of industrial
14 bitumen; approximately 17% of lighter oils and industrial bitumen of 90/15 grade
15 were obtained by vacuum distillation. The usefulness of the industrial bitumen
16 produced was tested in the preparation of bituminous paints. Thermal treatment of
17 oily sludge can irreversibly change the content of heavy components, and enhance its
18 bond capacity. However, compared to refiner sludge, there are more low-molecular
19 hydrocarbon components of petroleum in oily sludge from flotation cell or settling
20 tank during crude oil production.

21 Thermal treatment of oily sludge involves torrefaction, direct distillation, pyrolysis
22 and carbonization process. Temperature is the most important parameter in an

1 experimental design. Deng et al.¹² performed experimental and modeling study of the
2 long cylindrical oily sludge drying process. The study presented a Boltzmann drying
3 model, and predicted the air drying behavior of the long cylindrical oily sludge at
4 105-250 °C. Conesa et al.¹³ determined the pyrolysis of sludge from wastewater
5 treatment plant of an oil refinery at 350, 400, 470 and 530 °C in nitrogen atmosphere.
6 The study showed that in the liquids, the light hydrocarbon yield increased within
7 increasing temperature, whereas the aromatic compounds diminished. The
8 decomposition of the solid fraction proceeded through the pyrolysis of the char and
9 later combustion of the residue formed. Furthermore, the reactivity of the chars vs. the
10 oxygen was very high despite less of the conditions they were produced. Chang et
11 al.¹⁴ investigated the pyrolysis of oil sludge at the temperature range 378-873 K. They
12 concluded that the pyrolytic reaction was complex and significant in the range
13 450-800 K. The residues of oily sludge pyrolysis exhibited very high viscous form
14 below 623 K. Andrade et al.¹⁵ designed a set of heat-treated at different temperatures
15 (400, 500, 600, 700 and 900 °C) and obtained conductive carbon-clay nanocomposites.
16 In a word, analysis of all the products obtained (gases, liquids and chars) usually were
17 investigated and characterized during the complex thermal treatment process.
18 However, two problems need to be solved: the change of oily sludge during thermal
19 modification is required, and a suitable approach to the application of the modified
20 residual solid (asphalt-like emulsion) must be identified.

21 Distillation is probably the most often used process to produce asphalt from heavy
22 crude oil.^{16, 17} Also, it has been used in studies on the fuel recovery for oily sludge

1 treatment.^{18, 19} Reduce of the light hydrocarbons composition will be beneficial
2 to optimize the properties of asphalt-like emulsion. Accordingly, the increase of the
3 resin and asphaltenes content by thermal treatment is necessary. In addition, oxygen
4 plays an important role in determining the properties of asphalt.²⁰ The interaction
5 of oxygen and hydrocarbons can generate oxygen-containing compounds, which
6 contained carboxylic acids, phenols, ketones and esters et al. Among, esters are main
7 component. The ester groups can connect two different molecules to produce a new
8 material with higher molecular weight. This process enhanced the content of asphalt
9 in the hydrocarbons, and changed the colloidal structure and chemical composition of
10 asphalt.²¹ It has been reported that the softening point–penetration ratio of the residual
11 emulsion has been bringing about appreciable variation during the distillation
12 process.²² However, there is lack of analysis regarding the light oil and heavy
13 components of oily sludge after thermal treatment.

14 Because of its highly hydrophobic and extraordinarily stable chemical and
15 biological features, asphalt emulsion can be applied to control and decrease the
16 release of hazardous material with a variety of structural and compositional
17 characteristics. For example, PCS, galvanic sludge, incinerator bottom ash, and heavy
18 metals contaminated soil have all been treated by asphalt emulsions to control the
19 release of hazardous materials.^{23–27} In addition, previous results have also indicated
20 that asphalt can decrease the leaching rates of inorganic pollutants during
21 stabilization/solidification (S/S), because of its high content of resin and asphaltene.^{28,}
22 ²⁹ Meanwhile, applying asphalt in waste S/S prevented the risk of salinity and

1 inorganic anions causing interference in the concrete hardening process.^{7, 30} However,
2 as petroleum resources decline, it is important to look for alternatives to bitumen. This
3 is the reason why many researchers have focused on the use of cheaper materials for
4 S/S. From this point of view, a modified residual solid (asphalt-like emulsion) appears
5 to be an ideal candidate material for S/S treatment process.

6 The present study provides useful information on the modification of heavy oily
7 sludge and its potential use as a stabilization/solidification material. The purpose of
8 the research was to investigate the effect of thermal treatment on the properties of the
9 residual asphalt-like emulsion. In addition, the modified residual emulsion was test
10 during potential solidification process, and an attempt case was also made to gain an
11 insight into the leaching behavior of heavy metals in the mixture of the bottom ash
12 with the modified oily sludge.

13 **2. Materials and Methods**

14 **2.1. Materials**

15 Oily sludge: Several batches of random representative oily sludge, generated from
16 alum coagulation and the dissolved air flotation (DAF) cell, were collected from a
17 heavy oil produced water plant located in the Liaohe Oilfield, Liaoning Province,
18 northeastern China. The sludge had been dewatered by pH adjustment and pressure
19 filtration. Prior to distillation, physicochemical property tests of the samples were
20 carried out. Analysis results of the experimental sludge: pH, 6.2 ± 0.4 ; water content,
21 $63.7 \pm 0.4\%$ (w/w); total solid content, $11.7 \pm 0.5\%$ (w/w); oil content, $24.6 \pm$
22 0.3% (w/w). The saturated compounds, the aromatics, the resins and asphaltenes of oil

1 in the original sludge is 33.2%, 37.7%, and 29.1%, respectively.

2 Bottom ash: The ash was produced by the incineration of petroleum industry solid
3 waste. Table 1 shows the main heavy metals present in the bottom ash. The solid
4 samples were firstly dissolved in concentrated nitric acid solution ($\text{HNO}_3\text{-HF-HClO}_4$)
5 while being heated and were then analyzed with an ionization coupled plasma (ICP)
6 or atomic emission spectrophotometer (AES).³¹

7 **Table 1**

8 **2.2. Experiment design**

9 A distillation thermal treatment system was designed and manufactured to carry out
10 the oily sludge modification experiment. A schematic representation of the system is
11 shown in Fig. 1. Basically, the reactor of the system had a cylindrical shape whose
12 inner diameter was 22 cm and effective chamber length was 40 cm. It included an
13 electric heater, which could be used to heat the sludge up to 850 K. The electric heater
14 contained an electrical resistance heater, and a voltage controller. An agitator was
15 employed for blending the oily sludge to obtain uniform temperature distribution in
16 the reactor. A thermocouple was placed in the middle of the reactor to reflect the
17 heating temperature. In addition, an air pump was set to supply air to the reactor.
18 Concentrated H_2SO_4 was used to absorb moisture in the air. The final component of
19 the system was the condenser unit, in which a water-cooled condenser (condenser
20 tube, 0.6 m) was used to condense the vaporized light oil. The temperature of
21 circulating cooling water is 18 °C.

22 **Figure 1**

1 Before adding the oily sludge to the distillation reactor, it was dried at 105°C for
2 about 30 min, to separate the water content. Then, 2 kg of the oily sludge was added
3 into the reactor. The thermochemical process of the samples was performed in the
4 presence of O₂ (the air flow rate: 2 L/min), with continuous mixing. Four distillation
5 temperatures (453, 493, 533 and 573 K) were designed. The sludge was heated at 10
6 k/min from original temperature. When it was reached at desired temperature, a
7 temperature-controlled system was used for keeping the variation less than 3 °C.
8 Rapid condensation of light oil was collected in a container. Experimental replicates
9 were done using the same lot sludge for three times. The oily sludge was treated in the
10 actor for three individual distillation processes by the same experimental parameters.
11 Then the recovered light oil and the asphalt-like emulsion from three experiments
12 were collected to test the data through homogeneous mixing. Quantitative analysis of
13 hydrocarbons was carried out to compare the recovery rate of light oil. After
14 distillation treatment, the residual emulsion was collected for analyzing the softening
15 point, penetration and other characteristics.

16 The procedure used to mix the bottom ash with the modified oily sludge was based
17 on empirical findings of the S/S of ash and salt from a waste incinerator,²⁸ and of
18 noncombustible industrial waste.³² The process involved mixing the bottom ash with
19 the modified oily sludge at the chosen ratio (0.2–0.6) and homogenizing the mixture
20 for approximately 15 min. This process kept the temperature about 120–140 °C. The
21 viscous residual sludge was stirred continuously, and the bottom ash was thrown into
22 the actor uniformly. The mixture was subsequently put into a solidification pattern. It

1 was compacted under a pressure of about 0.4 MPa, and then pushed out. The
2 solidification pattern was a rectangle of 10 cm width and 15 cm length. The thickness
3 of the compacted mixture in each pattern was 1 cm.

4 The leaching tests were conducted using a horizontal vibration extraction procedure.
5 The aim was to study the potential use in controlling the release of heavy metals from
6 the composite mixture. The leaching solution was prepared using a standard leaching
7 test, and the heavy metal content in the leachate was determined (TCLP, EPA method
8 1311). Then it was compared with threshold limits required in Identification standard
9 for hazardous wastes–Identification for extraction procedure toxicity (Chinese
10 national standard GB 5085.3-2007).

11 ***2.3. Analysis methods***

12 The content of the oil and moisture was determined according to existing
13 procedures,³³ as was the content of the saturated compounds, the aromatics, the resins
14 and asphaltenes of the modified oily sludge.³⁴ The value of pH was monitored using a
15 pH meter (PHS-3B, Shanghai). The characteristics of the modified sludge were
16 analyzed following previously used methods,³⁵ and the mass of distilled light oil was
17 determined by weighting.

18 **3. Results and discussion**

19 ***3.1 Modification of heavy oily sludge***

20 ***3.1.1 Separation of light oil in oily sludge***

21 Distilled light oil samples were collected by the accumulation sampling method at the
22 test temperatures (453, 493, 533 and 573 K). Quantitative analysis of the production

1 was carried out to compare the recovery rate of light oil. In this study, M_{TS} , M_{DO} and
2 M_{RS} represent the masses of total initial sludge (dewatered sludge before distillation),
3 distillation-recovered oil and residual sludge, respectively. The variation of the
4 M_{DO}/M_{TS} ratio at various distillation temperatures is illustrated by a second-order
5 polynomial trend line in Fig. 2, at a heating rate of 10 K/min. The results showed that
6 the ratio curves of the four distillation experiments all exhibited similar trends, despite
7 slight variability between 453 K and the other temperatures. The effect of the lowest
8 temperature (453 K) was extremely poor, and less light oil was recovered. In contrast,
9 the ratio at the higher temperatures (493, 533 and 573 K) was more pronounced. This
10 could be attributed to the fact that, at lower temperatures, it would be difficult to
11 undergo many successive adsorption and desorption from the sludge.¹³ There was a
12 regular rise in the mass of recovered oil when the distillation time was longer than 60
13 min; the ratio of M_{DO}/M_{TS} at 533 K was larger than at 493 or 453 K. After 180 min,
14 the ratio of M_{DO}/M_{TS} reached 0.292, 0.334, 0.360 and 0.392 at the four test
15 temperatures, respectively. Thus, the light oil, approximately 39.2% of the oily sludge
16 could be separated after distillation treatment. Higher-temperature treatment was more
17 effective in improving the rates of recovered oil. However, the recovery of too much
18 light oil may negatively impact the residual emulsion. The results and observations
19 described above reveal that, in the present set of experiments, the recovery of light oil
20 in the sludge was highly influenced by temperature. In addition, the characteristics of
21 liquid product (condensate of gas at 298 K) from the oily sludge were shown in Table
22 2. It indicated that the properties of light oil are close to those of diesel oil.

1 **Table 2**

2 **Figure 2**

3 The ratio of light oil recovery after distillation in the present study was not in
4 agreement with previous results.^{36, 37} These studies focused on utilizing thermal
5 treatment of oil sludge to enhance the rates of pyrolysis and oxidative reactions in the
6 oily sludge, which was taken from the crude oil storage tank of a typical petroleum
7 refinery plant. The crude oil tank bottom sludge contained more solid content (i.e.
8 15%) than that of the dewatered DAF sludge used in our work (i.e. 11.7%), especially
9 more clay found in DAF sludges. In addition, the object of the oily sludge treatment
10 was different. The recycling and reuse of residual emulsion was considered as the
11 most important aspect in our study. Therefore, much light oil was recovered mainly
12 through direct distillation, rather than promoting the pyrolysis of heavy components
13 through increasing temperature. In fact, when the distillation temperature was lower
14 than 550 K, it did not cause the decomposition of heavy petroleum hydrocarbons. Liu
15 et al.³⁸ reported that the pyrolysis process of oily sludge can be divided into three
16 main stages within the temperature range for all heating rates. A second stage of
17 decreasing mass is observed between 393 and 805 K and involves a very important
18 weight loss (around 18 wt.% of the original weight) mainly related to the
19 volatilization and decomposition of organic matter in the oily sludge. As a result, it
20 was observed that the total petroleum hydrocarbon concentration in the separated
21 aqueous phase in triangular flask for the distillation method was much lower (i.e. 200
22 mg/L) than that for pyrolysis (i.e. 1550 mg/L). This was in agreement with previous

1 studies showing that the distillation method was effective for separating oil from the
2 aqueous phase.¹⁹ In addition, if the temperature was enhanced, pyrolysis of the oil was
3 obvious. Previous paper reported that in pyrolysis process, about 80% of total organic
4 carbon content in oily sludge converted into hydrocarbons and an important
5 hydrocarbon yield occurred at temperatures between 327 °C and 450 °C.³⁸

6 ***3.1.2 Properties of residual emulsion after oxidation modification***

7 Besides considering the amount of recovered light oil, the main physicochemical
8 properties of the residual emulsion were the most important concern. The modified
9 residual emulsion was analyzed for the amounts of saturates, aromatics, resins and
10 asphaltenes. The results are provided in Fig. 3. 493 K and 573 K were selected as test
11 temperature. The content of saturates in the modified residual emulsion at the two
12 temperatures were 23.2% and 18.2%, which was lower than the content (33.2%) of
13 the original sludge. Also, the levels of aromatics decreased with temperature after a
14 longer distillation treatment. It decreased from 37.7% to 29.3% at 493 K and to 25.5%
15 at 573 K after 180 min. This indicates that a greater proportion of ring-containing
16 hydrocarbons, usually high-molecular-weight hydrocarbons, are extracted when a
17 lower temperature is used. A similar pattern was observed for both resin and
18 asphaltene content. The ratio of resins increased from 26.6% to 38.6% and 44.6% in
19 the residual emulsion at the two temperatures at 180 min. Furthermore, the ratio of
20 asphaltenes increased from 2.5% to 8.9% and 11.7%. A possible explanation for the
21 change of behavior is that, under low temperature, the heavier hydrocarbons feature a
22 much more complicated reaction instead of direct distillation from the reactor. By

1 contrast, resin is characteristically unstable in oily sludge. To consider this possibility,
2 asphaltene, as a representative high-molecular-weight hydrocarbon, was further
3 evaluated and little change was found in its content. This result is in accordance with
4 a previous study in which it was reported that the process would mainly include
5 physical volatilization below 623 K.¹⁴

6 **Figure 3**

7 Two important parameters of the residual asphalt-like emulsion, penetration and
8 softening point, which determined the binder and embedding characteristics, were
9 analyzed to investigate the impact of oxygen with distillation process. As previous
10 reports, the relationship of penetration and softening point was significant during
11 evaluating the properties of asphalt.^{39, 40} The results (Figs. 4 and 5) show that the
12 value of penetration decreased, and the softening point enhanced with distillation time.
13 They were clearly influenced by temperature. After 180 min, the two values varied
14 slightly with distillation time. Compared to the findings of Kuriakose and
15 Manjooran,¹¹ the modified oily sludge was different from industrial bitumen produced
16 by vacuum distillation with catalysts. The main reason was that the aim of our
17 research was to investigate the feasibility of oily sludge modification and its potential
18 use in the S/S of other hazardous wastes by simple distillation without separating clay.
19 Also, the aforementioned study described how the residual sludge, after the removal
20 of lighter oils, was converted into different grades of industrial bitumen via heat
21 treatment at temperatures ranging from 200 to 250 °C, with AlCl₃ as the catalyst, for
22 time periods ranging from 2 to 3 h.¹¹ Certainly, regardless of the cost, the addition of

1 AlCl₃ as the catalyst can convert the oily sludge into some useful grades of industrial
2 bitumen. However, this needs further testing on optimized parameters and strict
3 catalyst condition in future research. In addition, a higher temperature of 573 K, as
4 well as a lower temperature of 493 K, probably should not yield a better softening
5 point–penetration relationship.

6 **Figure 4**

7 **Figure 5**

8 Besides the ratios of compounds, some parameters are usually measured to
9 compare with the standard of industrial bitumen. After distillation at the four
10 temperatures, residual oily sludge parameters such as penetration and softening point
11 were determined, and the results revealed distinct differences in the penetration for the
12 different samples; higher distillation temperatures yield lower values of the residual
13 emulsion. During the modification process, penetration is perhaps the best indicator
14 for the thermal treatment of oily sludge. In this study, the temperature of 493 K and
15 duration time of 2.5 h were considered as the optimal conditions for preparing grades
16 of industrial bitumen of lower penetration and higher softening point. The values of
17 penetration and softening point of the modified oily sludge were 88 and 48.5, which
18 fall within the requirements of bitumen 100# (pavement petroleum asphalt, SH0522,
19 China).

20 Next, selected physicochemical properties of the residual emulsion after distillation
21 at 493 K were characterized and summarized (Table 3). Compared with its parent oily
22 sludge, the residual viscous asphalt-like emulsion contained higher concentrations of

1 polar macromolecules (e.g., asphaltenes), which was in agreement with their higher
2 molecular weight. It is accepted that heteroatoms are primarily concentrated in heavy
3 oil components. The differences between the residual sludge and its corresponding
4 parent oily sludge suggested that the increase of resins and asphaltenes caused the
5 enhancement of cohesiveness. After distillation treatment for 180 min, the residual
6 emulsion was highly viscous. This is consistent with previous reports showing that the
7 pyrolysis residues of oily sludge exhibited highly viscous forms below 623 K
8 (pyrolysis temperature), while less viscous or solid forms above 713 K.¹⁴ These
9 variations in properties reflect the potential solidification characteristics of oily
10 sludge.

11 **Table 3**

12 **Figure 6**

13 *3.1.3 Mass balance of liquid oil and solid residues*

14 In addition, mass balance of residual emulsion and liquid oils was calculated. Under
15 the distillation temperatures of 453-573 K after 180 min, the variations of mass
16 fractions of products with temperature for treatment of oily sludge are shown as
17 follow: At 453 K, the final product distributions relative to the initial dry oil sludge, in
18 wt %, are about 30.5 liquid oils and 67.6 solid residues, respectively. The total
19 recovery is 98.1 wt %. At 493 K, the value of liquid oils and residual emulsion were
20 33.4% and 63.4%. The total recovery is 96.8 wt %. At 533 K, the value of liquid oils
21 and residual emulsion were 37.4% and 60.5%. The total recovery is 97.9 wt %. At
22 573 K, the value of liquid oils and residual emulsion were 39.2 and 58.2%. The total

1 recovery is 97.4 wt %. The unrecovered mass maybe attributed to the missed gaseous
2 products and experimental errors.

3 ***3.2 Leaching of heavy metals in bottom ash after mixing with modified oily sludge***

4 The results of the leaching tests are presented in Table 4. For the TCLP test,
5 solidification based on modified oily sludge reduced all the metals in the leachate
6 from the solidified matrices. These results are in agreement with several other
7 studies,^{41,42} and can be attributed to the strong detention capacity. An ideal ratio was
8 achieved at 0.5 for controlling the release of heavy metals. When the ratio of modified
9 oily sludge is less than this ratio, the release of several heavy metals will improve. Of
10 course, among the six kinds of heavy metals detected, the environmental toxicological
11 effects of Cd and Cr are the strongest. When the modified oily sludge was added in
12 sufficient quantity to immobilize the ash completely, the concentration of heavy metal
13 leaching was reduced. Therefore, a higher concentration of the modified sludge in the
14 solidified products will result in lower leachability. Certainly, if the proportion of the
15 modified sludge was decreased, coating the bottom ash would be an ideal way to
16 control the release of heavy metals. A previous study reported how an asphalt coating
17 was produced to form an immobilizing barrier against pollutant leaching, and the
18 results showed that the quantity of emulsion needed to prepare an asphalt coating is
19 relatively low.³² Based on comprehensive consideration of the compressive strength
20 and leaching concentration of heavy metal ions of the modified sludge, it is confirmed
21 that under the premise of non-hazardous to the environment, it represents an effective
22 way to improve the disposal and utilization of oily sludge in controlling the release of

1 heavy metals.

2 **Table 4**

3 **4. Conclusions**

4 This study investigated the feasibility of heavy oily sludge modification and its
5 application in controlling the release of heavy metals as a stabilization/solidification
6 material. From the results, the following main conclusions can be drawn:

7 (1) The changes of the heavy oily sludge were the increase of heavy components
8 ratio and the change of penetration and softening point. Among, the temperature of
9 493 K and duration time of 2.5 h were considered as the optimal conditions for
10 preparing grades of industrial bitumen of lower penetration and higher softening point.
11 The main physicochemical properties of the asphalt-like emulsion were in accordance
12 with bitumen 100#.

13 (2) An ideal ratio was achieved at 0.5 for controlling the release of heavy metals
14 during solidification. In addition, the increase of modified oily sludge ratio or coating
15 method can achieve an acceptable performance in the leaching test, meaning the
16 modified oily sludge demonstrated improvement in terms of the S/S of heavy metals.

17 (3) This study has important environmental engineering significance. Future studies
18 could include, for example, the ratio of oxygen, the application of a catalyst, and the
19 use of a better reactor, etc. In addition, the best ratio of embedded and long-term
20 monitoring of the solidification based on modified oily sludge should be studied.

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Table 1 Content of heavy metals in bottom ash from the petroleum industrial incineration waste

	Cu	Zn	Pb	Cd	Ni	Cr
Bottom ash (mg/kg)	151.47	657.33	25.60	5.95	83.7	128.33
TCLP of bottom ash (mg/L)	24.6	134.5	3.48	1.25	6.43	18.34
GB5085.3-2007 (mg/L)	100	100	5.0	1.0	5.0	15.0
Limit value (EPA) (mg/L)	/	/	5.0	1.0	/	5.0

Table 2 Properties of light oil (493 K)

Item	Value
Iodine value ($\text{gI} \cdot 100 \text{g}^{-1}$)	36.72
Oxidation stability ($\text{mg} \cdot 100 \text{mL}^{-1}$)	1.1
Freezing point ($^{\circ}\text{C}$)	1.0
Flash point ($^{\circ}\text{C}$)	105.0
Acidity ($\text{mg KOH} \cdot 100 \text{mL}^{-1}$)	21.42
Existent gum ($\text{mg} \cdot 100 \text{mL}^{-1}$)	22.6
Total sulfur (% wt.)	0.0461
Ash content (% wt.)	0.004
Cold filter plugging point ($^{\circ}\text{C}$)	3.0
Cetane number	51.2
Density ($20^{\circ}\text{C}/\text{kg} \cdot \text{m}^{-3}$)	0.8206

Table 3 Characteristics of the residual solid of oily sludge by distillation and oxidation (493 K)

Item	Value
Pour point ($^{\circ}\text{C}$)	42
Wax (% wt.)	6.0
Asphaltenes (% wt.)	8.9
Acidity (mg KOH/g)	4.3
Flash Point ($^{\circ}\text{C}$)	200
Kinematic viscosity (cst, 100°C)	30.33
Total sulfur (% wt.)	3.43
Ash content (% wt.)	4.8

Table 4 Concentration of heavy metals in leachate with different ratios of modified oily sludge and bottom ash (493 K, 180 min)

$M_{\text{Residual solid}} / M_{\text{Bottom}}$	Concentration of metals in leachate (ppm)
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ash+ Residual solid	Cu	Zn	Pb	Cd	Ni	Cr
0.2	10.3	92.12	2.17	0.87	4.12	14.84
0.3	8.34	64.34	1.86	0.64	2.71	10.25
0.4	7.02	46.32	1.74	0.42	0.85	7.37
0.5	2.68	18.62	1.16	0.20	0.41	4.46
0.6	1.35	7.53	1.04	0.15	0.33	3.22
GB5085.3-2007	100	100	5.0	1.0	5.0	15.0
Limit value (EPA)	/	/	5.0	1.0	/	5.0

Figure legends

Figure 1. Experimental system of the distillation treatment for oily sludge

Figure 2. Rate of light oil recovery at various distillation temperatures (Experimental conditions: heating rate of 10 K/min, stirring speed of 120 rpm, air volume of 2 L/min)

Figure 3. Effect of different modification temperatures on the ratio of four components of oily sludge (a: 493 K; b: 573 K. Experimental conditions: heating rate of 10 K/min, stirring speed of 120 rpm, air volume of 2 L/min)

Figure 4. Effect of different modification temperatures on penetration properties of residual sludge

Figure 5. Effect of different modification temperatures on softening point properties of residual sludge

Figure 6. Appearance of oily sludge (A: Raw sludge; B: Modified sludge)

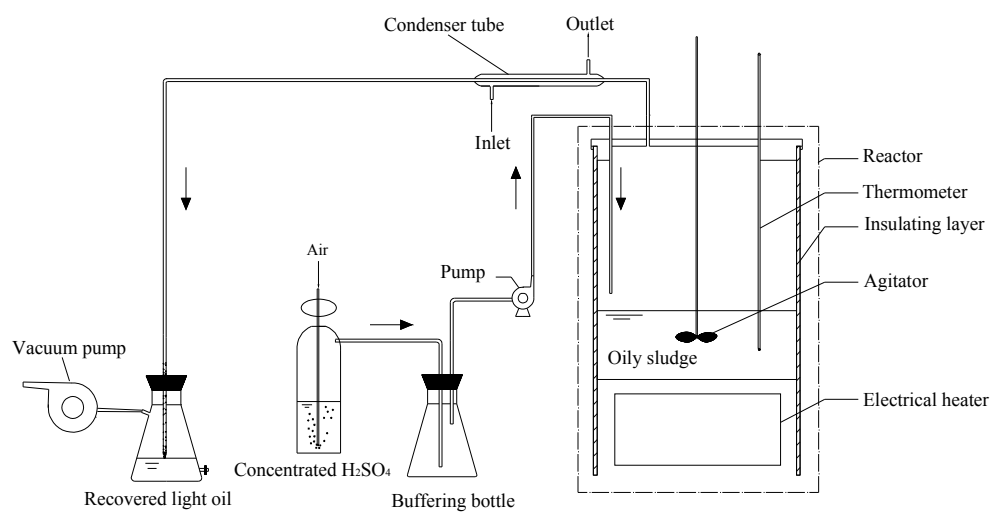


Figure 1 Experimental system of the distillation treatment for oily sludge

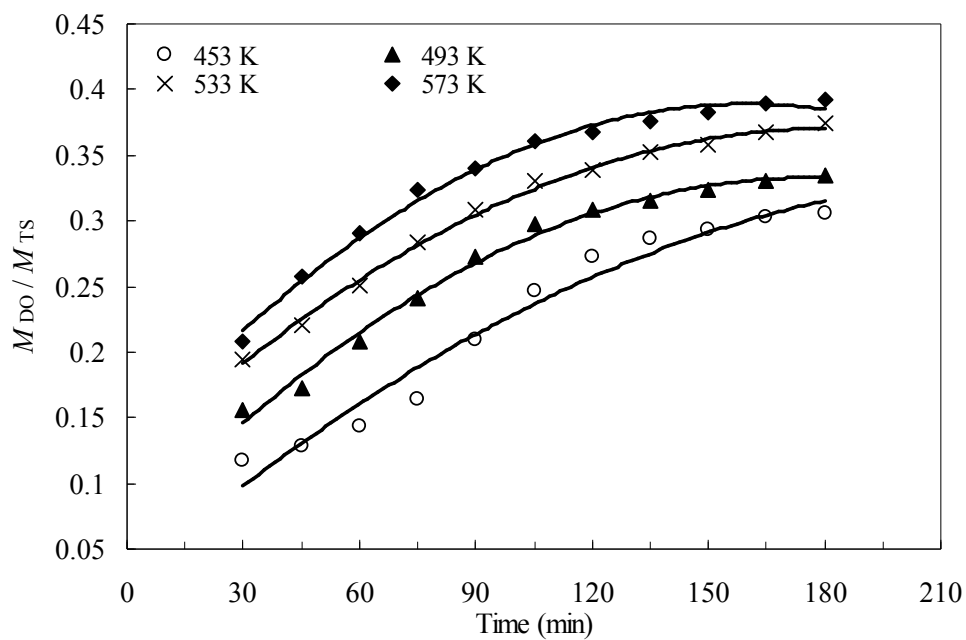


Figure 2 Rate of light oil recovery at various distillation temperatures (Experimental conditions: heating rate of 10 K/min, stirring speed of 120 rpm, air volume of 2 L/min)

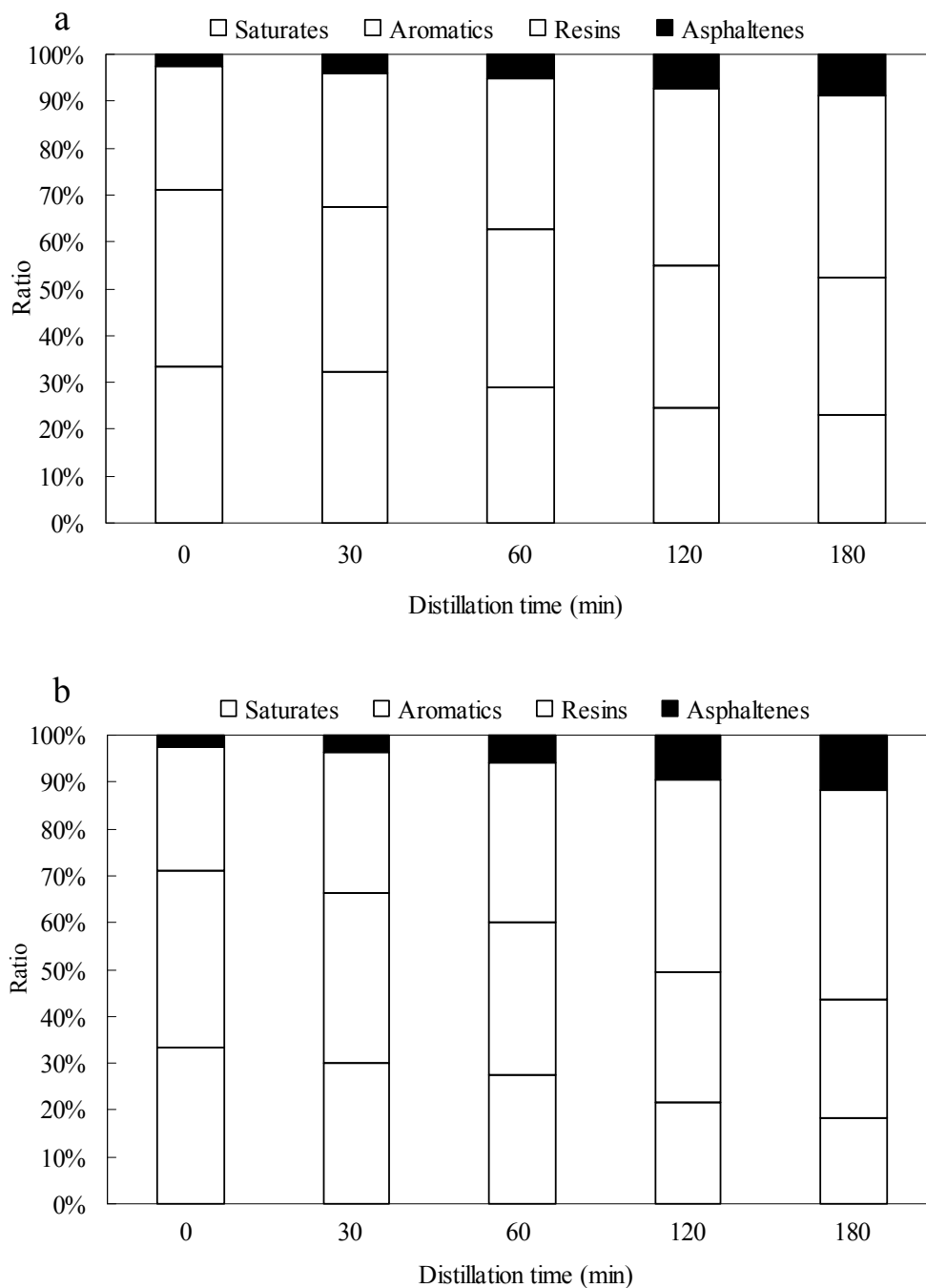


Figure 3 Effect of different modification temperatures on the ratio of four components of oily sludge (a: 493 K; b: 573 K. Experimental conditions: heating rate of 10 K/min, stirring speed of 120 rpm, air volume of 2 L/min)

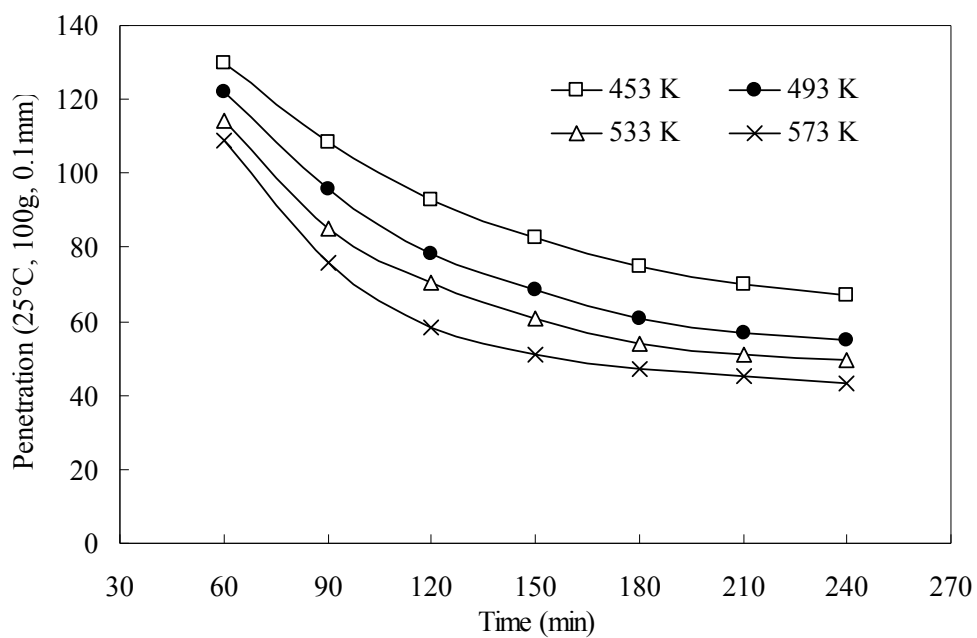


Figure 4 Effect of different modification temperatures on penetration properties of residual sludge

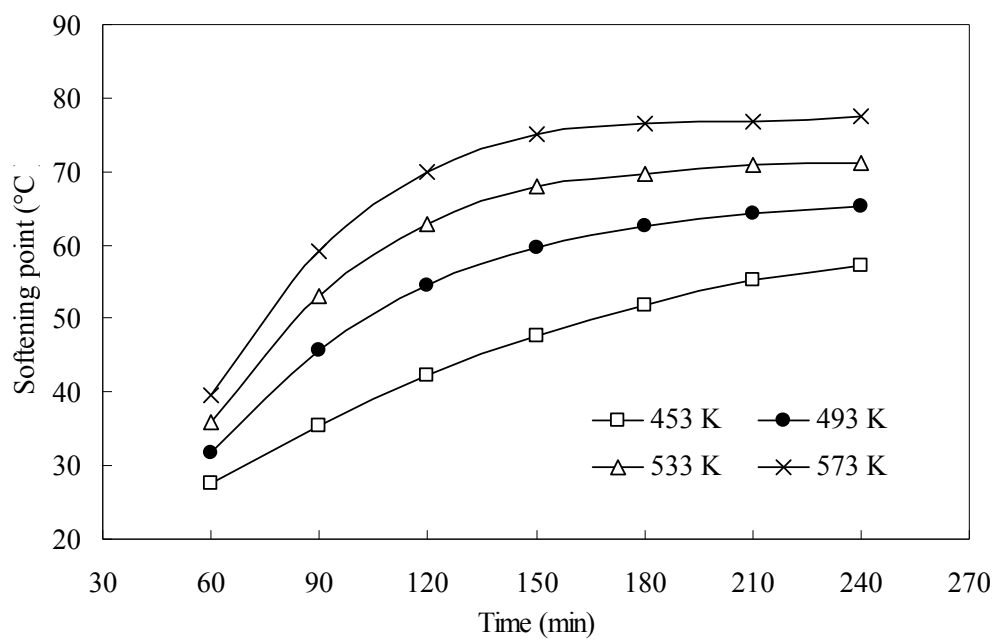


Figure 5 Effect of different modification temperatures on softening point properties of residual sludge



Figure 6 Appearance of oily sludge (A: Raw sludge; B: Modified sludge)