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## Characterization of Oil Sludges from Two Oil Fields in China

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Formation of oil sludges during oil production, transportation, and storage processes has become one of the severest problems in oil production and refinery plants in China. In the current study, compositions of two oil sludges collected from oil fields in China were characterized to assess the amounts of oil that can be potentially extracted for energy reuse. The mineral-containing solids separated from these samples were also characterized, and their role in stabilizing oil emulsions was interpreted. Experimental results showed that both oil sludges contained significant amounts of oil that could be potentially extracted for energy reuse. Solids separated from these sludges contained significant amounts of mineral fines that were oil-wet due to adsorption of polar macromolecules. These oil-wet mineral fines, together with the oil polar macromolecules, were suggested to be responsible for the water-in-oil (W/O) emulsions of the oil sludges studied.

### Introduction

Oil sludge, a complex mixture consisting of oil, water, and solid, is a product generated from the bulk oil in a number of processes, including oil production, transportation, and storage.<sup>1,2</sup> Oil storage tanks and oil–water separation systems in oil fields are among the largest sources producing oil sludges.<sup>3</sup> Accumulation of oil sludges at the tank bottom occupies a large fraction of tank space and consequently substantially lowers the tank capacity. When the sludge fraction reaches a certain level of a tank, tank operations have to be shut down to physically remove the sludge from the tank.<sup>4</sup> Large amounts of oil sludges are generated in China each year during oil production and processing. For instance, Shengli oil field, one of the largest oil fields in China, generates about 120 thousand tons of oil sludge a year.<sup>5</sup> These oil sludges need to be properly handled to prevent soil/groundwater contamination and to potentially use the valuable oil fraction for energy reuse.

Numerous methods have been investigated to treat oil sludges. These include incineration,<sup>6</sup> pyrolysis,<sup>7–9</sup> oxidative

thermal treatment,<sup>10</sup> centrifugation,<sup>4</sup> electro-demulsification,<sup>11</sup> landfarming,<sup>12</sup> and landfill.<sup>10</sup> Currently, no cost-effective technology exists to extract the valuable fuel from oil sludges.<sup>11</sup> Regardless of the technologies to be adopted for oil sludge treatment, minimization of the sludge volume is expected to help decrease the overall processing cost. Understanding the emulsion properties of oil sludges will greatly facilitate waste minimization by demulsification before many technologies can be used to effectively process these waste materials.

Precipitation of organic solids from their parent crude oils has been linked to oil instability. Characterization of these organic solids indicates that they contain significant amounts of asphaltene and/or wax fractions.<sup>2,13–17</sup> However, detailed characterization of the inorganic solids and their role in oil emulsion stability are lacking, although the mineral matter content and the abundance of insoluble organics contained in the solid deposits were found to be well correlated.<sup>2</sup> In bitumen-sand industry, it has been reported that fine mineral particles, such as clay, play a decisive role in oil–solid–water interactions.<sup>18–20</sup> Oil sludges from oil–water separation systems and oil storage tanks contain a lot of mineral particles trapped from reservoir materials during oil mining. It is, thus, speculated that mineral particles in these oil sludges would

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alter their wetting preference upon adsorption of polar macromolecules and consequently influence oil emulsion stability.

The objectives of this study were to (1) identify the compositions of two oil sludges from oil fields in China to assess the amounts of oil that can be potentially extracted for energy reuse and (2) characterize the mineral-containing solids separated from these oil sludges and interpret their role in stabilizing the oil emulsions. To meet these objectives, oil sludges were fractionated into four fractions: toluene soluble, toluene insoluble–tetrahydrofuran soluble, solids, and water. Selected physicochemical properties of the separated sludge oils and their parent crude oils were characterized to facilitate interpreting the interaction between oil macromolecules and mineral particles. The solid particles were characterized by a number of instrumentation methods to help interpret their role in stabilizing the oil emulsions.

### Experimental Section

**Materials.** Oil sludge samples and their parent crude oils were collected from two of the largest oil fields in China. Oil sludge A was collected from the tank bottom of an oil–water separator at an oil production plant in Heilongjiang Province, while oil sludge B was collected from the bottom of an oil storage tank at a united station in Shandong Province, both in China. The two parent crude oils (labeled crude oil A and crude oil B) have been used in a previous study<sup>21</sup> where they were designated differently as crude oil B and crude oil C, respectively. To prevent potential oil weathering, both oil sludges were collected right after the shutdown of their corresponding facilities for regular cleanup. To assess the enrichment of polar macromolecules in the oil sludge samples, their parent crude oils from their corresponding oil fields were also collected and analyzed. All samples were kept in a refrigerator at 4 °C and homogenized manually before use.

**Characterization of Oil Sludge Compositions.** Oil sludge samples were fractionated into four major components by sequential solvent extractions<sup>22</sup> with toluene and tetrahydrofuran (THF): toluene soluble (TS), toluene insoluble–tetrahydrofuran soluble (TIS–THFS), solids (THF insoluble), and water. Multiple tests (at least three) were conducted for these fractionation experiments. In a typical test, 25 g of oil sludge sample was placed in an extraction thimble and first extracted with 100 mL of toluene for 10 h in a Dean–Stark apparatus<sup>23</sup> under reflux until the refluxed toluene became colorless. The extractant was then transferred to a flask equipped on a rotating evaporator to remove the solvent, and the residue was designated TS. The volume of water was read directly from the water trap. The left material after toluene extraction was subsequently extracted similarly with 100 mL of THF followed by solvent evaporation to prepare the TIS–THFS fraction. The final solid residue was dried to a constant weight and designated as solids. Of these separated fractions, TS was considered as the oil fraction and named sludge oil, while TIS–THFS represented the relatively polar hydrocarbons further extracted from the oil sludge with a more polar solvent THF. Water extracted from the sample reflects the amount of water incorporated into W/O (water-in-oil) emulsions in the oil sludge.

**Characterization of Oils.** Selected physicochemical properties of the separated sludge oils and their corresponding parent crude oils were characterized. Densities of oil samples were

measured by a DMA5000 density meter (Anton Paar, Austria) based on U-tube oscillation. Weight-averaged molecular weight ( $MW_w$ ) was analyzed by size exclusion chromatography (SEC) on a Waters 515 (Waters, US) equipped with a Wyatt Technology Optilab rEX refractive index detector (Wyatt, Germany). Before tests, the columns (Styragel HR3, HR4 and HR5, Waters, U.S.) were calibrated by polystyrene standards with molecular weights in the range of 900 to  $1.74 \times 10^6$  g/mol. Heteroatom contents of oil samples, represented by NOS mass %, were determined on a CHN-O-Rapid elemental analyzer (Heraeus, Germany) with a thermal conductivity detector (TCD). Elemental compositions of C, H, N, and S were determined directly by the analyzer, while O content was assessed by conducting a mass balance. The asphaltene concentration was determined by precipitating the crude oil with *n*-heptane following the ASTM D6560-00 (IP 143/01) standard method. Acid number (AN) of oil samples was determined by nonaqueous titration following the procedures described by Zheng et al.<sup>24</sup> Analysis of these selected physicochemical properties was aimed primarily to evaluate the enrichment of polar macromolecules in the sludge oils and to facilitate interpreting the interaction between oil polar macromolecules and mineral particles in the oil sludges.

**Characterization of Extracted Solids. Particle Size Distribution.** Particle size distributions of the two extracted solid samples were determined by Malvern Mastersizer 2000 (Malvern, U.K.). Before tests, samples were pretreated with 10%  $H_2O_2$  on a hot plate to further remove from the solids the organic substances that survived after toluene and THF extraction. The resultant sample was then transferred to a beaker containing 0.05 M sodium hexametaphosphate followed by a 10 min sonication (KQ-100KDE, Kunshan Sonicor Instrument Corp. Ltd. China) to allow the particles to be well dispersed prior to particle size analysis.

**X-ray Fluorescence Spectrometry (XRF) and X-ray Diffraction (XRD).** XRF and XRD were used to analyze the chemical components and mineralogical constituents of the extracted solids. Analysis for major oxides was conducted on a model ARL 9800 X-ray fluorescence spectrometer (ARL, Switzerland) equipped with an X-ray tube with a Rh anode (40 kV, 60 mA) and a Be window (0.075-mm) by the fused disk method. XRD was performed on a wide-angle goniometer (D/Max-3C, Rigaku, Japan) using Cu K $\alpha$  radiation. X-ray intensity was recorded as a function of  $2\theta$  angle in the range of 3.00–70.00° with a step size of 0.02°. The applied voltage and current were 37.5 kV and 20 mA, respectively.

**X-ray Photoelectron Spectroscopy (XPS).** XPS surface spectra of the extracted solids were collected using a VG ESCALB MK-II Instrument (VG, U.K.). Both survey and high-resolution scans (C, Si, Ca, Al, Fe) were conducted. All binding energies were referenced to the neutral  $C_{1s}$  peak at 284.6 eV to compensate for surface charging effects. XPS spectra were used to identify the surface elemental compositions of C, Si, Ca, Al, and Fe of the extracted solids both before and after  $H_2O_2$  oxidation.<sup>19</sup> Changes in surface elemental concentrations by  $H_2O_2$  oxidation were used to identify whether an organic film exists, possibly due to adsorption of polar macromolecules on the solid surfaces. The existence of organic film on the solid surfaces is a good indication of their oil-wet properties.

**Visual Observation of Wetting Properties of the Extracted Solids.** Wetting preference of the extracted solids was assessed by visually observing their distribution between toluene and water phase according to the method described by Sparks et al.<sup>20</sup> with minor modification. Toluene was selected as the model oil phase, while 0.01 M NaCl solution was used as the water phase. Briefly, 0.1 g of extracted solids was added to a glass tube containing 1 mL of toluene and 5 mL of water. The mixture was

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**Table 1. Composition Analysis of Oil Sludges by Toluene and THF Sequential Extraction, % by Mass**

oil sludge	TS, %	TIS–THFS, %	water, %	solid, %	density <sup>a</sup> , g/cm <sup>3</sup>
A	56.1 ± 0.6	0.2 ± 0.12	16.2 ± 0.6	27.5 ± 0.2	1.06
B	26.3 ± 0.9	0.1 ± 0.01	27.6 ± 1.0	46.0 ± 0.3	1.36

<sup>a</sup> Average density of the oil sludge was assessed on the basis of its mass contents of the four separated fractions by assuming their densities as follows: TS and TIS–THFS of the same oil sludge having the same density (i.e., 0.83 g/cm<sup>3</sup> for A and 0.94 g/cm<sup>3</sup> for B), water 1.00 g/cm<sup>3</sup>, and both solids having the same density of 2.60 g/cm<sup>3</sup>.

**Table 2. Properties of Separated Sludge Oils and Their Parent Crude Oils**

oil samples	density at 50 °C, g/cm <sup>3</sup>	MW <sub>w</sub> <sup>a</sup>	asphaltene, %	AN <sup>b</sup> , mg KOH/g	NOS <sup>c</sup> , mass %
crude oil A	0.8267 <sup>d</sup>	1454	0.14 <sup>d</sup>	0.09	1.74
sludge oil A	0.8340	2017	0.38	4.93	2.69
crude oil B	0.9425 <sup>d</sup>	2302	3.82 <sup>d</sup>	2.03	2.93
sludge oil B	0.9433	2634	6.14	8.13	4.79

<sup>a</sup> MW<sub>w</sub>: weight-averaged molecular weight. <sup>b</sup> AN: acid number. <sup>c</sup> NOS: total concentration of nitrogen, oxygen, and sulfur by elemental analysis.

<sup>d</sup> Cited from ref 21.

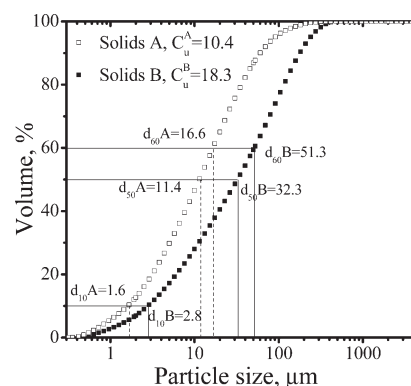
then subjected to 5 min of vortex mixing (vortex mixer, WH-1, Shanghai Huxi Analysis Instrument Corp., Ltd.). This resultant mixture was allowed to stand still for different periods of time, and a photo was captured at the end of each period. A short period (5 min) and a long period (3 days) were selected to assess qualitatively the stability of the resultant W/O emulsions stabilized by the extracted solids.

## Results

**Compositions of Oil Sludges.** Sequential solvent extractions by toluene and THF (Table 1) show that both oil sludges contain significant amounts of oil (TS), i.e., 56.1% for A and 26.3% for B. Although toluene can extract most of the bulk oil from both oil sludges, there are still some polar components left unextracted. Further extraction with THF, a more polar solvent than toluene, yields an additional 0.2% and 0.1% of polar components from oil sludge A and B, respectively.

Extraction tests (Table 1) also show that both oil sludge samples contain large amounts of water and solids. Oil sludge A contains 16.2% water and 27.5% solids, while B has much higher concentrations for both components (e.g., 27.6% and 46.0%). Incorporation of these components, especially the solids fraction, into the oil sludges significantly increases the sludge density as compared to their parent crude oils. The estimated density is 1.06 and 1.36 g/cm<sup>3</sup> for oil sludge A and B, respectively.

**Characterization of Oils.** Selected physicochemical properties of the separated sludge oils and their parent crude oils were characterized and are summarized in Table 2. Compared with their parent oils, the extracted sludge oils contain higher concentrations of polar macromolecules (e.g., asphaltenes), in agreement with their higher MW<sub>w</sub>, and increased concentrations in heteroatoms (N, O, S) and acidic components (AN). It has been accepted that heteroatoms are primarily concentrated in heavy oil components, such as asphaltenes.<sup>25</sup> The observed differences in selected physicochemical properties between the sludge oils and their corresponding parent oils suggest that heavy oil and particularly polar components in the crude oil are apt to precipitate during oil production and storage processes.



**Figure 1.** Particle size accumulation curves of extracted solids A and B. Uniformity coefficient ( $C_u = d_{60}/d_{10}$ ) was used to describe the uniformity of particle size distribution of separated solid samples.

**Characterization of Extracted Solids.** Particle size analysis (Figure 1) shows that both extracted solids have wide particle size distribution, from submicrometer to as large as 200 μm. The median particle size ( $d_{50}$ ) is 11.4 μm for solids A and 32.3 μm for solids B. Both extracted solids contain significant amounts of fine mineral particles in the micrometer range ( $d_{10A} = 1.6$  μm,  $d_{10B} = 2.8$  μm). Particle size distribution of solids A is more uniform than solids B, as indicated by its lower uniformity coefficient ( $C_u = d_{60}/d_{10}$ ). The difference in particle size distribution for the extracted solids might originate from the differences in their parent reservoir properties.

Chemical compositions of the two extracted solids were analyzed by XRF. Results (Table 3) show that both samples have higher concentrations of Si and Al elements. These samples also have high loss on the ignition (LOI) index. It is possible that both extracted solid samples contain considerable amounts of insoluble organic compounds on their surfaces, although calcite might also contribute to the elevated LOI, especially for solids A.

XRD spectra of solids A and B were collected to interpret qualitatively their mineral compositions. As both samples are complex mixtures consisting of minerals that can be traced back to their respective parent reservoirs, their XRD spectra are expected to be complicated. Results (Figure 2) show that major minerals contained in both samples are quartz, feldspar (including orthoclase and albite), and clays. Solids A contain significant amounts of calcite while solids B are rich in feldspar and clays (e.g., Illite and kaolinite).

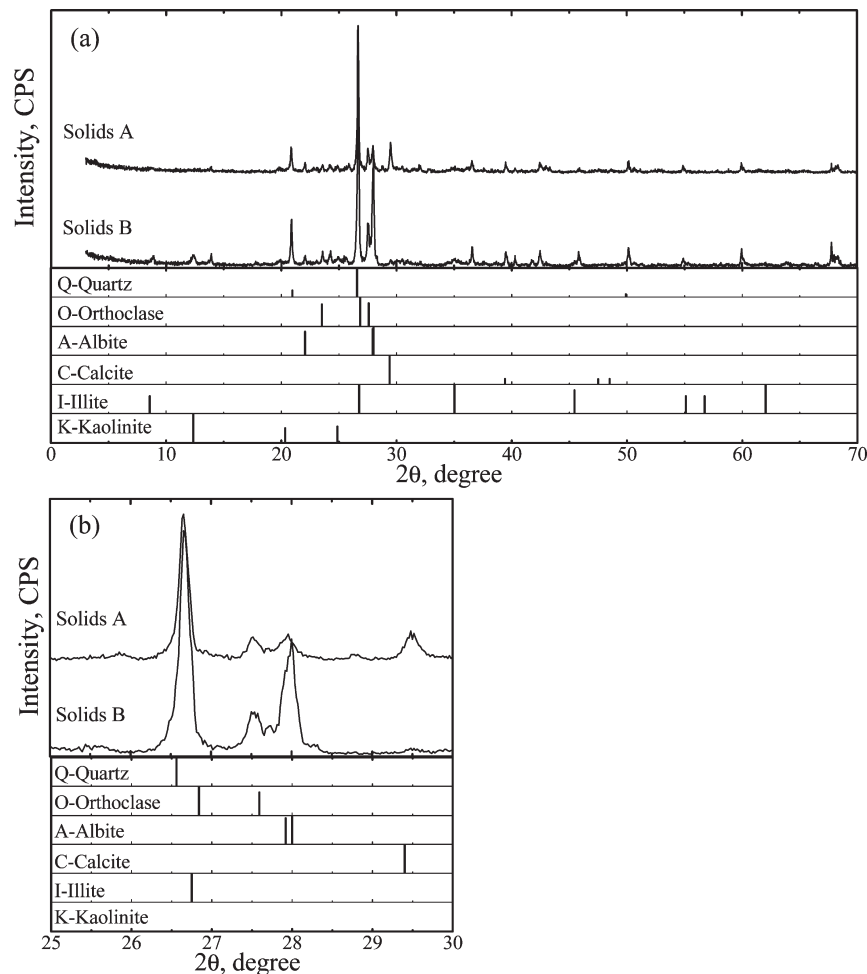
XPS analysis was performed to identify possible interactions between polar organic compounds and surfaces of the extracted solids. Shown in Figure 3a,b are sample A's XPS survey scans and summarized surface atomic concentrations calculated from its high resolution spectra both before and after H<sub>2</sub>O<sub>2</sub> digestion. The atomic concentration of the carbon element on surfaces of solids A is 65%. After H<sub>2</sub>O<sub>2</sub> digestion, however, its surface concentration is sharply

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**Table 3. Major Element Compositions of Extracted Solids, Mass %**

solids	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	MgO	MnO	TiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	LOI
A	47.62	9.06	4.49	12.61	0.10	0.14	0.42	2.21	2.05	0.18	5.55	10.26
B	62.12	13.06	1.71	5.97	0.91	0.06	0.60	2.55	2.84	0.12	0.70	9.32

**Figure 2.** XRD patterns of extracted solids A and B in the whole scanning range (a) and within 25–30 degrees (b). Standard diffraction lines for the several detected components were also included perpendicular to the  $2\theta$  axis with only the three strongest lines being presented.

decreased below 40%. This evidences the existence of organic compounds on the solids surfaces, possibly polar macromolecules, which have survived the sequential extractions by toluene and polar solvent (THF). This result is in accordance with the observed increase in surface concentrations of other elements (e.g., Si, Al, Fe, Ca) after the sample was digested by H<sub>2</sub>O<sub>2</sub>, which can partially decompose the adsorbed organic substances resulting in cleaner mineral surfaces. It is interesting to note that the N<sub>1s</sub> peak (399–401 eV) is significantly decreased after the solids sample was digested by H<sub>2</sub>O<sub>2</sub>, suggesting that N-containing organic compounds are adsorbed on solids surfaces. Similar phenomena were observed for the solids extracted from oil sludge B.

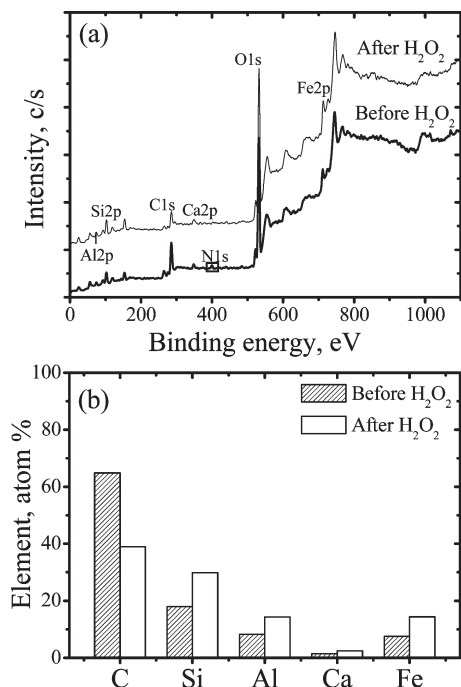
Wetting preference of the extracted solids was assessed qualitatively by visually observing the distribution of the solid grains between toluene and water phases contained in a glass tube. As demonstrated in Figure 4, in the absence of extracted solids, oil and water are immiscible and no emulsion is observed. Upon addition of solids A or B, large amounts of water-in-oil emulsion droplets are formed, particularly for solids A. These emulsion droplets are quite

stable even after 3 days, although some solid particles are found accumulated at the bottom of the test tubes. It is suggested that the surface properties of some fine mineral grains in the extracted solids have been modified by adsorption of polar macromolecules, changing their wetting preference from water-wetting to oil-wetting.

## Discussion

Analysis of the collected oil sludges indicated that they varied substantially in compositions while also shared some common features. Both oil sludge samples contained significant amounts of oil that could be potentially extracted for energy reuse, although oil concentration in sample B was less than half of sludge A. Compared with their parent crude oils, heavy polar compounds were enriched in the extracted sludge oils as demonstrated by their increased MW<sub>w</sub> and significantly higher concentrations in asphaltene, NOS, and acidic fractions. Higher content of solids for sample B might stem from the loose nature of its corresponding reservoir minerals.

Characterization of the two solid samples separated from the collected oil sludges showed that both of them contained

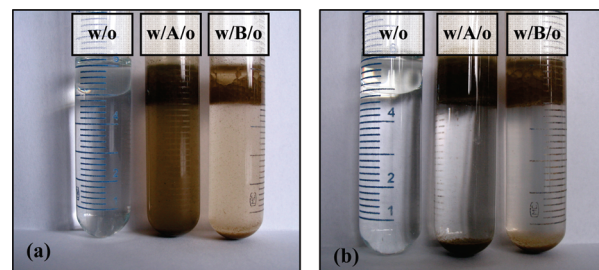


**Figure 3.** XPS survey-scan spectra (a) and calculated atomic ratios of surface elements (b) on extracted solids A both before and after  $H_2O_2$  digestion. Atomic ratios of surface elements were determined from the high-resolution scan spectra of the respective elements.

significant amounts of small particles (Figure 1) that were able to stabilize W/O emulsions. Because of their relatively large surface areas, these fine mineral particles tend to adsorb polar macromolecules on their surfaces. Surface XPS spectra (Figure 3) clearly demonstrate the existence of nitrogen-containing organic substances on the solid surfaces. Adsorption of these polar macromolecules can modify the wettability of these small mineral particles from water-wetting to oil-wetting, causing the W/O emulsion to be stabilized (Figure 4). It has been reported that mineral particles (e.g., silica, clay, iron oxides) contained in crude oils can become oil-wet due to their long-term exposure to the bulk oil and can stabilize W/O emulsions when these particles are sufficiently small.<sup>26</sup>

The current study suggested both small oil-wet mineral particles and polar macromolecules (e.g., asphaltene) would be responsible for the formation of W/O emulsions in the oil sludges investigated. The enriched asphaltene molecules in the sludge oils (Table 2) can not only interact with small mineral particles to generate oil-wet fines (Figure 4) but also accumulate preferentially on the oil–water interface. The existence of both asphaltenes and oil-wet fines on the oil–water interface can work jointly to enhance W/O emulsion stability.<sup>26</sup> Similar findings were reported by Yan et al.<sup>27</sup> and Sztukowski and Yarranton,<sup>28</sup> who reported that both asphaltenes and fine solids were responsible for the stability of water-in-oil emulsions.

A general picture for generation of tank oil sludges is depicted as follows. Generally, water and solids are present throughout crude oil production, transportation, and storage



**Figure 4.** Distribution of extracted solids A and B between water and oil phases. (a) 3 min after mixing: no solids added in the toluene–water system (left tube), solids A added to the system (middle tube), and solids B added to the system (right tube). (b) 3 days after mixing (other conditions fixed). 0.01 M NaCl solution was used as the aqueous phase, while toluene was selected as the oil phase. The volume ratio between oil and water was fixed at 1:5, and 0.1 g of solids were used throughout the tests.

processes. Water is entrapped into the bulk oil in the form of tiny emulsion droplets, which are quite stable due to accumulation on the oil–water interface of small oil-wet mineral particles and polar macromolecules, such as asphaltenes. However, these W/O emulsion droplets are metastable from the thermodynamic point of view. During the long-term storage process, tiny W/O emulsion droplets would finally aggregate to form larger droplets, which could not be effectively dispersed when significant gravity force is built on these aggregated emulsion droplets. These large droplets would then gradually separate from the bulk oil and accumulate on the tank bottom as heavily emulsified W/O oil sludges.

The current study showed that the two oil sludges contained large fractions of sludge oil (56.1% for A and 26.3% for B) that could be potentially extracted for energy reuse. However, both samples were in a heavily emulsified state, containing significant amounts of water (16.2% for A and 27.6% for B) and solids (27.5% for A and 46.0% for B) stabilized by fine oil-wet mineral particles and polar macromolecules. It is expected that these heavy W/O emulsions would pose great challenges for oil separation. It is suggested that pretreatment by demulsification would greatly help to reduce the overall cost for oil sludge processing. For example, a binary system consisting of a demulsification and centrifugation process could be tested in the future to separate these types of oil sludges. In the first process, the oil sludge can be demulsified by adding demulsification reagents and/or recyclable solvents or using electro-demulsification. The destabilized oil sludges could then be separated into their components by the subsequent centrifugation process. The separated solid fraction can be further treated by bioremediation to degrade the residual oil still associated with mineral particles. The separated sludge oil can be used for heating purposes. Oil sludge separation is beyond the scope of the current study. Future work needs to be conducted to test the feasibility of separating these oil sludges, for example, by the binary system proposed above.

## Conclusions

Characterization of the two oil sludges showed that both samples contained significant amounts of oil, which could be potentially extracted for energy reuse. These samples also contained large fractions of water and solids, suggesting they were both in heavily emulsified state. Both extracted sludge oils contained higher concentrations of heavy polar

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components than their parent crude oils. Solids separated from the two oil sludges were rich in oil-wet mineral fines due to adsorption of polar macromolecules. These oil-wet mineral fines, together with the asphaltene molecules were suggested to be responsible for the W/O emulsions formed in the oil sludges investigated.

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