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Analysis of Pyrolysis Characteristics of Oily Sludge in Different Regions and Environmental Risk Assessment of Heavy Metals in Pyrolysis Residue

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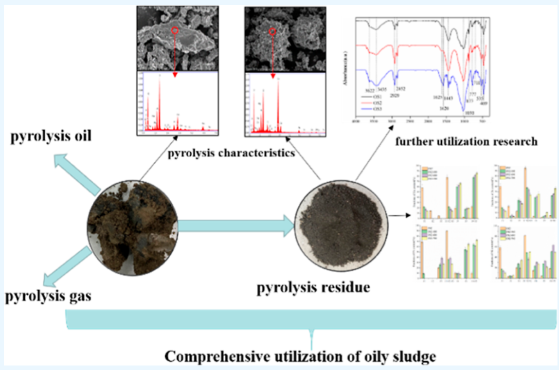
ABSTRACT: As a resource treatment method, pyrolysis realizes the recovery of oil and immobilization of heavy metals in oily sludge (OS). The results showed that the composition of OS had little effect on the trend of the whole pyrolysis process, but it had different effects on the mass loss and maximum weight loss rate at each pyrolysis stage. SEM−EDS results showed that the pyrolysis residue had a porous internal structure, which was similar to that of activated carbon. The elements S, Ca, O, Fe, Al, and Si were embedded in the carbon skeleton. After OS pyrolysis, the oil content of the solid residue was far less than 2%, which met the pollution control requirements for comprehensive utilization specified in China's oil and gas industry standard. At the same time, the ratio of exchangeable fraction decreased and the ratio of residual fraction increased after OS pyrolysis. The potential ecological hazard coefficient (E_r) of Cd in OS2, OS2-500, and OS2-600 was greater than 40, which were strong and medium hazards. The E_r values of OS2-700 and other metals were far lower than 40, which were low hazards. With the increase of pyrolysis temperature, the comprehensive ecological hazard index (RI) of heavy metals in the residue gradually decreased and the RI value of OS2-700 decreased to 28.01. Therefore, the pyrolysis residue had an internal porous structure and controllable environmental risk. It could be used as an adsorption material for heavy metals to realize the comprehensive utilization of OS.



1. INTRODUCTION

Oil and gas mining industry is a mineral mining industry that provides important energy and raw materials for the national economy.[1] It plays an extremely important role in the national economy. With its rapid development, the petrochemical industry has also brought many problems, such as resource waste and environmental pollution.[2,3] Oily sludge is a huge amount of solid waste produced in the petroleum and petrochemical industry, which has high resource recycling value. Because it contains high concentrations of hydrocarbons and other refractory organic and heavy metal components, oily sludge is classified as hazardous waste in many countries.[4−6] According to statistics, China produces about millions of tons of oily sludge every year, and the output is still increasing year by year.[7,8] Although the organic pollutants in oilfield sludge will cause serious damage to the environment, the components such as petroleum substances, metals, and other inorganic minerals have important value in oil and gas recovery and comprehensive utilization of inorganic components. Due to the different sources and processing processes of oilfield sludge, its chemical composition is complex. For example, the mass fraction of total petroleum hydrocarbons in oilfield sludge ranges from 5 to 86%, but it is usually 10 to 50%. The mass fraction of solid particles in oilfield sludge is 5 to 46%, and the content of water varies greatly.[9−11] In the contemporary society of increasing energy shortage, if we cannot effectively use the oil and other substances in the oily sludge, it will be a serious waste of resources and cause serious damage to the environment. Therefore, oilfield sludge is a "resource" misplaced, and the scientific treatment of oily sludge is of great significance.[9−13]

At present, the treatment methods of oily sludge mainly include incineration, solidification, solvent extraction, pyrolysis, and membrane separation.[6,14−16] Among them, pyrolysis technology has the characteristics of complete treatment effect, less pollution, and oil resource recovery, which has become a research hotspot of scholars at home and abroad.[17] Oily sludge pyrolysis is a series of physical and chemical changes of different components of oily sludge at high temperatures without oxygen. Many scholars have analyzed the thermal characteristics and dynamics of the oily sludge pyrolysis

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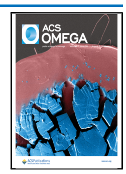

process and investigated the effects of operating conditions on pyrolysis products, such as heating rate, residence time, pyrolysis temperature, and type and quantity of catalysts.[18−21] The current research focuses on the impact on pyrolysis oil and pyrolysis gas and analyzes the release characteristics of heavy metals and some pollutants in oily sludge.[22] The study on the release properties of N/S/Cl pollutants in oily sludge shows that there are three typical decomposition steps in the pyrolysis and combustion process. At the same time, it is pointed out that organic N/S/Cl component is the main cause of N/S/Cl pollution.[22] In addition, some literature have studied the influence of adding fly ash on the quality of pyrolysis products. The fly ash used in one study is the product of gasification of sewage sludge in a fluidized bed reactor. The research shows that the addition of fly ash can promote the yield of pyrolysis products of oily sludge. When the proportion of fly ash is increased to 50.0 wt %, the yields of pyrolysis oil and gas can reach the highest, which are 30.43 and 11.56 wt %, respectively. The FTIR spectra analysis showed that with the addition of fly ash from 16.7 to 50.0 wt %, the content of aromatic hydrocarbons in pyrolysis products increased and the molecular mass of unbranched alkanes decreased.[23] The co-pyrolysis of organic matter and oily sludge also showed that the increase of pyrolysis temperature led to the decrease of pyrolysis oil recovery, but the non-bioavailable metal forms in pyrolysis residue increased. The metals in the oily sludge were fixed during pyrolysis.[24]

Previous studies focused on pyrolysis oil and pyrolysis gas, and analyzed various characteristics and laws of oily sludge pyrolysis.[17,23,25−27] Considering the comprehensive utilization of resources in the whole process of oily sludge treatment, the utilization of pyrolysis residue is also a key research direction. According to the previous study on the pyrolysis mechanism of oily sludge, heavy metals are accumulated in the pyrolysis residue. Once handled improperly, it will cause certain harm to the surrounding environment and human health.[28] The solid residue is the main component after pyrolysis of oily sludge, and the heavy metals are immobilized during the pyrolysis process. The study of its environmental risk is of great significance for the resource treatment of oily sludge.[29] Therefore, this paper will study the pyrolysis characteristics of oily sludge in three different regional oilfields and take the pyrolysis residue as the key research object. By analyzing the changes of appearance, composition, migration, and distribution of heavy metals and environmental risk of oily sludge and solid residue, the characteristics of residue in pyrolysis process were revealed, so as to provide scientific guidance for the subsequent utilization of residue.

2. MATERIALS AND METHODS

2.1. Materials. The oily sludge samples OS1, OS2, and OS3 used in the experiment were collected from Tahe oilfield, Fengcheng oilfield, and Tarim oilfield in Xinjiang Uygur Autonomous region, China. The oily sludge samples were all ground sludge. The oily sludge OS1 and OS3 were yellowish brown and sandy solid substances, and OS2 was a dark brown and sticky solid substance. Table 1 describes the basic characteristics of oily sludge samples adopted in this paper. The basic analysis such as oil content, proximate and ultimate analysis, and lower heating value (LHV) was performed. Soxhlet extraction method was used to analyze the oil content of the sample. Proximate analysis of oily sludge refers to the proximate analysis standard of solid biofuels (GB/T 28731-2012), and muffle furnace was used for relevant analysis (KSL-1200X, China). In this proximate analysis, the air drying method was used to determine the moisture, the slow ashing method was used to determine the ash, and the subtraction method was adopted to calculate the fixed carbon. The ultimate analysis was carried out by a CHNS element analyzer (VARIO EL cube, Germany), and LHV was determined by a full-automatic calorimeter (ZDHW-A9, China). In this paper, three groups of parallel experiments were carried out, and the average value was taken as the analysis data.

Table 1. Basic Characteristics of Oily Sludge Samples Adopted in This Paper

Sample name	Source	Sample description	Appearance morphology
OS1	Tahe oilfield	Yellowish brown, uneven granular soil	
OS2	Fengcheng oilfield	Dark brown, sticky block	
OS3	Tarim oilfield	Yellowish brown, fine sand	

2.2. Experimental Apparatus and Method. In this paper, the fixed bed pyrolysis reactor of tubular furnace (quartz tube length: 310 mm, Ø: 45 mm; OTF-1200X, China) was used to pyrolysis oily sludge. In order to ensure that the whole pyrolysis process was in an inert environment, high-purity nitrogen was introduced into the tubular furnace at a certain flow rate before and during pyrolysis. The flow rate of nitrogen was set at 125 mL/min, and the heating rate of pyrolysis process was 20 °C/min. The pyrolysis reaction temperature of the sample was set at 500, 600, and 700 °C, respectively, and the constant temperature reaction time was 180 min. In each experiment, 80 g oily sludge sample was weighed for pyrolysis. After the pyrolysis reaction, the cooled residue was collected for subsequent property analysis.

2.3. Analysis of Pyrolysis Characteristics. In this paper, the effects of pyrolysis temperature and oily sludge composition on pyrolysis were studied. The main characterization factors were the oil content, internal structure, and surface functional groups of the residue. The representative pyrolysis residue samples were further selected to analyze the immobilization mechanism of heavy metals in the pyrolysis process and the controllability of environmental risk of the residue. The forms of heavy metals were obtained by a five-step extraction method, and the environmental risk was evaluated by potential ecological risk index (RI). The main analysis indexes include oil content, thermogravimetric (TG) analysis, X-ray fluorescence spectrometry (XRF), scanning electronic microscopy combined with energy dispersive spectroscopy (SEM−EDS), and Fourier transform infrared (FTIR) spectroscopy. The oil content was still determined according to the method in Section 2.1. The thermal characteristics of oily sludge were characterized by TG analysis. The temperature rise rate of the TG analyzer was 10 °C/min, and the temperature range was 30−1000 °C. The flow rate of

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nitrogen into the furnace was 40 mL/min (STA-449C, Netzsch, Germany). The elemental analysis of oily sludge was determined by XRF (S8 TIGER, Bruker, Germany). The morphology of oily sludge and residue was observed by SEM−EDS (S-4800, Hitachi, Japan). The group structure of oily sludge and residue was obtained by FTIR (Tensor27, Bruker, Germany). The contents of Cu, Zn, Pb, Ni, Cr, and Cd in the samples were determined by inductively coupled plasma emission spectrometry (ICP−OES) (Optima 7000DV, PerkinElmer, USA), while the contents of Hg and As were analyzed by atomic fluorescence spectrometry (AFS-8520, Haiguang, China). The oily sludge samples used for TG, XRF, SEM−EDS, and FTIR analysis were all dried samples, in which the drying temperature was 105 °C and the drying time was 4 h.

2.4. Speciation and Distribution of Heavy Metals. Tessier five-step sequential extraction method was adopted to represent the speciation of heavy metal changes before and after pyrolysis of oily sludge at different temperatures.[30] The effect of pyrolysis temperature on the immobilization of heavy metals in oily sludge was further analyzed. The operation methods and corresponding forms of sequential extraction are shown in Table 2. The proportion of each fraction was the ratio of the extraction concentration of the corresponding fraction to the extraction concentration of the five fractions. The content of extracted heavy metals was determined by ICP−OES (Optima 7000DV, PerkinElmer, USA).

Table 2. Explanation of Tessier 5-Step Sequential Extraction

heavy metal speciation	extractant	operating conditions
exchangeable fraction	8 mL of 1.0 M $MgCl_2$ (pH = 7.0)	shake at 25 ± 1 °C for 1 h
carbonate fraction	8 mL of 1.0 M NaAc (pH = 5.0)	shake at 25 ± 1 °C for 5 h
Fe−Mn oxide fraction	20 mL of 0.04 M $NH_2 \cdot OH \cdot HCl$ in 25% (v/v) HAc	shake at 96 ± 3 °C for 6 h
	3 mL of 0.02 M HNO_3, 5 mL of 30% (v/v) H_2O_2 (pH = 2.0)	shake at 85 ± 2 °C for 2 h
organic matter bound fraction	3 mL of 30% H_2O_2 (pH = 2)	shake at 85 ± 2 °C for 3 h
	5 mL of 3.2 M NH_4Ac, add 20% (v/v) HNO_3 and dilute to 20 mL	shake at 25 ± 1 °C for 30 min
residual fraction	aqua regia	ISO specification (11466)

2.5. Determination of Potential Ecological Risk Index. The potential ecological hazard index method was a set of evaluation methods established by the Swedish scholar Hakanson in 1980.[31] This method applied the principle of sedimentology to evaluate heavy metal pollution and ecological harm. According to the properties of heavy metals and the characteristics of environmental behavior, it was proposed from the perspective of sedimentology to evaluate the heavy metal pollution in the medium. Its calculation formula is shown in eq 1.

$$\mathrm{RI} = \sum_{i=1}^{m} E_{\mathrm{r}}^{i} = \sum_{i=1}^{m} T_{\mathrm{r}}^{i} C_{\mathrm{f}}^{i} = \sum_{i=1}^{m} T_{\mathrm{r}}^{i} \frac{C^{i}}{C_{n}^{i}} \quad (1)$$

where RI is the comprehensive ecological hazard index; C^i is the measured value of single heavy metal;C_n^i is the evaluation standard value of heavy metals, which refers to the relevant quality standards of sludge for forestland (CJ/T 362-2011);[32] E_r^i is the single factor potential ecological hazard coefficient; T_r^i is toxicity response coefficient of heavy metals; and C_f^i is the single factor pollution coefficient.

3. RESULTS AND DISCUSSIONS

3.1. Analysis of Oily Sludge Samples. *3.1.1. Physical and Chemical Characteristics.* Table 3 shows the chemical characteristic analysis of oily sludge in three different regions. Proximate analysis showed that the ash content in oily sludge samples was high, and the ash content in OS3 was as high as 88.60%. Considering that the oily sludge was mainly composed of soil and crude oil, the sand content was high in the samples used in this study. The main volatile components of oily sludge were petroleum organics, which were 11.80, 13.93, and 6.27%, respectively. The water content of oily sludge samples was 16.37, 18.99, and 2.26%, respectively, which mainly comes from rainwater and crude oil exploitation. The water content in OS3 was low and presented the appearance of fine sand, as shown in Table 1. The content of fixed carbon in oily sludge was less, accounting for 0.23, 0.81, and 2.87%, respectively. According to the results of ultimate analysis, the content of C element in oily sludge was the highest, which was 4.87, 7.43, and 5.60%, respectively. The content of H element was 0.94, 1.59, and 1.09%, respectively. In addition, it contained small amounts of elements N and S. The oil content of oily sludge obtained by Soxhlet extraction method was 8.56, 10.5, and 6.43%, respectively. The LHV of oily sludge was 3.47, 4.26, and 2.61 MJ/kg, respectively.

The oily sludge of the three oilfields was ground oily sludge, and its composition difference was closely related to the local soil composition. According to the analysis results of oily sludge from three different oilfields, OS3 had higher fixed carbon content but lower oil content and heating value. It could be inferred that the organic carbon in OS3 was lower than that in OS1 and OS2. The results of elemental analysis of dried oily sludge are shown in Table 4. Elemental analysis data showed that the Si content in OS3 was as high as 25.23%. The content of inorganic components was high, and the recyclable oil component was relatively low. The following content of this paper makes an in-depth analysis and discussion of the composition of organic matter in oily sludge of different oilfields.

3.1.2. Thermogravimetric Analysis. A series of complex physical and chemical reactions occur with the thermal cracking process of oily sludge. In this paper, a more appropriate TG/derivative TG (DTG) analysis technology

Table 3. Chemical Characteristics of the Oily Sludge

	proximate analysis[a] (wt %)				ultimate analysis[a] (wt %)					
sample	moisture	volatile	ash	fixed carbon[c]	C	H	N	S	oil content (%)	LHV[b] (MJ/kg)
OS1	16.37	11.80	71.60	0.23	4.87	0.94	0.09	2.72	8.56	3.47
OS2	18.99	13.93	66.27	0.81	7.43	1.59	0.11	0.70	10.5	4.26
OS3	2.26	6.27	88.60	2.87	5.60	1.09	0.09	0.49	6.43	2.61

[a]Receive basis. [b]Lower heating value. [c]Calculated by difference.

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Table 4. Elemental Analysis of Oily Sludge Detected by XRF (on Dry Basis)

	content (%)				content (%)		
element	OS1	OS2	OS3	element	OS1	OS2	OS3
Si	15.78	16.03	25.23	Sr	0.103	0.0449	0.0452
Ca	9.03	7.77	2.78	P	0.0524	0.0945	0.0771
Al	5.30	5.87	7.37	Cr	0.0107	0.0047	0.0043
Fe	4.14	3.33	2.98	Cu	0.0125	0.0048	0.0039
S	2.02	1.05	0.939	W	0.0099		0.0351
Mg	1.93	1.22	1.21	Zr	0.0093	0.0090	0.0176
Na	1.93	1.20	1.26	I	0.0119		
Cl	2.69	0.433	0.303	Ni	0.0075	0.0062	0.0043
Ba	2.41	0.432	0.0881	V	0.0053	0.0134	0.0086
K	1.70	1.44	2.17	Pb	0.0078		
Ti	0.245	0.285	0.446	Rb		0.0038	0.0062
Mn	0.171	0.0766	0.0535	Ga			0.0033
Zn	0.154	0.778	0.0100				

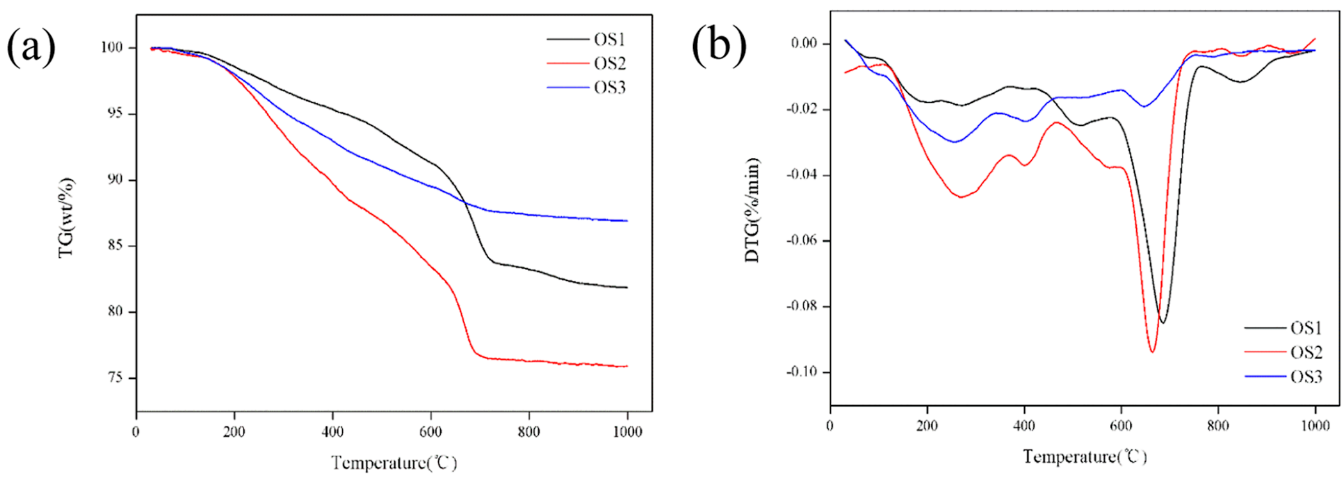

Figure 1. TG analysis curves of the oily sludge. (a) TG curves; (b) DTG curves.

was selected to analyze the quality change of the oily sludge pyrolysis process. The details of the variation of oily sludge quality with temperature were obtained. Figure 1 shows the TG and DTG curves of oily sludge samples under the condition of high-purity nitrogen. According to the results of TG curves and the properties of oily sludge, the pyrolysis process of oily sludge could be divided into five stages: drying degassing stage (30−180 °C), light oil volatilization stage (180−400 °C), heavy oil decomposition stage (400−520 °C), pyrolysis semi coking stage (520−650 °C), and mineral decomposition stage (650−1000 °C). The above stages were carried out by multiple reactions, but one reaction was the main reaction in a specific temperature range.[33] Therefore, each pyrolysis stage was divided according to the main reaction of corresponding substances in different temperature ranges.

As shown in Figure 1, the trend of TG and DTG curve of oily sludge samples in different regions was similar, indicating that the composition and properties of oily sludge studied in this paper had little effect on the trend of the whole pyrolysis process. Therefore, only OS2 was selected as the object of the following pyrolysis residue characteristics research. However, the mass loss and maximum weight loss rate of oily sludge with different properties were different in each stage. As the samples were dried for TG analysis, the first stage was mainly the volatilization of chemically bound water and some low boiling alkanes. The weight loss rates of OS1, OS2, and OS3 in the first stage were 1.05, 1.52, and 1.47% respectively, indicating that there were few chemically bound water and small molecular compounds in the oily sludge. On the basis of proximate analysis results, the water in the oily sludge was mainly free water. The second, third, and fourth stages of oily sludge pyrolysis accounted for a large proportion and were the main components of oily sludge weight loss. In these stages, the organic matter in the oily sludge volatilized directly, or some macromolecular organic matter volatilized after pyrolysis reaction to form components with relatively small molecular weight.[34]

DTG curve showed that there was a large peak in the second stage of oily sludge pyrolysis. This stage was a rapid weight loss stage of pyrolysis, which mainly comes from the volatilization of low boiling point hydrocarbons. There was also a small peak in the temperature range of the third stage of oily sludge pyrolysis, which was the main reaction stage of oily sludge pyrolysis. At this stage, a large number of alkanes were produced.[33] The C−C bond of macromolecules was broken, and small alkanes were generated to escape. At the same time, the C−H bond broke to produce olefins, and cyclization reaction also occurred at this stage to produce aromatic hydrocarbons.[35] The mass loss in the fourth stage of oily sludge pyrolysis may mainly come from the decomposition reaction of complex refractory organic compounds. In the fifth stage of oily sludge pyrolysis, the mass loss was small and then

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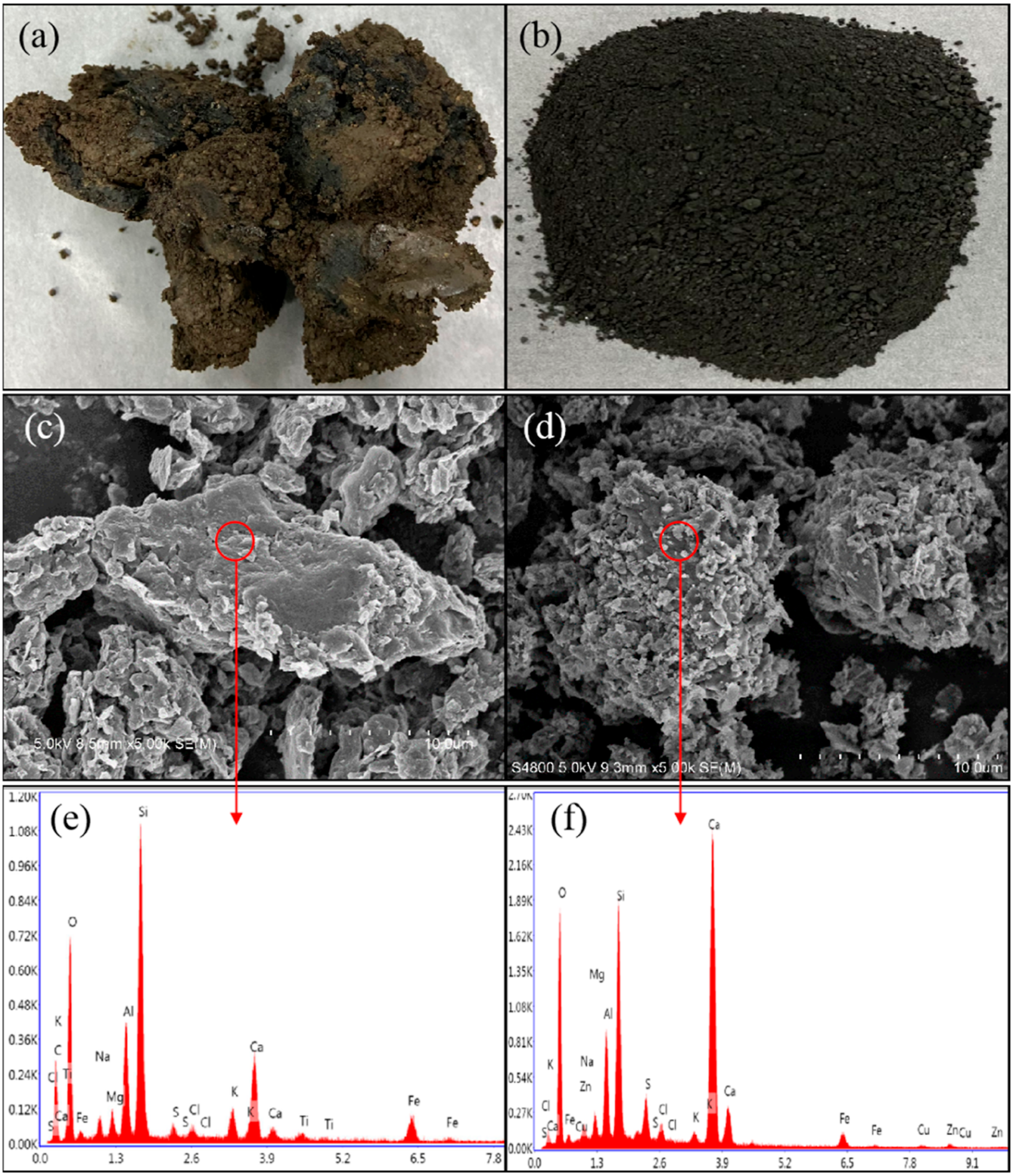

Figure 2. Appearance and SEM−EDS images of oily sludge before and after pyrolysis. (a,c,e) OS2; (b,d,f) solid residue after OS2 pyrolysis.

the mass tended to be stable. This stage was mainly caused by the decomposition reaction of inorganic carbonate in oily sludge.

The weight loss rates of OS1, OS2, and OS3 were 18.13, 24.11, and 13.09%, respectively, at the pyrolysis temperature ranging from 30 to 1000 °C. Compared with other oily sludge samples, OS3 had lower weight loss rate and less volatilization and decomposition of organic matter, indicating that the oil content was low. The above results were consistent with the analysis conclusion of organic matter in oily sludge samples in Section 3.1.1.

3.2. Analysis of Pyrolysis Characteristics. *3.2.1. Morphology Analysis.* Considering the similarity of pyrolysis trend of oily sludge samples, OS2 was only selected as the research

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object of pyrolysis residue. Figure 2 shows the appearance and SEM−EDS of OS2 before and after pyrolysis. It could be seen from Figure 2 that the oily sludge was a yellowish brown and viscous solid material. The residue was non-uniform particles, and the surface of the particles was velvet carbon. At the same time, the pyrolysis residue had no special smell, and the SEM image showed that it had rich porosity, similar to the structure of activated carbon. According to previous studies, the porous structure skeleton of the pyrolysis residue was composed of C elements, and it could be seen from its EDS that S, Ca, O, Fe, Al, and Si elements were embedded in the carbon skeleton structure.[36] Most of the embedded elements existed in crystalline minerals and amorphous compounds of inorganic salts, so the pyrolysis residue could be considered as an adsorption material for heavy metals.[37] However, more importantly, the environmental risk caused by residues should be fully considered. Section 3.3 of this paper will evaluate the environmental pollution risk of the residue.

3.2.2. Oil Content and FTIR Analysis. Table 5 shows the oil content of oily sludge and solid residues. It could be seen that

Table 5. Oil Content of Oily Sludge and Solid Residue

oily sludge	oil content (%)	solid residue	oil content (%)
OS1	8.56	OS1-500	0.1270
		OS1-600	0.0870
		OS1-700	0.0587
OS2	10.5	OS2-500	0.0850
		OS2-600	0.0839
		OS2-700	0.0674
OS3	6.43	OS3-500	0.0697
		OS3-600	0.0530
		OS3-700	0.0468

the oil content of the residue in different regions was low, which was less than the requirement of no more than 2% specified in China's oil and gas industry standard (SY/T 7301-2016). When this provision was met, the residue could be used to lay the well way and pad the foundation materials of the well pad. At the same time, the pollutants in the leaching solution of the cured formed subgrade shall meet the requirements of GB 8978-1996 "integrated wastewater discharge standard".

Figure 3 shows the characteristics of organic functional groups of oily sludge and solid residues by FTIR spectra. The FTIR spectra analysis in Figure 3a showed that oily sludge samples in different regions had similar absorption peaks, but the absorption intensity was different. The FTIR spectra of oily sludge showed that there were many kinds of absorption peaks, indicating that the composition of organic matter in the solid waste was complex. Among them, the absorption peaks at 3622 and 3435 cm^{-1} were hydroxyl functional groups, which generally existed in the form of a free, intramolecular association or an intermolecular association. The absorption peaks at 2929, 2852, and 1443 cm^{-1} might be aliphatic functional groups. The absorption peaks at 2929 and 2852 cm^{-1} corresponded to $-CH_3$ and $-CH_2$, respectively. The absorption peak at 1443 cm^{-1} was considered to be alkane or olefin. The absorption peaks at 1625 and 1620 cm^{-1} were C=C of aromatic hydrocarbons and olefins. The absorption peak at 1030 cm^{-1} was the stretching vibration of C−O, which may come from alcohols, ethers, or esters. The peaks around 877, 777, and 711 cm^{-1} were ascribed to the bending mode of out-of-plane C−H. The last bands at 535 and 469 cm^{-1} were bending vibration of C−C=O, that is, aldehydes and ketones.[38−41]

Figure 3a shows that the organic components of oily sludge in different regions are similar. In the follow-up study, only the composition and structure of residue after OS2 pyrolysis were analyzed. The relevant FTIR spectra are shown in Figure 3b. The results showed that the infrared peak intensity of pyrolysis residue at 2929, 2852, and 1443 cm^{-1} gradually decreased or even disappeared at the pyrolysis temperature ranging from 500 to 700 °C. The peak band of pyrolysis residue at the above wavelength disappeared completely at 700 °C. The peak bands with this law also appeared at 3622, 877, 711, and 535 cm^{-1}. The FTIR spectra of oily sludge and pyrolysis residue showed that alcohols, phenols, aliphatics, aldehydes, and ketones in oily sludge were gradually decomposed during pyrolysis. The higher the pyrolysis temperature, the more thorough the decomposition of organic compounds. This conclusion could also be seen from the TG/DTG curve in Figure 1. Compared with the above analysis of the pyrolysis stage of oily sludge, oily sludge began to enter the heavy oil decomposition and pyrolysis semi-coking stage when the pyrolysis temperature was higher than 400 °C. On the contrary, the peak of pyrolysis

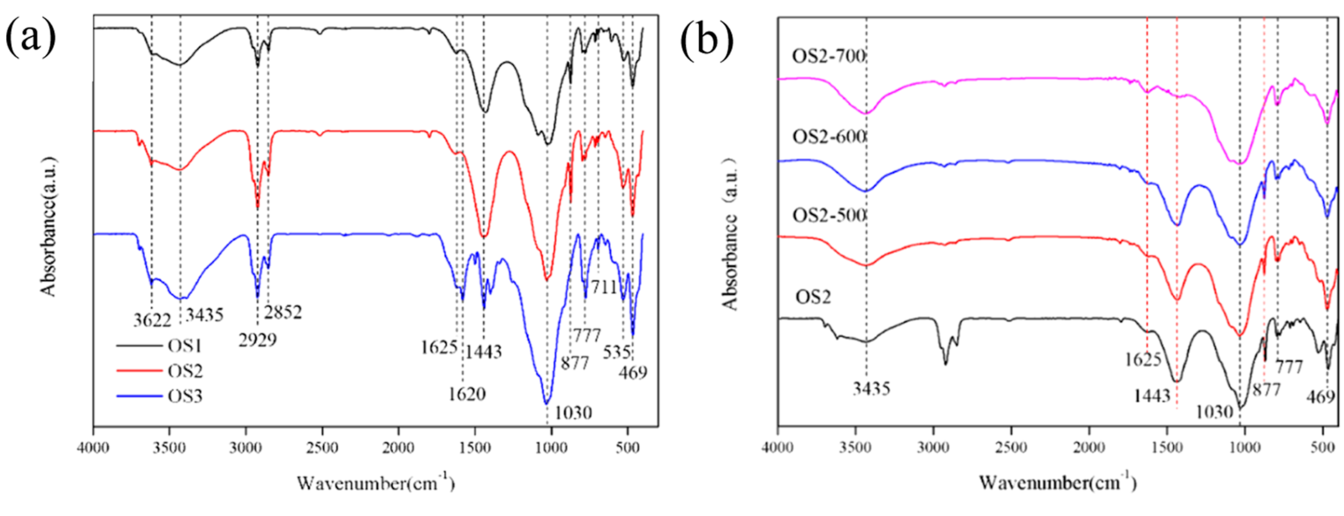

Figure 3. FTIR spectra of oily sludge (a) and solid residue (b) at different pyrolysis temperatures.

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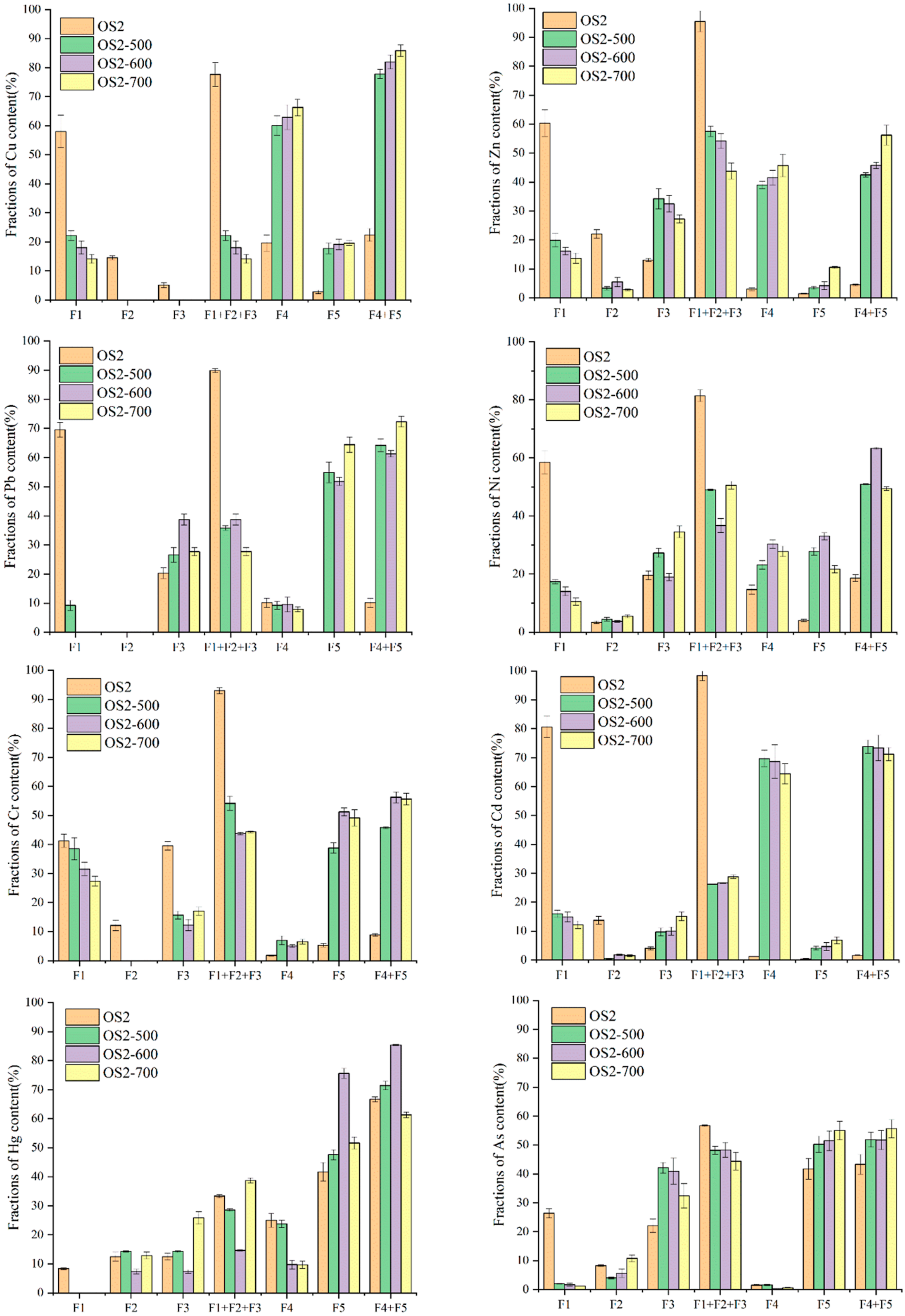

Figure 4. Fraction distribution of heavy metals in oily sludge and solid residue at different pyrolysis temperatures.

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Table 6. Heavy Metals in Oily Sludge and Pyrolysis Residue

concentration of heavy metals in oily sludge and pyrolysis residue (mg/kg)								
sample	Cu	Zn	Pb	Ni	Cr	Cd	Hg	As
OS2	29.2	7140	13.4	49.9	44.3	58.2	0.516	17.6
OS2-500	31.3	4850	17.9	50.0	47.4	42.9	0.197	12.4
OS2-600	36.4	7210	18.1	68.6	54.8	55.3	0.131	21.1
OS2-700	37.7	7990	19.4	55.5	52.7	14.5	0.072	12.7
CJ/T 362-2011	1500	3000	1000	200	1000	20	15	75

classification standard of potential ecological hazard index								
heavy metals	Cu	Zn	Pb	Ni	Cr	Cd	Hg	As
T_r	5	1	5	5	2	30	40	10
C_n	1500	3000	1000	200	1000	20	15	75

E_r	pollution degree	RI	risk degree
$E_r < 40$	slight	RI < 150	slight
$40 \le E_r < 80$	medium	150 ≤ RI < 300	medium
$80 \le E_r < 160$	strong	300 ≤ RI < 600	strong
$160 \le E_r < 320$	very strong	RI ≥ 600	very strong
$E_r \ge 320$	extremely strong		

the potential ecological risk evaluation in oily sludge and pyrolysis residue										
	E_r									
sample	Cu	Zn	Pb	Ni	Cr	Cd	Hg	As	RI	risk degree
OS2	0.10	2.38	0.07	1.25	0.09	87.30	1.38	2.35	94.90	slight
OS2-500	0.10	1.62	0.09	1.25	0.09	82.95	0.53	1.65	88.28	slight
OS2-600	0.12	2.40	0.09	1.72	0.11	64.35	0.35	2.81	71.95	slight
OS2-700	0.13	2.66	0.10	1.39	0.11	21.75	0.19	1.69	28.01	slight

residue at a wavelength of 1625 cm^{-1} gradually increased with the increase of temperature, indicating that the aromatization of pyrolysis residue increased with the increase of temperature. At 1030 cm^{-1}, the change of peak intensity was not obvious, indicating that the pyrolysis temperature had little effect on C−O bond.[42]

3.3. Environmental Risk Assessment. *3.3.1. Heavy Metal Speciation Characteristics.* Figure 4 presents the distribution of heavy metals speciations in oily sludge and solid residue at different pyrolysis temperatures. The ratio of $(F_1 + F_2 + F_3)$ represented the chemical speciation that was easy to enter the environment, and the ratio of $(F_4 + F_5)$ represented the chemical speciation that was relatively stable for heavy metals and low environmental risk. The speciation distribution analysis showed that Cu, Zn, Pb, Ni, Cr, and Cd in OS2 mainly existed in exchangeable fraction (F_1), accounting for 58.04, 60.33, 69.57, 58.47, 41.30, and 80.65%, respectively. Hg and As mainly existed in the residual fraction, accounting for 41.67 and 41.75%, respectively. In the pyrolysis temperature range of 500−700 °C, the ratios of exchangeable fraction (F_1) and $(F_1 + F_2 + F_3)$ of heavy metals in the solid residue gradually decreased, and the ratios of residual fraction (F_5) and $(F_4 + F_5)$ increased at the pyrolysis temperature ranging from 500 to 700 °C. The above results mainly take into account the changes of oily sludge during pyrolysis. On the one hand, heat treatment changed its physical properties, such as density and moisture content. On the other hand, pyrolysis promoted the decomposition of heavy metal compounds in oily sludge. Heavy metals were gradually transformed into more stable chemical forms during pyrolysis, such as oxides.[43−46] The above results indicated that pyrolysis could immobilize heavy metals and weakened their migration ability in the environment. The environmental risk of heavy metals in the solid residue was reduced.[24,44] In addition, it was noteworthy that Hg volatilized rapidly into pyrolysis oil and pyrolysis gas during pyrolysis, so the Hg content in solid residue gradually decreased with the pyrolysis process. The ratio of $(F_1 + F_2 + F_3)$ of Hg increased greatly at 700 °C, which was manifested in the increase of carbonate fraction (F_2) and Fe−Mn oxide fraction (F_3). The above chemical speciation changes of Hg in solid residue were closely related to the valence conversion of Hg during pyrolysis. When the pyrolysis temperature was 500 and 600 °C, a large amount of reducing gas was generated to reduce the high valence Hg to Hg^0. When the pyrolysis temperature was 700 °C, the volatile had basically escaped and the reduction effect on Hg was weakened. At the same time, Hg^0 continued to enter the pyrolysis gas with the progress of pyrolysis, resulting in the decrease of the proportion of Hg^0. Therefore, the proportion of unstable form $(F_1 + F_2 + F_3)$ of Hg in OS2-700 increased.[45]

3.3.2. Potential Ecological Risk Assessment of Oily Sludge and Solid Residue. The potential ecological risk assessment of oily sludge and its solid residue is shown in Table 6. Compared with oily sludge, the contents of Cu, Zn, Pb, Ni, and Cr in pyrolysis residue were higher, which indicated that the metals had been gradually enriched in the residue during pyrolysis.[47] For example, the contents of Cu and Zn in OS2 increased from 29.2 and 7140 to 37.7 and 7990 mg/kg in OS2-700, respectively. In the pyrolysis process, heavy metals not only enriched in the solid residue but also entered the pyrolysis oil and gas due to volatilization. Once the volatilization of heavy metals was greater than the accumulation, the content of heavy metals in the pyrolysis residue decreased. For example, the contents of Hg and Cd in OS2 decreased from 0.516 and 58.2 to 0.072 and 14.5 mg/kg in OS2-700, respectively. In addition, the volatilization of Ni and Cr was higher than its pyrolysis enrichment effect at the pyrolysis temperature ranging from 600 to 700 °C. The contents of Ni and Cr decreased from 68.6 and 54.8 mg/kg in OS2-600 to 55.5 and 52.7 mg/kg in OS2-700, respectively. Therefore, with the increase of pyrolysis

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temperature, the content of heavy metals in the residue changes continuously under the combined action of volatilization and accumulation. The higher the temperature, the stronger the volatilization. When the temperature rises to a certain temperature, its volatility increases and the content of heavy metals in the residue decreases significantly. For example, when the pyrolysis temperature was increased to 700 °C, the content of Cd in the residue was greatly reduced. The change of heavy metal content indicated its complex migration and transformation in the pyrolysis process, which played a guiding role in the risk assessment of heavy metals.

During the calculation of the potential ecological RI, the evaluation standard value C_n of heavy metals referred to the relevant quality standards of sludge for forestland (CJ/T 362-2011). The evaluation criteria for pollution degree and risk degree of heavy metals are shown in Table 6. The average value of heavy metals E_r in solid phase residue was in a descending order: Cd > Zn > As > Ni > Hg > Cu > Cr > Pb. The average E_r value of Cd was 56.35, which was a medium ecological hazard. The E_r values of Cu, Zn, Pb, Ni, Cr, Hg, and As were far lower than 40, which was a slight ecological hazard. The comprehensive ecological risk assessment results showed that the RI values of heavy metals (Cu, Zn, Pb, Ni, Cr, Cd, Hg, and As) of OS2, OS2-500, OS2-600, and OS2-700 were less than 150, indicating that the potential ecological risk of oily sludge and pyrolysis residue to the environment was low.

4. CONCLUSIONS

This study showed that there were great differences in the composition of oily sludge in different regions due to different local soil components, but it had little effect on the trend of the whole pyrolysis process. TG analysis showed that the pyrolysis process of oily sludge consisted of five stages, among which light oil volatilization stage, heavy oil decomposition stage, and pyrolysis semi-coking stages were the main components of weight loss of oily sludge. The results of five-step sequential extraction of oily sludge and residue showed that the metal in oily sludge was immobilized after pyrolysis, and the proportion of stable components such as residue increased. The potential ecological hazard assessment of heavy metals showed that heavy metals in oily sludge migrated and transformed due to enrichment and volatilization during pyrolysis, and most of them were enriched in the solid-phase residue. Among them, the harm degree of Cd in OS2 and OS2-500 was strong ($80 \leq E_r < 160$), and the harm degree of Cd in OS2-600 was medium ($40 \leq E_r < 80$). Due to volatilization, the E_r value of Cd decreased from 87.30 in OS2 to 21.75 in OS2-700. In general, the potential ecological risk of pyrolysis residue to the environment was controllable (RI < 150), and further utilization research could be carried out according to the structural properties of the residue.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01994.

Content of heavy metals in oily sludge and pyrolysis residue and recovery ratio of heavy metals after five-step extraction, QA/QC for concentration of heavy metals in oily sludge and pyrolysis residue, and QA/QC for concentration of heavy metals extracted in 5-step sequential extraction (PDF)

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Notes

The authors declare no competing financial interest.

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