Scientific article
UDC 665.6/.7:543.48
DOI: 10.52957/2782-1900-2024-5-2-127-132

POSSIBILITIES OF SPECTRAL ANALYSIS METHODS FOR THE OIL SLUDGE RESEARCH

E. L. Nikitina, V. A. Smirnova, A. S. Danilova

Elena L. Nikitina, Candidate of Technical Sciences, Associate Professor; **Valeria A. Smirnova**, Student; **Angelina S. Danilova,** Engineer
Yaroslavl State Technical University, Yaroslavl, Russia
nikitinael@ystu.ru, smirnova.lera-2010@yandex.ru, danilovaas@ystu.ru

Keywords: *cake, tricanter, oily waste, X-ray fluorescence spectrometry, spectral analysis*

Abstract. *The paper considers the problem of utilisation and neutralisation of oil sludge at oil producing and refining enterprises. Oil sludge is a complex heterogeneous mixture consisting of high-molecular oil compounds, mineral particles of different composition, and water. The authors studied the elemental composition of oil sludge of different storage periods for oil refinery production by modern analytical methods: IR spectroscopy and X-ray fluorescence spectrometry. According to the research, the main composition of the oil residue, represented by the hydrocarbon component, contains paraffin-naphthenic and heavy aromatic hydrocarbons. Moreover, its non-hydrocarbon component contains compounds Si, Al, Ca, Fe, S, Ba.*

For citation:
Nikitina, E.L., Smirnova, V.A. & Danilova, A.S. (2024) Possibilities of spectral analysis methods for the oil sludge research, From Chemistry Towards Technology Step-By-Step, 5(2), pp. 127-132 [online]. Available at: https://chemintech.ru/ru/nauka/issue/5176/view

Introduction

The Russian Federation is a leader in oil production and refining. Oil companies in Russia produce 600 thousand tonnes of oil sludge annually; the total volume worldwide is 6 million tonnes. Oil producing companies account for more than 1 million tonnes of oil sludge and oil-contaminated soils; oil refineries – 0.7 million tonnes; oil depots – 0.3 million tonnes; other sources (railway transport, airports, seaports) – 0.5 million tonnes [1-3]. Oily waste disposal facilities occupy dozens of hectares of territories separated out of economic use and are characterised by ecological, fire, and sanitary-hygienic danger. When oil sludge penetrates into the soil, deep irreversible changes of physical, physicochemical, and microbiological properties occur. It causes the loss of soil fertility [4, 5]. The recovery period of oil-contaminated soils is 2-15 years.

Notwithstanding the significant amount of waste, rational methods of its recycling in our country are still underdeveloped. Most often inexpensive methods of disposal are used in Russia. They are incineration and landfilling [6]. One of the reasons for limited use of promising oil sludge processing technologies is poorly studied component composition of sludge, and practical absence of separate collection of oil-contaminated soils. Separate collection depends on the amount of oil products. They provide low efficiency of measures taken for their processing. Eventually, the companies use those technologies ensuring maximum economic efficiency and minimum processing costs [7, 8]. Oil sludge is the most dangerous pollutant practically for all components of the natural environment – surface and ground waters, soil, atmospheric air.

Main body

The composition of oil sludge is very diverse. It represents a complex heterogeneous system consisting of mechanical impurities, mineralised water, and oil products. The ratio of these components depends on the source of formation, conditions, and duration of storage [9, 10]. The properties of oil sludge, which have been stored in sludge reservoirs for years, differ significantly. Light volatile hydrocarbons evaporate out of the sludge during storage, the liquid fuel oil fraction penetrates into the soil and is supplemented by atmospheric precipitation, mechanical impurities, etc. [11]. There is 7 kg of oil sludge per tonne of refined oil. It causesits large accumulation in the earth pits of oil refineries [12-14]. The purpose of the research is to analyse oil sludge of different storage periods generated in the process of separation at PAO "Slavneft-YaNOS", Yaroslavl, Russia. The principle of the unit operation is reduced to separation of mechanical impurities of oil products in the tricanter by the method of technophase separation. Oil sludge with oil products is separated into three phases: oil product, water (fugate), and mechanical impurities (cake). The advantages of the unit are reduction of waste and utilisation of treated water in the technological cycle.

The composition of mineral components of different storage periods slurries was analysed in the ash formed by burning the cake at 600 ^{0}C on X-ray fluorescence spectrophotometer EDX6000B with SDD-silicon detector EDX Pocket Series. We have found that oil sludge has a significant amount of mineral components represented by calcium, silicon, iron, aluminium compounds (Table 1). Apparently, it is reasonable to use sludge as an additive to asphalt concrete compositions.

Table 1. Physico-chemical parameters of oil sludge of different storage periods

Name of parameter	Oil sludge of PAO "Slavneft-YaNOS" for long-term storage	Oil sludge of PAO "Slavneft-YaNOS" for current production
Density, kg/m^3	1,450±73	1,382±63
Acid number, mgKOH/g	4.33±0.02	3.56±0.02
Mass fraction of the component, %:		
Water	3.9±0.2	26.8±1.1
Organic content	54.6±0.5	27.2±0.09
Mineral content	41.47±2.3	46.1±2.6
(in terms of silicon oxides), % wt.:	5.342±1.3	6.714±1.1
calcium oxide	7.164±0.2	8.872±0.2
ferrum oxide	7.703±0.2	8.904±0.3
aluminium oxide	6.316±0.6	6.987±0.44
copper oxide	0.091±0.01	0.088±0.01

Name of parameter	Oil sludge of PAO "Slavneft-YaNOS" for long-term storage	Oil sludge of PAO "Slavneft-YaNOS" for current production
zinc oxide	0.514±0.13	0.571±0.11
plumbum oxide	0.051±0.01	0.057±0.01
magnesium oxide	0.918±0.08	1.307±0.09
molybdenum oxide	0.329±0.07	0.340±0.05
phosphorus oxide	0.316±0.01	0.404±0.04
sulphur oxide	8.015±0.11	8.853±0.12
potassium oxide	0.787±0.07	0.894±0.04
titanium oxide	0.228±0.06	0.324±0.06
vanadium oxide	0.052±0.01	0.064±0.01
barium oxide	1.873±0.1	1.721±0.09

The oil and oil products acidity depends on the content of naphthenic, carboxylic, and oxycarboxylic acids and acidic compounds. The naphthenic acids are the dominant of these compounds. Acidity of oil sludge can be caused by the presence of sulphuric acid or its derivatives (sulphonic acids, sulphuric acid esters).

We analysed the organic content of oil sludge obtained by extracting it in chloroform after evaporation of the solvent. IR spectra of the extracts we obtained on an RX FT-IR spectrometer (Perkin Elmer) at the frequency range of 500-4000 cm^{-1}. We found that a significant proportion of the organic content of the sludge is represented by aromatic naphthenic and paraffinic compounds (Table 2).

Table 2. Hydrocarbon content in sludge of different storage periods

Name	Hydrocarbon content in oil sludge, % wt.		
	aromatic	paraffinic	naphthenic
Oil sludge of current production	5.19–5.7	29.13–35.83	58.98–65.68
Oil sludge of long-term storage	12.96–16.92	18.4–22.36	60.72–64.68

We used the spectrophotometric method to determine the percentage of carbon in aromatic, paraffinic and naphthenic structures of oil residues of primary and secondary sludge origin of different storage periods. We chose two absorption bands for the study of oil residues: one for the determination of carbon in aromatic structures the band – 1600 cm^{-1}, corresponding to the valence vibrations of aromatic rings, and another for the determination of carbon in paraffinic structures the band – 2850 cm^{-1}, corresponding to the valence vibrations of CH-bonds of aliphatic compounds. We recorded IR spectra in solutions because heavy oil residues are highly viscous. We used the solvent carbon dichloride with a concentration of 8 g/l in a 0.04 cm cuvette to analyse the paraffin fraction; for the aromatic fraction we used methylene chloride with a concentration of 30 g/l in a 0.1 cm cuvette. We compared the ratios in the maxima of the absorption bands at 1600 and 2850 cm^{-1} with the carbon content of the aromatic and paraffinic structures calculated using the densimetric method.

There are strong absorption bands in the range 2850-2950 cm^{-1}, characteristic for symmetric and asymmetric valence vibrations of CH_2;the absorption bands in the range 1455 and 1380 cm^{-1}, characteristic for deformation vibrations of CH_2-, CH_3-bonds. Moreover, the intensity of absorption bands in the sludge of long-term storage is more significant compared to the oil sludge of current production (Fig. 1).

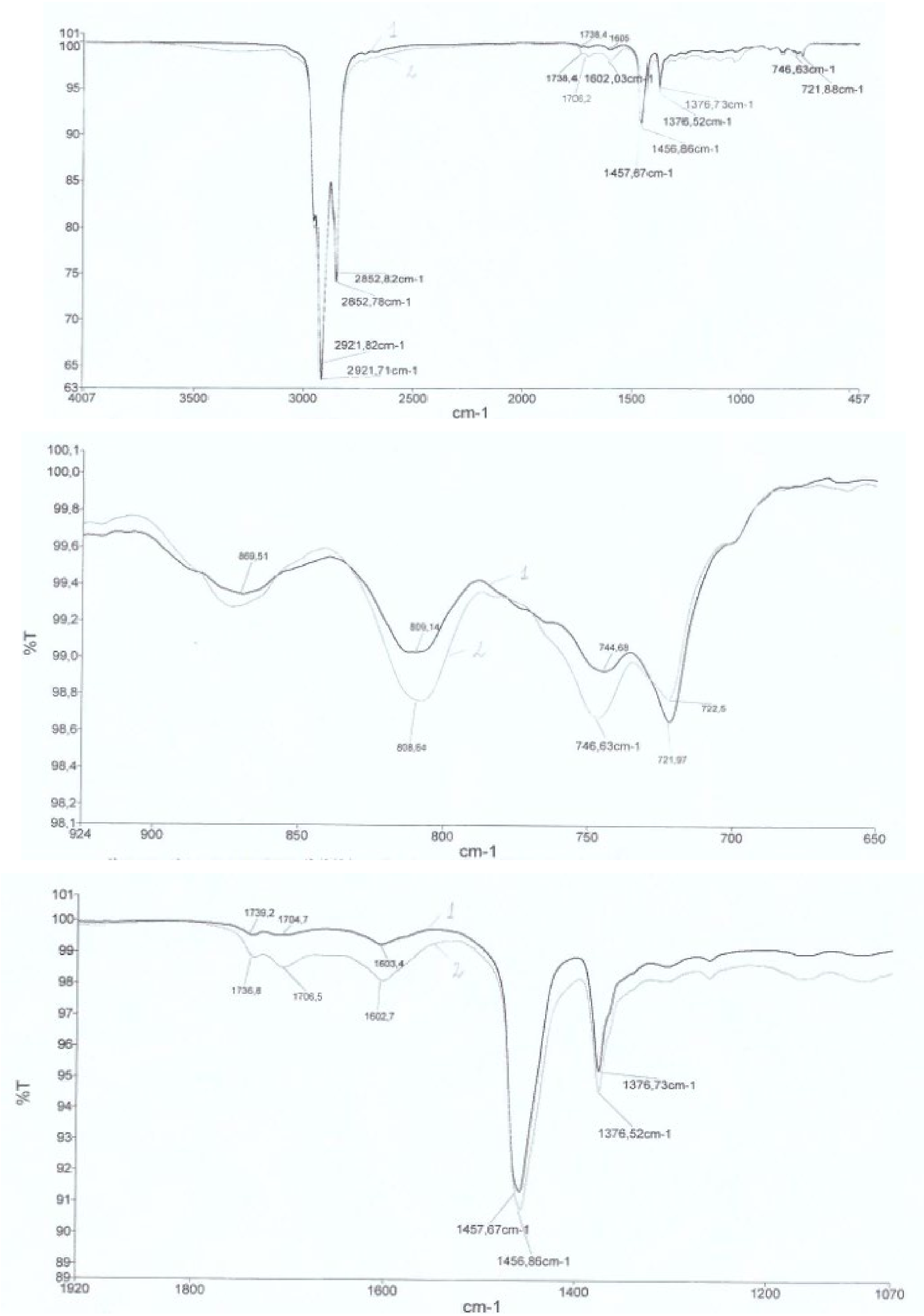

Fig. 1. IR spectrum of oil sludge extracts: 1 – current production; 2 – long-term storage

The amount of aromatic fractions in oil sludge of the current production is insignificant. This is indicated by oscillations in the aromatic ring at the band 1600-1605 cm^{-1}. The highest intensity of absorption bands in the aromatic ring is significantly observed in the extract obtained using long-term storage sludge. This is in correspondence with the quantitative calculation and the larger fraction of aromatic fractions in the samples of long storage sludge (see Table 2). Slurries of both current production and long-term storage are susceptible to isomerisation. This is due to the action of atmospheric factors, as evidenced by the following frequency bands: branching at the quaternary atom at the 746 cm^{-1} band, one hydrogen atom corresponding to the 870 cm^{-1} absorption band with isomers at the double bond $(CH_2)_n \geq 5$, as well as 1,4-substitution in the aromatic ring at the 809 cm^{-1} absorption band (see Fig. 1). A greater degree of paraffinic structures branching is observed in oil wastes of long storage period. It is assessed by the intensity of absorption bands at the quaternary carbon atom 746.744 cm^{-1}. Under the influence of atmospheric factors, components of oil sludge are able to transform into other compounds due to condensation, polymerisation, isomerisation processes. The presence of a large amount of paraffins indicates good anti-corrosion and waterproofing properties of oil sludge. These properties can be manifested in the materials for a long period of time.

Conclusions and recommendations

Thus, we have studied the composition of oil sludge of different storage periods, formed after three-phase separation at the refinery by methods of IR spectroscopy and X-ray fluorescence spectrometry. The hydrocarbon component of oil sludge is represented by paraffin-naphthenic hydrocarbons (more than 80%), the aromatic component accounts for less than 15%. The mineral component of oil sludge includes mainly silicon, iron, calcium, aluminium, sulphur, and barium compounds. Significant amount of mineral components together with organic components in oil sludge composition can find practical application in road construction. Moreover, effective neutralisation of oil waste and elimination of storage pits remains an urgent task for petrochemical enterprises. On the one hand, this is due to the high resistance of oil sludge to destruction, their composition and properties. Those are constantly changing under the influence of weather conditions and processes occurring in them [15-17]. On the other hand, oil refineries, when handling oil waste, should minimise its quantity and develop their own economically available and technically feasible technologies to involve waste into resource turnover.

References

1. **Khusnutdinov, I.Sh., Safiulina, A.G., Zabbarov, R.R. & Khusnutdinov, S.I.** (2015) Methods of utilisation of oil sludge, *Izvestiya vuzov. Khimiya i khimicheskaya tekhnologiya,* 58(10), pp. 3-20 (in Russian).
2. **Abdrakhmanov, N., Abdrakhmanova, K., Vorohobko, V., Abdrakhmanova, L. & Basyirova, A.** (2017) Development of Implementation Chart for Non-Stationary Risks Minimization Management Technology Based on Information-Management Safety System, *Journal of Engineering and Applied Sciences,* (12), pp. 7880-7888. DOI: 10.3923/jeasci.2017.7880.7888.
3. **Semchenkova, D.N., Rastoskuev, V.V., Abdrakhmanov, N.Kh. & Kolobov, N.S.** (2008) Complex express-evaluation of ecological risks in industry, *Neftyanoe hozyajstvo,* (8), pp. 104-105 (in Russian).
4. **De Quadros, P.D., Cerqueira, V.S., Cazarolli, J.C., Peralba, R.M.C., Camargo, F.A.O., Giongo, A. & Bento F.M.** (2016) Oily sludge stimulates microbial activity and changes microbial structure in a landfarming soil, *Int. J. Biodeterior. Biodegrad,* 115, pp. 90–101.

5. **Koshlaf, E. & Ball, A.S.** (2017) Soil bioremediation approaches for petroleum hydrocarbon polluted environments, *AIMS Microbiol.,* 3(1), pp. 25–49.
6. **Gron, V.A., Korostovenko, V.V., Shakhrai, S.G., Kaplichenko, N.M. & Galaiko, A.V.** (2013) Problem of formation, processing and disposal of oil sludge, *Uspekhi sovremennogo estestvoznaniya,* (9), pp. 159-162 (in Russian).
7. **Afanasyev, S.V., Volkov, D.A., Trifonov, K.I. & Volkov, V.A.** (2019) *Physico-chemical bases of natural and anthropogenic processes in the technosphere.* Samara: Izd-vo Sam. nauch. centra RAN (in Russian).
8. **Yankovoy, D.S., Ladygin, K.V. & Stompel, S.I.** (2014) New technology of oil sludge recycling, *Ekologiya proizvodstva,* (9), pp. 47-51 (in Russian).
9. **Ivshina, I.B., Kuyukina, M.S., Krivoruchko, A.V., Elkin, A.A., Makarov, S.O., Cunningham, C.J., Peshkur, T.A., Atlas, R.M. & Philp, J.C.** (2015) Oil spill problems and sustainable response strategies through new technologies, *Environ. Sci: Processes & Impacts,* 17(7), pp. 1201–1219.
10. **Lapidus, A.L., Gyulmaliev, A.M., Poletaeva, O.Yu., Kolchina, G.Yu., Guseynova, S.N. & Movsumzade E.M.** (2019) Dependence of Reactivity on the Structural and Physicochemical Characteristics of Heavy Highly Viscous Oil Components, *Solid Fuel Chem.,* (2), pp. 23-29. DOI: 10.3103/S0361521919020083.
11. **Xu, Y. & Zhou, N.Y.** (2017) Microbial remediation of aromatics-contaminated soil, *Front. Environ. Sci. Eng.*, 11(2), pp. 1–9.
12. **Ivshina, I., Kostina, L., Krivoruchko, A., Kuyukina, M., Peshkur, T., Anderson, P. & Cunningham, C.** (2016) Removal of polycyclic aromatic hydrocarbons in soil spiked with model mixtures of petroleum hydrocarbons and heterocycles using biosurfactants from Rhodococcus ruber IEGM 231, *J. Hazard. Mat.,* 312, pp. 8–17.
13. **Saikia, N.J., Segupta, P., Gogoi, P.K. & Borthakur, P.C.** (2001) Physico-chemical and cementations properties of sludge from oil field effluent treatment plant, *Cement Concrete Res.,* 31, pp. 1221–1225.
14. **Morelli, I.S., Vecchioli, G.I., Del Panno, M.T., Garre, M.I., Costanza, O.R. & Painceira, M.T.** (1995) Assessment of the toxic potential of hydrocarbon containing sludges, *Environ. Pollut.*, 89(2), pp. 131–135.
15. **Smirnov, M.B. & Vanyukova, N.A.** (2017) Dependencies between the main structural-group parameters of the composition of oils of the Volga-Ural oil and gas basin according to 1H and 13C NMR, *Neftekhimiya,* 57(3), pp. 269–277. DOI: 10.7868/S0028242117010130.
16. **Orellana, R., Cumsille, A., Rojas, C., Cabrera, P., Seeger, M., Cárdenas, F., Stuardo, C. & González, M.** (2017) Assessing technical and economic feasibility of complete bioremediation for soils chronically polluted with petroleum hydrocarbons, *J. Bioremed. Biodegrad,* 8: 396. DOI: 10.4172/2155-6199.1000396.
17. **Ubani, O., Atagana, H.I. & Thantsha, M.S.** (2013) Biological degradation of oil sludge: A review of the current state of development, *African J. Biotechnol.*, 12(47), pp. 6544–6567.

Received 09.04.2024
Approved 30.05.2024
Accepted 22.05.2024