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Assessment of the Opportunity of Obtaining Flotation Reagents Based on Products of Ozonation of Sapropelite Coal and Oil Shale

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Аннотация

Abstract

The paper carries out the comparative analysis of products composition of ozonolytic destruction of sapropelite coal and oil shale kerogen from various fields of Russia. Sapropelite ozonation products could be used as substitutes for fatty acid and other traditional flotation reagents based on oil during enrichment of metal ores and fossil fuels, as demonstrated. Thus, sapropelite solid fossil fuels (properly sapropelite coal and non-sulphurous shale) that have a relatively regular structure of organic substances and oxidation products of uniform composition (mainly aliphatic mono- (C_9 – C_{25}) and dicarboxylic (C_2 – C_{12}) acids) could be considered as raw materials for obtaining analogues of oil-based flotation reagents that are used during enrichment of oxidized ores of non-ferrous metals, alkaline earth metal non-silicate salts and ferrous metal carbonates. Products of ozonation of Barzas sapromixite (aliphatic, aromatic, and hydroaromatic acids) of humus-sapropelite nature may show shorthand and foaming properties in the flotation of oxidized metallic ores and solid fossil fuels (coal and shale). Product composition of ozonation of Kashpirsk sulphur shale (aliphatic and sulphonic acids) allows obtaining sulpho-containing flotation oxyhydril reagents based thereon. The latter can be used as collectors of non-sulphide minerals and emulsifiers.

It is concluded that the industrial development of Dmitrievsky oil shale and Barzas sapromixite deposits is promising. They are compactly located in the territory of the Kuznetsk Coal Basin with developed transport infrastructure and the presence of concentration plants in order to obtain chemicals and flotation reagents therefrom.

Keywords: ozonation, oil shale, flotation reagents

INTRODUCTION

According to the reserves of oil shale (OS), Russia is among the world leaders and has a great experience in the area of its processing. Organic matter (OM) of OS and sapropelite coal representing transformation products of algae and lower aquatic organisms, attract researchers' attention in opportunity for its use as raw materials for chemical and other

industries. Traditions of the study of OM of sapropelite solid fossil fuels (SFF) were founded by scientists in the Baltic republics of the former Soviet Union [1, 2], Leningrad Technological Institute named after Lensoviet [3, 4], and the Irkutsk Polytechnic Institute [5, 6]. The current development of ideas about the structure, physicochemical properties, and reactivity of OM of sapropelites during thermochemical impact is also reflected in

papers [7–9] etc.

The most promising and almost implemented area of processing of OS is gasification, during which their OM turns into a mixture of carbon oxides and hydrogen and pyrolysis with the formation of gaseous, liquid, and solid products. Fuel oil, Ichthyol (the scope is medicine), sodium Ichthyol (agriculture), Teepol detergents and surfactants, sulphanol (ore and SFF dressing), softener (rubber industry), tanning agent (leather industry), bitumen (manufacture of rechargeable tanks), toothpaste, insecticide (agriculture), albichtol, plasticate (cable industry), binder (foundry) are commercial products of industrial processing of OS [10, 11].

The main difficulty of shale processing technology is related to a high content (to 70 %) of the mineral component, in which OM is finely dispersed. Some of the best results in the technology of enriching shale have been obtained in case of utilising the flotation method with the use of shale processing products, i.e. shale resin fractions with different boiling points (as the collector) and shale phenols (as a foaming agent) [11]. Concentrates of sapropelite dicarboxylic acids and oxidation product extracts produced from Irkutsk sapropelites also showed efficient flotation properties in the dressing of non-ferrous metal ore and coal [6]. The complexity of producing mineral concentrates determines the requirement of the search for new efficient flotation agents including those that are obtained on the grounds of processing of sapropelite raw materials.

To obtain lower molecular mass products from sapropelite OM that is presented by high-molecular-mass spatial structure

thermochemical [8, 12, 13] and oxidative [3, 5] methods are used. Ozonation is one of the traditional methods of soft destructive impact used for both studying the structure of the organic matter of fossil fuels and producing oxygen-containing soluble products based thereon [14–17].

The present paper summarizes the results of ozonation of oil shale kerogen and sapropelite coal from various Russian deposits and carries out assessments of producing oxyhydrilic flotation reagents based thereon.

EXPERIMENTAL

Solid fossil fuels of sapropelite type, such as OS (the Dmitrievskoe and Kashpirskoye deposits in Kuznetsk and Volga basins, respectively), boghead (the Taimilir deposit, Yakutia), and sapromixite coal (the Barzas deposit, Kuznetsk Basin) were used as study objects. These SFF (except for sulphur oil shale of Volga) are currently not being developed due to geographical deposit remoteness or the prevalence of alternative fuel types in the territory of their bedding.

Kerogen was produced by acid demineralization of powdery (0–0.063 mm) samples by hydrochloric and hydrofluoric acids. Table 1 gives characteristics of kerogen samples.

Ozonation of SFF samples (fraction ≤ 0.063) was carried out in a rotating reactor in an ozone/O₂ stream (1.0–1.5 vol. % of ozone). The reaction medium is CHCl₃ and cycle time is 5 h. Compounds insoluble in chloroform were extracted from the oxidized sample of SFF with

TABLE 1
Characteristics of sapropelite kerogen

Samples	Ash content A^d , %		Yield of volatiles, V^{daf*}	Elemental composition, % per daf				H/C	A_{2920}/A_{1600}
	Initial OS	Kerogen		C	H	S	O+N		
Dmitrievsky OS	72.9	8.5	81.0	77.9	10.0	0.2	11.9	1.55	2.83
Kashpirsky OS	70.0	13.5	78.5	65.4	7.8	15.5	11.3	1.43	2.57
Taymylyr boghead	3.5	3.5	79.1	82.3	9.7	0.2	7.8	1.41	2.80
Barzas sapromixite	37.0	3.3	48.1	82.7	7.2	0.3	9.8	1.04	1.57

* The value is given for the dry ash-free state of fuel.

acetone. The resulting products were divided into solid insoluble residue and chloroform-soluble and soluble in acetone; acetone-soluble compounds were broken down into water-soluble (WS) and water-insoluble (WI).

The chromato-mass-spectrometric analysis was carried out using a 19091S-433 device (Agilent) in a range of 15–500 amu; HP-5MS capillary column (5 % of diphenyl and 95 % of dimethylsiloxane), 30 m × 0.25 mm × 0.25 μm; helium carrier gas. Chromatographed oxygen-containing products were pre-esterified with a solution of HCl in methanol, rinsed with distilled water, and extracted with hexane. Infrared diffuse reflectance spectra were recorded using Bruker Tensor 27 spectrometer. Carbonyl groups were analyzed by the reaction with hydroxylamine hydrochloride, carboxyl – using an acetate method, total acidity was determined by ion exchange with NaOH.

RESULTS AND DISCUSSION

Common characteristics of sapropelite SFF are elevated yields of volatile matter (V^{daf}), hydrogen content, and the H/C atomic ratio relatively to humic coal. However, despite a close stage of chemical maturity (from brown coal to long-flame coal), the composition of their organic part composition and mineral fraction amount are substantially different (see Table 1), which is driven by facial conditions of the formation of coal- and shale-bearing strata.

According to IR spectral data (Fig. 1), the most intense absorption bands of aliphatic CH_n bonds (2930, 2855, 1460, 1380, 720 cm^{-1}) are typical for SFF samples, which indicates the presence of long methylene chains in their OM. Distinct absorption bands of C–O–C bonds of aliphatic linear (1180 and 1050 cm^{-1}) and cyclic (1090 and 830 cm^{-1}) ethers attest to the contribution of ether oxygen to the construction of sapropelite kerogen macromolecules. A distinctive characteristic of the spectrum of Barzas sapromixite is the presence of more intense absorption bands of aromatic C–H (3040 cm^{-1}) and C=C bonds (1610 cm^{-1}) compared to the other studied SFF, which points to elevated content of aromatic fragments in its structure. The data of the IR spectral parameter $A_{2920}/$

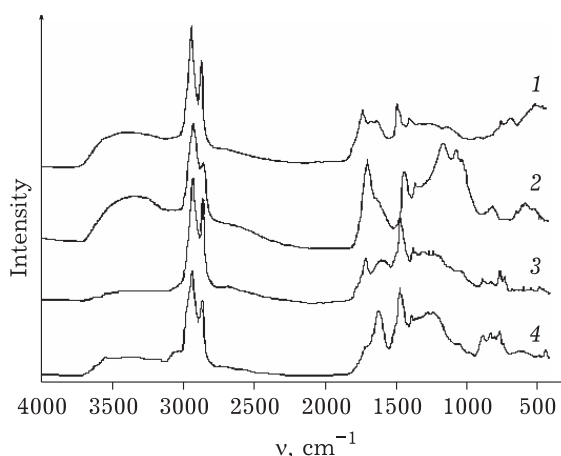


Fig. 1. IR spectra of the studied samples of sapropelite kerogen: Dmitrievsky oil shale (1), Kashpirsky oil shale (2), Taymylyr boghead (3), and Barzas sapromixite (4).

A_{1600} that reflects aliphatic fragment fraction in the organic matter of fossil fuels relatively to aromatic, and also V^{daf} values minimum for this SFF indicate the same (see Table 1). Absorption bands of C–S and S–O bonds (530–580 cm^{-1} and 850–900 cm^{-1} , respectively) that point out to the presence of sulphur heteroatoms in the composition of thiophenes, sulphide bridges, and sulpho groups in the organic matrix of kerogen additionally appear in the IR spectrum of Kashpirsky oil shale [18].

Differences in the chemical composition of kerogen species affect the yield and composition of their ozonolytic destruction products. Sapromixite demonstrates the highest yield of soluble products (94 mass %) for 25 h of ozonation in chloroform (5 cycles of 5 h each) and boghead – minimum (45.5 mass %, Table 2). A decrease in the yield of the ozonation products with increasing the H/C atomic ratio for SFF samples under study may be due to a decrease in the number of sterically available structural fragments and chemical bonds (C=C bonds in saturated alkyl chains and weakly condensed aromatic structures [19]) in OM of boghead and OS.

Relatively high-molecular-mass WI compounds prevail among the ozonation products of sapropelites (see Table 2), which may point out to soft ozonolytic destruction of shale OM. The ozonation products of Kashpirsky oil shale, in which the fraction of WS substances is significantly higher, are an exception.

Compounds soluble in chloroform that is used as an ozonation medium mainly contain the carboxyl functional group with a lower contribution of hydroxyl and carbonyl groups (see Table 2). *n*-Monocarboxylic acids (*n*-MCAs) with chain length from C₉ to C₂₂ (from pelargonic to behenic) prevail among compounds identified by GC-MS [14, 15]. Saturated dicarboxylic and benzenedicarboxylic acids and long-chain polyunsaturated compounds of acyclic terpene series are present in less significant amounts.

Water-soluble products of acetone extract of kerogens represent the most oxygen-saturated fraction with atomic ratio O/C ~ 1 (see Table 2), which points out to the presence of lower dicarboxylic acids. Carboxyl and carbonyl groups prevail in the functional composition of WS compounds. Mono and dicarboxylic acids traditional for redox processes were identified

by GC-MS (Table 3) [14–17]. Monocarboxylic acids have a hydrocarbon chain length from C₉ to C₂₂; acids with the composition of C₂–C₁₁ prevail among dicarboxylic acids. Judging by a high fraction of C₄ succinic, C₆ adipic and C₉ azelaic in products, they can be formed from polymerization products of unsaturated higher acids (e.g. C₁₈ – oleic, linoleic, linolenic) [20].

Water-soluble products of Dmitrievsky oil shale and Taymylyr boghead almost entirely consist of aliphatic mono- and dicarboxylic acids of normal structure with a prevalence of adipic (C₆) (see Table. 3). A distinctive characteristic of WS products of Kashpirsky oil shale is the presence of a wide range of branched aliphatic acids (including tricarboxylic), and also keto and hydroxy acids. High content of oxalic acid in products may be due to destruction of non-condensed benzene rings with ozone.

TABLE 2
Characteristics of products from ozonation of fossil fuels

Products	Sample of fossil fuel	V*	C	Elemental composition			H/C	O/C	Functional composition, mg-equ/g		
				% per daf					COOH	OH	CO
				C	H	O+N+S**					
Insoluble residue	Dmitrievsky OS	57.8	40.8	55.0	7.1	37.9	1.55	0.50	3.80	6.23	4.07
	Kashpirsky OS	64.3	53.4	49.7	5.9	50.3	1.42	0.49	4.58	3.70	5.00
	Taymylyr boghead	55.5	40.8	61.1	7.3	31.6	1.43	0.38	2.86	1.15	2.90
	Barzas sapromixite	10.7	8.0	61.8	5.8	32.4	1.13	0.37	2.47	3.46	4.11
CHCl ₃ soluble	Dmitrievsky OS	22.1	16.6	58.5	7.1	34.4	1.46	0.44	6.08	3.27	4.71
	Kashpirsky OS	6.7	5.6	49.9	6.7	43.4	1.61	0.65	8.31	3.00	6.75
	Taymylyr boghead* Barzas sapromixite*										
Acetone-soluble, therefrom:											
Water-soluble	Dmitrievsky OS	10.8	5.6	40.5	4.6	54.9	1.36	1.02	9.40	4.36	3.65
	Kashpirsky OS	36.0	18.8	31.3	5.0	63.7	1.91	1.31	10.99	3.83	6.42
	Taymylyr boghead	17.2	10.7	51.1	4.9	44.0	1.15	0.65	7.21	0.67	4.73
	Barzas sapromixite	15.5	7.8	41.9	4.1	54.0	1.17	0.97	8.29	1.03	8.97
Water-insoluble	Dmitrievsky OS	20.6	17.1	64.5	7.1	28.4	1.32	0.33	3.02	3.82	3.72
	Kashpirsky OS	17.3	15.5	53.5	7.3	39.2	1.64	0.45	3.03	3.70	5.72
	Taymylyr boghead	28.3	20.5	59.5	5.7	34.8	1.15	0.44	3.57	3.04	3.63
	Barzas sapromixite	78.5	58.9	62.1	5.2	32.7	1.00	0.39	3.28	1.34	4.53

Notes. V – yield, mass. % per daf; C – carbon content in products, % of initial.

* CHCl₃ soluble ozonolysis products in experiments with Taymylyr boghead and Barzas sapromixite were combined with acetone-soluble.

** Sulphur content in products of ozonation of Kashpirsky oil shale, %: oxidate 11.6, H₂O-soluble 9.0. Total sulphur content (S_{tot}) in other products was not determined due to their low yields.

Sulphuric acid fraction identified as dimethyl sulphate reaches 25 % (see Table 3). The lack of other soluble forms of sulphur (sulphenes and sulfoxides) in products points out to destruction (*e.g.* C–C bonds in thiophenes) or additional oxidation of sulphur-containing fragments with ozone to H₂SO₄ [19]. Mono- (C₁₆ palmitic and C₁₈ stearic) and dicarboxylic (C₅–C₁₂) aliphatic acid with a higher proportion of C₆ and C₉, steroid (hydrophenanthrenecarboxylic) acids, and derivatives of aromatic phthalic acid were identified in the composition of WS products of ozonation of Barzas sapromixite (see Table. 3). Herewith, the fraction of benzenecarboxylic acids in sapromixite products was ca. 50 %, which is consistent with the idea of a more aromatic structure of its OM compared to pure sapropelite SFF [17].

Product composition of SFF samples under study is characterized by a significantly higher diversity of classes of organic compounds

compared to WS fraction; both oxidation products and unreacted hydrocarbons are present among them [14–17]. Oxygen content and the number of carboxyl groups in WI substances are almost twice lower than in WS (see Table 2). Aliphatic acids are presented by higher saturated and unsaturated C₁₂–C₂₅ acids with a prevalence of palmitic (C₁₆), stearic (C₁₇) and linoleic (C₁₈) acids. Hydrocarbon fraction of WI compounds consists of long-chain C₂₀–C₃₀ *n*-alkanes, alkenes, and aryl-substituted two- and triannulated arenes. The heteroatoms O and N in phenols, ketones, and ethers and carbazoles and acridines, respectively are a part of aromatic and hydroaromatic compounds.

The products of ozonation of sapropelite SFF kerogens are similar to oil oxidation products in their composition, therefore, they may be regarded as probable complex substitutes for heteropolar flotation reagents based on oil raw materials used in the practice of

TABLE 3

Results of gas GC/MS analysis of water-soluble (WS) substances

Class of compounds	Component composition of esterified WS products, rel. % to total chromatographed			
	Dmitrievsky OS	Kashpirsky OS*	Taymylyr boghead	Barzas sapromixite
Dimethyl sulphate	2.2	24.9	–	–
Methyl esters				
of aliphatic acids C ₉ –C ₂₂	43.5	8.1	–	1.9
Methyl esters of aliphatic hydroxy and ketoacids	1.2	3.6	7.8	–
Dimethylesters:				
of oxalic acid	3.0	18.1	11.6	3.5
of aliphatic acids C ₃ –C ₁₂	45.3	39.4	79.1	48.0
Dimethyl esters				
of aliphatic hydroxy- and ketoacids C ₄ –C ₇	–	3.2	–	–
Trimethyl esters				
of aliphatic acids C ₃ , C ₄	–	0.9	–	–
Dialkyl phthalates	3.5	1.4	1.2	40.2
Oxy- and oxoaromatic acids	1.3	0.4	0.3	2.2
Methyl ester				
of hydrophenantrenic acid	–	–	–	4.2

Notes. Dash means not determined

*In ozonation products of Kashpirsky OS acids with normal and branched structure are summed.

minerals separation (including OS). Herewith, hydrocarbon component of ozonation products may act as collectors, and polar one as foaming agents.

It is known that flotation quality is largely determined by the success of the selection of flotation reagents and reagent flotation modes [21–23]. Shorthand properties of polar reagents are driven by the chemical activity of functional groups, hydrocarbon radical length, the presence of carbon-carbon bonds therein, electron-donor substituents, and also hydrocarbon chain branching [24, 25]. Saturated carboxylic acids with the number of atoms in the radical of 12–14 have the maximum flotation activity. Weak flotation activity of acids with an atom number of less than 8 is related to their high solubility and the impossibility of film development on the water surface. Flotation activity decrease of reagents with carbon atom number of over 16 is associated with a decrease in activity of fatty acids, surface pressure decrease in the film, and its low spreading rate. The presence of a large number of polar groups in hydrocarbon species violates asymmetry and weakens molecule ability towards orientation in surface layers of the mineral. For acids that have a branched structure or the C=C double bond, there is an increase in their collective capacity due to better fastening in the mineral surface. The availability of electron-donor substituents, such as CH₃, C₆H₅, etc. in collector hydrocarbon chain contributes to its chemisorption by the mineral surface with increasing its hydrophobicity [21–23]. The occurrence of sulphate ion containing compounds (to a greater or lesser extent, flotation poisons) contributes to mineral surface hydrophysics; SO₃H substituents increase

reagent solubility, which leads to a decrease in its shorthand properties [21]. At the same time, sulpho acids are characterized by high foaming and emulsifying properties [24]. It is also known that the use of several acids or a mixture with different hydrocarbon skeletons simultaneously increases the yield of the collected product, however, process selectivity is lower [25].

Unsaturated fatty acids, such as oleic acid (C₁₇H₃₃COOH) with one double bond in the hydrocarbon chain, linoleic acid (C₁₇H₃₁COOH) with two double bonds and linolenic acid (C₁₇H₂₉COOH) with three double bonds that are met in natural products, and also some saturated high-molecular-mass acids and their derivatives are most widely used as oxyhydrilic reagents [24, 25]. These acids are of the greatest practical interest for flotation of alkaline earth metals non-silicate salts and ferrous metals carbonates, such as calcite (CaCO₃), fluorite (CaF₂), scheelite (CaWO₄), apatite (Ca₅(PO₄)₃(F, Cl, OH)), barite (BaSO₄), witherite (BaCO₃), siderite (FeCO₃), and rhodochrosite (MnCO₃). Substitutes for oleic acid in the industry are fatty acids-containing products of various industries, such as oleine, sulphate soap, tall oil, naphthenic acids, synthetic fatty acids (SFA), still bottoms of synthetic fatty alcohols, oxidized hydrocarbons, wastes of oil-fat and other chemical industries [25]. Being foaming agents and anion collectors, alkyl sulphates, alkyl sulphonates, sulpho-carboxylic acids, and their salts are widely used in the flotation of non-sulphide minerals, especially in the separation of barite from calcite and other minerals. As weaker but more selective collectors compared to fatty acids, sulpho-containing reagents are often used in parallel with fatty-acid ones. In this form they are used as emulsifiers of

TABLE 4

Results of flotation of quartz-fluorite ore using various flotation reagents [6]

Flotation reagents	Optimal consumption, g/t	Concentrate yield, %	Content, %	Extraction, %
Sodium oleate	400	49.7	79.3	96.8
Oleic acid emulsion	200	48.8	79.8	96.6
Saponified petrolatum	1000	47.6	80.0	96.2
Emulsol	1000	46.2	80.6	92.3
Sapropelite dicarboxylic acids	300	54.7	71.8	96.2

hydrocarbons and fatty acids [24, 25].

Oxidation products of Irkutsk sapropelite coal (concentrates of dicarboxylic acids, organic extracts of oxidation product) were tested as flotation reagents during flotation of coal and quartz-fluorite ore (Table 4) [6]. Unlike traditional flotation reagents, sapropelites oxidation products demonstrated comparable or higher (emulsol) collecting capacities at lower reagent consumption. The ether extract is recommended as a substitute for oleic acid during plumbojarosite flotation. Acetone extract is more active in coal flotation. Methyl-ethylketone extract is similar to pine oil in foaming properties and has higher collecting capacities in relation to coal and oxidized fluorite ores [6].

CONCLUSION

Proceeding from the ideas about the collecting capacity of oxyhydrilic reagents [21–25], it follows that properly sapropelite coal and non-sulphurous shale that have a more regular structure of the organic matter (OM) and yield oxidation products of uniform composition can be regarded as raw materials to produce oxyhydrilic reagents during flotation enrichment of non-ferrous and ferrous metals ores. The presence of hydroaromatic (naphthenoaromatic) and heterocyclic acids alongside with aliphatic acids in the composition of Barzas sapromixite is also likely to contribute to shorthand properties during flotation of both oxidized metal ores and fossil fuels. Sulphur Kashpirsky oil shale, chemical, and energy processing of which is currently being carried out on an industrial scale is also likely to be suitable for obtaining oxyhydrilic flotation reagents. The latter are characterized by a high content of sulphate ions, and therefore, can be used as collectors of non-sulphide minerals and emulsifiers [23, 25].

Considering compact location of two sapropelite deposits (Dmitrievsky oil shale and Barzas sapromixite), developed transport infrastructure of the Kuznetsk basin and the presence of coal-mining and concentration plants in the territory of the Kemerovo area, one can make a conclusion about high prospects of the industrial development of these deposits

including the production of chemicals and flotation reagents [6, 26].

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