Organic matter of mine water and mining waste

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Abstract

A features study of organic pollution from wastes, mine water, and mining effluents caused by extraction and processing of various types of minerals has been performed. The organic pollution characteristics of waste and effluents from the mining industry within the Kizel coal basin and the Verhnekamsky potassium salt deposit differed in applied technologies of ore processing and beneficiation are considered. It has been found that along with natural organic compounds specific for extracted mineral raw materials, technological reagents are a substantial source of organic pollution of wastes and effluents. Laboratory waste leaching test has shown that transformations of organic matter into water-soluble forms is accompanied by reactions of biochemical and physicochemical nature leading to generations of new compounds which are absent in the host minerals. The environmental significance of organic compounds entering the hydrosphere was assessed. Some of them have been revealed to be the persistent organic pollutants which cause substantial pollution of surface water and groundwater connected with waste storage facilities of mining industry.

Keywords: mining waste, organic pollutant, leaching, dissolved organic matter composition, geochemical markers.

Introduction

One of the features of mining technogenesis is a sharp increase in the number of substances in geochemical circulation, leading to toxic components entring the hydrosphere. The most powerful source of pollutant emissions is mining wastes characterized by the accumulation of a wide range of hazardous components. Among the least studied pollutants are organic compounds, in most cases not included in control scopes. Despite the fact that, in many cases, these compounds belong to the category of micro impurities in the extracted mineral raw materials (Greenwood et al. 2013), the technologies used for its beneficiation and processing quite often lead to substantial organic pollution of the generated waste (Bachurin 2005). It is facilitated by the use of a wide range of organic reagents (collectors, modifiers, frothers, etc.) in the beneficiation technological processes. Many of the used reagents has been established to be complex mixtures of compounds (polycyclic aromatics, hydrocarbons, phenols, amines, etc.) and serve as a source of hazardous compounds in wastes (Bachurin et al. 2013). The interaction of natural and technological compounds leads to the formation of multicomponent organo-mineral complexes in wastes which have no natural analogs and require the investigations of their hazards and behavioral features in the environment. One feature of organic pollutants should be noted – the ability of rapid geochemical transformation under the influence of exogenous factors resulting in new transformation products (TPs) including a substantial proportion of unregulated chemicals many of which can be equally or even more persistent and toxic than the original substances (Bachurin et al. 2013).

Methods

Studies (Bachurin et al. 2013, 2014) have shown that the real environmental assessment of organic pollution within the hydrosphere of mining areas is possible only when taking into account the particular characteristics of the waste composition and the nature of their transformation in the water environment. Practical implementation of given methodological approach was performed on the basis of laboratory studies of "waste – water" systems and an informational database created on the results of hydrogeochemical investigations in mining regions. This made it possible to obtain basic analytical characteristics of pollutants (geochemical markers), reflecting both the particular nature of the extracted raw materials and the technology of its beneficiation which control pollutants accumulation in wastes (Bachurin et al. 2013). A laboratory waste leaching test was carried out in static conditions by successive three-step dissolution of solid mixtures in distilled water (the initial ratio of water to waste is 30 : 1). This simulation imitates the precipitation effect on waste-rock dumps stored on the surface. In the case of some organic reagents using in the technological process, the composition of their aqueous solutions and the nature of transformation after 1, 7 and 21 days were investigated.

The main studied objects in the tests and experiments were the most capable to migration components of organic matter – bitumens, which constitute the sum of organic compounds extracted from an analyte by chloroform (B_C) or hexane (B_H). The investigations of bitumens were carried out using analytical chemistry methods allowing to judge the structural-group and individual composition of organic compounds: thin-layer chromatography TLC, FT-IR spectroscopy, gas chromatography–mass spectrometry GC–MS (Agilent Technologies 6890N, MSD 5975B). As additional criterions reflecting the level of organic pollution of the studied objects, we used total petroleum hydrocarbons (*TPH*), phenols, benzo(a)pyrene, Corg. A brief description of the results obtained for the two Urals mining areas is provided below showing differing composition of natural organic compounds in extracted minerals and the technologies used for ore preparation and beneficiation.

Kizel coal basin has been the oldest coal-mining region of Russia. Cessation of mining did not solve the complex environmental problems that emerged during the long-term basin operation. This is caused by continued mine water outflow to the surface with total discharge volume ranging from 1,328 to 2,650 m^3/h. Effluents from waste-rock dumps are other sources of pollution, the total discharge of which reaches 27.9-37.3 m3/h. Like it was during the operation of coal mines enterprises, mine waters and effluents have an acidic reaction (pH = 2-3), sulphate composition and high content of iron, aluminum, and a number of microcomponents (beryllium, manganese, cobalt, nickel, etc.).

Information about organic pollution level of coal mining waste in the Kizelovka basin is practically absent. There is however, the recorded presence of bituminous substances (B_C 0.30-12.33 mg/dm^3), TPH (0.05-1.87 mg/dm^3), and low molecular weight aromatic hydrocarbons (0.09-0,39 mg/dm^3) in mine drainage (Bachurin 2018). The content of chloroform extracted bitumens (B_C) in the rocks of 8 surveyed uneven-aged dumps is relatively small – 0.5-6.0 g/kg, of which TPH accounts for 0.04-2.39 g/kg (2-13% B_C). Analysis of the hexane fraction of bitumens (BH) of the rocks using the GC – MS method have shown that the share of hydrocarbon compounds is 48-62%, most of which are represented by aliphatic structures (Table 1). Aliphatic hydrocarbons are presented by a series of C_{11}-C_{43} with a maximum content of short-chain homologues of C_{13}-C_{18}. Aromatic structures (64.8-159.0 mg/kg) are predominantly polycyclic and are presented by alkyl-substituted biphenyl, naphthalene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, 3,4-benzpyrene (13-104 mg/kg). The heterostructures of bitumens of the waste-rock dumps are represented by a wide group of oxygen-containing compounds (O-), dominated by carboxylic acids and their derivatives. In some samples, a high content of sulfur-containing compounds (S-) was recorded that is explained by the high sulfur content in coal. Nitrogen- and halogen-containing structures (N-, Hal-) are present in a subordinate amount.

According to laboratory tests data, water extracts from waste rocks of dumps are characterized by the following criteria: the content of bitumen BC ranges between 0.60-2.35 mg/dm^3, TPH between 0.05-0.80 mg/dm^3, and 0.002-0.10 mg/dm^3. According to GC – MS, bitumens of water extracts from dump

Table 1 *The composition of bitumens (%) in wastes and effluents of the Kizel coal basin.*

	Alkanes	Naphthenes	Arenes	O-	N-	S-	Hal-
Rock of dumps	42,8-52,7	1,2-1,7	4,6-7,3	15,4-49,2	0,8-1,9	0-10,1	1,4-3,1
Water extract	54,6-62,5	1,7-1,8	none	33,2-34,4	0-0.2	none	1,4-6,6
Leachates of dumps	16,0-24,2	0-1,1	0,3-0,5	65,1-65,4	4,5-9,7	0-4,1	отс.
Mining water	6,4-19,5	0,6-3,2	0-1,1	70,0-84,6	0,4-3,0	0-1,5	0,2-2,8

phenols between rocks are mainly presented by aliphatic hydrocarbons and hetero compounds with obvious dominance of oxygen-containing structures (Table 1). When leaching, aliphatic hydrocarbons of the C12-C44 series (1.3 mg/dm^3) and O-containing structures, among which adipates and phthalates (0.7 mg/dm^3) predominate, enter into the aqueous phase with exceedances of the maximum allowable concentrations (MAC). The mono- and bicyclic aromatics in water are stable in an ester form (adipate, phthalate). Thus, the dump rocks leaching test has shown that seeping water carries away a whole range of organic compounds many of which are scarcely studied from the environmental perspectives.

The study of the dump leachates composition confirmed a high loading of organic compounds in them: the content of bitumens B_C is 0.80-11.38 mg/dm^3, *TPH* – 0.20-1.75 mg/dm^3, benzene – 0.36-0.39 mg/dm^3, toluene - 0.11-0.17 mg/dm^3, phenols – 0.03-0.06 mg/dm^3. The abundance of amines, pyridines, indoles, and quinolines (0.2 mg/dm^3) which have quite strict health standards calls attention. At the same time, the bitumens of the dump leachates, in contrast to the waste rocks water extracts, are more oxidized. According to GC – MS, non-hydrocarbon structures dominate in the bitumens composition with a subordinate content of hydrocarbons represented mainly by n-alkanes of the C_{17}-C_{35} series. Phthalates, which account for 12.2-51.4% of bitumens, dominate in the group of heterocompounds as well as in water extracts from rocks. The high content of these compounds, which, apparently, are products of the transformation of the aromatic structures, is due to their stability under conditions of hypergenesis. In addition, the leachates of the dumps carry into the hydrosphere a wide variety of other aromatic ecotoxicants – alkylated biphenyls and anthracenes, pyrene, fluoranthene, halogenated benzenes, benzamins and benzonitriles, piperidines, arylsulphonic acids, etc. Besides the esters, other acid derivatives being products of deeper transformations of carboxyl, aliphatic and aromatic structures are also environmentally hazardous. Of their variety, amides and nitriles of acids, halogenated, and sulphonated esters are emphasized. Apparently, this phenomenon is caused by multiple precipitations events that affect rock dumps leading to aqueous phase entry not only of easily soluble compounds, but also the structures strongly associated with the mineral matrix.

The results mentioned above show that the changes of coal-bearing rocks in dumps under hypergenesis conditions lead to a chemical transformation of natural organic compounds with the formation of a wide range of structures predominantly of the oxygen-containing type with high solubility and migration capacity in a water environment (Bachurin 2018).

Verhnekamsky potash salt deposit. The approved technology of potash processing in Verhnekamsk deposit provides for mineral's liberation (sylvinite, carnallite) using halurgic or flotation beneficiation methods. The beneficiation of potash produces wastes such as tailings stored in salt dumps, clay-salt sludges and brines merging into a sludge storage. The highest level of organic pollution is typical for the clay-salt sludges (B_H – 0.73-3.0 g/kg, *TPH* – 0.34-1.96 g/kg) due to accumulation of both natural organic of halopelites and technological reagents, most of which are categorized as synthetic surfactants (**Bachurin** et al. 2015). According to the GC–MS dates, saturated aliphatic and halogenated hydrocarbons of series C_4-C_{44} dominate the low content of naphthene and aromatic structures (Table 2).

Aliphatic hydrocarbons consist of normal and branched alkanes, alkens, and isoprenoids. Series of normal alkanes (27.1-

Table 2 *Bitumens composition (%) of ores and wastes in Verhnekamsky potash salt deposit*

	Hydrocarbons	O-	Hal-	others
Potash ores	83.3	7.1	3.1	6.4
Halite wastes	56.2	39.4	2.5	1.9
Clay-salt sludges	50.0	37.5	8.8	3.8
Liquid phase of sludges	8.2	89.8	1.2	0.8
Brines	15.8	79.7	2.0	2.5

34.9%) consists of homologues C_{13}-C_{34} with a maximum content of C_{18}, C_{17}, C_{20}. Due to the fact that the short-chain n-alkanes are few suggests that accumulation of these structures in sludges causes by the technogenic effect. Heterocompounds include predominantly O-containing structures, in which aliphatic and naphthenic alcohols, aliphatic, naphthenic, aromatic ketones and acid derivatives are identified. Among the last, acetates and phthalates are particularly noteworthy, which held 40-44% of all heterocompounds. Apparently, the formation of these structures is associated with the destruction of polyaromatic hydrocarbons and alcohols that make up the process reagents.

According to the GC-MS data, the reagents used in the desliming stage (carbamide-formaldehyde resin, polyacrylamide "Akkofloc A-110", aliphatic amines "Ethomeen", glycol ether) represent a complex multicomponent mixture, which, along with the declared reagents, contain a wide spectrum other compounds. Physico-chemical processes occurring in the "reagent - water" system lead to substantial changes in the chemical appearance of water-soluble organics. The main transformation products of the technological reagents examined are polyethoxylated compounds (polyglycols, polyoxyalkanols, and their ethers, dioxolanes, dioxanes and crown ethers), ammonium compounds and nitrogenous heterocycles, hydrocarbon structures, including polycyclic aromatics (Bachurin et al. 2015).

The results of laboratory testing of sludge leaching showed that despite the hydrophobicity of organo-mineral complexes formed in the waste, a certain part of organic compounds (from 5 to 33%) is water soluble. The quantity of B_C in the sludge-water extract ranges between 0.55-3.43 mg/dm^3, *TPH* – 0.02-1.13 mg/dm^3, phenols - 0.001-0.08 mg/dm^3, amines < 0.78 mg/dm^3, benzo(a) pyrene - 1.2-25.4 ng/dm^3. According to the GC – MS data, both the initial structure of the sludge and the products of hydrolytic processes are identified in the leaching products. The last ones consist of hetero compounds, with a total content from 69.5 to 84.0% B_C. Phthalates are distinguished by the total content in water extracts reaching 89%. Considering the low content of these compounds in water extracts of halopelites (less than 14%), it can be assumed that their appearance is associated with the reagents transformation in the aquatic environment. The increased content of these compounds in the aquabitumens, including brine of sludge storages, is most likely due to their high solubility and stability in aqueous solutions (Bachurin et al. 2015). Additionally, a group of carbohydrate compounds (derivatives of furanose, pyranose, galactose) was identified in the organic content of leached sludge, which is associated with the using of carbamide-formaldehyde resin in the technological cycle, and acetoacetic acid esters due to the transformation of flotation agents.

Research of clay-salt sludge - water extract shows that sludge is a potential source of a wide range of organic structures representing a "cocktail" of natural and technological compounds, and their transformation products entering the hydrosphere. The predominance of carbocyclic and heterocyclic compounds in the aquatic environment has shown that the biogeochemical transformations of natural and man-made organic waste occur mainly because of cyclization and condensation of structures which control the extent of migration and accumulation of pollutants. Among the compounds passing into the water phase, nanoscale crown ethers, aza-crown ethers, annihilates and naphthenic macrocycles, the uniqueness of which is due to the ability to form stable lipophilic complexes with cations of various metals and microelements, are found. The main markers of water pollution are polyethoxy structures represented by linear polyglycols, their esters and polyoxyalkols, and cyclic dioxolans, dioxanes and crown ethers. Among the other water-soluble compounds in clay-salt sludges it is interesting to note aliphatic halogen-containing structures of the C9-C18 series marking the syngenetic organics of halopellites, aliphatic and naphthenic hydrocarbons, polycyclic aromatics, aliphatic amines, ammonium compounds, and nitrogenous heterocycles, which are products of the transformation of flotation agents. We should note that most of these compounds are toxic substances, and has established hygienic standards, which allows them to be monitored according to regulated measurement techniques.

Conclusions

The results of the geo-ecological survey of the mining areas of the Ural show that industrial wastes contain natural and technogenic organic compounds that are readily soluble in water.

This causes the possibility of organic pollution of the hydrosphere in areas adjacent to waste storage facilities. In some cases, the content of water-soluble organic compounds exceeds the sanitary and health standards adopted in Russia (table 3).

The range of organic pollutants is largely determined by the processes of transformation of natural and technogenic compounds in the water environment. This requires special laboratory testing aimed at clarifying the leaching nature of organic compounds from waste and the possible transformation products. The subsequent environmental monitoring should be focused on the control of only those chemical compounds that may be dangerous to humans and to the environment (Chibwe 2017).

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***Table 3** Water-soluble organic compounds of mining wastes of the Ural*

Compounds	Quantity, mg/dm³	MAC, mg/dm³	Hazard category
TPH	0,05-4,15	27	4
Benzene and homologues	0,34-0,58	0,5	2
Phenols	0,03-0,10	0,1 (phenol)	2, 4
Aliphatic alcohols, oxo-compounds C_3-C_{44}	0,05-0,64	0,25 (propanol) 0,02 (propenal)	1, 4
Phthalic acid, phthalates	0,12-9,34	0,2 - 1,0	2
Nitrogen-containing C_5–C_{20}	0,35-0,96	0,05-0,1 (amines)	2, 4
Organic sulphur	0,02-6,38	$0{,}2\times10^{-3}$ (propentiol)	3
Halogenated hydrocarbons C_7–C_{18}	0,03-4,92	$2{,}5\times10^{-3}$ (tetrachlorhexane)	4
Aromatic N-, O-, S-containing	0,65-0,80	0,1 (naphthol)	2, 3

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