Natural Environmental Pollutants in the Black Shale Zones

B. M. Osovetsky[1], I. V. Badyanova[2]

[1]*Natural Science Institute of Perm State University, Genkel, 4, 614990, Perm, Russia, opal@psu.ru*
[2]*Natural Science Institute of Perm State University, Genkel, 4, 614990, Perm, Russia, kataev7@psu.ru*

Abstract

The main natural sources of water contamination in the areas of black shale rocks in the western slope of the Urals are considered. They are characterized by the presence of various toxic elements due to sorption activity by carbonaceous matter. A substantial increase in their concentrations with the transition to readily soluble forms occurs in the weathered rocks and karst cavities. The latter are eroded by streams, and solutions or suspensions with a high content of toxic elements are transported over long distances. Their most substantial concentrations are found in the clayey weathered rocks (especially for Zn, Hg, Pb, Ni, As, Cu, V). In many parts of the world the territory of black shale rocks are areas of intensive mining activity, the ecological condition of which requires constant monitoring.

Keywords: black shale formation, weathered rocks, toxic and radioactive metals

Introduction

The industrial and mining enterprises are usually considered as the main sources of contamination of natural waters. The latter are widely represented in such mining regions as the Urals and cause the intensive pollution of the environment. For example, substantial masses of toxic elements enter the natural waters and atmosphere in the Urals when developing copper and gold deposits. Difficult environmental conditions are sometimes created due to the air migration of fine asbestos. A high chromium content is observed in the waters of the areas where chrome ores are mined, etc.

Many deposits of diamonds, noble metals, copper, coal and other minerals have already been exploited, but substantial areas remain occupied by mining dumps. Suffice it to note the large areas of waste heaps left after the cessation of the development of a coal deposit in the Kizelovsky basin. There is a diverse complex of toxic elements in the natural waters of these areas.

There are high concentrations of toxic elements in certain areas of the Urals the sources of which are natural objects in addition to the technogenic contamination of natural waters. These include, first of all, specific rocks and mineral occurrences of minerals. O. Gryaznov (2014) shows typical associations of toxic and other small elements in the Urals rocks. In particular, a very wide range of toxic elements (Ta, Nb, Be, Mo, Pb, Zn, Co, Ni, Cr) is associated with alkaline feldspar metasomatites, which are widespread in the Urals.

Many toxic elements are concentrated in sulfides. They are not resistant to chemical weathering agents and are easily destroyed by oxidation, and toxic elements are converted into colloidal or true solutions. Being unstable to chemical weathering agents sulfides dissolve easily, and toxic elements become the components of colloidal or true solutions. Then they are deposited on certain geochemical barriers in the process of migration, where they may be concentrated.

The complexes of black shale formations, widely represented in the Urals, have long attracted attention as a promising source of useful minerals. Black shale rocks contain carbonaceous matter, which is a natural sorbent of potentially toxic metals, including toxic and radioactive ones. The weathered rocks are formed in the process of destruction of black shale rocks, in which the toxic components are accumulated. The weathered rocks are easily eroded by rivers and interseasonal water flows.

A concrete example is the area of the black shale rocks of the Fedotovskaya suite (Upper Riphean) on the western slope of the Middle Urals. This territory is a part of the Gornozavodsky district of the Perm Region with intensively developed mining activities of different profiles, saturated with numerous mining and production wastes. Earlier, gold and diamond deposits were developed on the territory, as a result of which a huge amount of dumps had been accumulated.

Methods

In the process of studying the material composition of the black shale rocks of the Fedotovskaya suite and the weathered rocks overlying them on the western slope of the Middle Urals, the content of toxic metals and radioactive elements was determined using electron probe spectroscopy methods. The JSM 6390LV scanning electron microscope (Jeol) with INCA 350 x-act energy dispersive device (Oxford Instruments) and the X-ray fluorescence spectrometer S8 TIGER (Bruker) are used. The main mineral forms of occurrence for toxic elements and their transformations into secondary products in the processes of chemical weathering have been investigated. In total, about 100 microprobe and over 1800 X-ray fluorescence analyses were performed.

Results

The minerals that carry most of the toxic metals in black shale rocks are sulfides. The mineral with many toxic elements (Ni, Co, As, Sb, Bi, Se) is pyrite. The total content of toxic impurity elements in pyrite is usually 0.3-0.5%, sometimes up to 2-3%. In addition to pyrite, many other sulfides containing toxic elements are presented in black shale rocks (galena, sphalerite, arsenopyrite, cinnabar, cobaltite, etc.) (tab. 1).

The form of occurrence for uranium in the black shale rocks of the Fedotovskaya suite is mainly uraninite, confined directly to inclusions of carbonaceous matter (fig. 1). The presence of uranium and thorium in organometallic compounds is assumed. Mercury is found in the form of droplets of native mercury, amalgams, and as part of aggregates with the participation of gold and silver micro- and nanoparticles. The mercury concentrator is probably carbonaceous as an active metal sorbent. It is also possible for it to enter the deep faults from the mantle during periods of tectono-magmatic activation of the territory (for example, in the Early Mesozoic).

The study of the distribution of toxic elements in the section of black shale rocks allows us to draw the following conclusions. Their concentrations within the black shale strata vary in wide limits, depending on

***Table 1** The average content of toxic elements in the sulfides of the black shale strata of the Fedotovskaya suite and detrital weathered rocks, %.*

Elements	1	2	3	4	5	6	7	8	9	10	11
S	18.11	20.36	19.67	15.87	16.19	44.56	53.45	53.41	39.64	34.51	19.66
Fe	9.29	6.13	4.33	0.60	0.60	36.17	45.10	45.59	33.76	2.99	5.92
Cu	0.48	0.29	0.82	0.84	0.18	0	-	0	25.59	0.28	0.37
Zn	-	-	0.51	0.82	0.17	-	-	-	-	61.27	71.03
As	32.18	42.46	42.26	4.11	0	0	-	-	-	-	-
Ni	6.95	4.87	2.85	0.73	-	-	0.14	-	-	-	-
Co	20.41	25.07	28.50	1.99	-	-	0.11	-	-	-	-
Ag	0	0	0	0.13	0.14	-	-	-	-	0.11	0
Se	-	-	-	-	0.28	-	-	-	-	-	-
Pb	-	-	-	73.56	78.61	15.79	-	-	-	-	-
Bi	-	-	-	1.36	3.22	-	0.87	0.87	-	-	-
Cd	-	-	-	-	-	-	-	-	-	0.31	0.67
In	-	-	-	-	-	-	-	-	-	0.09	1.79
Sn	-	-	-	-	-	-	-	-	-	0.13	0
Amount	87.42	99.18	98.94	100.01	99.39	96.52	99.67	99.87	98.99	99.69	99.44

Note: 1-3 - cobaltin, 4-5 - galena, 6 - galena in pyrite, 7-8 -pyrite, 9 - chalcopyrite in pyrite, 10-11 - sphalerite.
Analyst B.M. Osovetsky.

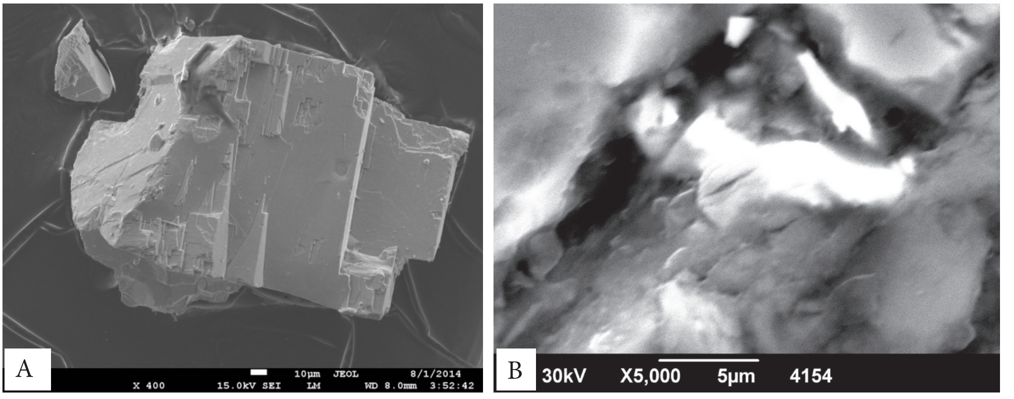

Figure 1 *Typical minerals of the black shale rocks: A - galena, B - uraninite (light) in a crack with organic matter*

the content of carbonaceous matter, the degree of metasomatic changes in the rock, hydrothermal and effusive activities. Metal concentrations decrease sharply in the calcite interlayers. For example, for zinc they are reduced to 16 ppm, instead of the usual concentration, ranging from 66 to 194 ppm (tab. 2).

The processes of substantial redistribution of toxic elements have been occurring in the weathered rocks. At the same time, they are usually insignificant in the detrital weathered rocks of aleurite composition and only for some elements marked changes are noted. Thus, the concentrations of V, Cr, and Co in the detrital weathered rocks are sharply reduced compared with those in the black shale rocks (see tab. 2).

The carbonaceous matter and sulfides are easily decomposed in the weathered rocks of the clay composition, and their components often become an integral part of colloidal solutions. Almost all toxic elements are found here. Galena in the weathered rocks decomposes to form easily soluble corkite $PbFe^{3+}_3[SO_4][PO_4](OH)_6$. The secondary pyrite of a colloform structure is also formed in the weathered rocks, in which high concentrations of some toxic metals are observed. Extremely high concentrations of zinc, nickel, vanadium, and lead have been found in individual layers of the weathered rocks (tab. 3).

The active migrant in the clay weathered rocks is mercury. The mineral forms of Hg occurrence are very diverse, including Hg_2Sn, Hg_3Pb, HgAu and other amalgams. The gold-mercury aggregates with globular structure, which are formed as a result of gradual merging of mercury droplets and

Table 2 *The average content of toxic elements in the black shale rocks of the Fedotovskaya suite and detrital weathered rocks, ppm.*

Interval, m	V	Cr	Co	Ni	Cu	Zn	As	Sn	Sb	Pb	Th	U	N
					Weathered rocks								
2.5-5.0	9	2	0	27	45	74	25	8	6	7	15	3	1
5.0-8.0	8	0	2	20	20	80	17	8	6	6	13	3	1
					Black shale rocks								
8.0-20.5	49	13	7	32	45	160	15	9	7	29	11	4	4
20.5-30.5	60	61	10	44	34	75	18	7	4	15	7	1	4
30.5-44.0	58	59	8	35	25	66	13	5	5	13	6	1	5
44.0-46.0	55	58	3	8	3	16	5	2	2	1	0	0	1
46.0-55.4	61	58	8	37	26	79	13	4	3	17	8	1	3
55.4-107.0	87	44	12	49	28	194	19	3	1	36	6	3	17

Note: N is the number of analyses (hereinafter). Analyst K.P. Kazymov.

Table 3 *The average content of pollutant elements in the Early Mesozoic clay weathered rocks, ppm.*

Interval, m	V	Cr	Co	Ni	Cu	Zn	As	Sn	Sb	Pb	U	N
6.0-14.0	75	16	27	111	61	695	7	5	5	6	5	2
28.5-40.0	19	4	2	3	21	15	5	4	5	6	0	4
41.5-42.0	25	1	0	14	23	14	5	6	6	17	1	1
44.3-49.3	34	11	0	12	36	21	5	4	5	35	1	4
49.3-54.6	116	15	1	21	30	19	7	7	7	75	1	3
54.6-59.0	73	10	0	16	18	13	6	4	4	22	0	3

Analyst K.P. Kazymov

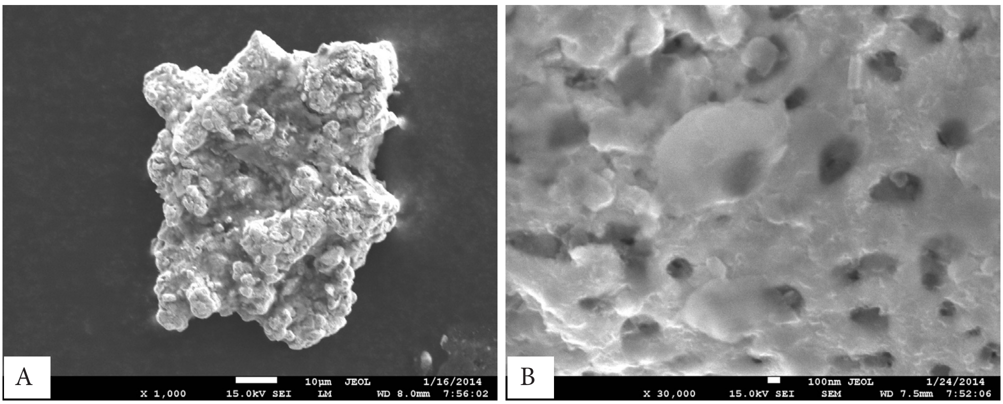

Figure 2 *Gold-mercury aggregate: A - general view, B - porous surface*

capturing of micro- and nanoparticles of gold, are characteristic new formations in the clay weathered rocks. On the way to such aggregates, clay, iron, silica, and other substances are also often captured. The fact of the formation of such aggregates is an evidence of the active migration of mercury. The gold-mercury phases gradually decompose with the release of mercury in the native state and in the gas phase, as evidenced by the numerous pores on the surface of the aggregates (Fig. 2).

An important role as an accumulator of toxic elements is played by karst cavities filled with the weathered rock products. They are found in large quantities in carbonate rocks in contact with black shale. There are very few toxic elements directly in carbonate rocks. But in the products of the weathered rocks displaced into karst cavities their concentrations sharply increase (for example, zinc percentage reaches 330 mg/L) (tab. 4).

According to the data of the Gornozavodsky municipal district in the spatial planning scheme for 2008, the Upper Riphean-Vendian aquifer complex is represented by hydrocarbonate and sulphate-hydrocarbonate sodium, calcium and magnesium waters with mineralization of 0.06-0.07 g/L, the upper Riphean-Vendian terrigenous aquiferous complex hydrocarbonate and sulphate-hydrocarbonate magnesium-calcium waters with mineralization of 0.02-0.05 g/L, rarely up to 0.2 g/L, the Klyktan terrigenous-carbonate aquifer complex presents detecting bicarbonate-calcium-magnesium water with a salinity of 0.1-0.3 g/L, complex uneven aquifer intrusive rocks represented hydrocarbonate (sodium, magnesium, calcium) to water with a mineralization 0.1 g/L. The trace element composition of surface waters in the study area is given in table 5.

Conclusions

The zone of black shale rocks on the western slope of the Middle Urals is characterized by elevated concentrations of toxic elements in the weathered rocks eroded by water courses. These natural sources of environmental contamination by the nature of their effect on ecosystems are almost as important as man-made sources.

Table 4 *The average content of pollutant elements in the Upper Riphean carbonates and the Early Mesozoic weathered rocks in karstic cavities, ppm.*

Interval, m	V	Cr	Co	Ni	Cu	Zn	As	Mo	Sn	Sb	Pb	N
					Carbonates							
7.0-15.5	6	0	0	2	3	11	4	1	5	6	2	6
					Weathered rocks							
15.5-28.5	85	24	58	97	92	330	12	0	7	9	13	7
					Carbonates							
28.5-40.3	14	0	0	4	4	13	4	1	5	6	3	6
					Weathered rocks							
40.3-54.0	70	113	47	85	57	272	11	0	6	9	10	5
					Carbonates							
54.0-168.7	7	0	0	2	3	11	4	1	4	5	3	20

Analyst K.P. Kazymov

Table 5 *The trace element composition of the surface waters of the Koiva River basin, mg/L.*

Place of selection	Cu	Zn	Pb	Cr
R. Koiva, estuary	0.005	0.014	<0.001	0.005
R. Koiva, left bank, Kuse-Aleksandrovsky	0.005	0.001	<0.001	<0.001
R. Koiva, above the “Upper R. Koiva”	0.005	0.012	0.001	0.001
R. Koiva, below the “Upper R. Koiva”	0.005	0.014	0.001	0.001

Black shale strata are widespread in the world. They are either already areas of active mining or are in the process of economic development. As to the western slope of the Urals, natural sources of environmental contamination can have a substantial effect on the ecological condition of the territory.

An important task is to develop a comprehensive environmental monitoring program in the areas of black shale rocks with an assessment of the contamination level of natural waters and bottom sediments with radioactive and toxic components.

Acknowledgements

The authors are grateful to S.Suslov, an employee of Geokarta-Perm JSC, for providing stone material and M.Volkova, K.P.Kazimov, staff of the Perm University Nanomeralogy Sector, for participating in sample preparation operations and performing analytical studies.

References

Badyanova IV (2015) Globular gold of black-shale strata. Geology and Mineral Resources of the Western Urals. Perm State University 15. p 3-5.

Gryaznov ON (2014) Natural sources of natural and environmental pollution. News of the Ural State Mining University 2(34). p 11-17.

Gryaznov ON (2014) Factors of engineering and geological conditions of the Urals. Regional geological factors. News of the Ural State Mining University 3(35). p 30-50.

Osovetsky BM (2017) Natural Nanogold. Springer Mineralogy. 145 pp.