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Geochemical barriers in the technogenic zone of tungsten deposits in Eastern Transbaikalia (Russia)

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Abstract. The relevance of the study is due to the need to protect the environment in mining regions in connection with the pollution of surface and groundwater. The conditions of the formation and influence of technogenic geochemical barriers on the physicochemical parameters of water developed in the areas of tungsten deposits in Eastern Transbaikalia have been studied. Locations of oxygen, sorption, alkaline, acidic and hydrodynamic type geochemical barriers have been identified. It has been shown that the most widespread barriers are complex geochemical barriers formed as a result of the superposition of several barriers.

1 Introduction

Environmental problems arising in the areas of mining enterprises necessitate, in addition to the assessment of drainage from ore deposits as a source of natural water pollution, the search for opportunities for their purification. One of the promising methods for preventing the spread of toxic elements is the use of geochemical barriers, defined as "sections of the earth's crust where there is a sharp change in the intensity of migration of chemical elements over a short distance, and as a result, their concentration" [1].

Natural barriers occurring in natural conditions and technogenic barriers formed as a result of the technogenic modification of the geochemical environment are distinguished. Mechanical, physicochemical, and biogeochemical types are distinguished in each of them. Physicochemical barriers are better studied and have significant practical value. They are divided into several types: oxygen barriers are formed in places where the reducing environment changes to an oxidizing one; hydrogen sulfide or peat barriers, on the contrary, are formed when oxidizing conditions change to reducing ones; alkaline barriers are formed when pH increases, while acidic barriers are formed when pH decreases. Sorption, evaporation, hydrodynamic, and other types of barriers are also distinguished [1-2].

The peculiar feature of technogenic geochemical barriers is the possibility of concentrating components that are not encountered in natural conditions, as well as the fact that concentrations of substances that deposit on them are usually significantly higher than on natural barriers. At present, a large number of studies are devoted to the study of natural

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and technogenic geochemical barriers aimed at solving environmental problems arising in mining regions [3-6].

Transbaikalia is the oldest mining region. Waste from mining production stored in the vicinity of mines and concentrators for many years serve as a source of pollution of all components of the environment, including surface and groundwater. The presence of sulfide mineralization within ore bodies as well as their localization in the near-surface layer of the earth's crust where they come into contact with oxygen and surface waters, contributes to the activation of oxidation and sulfide decomposition processes. This results in the technogenic transformation of water and the formation of acidic mine drainage with abnormally high metal concentrations. Environmental problems arising in this connection require the study of drainage from deposits as a source of natural water pollution and the search for ways to purify it.

The aim of the study was to investigate the geochemical barriers that have become most widespread in the mining regions of Transbaikalia using the example of two tungsten deposits.

2 Materials and methods

The areas of formation of geochemical barriers in the technogenic zone of the Bukuka and Spokoyninskoye tungsten deposits located in the Eastern Transbaikalia were studied (Figure 1). The deposits are associated with the development of Paleozoic and Mesozoic sandstone-shale deposits penetrated by Mesozoic granitic intrusions [7]. For the Bukuka vein quartz-wolframite-sulfide deposit, increased sulfide content is characteristic, represented by pyrite, galena, chalcopyrite, sphalerite, molybdenite, and others. Wolframite is the main mineral of the ore veins in the Bukuka deposit. At the Spokoyninsk greisen-wolframite deposit, sulfide mineralization has a significantly smaller distribution, with the main ore minerals being wolframite, beryl, bismuthite, vismutin, tantaloniabates, muscovite, quartz, and fluorite. The Bukuka deposit was developed by both underground and open-pit methods until the beginning of the 1960s. On the Spokoyninskoye deposit, tungsten mining was resumed after a short hiatus and continues to this day.

Fig. 1. Layout of tungsten deposits: SP – Spokoyninskoye; BK – Bukuka.

During the study, water and secondary formations samples were collected. Chemical water analysis was conducted using conventional methods [8-9] in the accredited laboratory of the Institute of Natural Resources, Ecology, and Cryology SB RAS (Chita, Russia). Metal and main cation concentrations were determined using the atomic absorption method on the SOLLAR 6M spectrophotometer. Chemical water analysis using the ICP-MS method was conducted at the A.P. Vinogradov Institute of Geochemistry SB RAS (Irkutsk, Russia) using the ELEMENT2 device. The analysis of mineral formations included the study of their chemical composition (GIN SB RAS, Ulan-Ude, Russia). The HydroGeo 32 software package was used for thermodynamic calculations [10].

3 Results and Discussion

In the Bukuka deposit area, acidic SO_4 and F-SO_4 Mg-Ca waters with increased mineralization and anomalously high concentrations of heavy metals (Table 1) have become widespread. The presence of sulfide mineralization in ore bodies led to such a transformation of the waters. In the disrupted territories of the Spokoyninskoye deposit, weakly alkaline and alkaline waters of SO_4-HCO_3 and HCO_3 Mg-Ca and Ca-Na composition with anomalously high contents of W, Mo, U, and As predominate.

Table 1. Variation range of water chemistry parameters.

Characteristics	Bukuka			Spokoyninskoye		
	Min.	**Max.**	**Mid.**	**Min.**	**Max.**	**Mid.**
pH	2.06	7.85	5.84	5.87	8.75	7.19
Eh, mV	211	574	375	-87	221	94
HCO_3^-, mg/L	2.4	120.8	21.1	21.3	686	141.7
SO_4^{2-}	1.87	1562	157.3	7.8	617	82.1
Cl^-	0.4	52.5	4.26	0.54	95.4	19.3
F^-	0.03	173.2	15.9	0.12	3.41	0.92
Ca^{2+}	0.4	339.3	56.1	0.60	237	34.4
Mg^{2+}	0.4	250.1	10.1	0.32	125	12.6
Na^+	0.2	55.2	6.45	0.6	77.4	16.8
K^+	0.1	13.4	1.89	0.45	14.1	3.36
Si	0.5	34.2	9.43	1.75	11.5	5.8
Salinity	11	2348	269.1	51.1	1069	306.5
Al, µg/L	0.1	131222	14562	10.4	468	211.1
Sr	5	2961	488.6	40	1679	560
Li	5	589	50.3	12	405	87.1
Be	12.2	50	29.4	0.02	2.74	0.99
Fe	20	75900	2768	20.8	9500	1194
Mn	0.03	16200	1403	3.2	2730	360
Cu	0.5	23224	1648	0.7	11	2.35
Zn	1.5	117226	8758	0.5	45.8	9.27
Cd	0.1	1323	61.3	8	12	9.8
Pb	0.89	3150	160.3	0.45	13.2	3.65
As	0.15	33.4	5.19	0.68	605.6	137
Ni	0.05	1151	94.7	0.75	51	6.29
Co	0.15	310	20.1	0.5	26	8.48
Ag	0.03	12.1	1.08	0.2	0.89	0.21
W	0.1	28.8	1.13	0.1	1544	6.22
Sn	0.1	5.67	0.84	0.12	2.45	0.61
Mo	0.02	240	5.26	0.11	76.2	6.48
Y	0.38	174	48	0.1	0.29	0.19
Th	0.02	50.3	14.7	0.006	0.11	0.04
U	1.59	117	41.2	2.98	1863	645.7
∑ REE	2.23	1071	295.8	0.15	0.71	0.35

The normalization of metal concentrations in the investigated waters relative to the average composition of leaching zone waters [11] showed that Cd, Cu, Zn, and Co accumulate to the greatest extent in Bukuka's acidic and weakly acidic waters, while W, U, As, and Mn accumulate in the weakly alkaline and alkaline waters of the Spokoyninskoye deposit [12].

In the process of investigating the hydrogeochemical fields of tungsten deposits, areas of formation of technogenic geochemical barriers of oxygen, alkaline, acidic, sorption, and hydrodynamic types were discovered [12]. The oxygen (oxidizing) barrier acts when non-oxygen-containing waters (with low positive Eh <250 mV) mix with oxygen-containing groundwater and surface waters. More soluble reduced compounds transform into less soluble oxidized compounds, which promotes their removal in the solid phase as precipitated hydroxides, which also act as sorbents. [1-2]. The most effective of them are hydroxides of iron, manganese, and aluminum, which sorb cations in alkaline media and negatively charged ions in acidic media. The spatial overlay of the oxygen and sorption hydroxide barriers allows them to be classified as a single complex geochemical barrier. The area of action of such a barrier under conditions of neutral and alkaline media was observed in the drainage of tailings at the Spokoyninskoye deposit (Figure 2a). The Eh value at the water outlet in the sands was 13 mV. Approximately 2 m later, an increase in this indicator to 136 mV was noted, and deposits of ochre-colored colloid particles appeared at the bottom. The saturation of water with oxygen in this case led to a sharp increase in Eh and the oxidation of iron, with the precipitation of solid-phase hydroxides, on contact with which a sorption hydroxide barrier arose, which was indicated by a decrease in metal concentrations (μg/L): Zn - 5.0-4.0; Cu - 3.0-1.0; Pb - 1.23-0.45, Ni - 50.0-22.0.

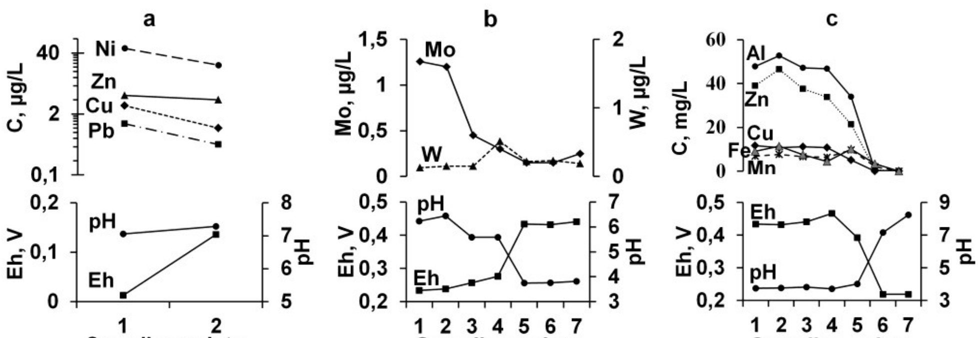

Fig. 2. Changes in the values of physics and chemical parameters of waters at the points of geochemical barriers action: of oxygen and sorption (a), of acid (b) and alkaline (c) types.

Complex barriers of this type, forming in acidic and weakly acidic media, are widely developed in the valley of the Kalenikha brook (Bukuka deposit), which drains the sands of the concentrator tailings. One of them formed with the overlap of oxygen, sorption hydroxide, and sorption clay barriers at the site of underground water discharge. Chemical analysis of the iron precipitation collected in this area showed the presence of Al, Si, Fe, Ca, Mg, Na, W, Ti , Mn, As, Cu, Zn, Pb, Sb, Cr, V, Mo, and others (in decreasing concentration). The highest content of precipitated ore elements is typical for tungsten, the best sedimentation for which in acidic waters is, known to be, iron hydroxide [2].The presence of metal cationogens in the precipitate composition is associated with the action of a sorption clay barrier, which is characterized in the hypergenesis zone by a predominantly negative charge. The possibility of clay precipitation formation is confirmed by the saturation of waters sampled in the barrier action area relative to clay minerals such as kaolinite, montmorillonite, and others [10].

The formation of an acidic geochemical barrier was detected when a water stream originating from an underground tunnel in the upper reaches of the Kalenikha floodplain (Bukuka) entered the tailings sand (Figure 2b). This resulted in a sharp decrease in pH values (from 5.59 to 3.75) and an increase in Eh (from 276 to 434). Anionogenic elements, such as molybdenum and tungsten, were concentrated in the acidic barrier, and their concentrations in the water significantly decreased (μg/L): W - 0.51-0.19; Mo - 1.26-0.15.

Sections of the formation of alkaline geochemical barriers have repeatedly been recorded in areas where acidic waters (pH < 4.0) mix with neutral background waters produced during filtration through tailings of the beneficiation plant at the Bukuka deposit. One example of such a barrier is the marshiness at the lower reaches of the Kalenikha floodplain where neutral fractured underground waters emerge (Figure 2c). Abundant iron deposits are formed along the stream bed in this area, and a significant increase in pH (from 4.01 to 7.17) and a decrease in Eh (from 392 to 219 mV) of the water are observed. There is also a change in the chemical type of water from SO_4 Mg-Ca to SO_4-HCO_3 Mg-Ca, and a noticeable decrease in mineralization (from 0.6 to 0.4 g/L) and heavy metal contents (mg/L): Al - 34-0.5; Fe - 10.2-3.42; Mn - 9.81-2.19; Cu - 5.07-0.03; Zn - 21.4-0.76. Thermodynamic calculations [10] showed that these waters are saturated with respect to iron and aluminum hydroxides [12].

The formation of a hydrodynamic barrier has been observed in the Kalenikha gorge, 50 meters below the tunnel. In this section, the stream valley is partially blocked by rockfall, resulting in the formation of a pool. The decrease in water flow velocity favored some stagnation of water, increased evaporation, and salt accumulation, leading to the formation of mineral deposits. Whitish deposits are clearly visible at the bottom of the pool, and ochre-coloured deposits can be seen when the upper film is removed. Equilibrium calculations in the "water-rock" system [10] showed that these waters were saturated with respect to iron and aluminum hydroxides (goethite, gibbsite) and clay aluminosilicates (kaolinite, montmorillonite, illite). This may indicate the joint action of hydrodynamic and sorption geochemical barriers.

4 Conclusion

The conducted research allowed us to obtain an idea of the main types of technogenic geochemical barriers, their prevalence, and role in purifying drainage water from tungsten deposits. One of the most common barriers in the surveyed areas are complex barriers formed as a result of the joint action of several overlapping different barriers: oxygen and sorption or oxygen, alkaline, and sorption. The study of geochemical barriers is one of the important directions in the development of effective methods for purifying drainage waters from mining territories. In the future, it is planned to continue work on identifying and more detailed research of geochemical barriers of different types.

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