

# Formation of the chemical composition of mining areas waters on the example of tungsten deposits of Eastern Transbaikalia

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**Abstract.** The chemical composition of waters in the mining areas of the four tungsten deposits (the Transbaikal region) are studied. Acidic sulfate waters with salinity (TDS) up to 2.7 g/L and abnormally high concentrations of Al, Zn, Fe, Mn, Cu, Pb, Cd and other metals were formed in the areas of Bukuka, Belukha and Antonova Gora Deposits. They are characterized by thermodynamic equilibrium with secondary aluminosilicates (kaolinite, montmorillonite), sulfates (gypsum, anglesite) and fluorides (fluorite, sellaite). These waters are characterized by the highest degree of nonequilibrium with primary minerals - anorthite, albite, muscovite, chlorite and others, which contributes to their further dissolution and accumulation of components in waters. Technogenic waters of the Spokojninskoe mine are characterized by neutral and alkaline reaction, moderate growth of salinity and active migration of U, W, As and Mo. They are saturated with respect to secondary aluminosilicates (montmorillonite, illite) and carbonates (calcite, dolomite, malachite, azurite, rhodochrosite, cerussite, siderite).

## 1 Introduction

Geochemical studies of drainage waters of mining areas in recent decades have been widely developed. This is mainly due to environmental problems that necessitate the assessment of drainage effluents from mines as a source of technogenic transformation of the natural environment. First of all, this applies to the areas of storage of waste production and processing of sulfide ores. Sulfide minerals, when coming out to the daylight surface, are actively oxidized, forming acid drainage runoff with abnormal concentration of pollutants. In international literature this phenomenon is known as "acid mine drainage" or "acid rock drainage" and lately is the most important subject of research, which is reflected in the works of C.O. Moses, D.K. Nordstrom, D.W. Blowes, B.G. Lottermoser, M.B.J. Lindsay, and others. In Russia, the theme is widely presented in scientific publications of V. N. Udachin, G. R. Kolonin, S. A. Bortnikova, O. L. Gas'kova, A. M. Plyusnin and many other researchers.

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The Transbaikal territory is the oldest mining region, which accounts for about a third of Russia's tungsten reserves. Its active mining was carried out in the last century and continues nowadays at some sites. Mining waste is a source of toxic elements entering the environment and polluting all its components, including natural waters. A significant part of the deposits is represented by sulfides, which contribute to the formation of acid drains with high concentrations of toxic components exceeding the permissible environmental standards.

The relevance of the topic under discussion is due to the need to understand the mechanisms of waters technogenic transformation for the subsequent prediction of changes in their quality in the mining process in these areas. The aim of the work is to study the formation of waters composition from the standpoint of water-rock interaction on the example of tungsten mines areas.

## 2 Objects and methods of research

In the present work the data of hydrogeochemical testing of four tungsten deposits located in the Eastern Transbaikalia are used. Three of them, belonging to the Kukulbeisky ore district – Antonova Gora, Belukha and Bukuka Deposits, were developed before the beginning of 1960. After their liquidation they were abandoned and more than fifty years served as sources of pollution of natural waters. In the Spokojninskoe mine belonging to the Aginsky ore district the tungsten mining was conducted prior to the beginning of this century, and after a short break were resumed. The drainage waters were sampled from mine galleries, rock dumps and tailings, as well as pit lakes and ponds of the tailing dumps.

The ore field of the Bukuka Deposit consists of mainly granodiorites and, to a lesser extent sedimentary rocks including shales, sandstones, and small-pebble conglomerates. The ore field of the Belukha Deposit is composed of biotite-hornblende diorites and, to a lesser extent, of porphyritic biotite granites. In general, the ores of these two deposits are characterized by an increased content of sulfides and fluorite [1, 2].

The Antonova Gora Deposit position located in fine-grained granites, which break through sand-shale massif [1]. The plagioclase, potassium feldspar, quartz, and biotite in mineral composition of granitoids of the Kukulbey ore region deposits are dominated. Minerals of ore veins are represented by wolframite, pyrite, quartz, pyrrhotite, chalcopyrite, sphalerite, galenite, and etc.

Within the Spokojninskoe Deposit there are two types of mineralization - greisens and quartz veins [2]. The mineral composition of greisens: quartz, muscovite, amphibole, pyrrhotite, apatite, garnet, wolframite, cassiterite, and etc. A small amount of sulfides and fluorite is one of the mineralogical features of the ore bodies of the Spokojninskoe Deposit. Wolframite is the main ore mineral in all the deposits under consideration.

The data of chemical analysis of 297 water samples were used. Chemical and analytical studies were carried out in the certified laboratory of the Institute of natural resources, ecology and cryology SB RAS (Chita) by conventional methods: potentiometry, colorimetry, turbidimetry. Determination of metal concentrations in water was carried out by atomic absorption spectrophotometry on a spectrophotometer SOLAAR M6. Additionally, water samples were analyzed by ICP-MS method at the Institute of Geochemistry SB RAS of Sciences (Irkutsk). The construction of phase diagrams was carried out using the tools of the software package Excel was carried.

### 3 Results and discussion

#### 3.1 The chemical composition of waters

Technogenic pollution of the environment by mining waste in the areas of tungsten deposits have led to changes in the water exchange conditions and groundwater pathways. These changes result of this was the to the formation of hydrogeochemical systems that differ significantly in their physical and chemical characteristics from natural ones.

The most common features of these differences are the increased water migration of chemical elements, especially heavy metals, and, for sulfide deposits, the occurrence of acid mine drainage [3-5].

The waters of technogenic streams of the Kukulbeyskiy ore district are characterized mainly by sulfate and hydrocarbonate-sulfate anionic composition, the decrease of pH to weakly acidic and acidic values, substantial, in the tens or more times, increase of salinity (table 1). The lowest pH values were recorded in waters filtrating through the waste rock dumps, sands of tailings, as well as in mine gallery at the Antonova Gora deposit, and in waters of pit lake Bukuka. The most highly mineralized acidic sulfate waters of the Bukuka mine are characterized by abnormally high concentrations of metals – Al, Zn, Fe, Mn, Cu, Pb, Cd, REE.

**Table 1.** Range of changes in physico-chemical parameters of mines waters compositions.

Parameter	Unit of measure	The tungsten mine				The middle values for waters of leaching zone[6]
		Bukuka	Antonova Gora	Belukha	Spokojninskoe	
pH	unit of pH	<u>2.06-7.17</u> 5.69	<u>2.65-6.75</u> 4.29	<u>3.63-7.54</u> 6.27	<u>5.87-8.75</u> 7.21	6.75
Eh	mV	<u>211-574</u> 375	<u>303-571</u> 462	<u>257-472</u> 326	<u>-87-221</u> 94	-
HCO <sub>3</sub> <sup>-</sup>	mg/L	<u>0.43-121</u> 19.4	<u>0.61-10.4</u> 4.95	<u>1.3-83.4</u> 15.2	<u>21.3-686.0</u> 144.3	146.0
SO <sub>4</sub> <sup>2-</sup>		<u>0.5-1562</u> 173.6	<u>0.8-613.1</u> 108.2	<u>1.90-244.1</u> 33.0	<u>7.80-617.0</u> 83.3	12.4
Cl <sup>-</sup>		<u>0.20-21.4</u> 0.40	<u>0.30-5.60</u> 1.17	<u>0.17-21.9</u> 2.84	<u>0.17-95.4</u> 19.0	10.1
F <sup>-</sup>		<u>0.03-173</u> 15.9	<u>0.01-19.0</u> 1.52	<u>0.14-8.10</u> 1.84	<u>0.12-3.97</u> 1.07	0.23
Ca <sup>2+</sup>		<u>2.50-339</u> 62.6	<u>7.92-177.9</u> 32.8	<u>2.90-101</u> 25.4	<u>0.10-236.6</u> 34.7	27.4
Mg <sup>2+</sup>		<u>0.4-250</u> 12.3	<u>0.10-46.8</u> 5.77	<u>0.30-12.1</u> 2.47	<u>0.32-125.1</u> 13.2	11.2
Na <sup>+</sup>		<u>0.20-55.2</u> 6.70	<u>0.50-13.0</u> 4.17	<u>1.20-15.9</u> 3.40	<u>0.58-77.4</u> 17.3	13.8
K <sup>+</sup>		<u>0.05-12.4</u> 1.79	<u>0.5-2.8</u> 1.08	<u>0.10-5.10</u> 0.88	<u>0.02-19.6</u> 4.00	1.84
TDS		<u>11-2709</u> 416.8	<u>7.89-901.0</u> 261.8	<u>15-490.0</u> 95.7	<u>51.1-1069</u> 332	239.0
SiO <sub>2</sub>		<u>1.07-73.2</u> 20.2	<u>11.8-43.9</u> 23.3	<u>10.3-20.7</u> 14.4	<u>1.07-24.6</u> 12.3	14.5
Al		<u>0.10-131</u> 14.4	<u>0.20-20.5</u> 5.64	<u>0.06-5.42</u> 0.83	<u>0.02-0.47</u> 0.18	0.19
Sr		<u>0.01-2.96</u> 0.44	<u>0.01-0.97</u> 0.11	<u>0.02-1.37</u> 0.19	<u>0.04-1.67</u> 0.58	0.09
Fe		<u>0.02-75.9</u> 2.77	<u>0.051-32.7</u> 2.91	<u>0.001-4.8</u> 0.28	<u>0.02-10.6</u> 1.41	0.42

Mn		<u>0.001-14</u> 1.31	<u>0.10-2.79</u> 0.64	<u>0.001-1.4</u> 0.08	<u>0.003-5.66</u> 0.48	0.03	
Cu		<u>0.001-23</u> 1.74	<u>0.05-3.80</u> 0.76	<u>0.0002-1.5</u> 0.09	<u>0.001-0.01</u> 0.002	0.004	
Zn		<u>0.02-117</u> 9.50	<u>0.15-10.7</u> 2.56	<u>0.005-4.6</u> 0.43	<u>0.001-0.26</u> 0.017	0.03	
Pb	mkg/L	<u>0.01-3150</u> 180.0	<u>0.14-90.0</u> 13.1	<u>0.2-15.0</u> 4.0	<u>0.11-13.2</u> 3.84	2.18	
Cd		<u>0.13-1323</u> 98.1	<u>0.21-182.0</u> 38.8	<u>0.13-25.0</u> 6.22	<u>0.31-12.0</u> 6.58	0.20	
As		<u>0.15-33.0</u> 7.26	<u>0.25-17.9</u> 3.24	<u>0.14-2.30</u> 0.58	<u>0.68-606.0</u> 137.0	1.34	
Mo		<u>0.05-240.0</u> 6.30	<u>0.13-40.7</u> 5.77	<u>0.10-15.9</u> 3.48	<u>0.11-76.0</u> 8.73	1.16	
W		<u>0.05-28.8</u> 1.30	<u>0.10-12.0</u> 1.12	<u>0.20-6.90</u> 1.44	<u>0.10-1544</u> 121.6	–	
U		<u>1.6-117.0</u> 41.2	<u>2.00-58.0</u> 17.0	<u>0.17-0.44</u> 0.26	<u>1.50-1863</u> 473.5	0.56	
ΣREE		<u>2.23-1072</u> 298.3	<u>2.50-21.0</u> 10.3	<u>1.40-8.40</u> 3.90	<u>0.15-0.71</u> 0.35	–	
Note: the minimum and maximum (in the numerator) and average (in the denominator) parameter values are shown; dash indicates no data.							

Within the Spokojninskoe mine areas neutral and slightly alkaline technogenic waters with a maximum salinity up to 1 g/l are mainly formed (table 1). The chemical composition of these waters is HCO<sub>3</sub>-Mg-Ca type, with the exception of the pit lake solution belonging to the SO<sub>4</sub>-Ca type. Geochemical conditions in the area of the Spokojninskoe Deposit are favorable for migration and accumulation in waters of anionic elements – U, W, As and Mo (Table 1).

### 3.2 The thermodynamic equilibrium in the water-rock system

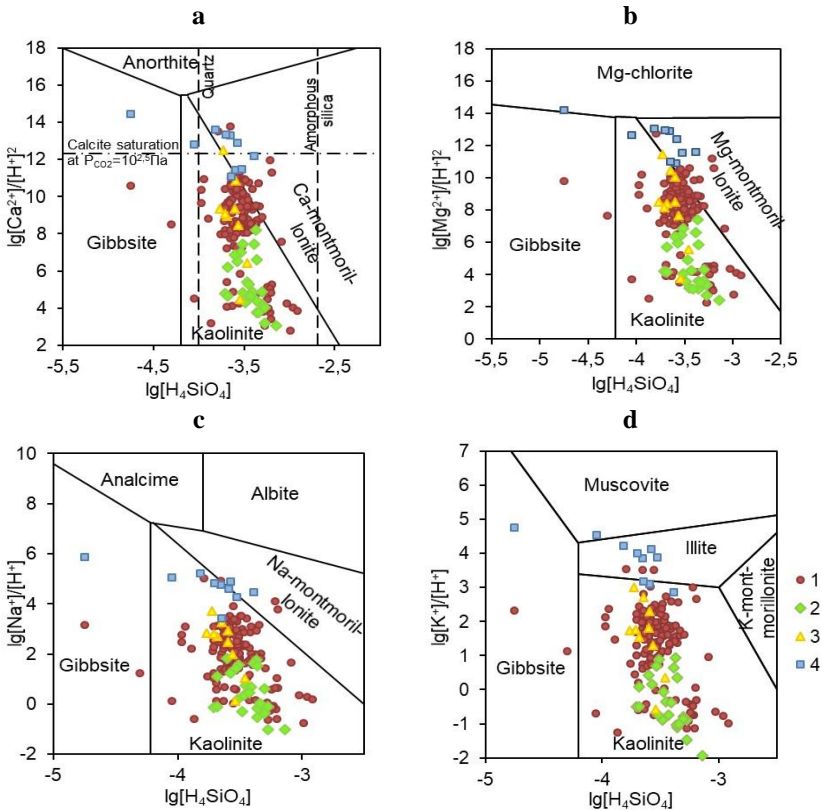
It has been shown earlier [7] that in formation of the chemical composition of waters in the studied areas water-rock interaction is the main factor. Features of the behavior of components in waters are determined by their migration abilities in different environments, and controlled by the ratio of climatic, geological and anthropogenic factors, with the leading role of the last one.

The water-rock system has twofold equilibrium-nonequilibrium nature, that is, there are nonequilibrium in “aqueous solution – primary mineral” system and equilibrium in “aqueous solution – secondary mineral” system at the same time. This interaction feature determines the continuous dissolution of the primary endogenous rock and the formation of a secondary hydrogenic-mineral complex, which is in strict dependence on the stage of this interaction [6, 8]. The concentration of the elements contained in the water, in this case, is nothing but the difference between their amount introduced into the solution during the dissolution of rocks and the amount deposited during the formation of the secondary mineral phase. The main processes of formation of the water composition are the hydrolysis of aluminosilicates and the oxidation of sulfide minerals. When sulfides are oxidized, the concentration of H<sup>+</sup>-ions increases in water, resulting in a decrease in the pH to the minimum values. The presence of carbonate minerals has a neutralizing effect on the increasing acidity of water; the actual pH of waters is determined by the ratio between the amount of sulfide and carbonate minerals [9, 10]. This explains an increased acidity of mine drains in Bukuka, Antonova Gora and Belukha mines, as well as the neutral and alkaline reaction of waters, formed in the area of the Spokojninskoe Deposit development.

The illustrations of the statement about the equilibrium-nonequilibrium nature of the interaction of water with rocks are presented below on the diagrams of the equilibria of the studied waters with the main aluminosilicate minerals (Fig.1 a-d), constructed by the method proposed by R.M. Garrells and C.L. Christ [11]. The vast majority of the waters composition points are located in the diagram section of kaolinite and montmorillonite. These minerals are widely distributed of in the oxidation zone of the studied areas. The composition points of acid sulfate waters of the Bukuka, Belukha and Antonova Gora mines almost completely fall into the field of kaolinite. The increase in pH values contributes to their shift towards equilibrium with montmorillonite and illite. These are usually weakly acidic and neutral waters formed within the undisturbed landscapes of the territories adjacent to the mines.

The neutral and alkaline waters of the mine Spokojninskoe are in equilibrium with montmorillonite and illite (Fig.1a-d). Two points of waters composition located in the diagram section of Mg-chlorite and muscovite (Fig. 1 b, d) characterize the condition of the waters of tailings pond and reservoir. These are shallow (up to 1-3 m), well-heated water bodies with a high degree of evaporation from the surface water. Several points of waters composition get into the stability field of gibbsite, which is due to the low activity of silicon ions in water ( $\text{SiO}_2 < 5 \text{ mg/L}$ ). However, this mineral in the precipitation is not fixed. The reason for this is probably the presence in the waters of a large number of fluorine ions that bind aluminum to stable aluminum-fluoride complexes [12, 13].

At the same time, there is a nonequilibrium of the investigated waters with the vast majority of primary aluminosilicates - anorthite, albite, muscovite, chlorite and many others (Fig.1a-d), which continue to dissolve, thereby contributing to the accumulation of components in the waters before saturation with clays and other minerals.



**Fig. 1.** Stability field diagrams at 25<sup>0</sup>C: a) the system H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-CO<sub>2</sub>-CaO-SiO<sub>2</sub>; b) the system H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-MgO-SiO<sub>2</sub>; c) the system H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-Na<sub>2</sub>O-SiO<sub>2</sub>; d) the system H<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-SiO<sub>2</sub> with the application data on the composition of the tungsten deposits waters: 1 – Bukuka, 2- Antonova Gora, 3 – Belukha, 4 – Spokojninskoe.

The main mechanism preventing the achieve an equilibrium of the waters with primary aluminosilicates is carbonate geochemical barrier, as evidenced by the position of the points of waters composition above the line of calcite saturation (Fig. 1a). The probability precipitation of this secondary mineral occurs by waters with an increase in the pH value of more than 7.5 and salinity values of more than 0.4 g/L. Also, the equilibrium of neutral and alkaline technogenic waters with other carbonate minerals – dolomite, malachite and azurite (Belukha, Bukuka, Spokojninskoe), rhodochrosite and cerussite (Bukuka, Spokojninskoe), siderite (Spokojninskoe) was fixed. The formation of carbonates, in this case, prevents further accumulation of calcium, magnesium, manganese, lead, copper and iron in the waters and contributes to the preservation of water nonequilibrium with primary minerals. The greatest degree of waters nonequilibrium with the primary aluminosilicates is characteristic for acid technogenic waters.

The presence of sulfides in the ore veins of the deposits contributes to the accumulation of SO<sub>4</sub><sup>2-</sup>-ions in the waters, which in combination with high concentrations of calcium can contribute to the achievement of an equilibrium of the waters with gypsum. This phenomenon was fixed in highly mineralized waters (with salinity more than 2.3 g/L), formed within the sands of tailing of the Bukuka mine. Also, these waters are in equilibrium with anglesite, in so doing the lead concentration was 1.63-3.15 mg/L.

Acid technogenic waters from Bukuka and Antonova Gora mines are in equilibrium with the fluorides – fluorite and sellaite. Saturation by fluorite was fixed in the neutral waters Spokojninskoe mine. The presence of clay phases, gypsum, anhydrite, fluorite, sellaite, jarlite, weak traces of scorodite and pharmacolite was shown by X-ray fluorescence analysis of sediment from mine drainage waters of these deposits. Another mechanism for removing components from the aqueous medium into the solid phase is the action of different types of geochemical barriers such as oxidative, alkaline, sorption and evaporation types, which are widespread in the mine areas [5].

## 4 Conclusions

Diverse in characteristics technogenic hydrogeochemical systems were formed in the areas of mining of tungsten. The greatest degree of technogenic transformation of waters was identified within the limits of deposits with the increased content of sulfides in ores - Bukuka, Belukha and Antonova Gora mines. They are characterized by high acidity and salinity, a change in the chemical type of waters, as well as a significant increase in the water migration of cationogenic metals. These waters have the highest degree of nonequilibrium with primary aluminosilicate minerals. The technogenic waters of Spokojninskoe mine have the neutral and alkaline reaction, more moderate growth of salinity and increased migration of anionic elements. One of the leading factors limiting the accumulation of components in the considered waters is the achievement of equilibrium in the system - aqueous solution – a secondary mineral.

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