Chemical composition and ecogeochemical assessment of water in quarry lakes of the Zavitinskoye and Ermakovskoye beryllium deposits (Russia)

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Abstract. The study presents the results of research on the chemical composition of water in quarry lakes of the lithium-beryllium Zavitinskoye and fluorite-beryllium Ermakovskoye deposits located in the Eastern and Western Transbaikalia, respectively. Currently, the mines are abandoned, and the quarry lakes are actively used by the population of nearby villages for domestic and recreational purposes. It was found that the water in the quarries of these deposits is brackish and fresh, belonging to the sulfate-magnesium-calcium and hydrocarbonate-sulfate-magnesium-calcium types with a neutral and slightly alkaline reaction and high contents of sulfates and certain metals (Li, Be, Zn, Al, Mn, Fe, Sr, etc.). Significant variations in the concentrations of trace elements in the identified types of water indicate the significant role of the hydrogeochemical environment (pH, Eh, mineralization, etc.) in their dispersion or accumulation. The beryllium content in the water of Zavitinskoye deposit quarries ranges from 0.35 to 10.1 μg/l, while in the Ermakovskoye quarry it ranges from 0.024 to 0.026 μg/l. The content of some regulated components in the water exceeds the maximum permissible concentrations established for fishery ponds and sanitary-hygienic norms by several orders of magnitude.

1 Introduction

Ecogeochemical issues of mining areas have remained relevant for many decades. One of these issues is related to the formation of technogenic reservoirs in the form of flooded quarries, formed as a result of open-pit mining of mineral deposits. Typically, the flooding of quarry excavations occurs due to the influx of atmospheric precipitation and groundwater. Often, the waters of quarry lakes are characterized by elevated levels of toxic elements in mobile forms, or conversely, by low-anomalous concentrations of many components. Furthermore, technogenic reservoirs exhibit fundamental similarities in hydrochemical, sedimentation, and bioproduction processes to naturally occurring water bodies. In this regard, the hydrochemistry of quarry lakes is of broad interest to many

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researchers for studying the peculiarities of their chemical composition formation and for ecogeochemical assessment of the surrounding environment.

Particular attention is given to the composition of ores and the presence of beryllium, as a highly toxic element, in the Zavitinsky lithium-beryllium and Ermakovskoye fluorite-beryllium quarry lakes located in Eastern and Western Transbaikalia respectively, whose open-pit mining operations date back to the last century.

The aim of this study is to investigate the chemical composition of waters in the quarries of the aforementioned deposits and evaluate the ecogeochemical consequences of their development.

2 Materials and Methods

Hydrogeochemical characteristics of the waters of the Zavitinskoye and Ermakovskoye beryllium deposits' quarry lakes have been previously discussed in works. Their geological structure, ore composition, and genesis have been studied by various researchers.

The Zavitinskoye rare-metal deposit is known for its rich complex ores containing typical rare elements (lithium, beryllium, tantalum, niobium, etc.). Discovered in 1897, the deposit is located in the Shilkinsky district of Zabaikalsky Krai (north of the Pervomaisky settlement). Ore extraction at the Zavitinskoye deposit was carried out from 1937 to 1997 by the Zabaikalsky Mining and Processing Plant (ZabGOK), producing spodumene, tantalum-niobium, beryllium, and quartz-feldspar concentrates. From 1980 to 1989, the concentrator also processed ores from the Ermakovskoye fluorite-beryllium deposit and fluorspar ores from Mongolian deposits.

Currently, within the deposit boundaries, there are overburden dumps, tailings storages, and two quarry lakes (upper and lower). Over the 40 years of Zavitinskoye deposit mining, a significant amount of ZabGOK waste, estimated at 11.815 thousand tons, has been accumulated. These mining wastes suggest that the Zavitinskoye deposit can be considered a comprehensive geotechnical complex with further prospects for constructing a new concentrator and producing lithium concentrate from processed ore.

The Ermakovskoye fluorite-bertrandite-phenaclidite deposit, notable for its diverse beryllium minerals, was discovered in 1964 and is located in the Kizhinginsky district of the Republic of Buryatia (north of the Novokizhinginsky settlement). Similar to the Zavitinskoye deposit, it was open-pit mined from 1975 to 1989. The main valuable components in the ores are beryllium and spar. During the development of the deposit, approximately 60% of the explored mineral reserves were extracted. The mine is currently decommissioned, and a stagnant reservoir (lake) has formed at the bottom of the remaining quarry, approximately 70 meters deep. The Ermakovskoye deposit is also seen as a highly profitable facility for resuming beryllium mining operations.

After the closure of the aforementioned mines, no reclamation and restoration work of the mining landscape areas has been carried out. The quarry lakes of the deposits are actively used by the local population of nearby villages for recreation and fishing, and numerous instances of spontaneous waste dumping have been noted.

Hydrogeochemical testing of the technogenic reservoirs of the mentioned deposits was carried out during the summer periods from 2016 to 2023. Water samples were collected from the shoreline and central (deepwater) zones of the quarry lakes. In-situ measurements included water temperature (T, °C), pH values, and redox potential (Eh). The depth of the water bodies was measured using an echo sounder. Chemical-analytical studies of water samples were conducted according to standardized methods in the accredited laboratory of Geoecology and Hydrogeochemistry of the Institute of Natural Resources Ecology and Cryology, Siberian Branch of the Russian Academy of Sciences (Chita) and at the

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analytical center of the A.P. Vinogradov Institute of Geochemistry of the Siberian Branch of the Russian Academy of Sciences (Irkutsk).

3 Results

The obtained results on the macro- and microcomponent composition of the sampled waters from the quarry lakes of the Zavitinskoye and Ermakovskoye beryllium deposits and some of their physicochemical characteristics are presented in Table 1.

Table 1. Physical and chemical parameters and the content of macro- and certain microelements (min-max) in the waters of the Zavitinskoye and Ermakovskoye deposits quarries (mg/L).

Parameters	The quarries of the Zavitinskoye deposit		The quarry of the Ermakovskoye deposit	MPC */**, mg/dm^3
	upper	lower		
T, °C	8.9 – 22	6.9 – 21	21.5 – 21.8	n.n./n.n.
H, m	11.3	33	-	n.n./n.n.
pH	6.64 – 7.59	7.39 – 8.35	8.14 – 8.23	fon/from 6 to 9
Eh, mV	87 – 281	-30 – 157	197 – 289	n.n./n.n.
CO_2, mg / L	6.39 – 13.1	3.87 – 15.9	0.88 – 1.41	n.n./n.n.
HCO_3^-	25.9 – 46.1	109 – 152	210 – 212	n.n./n.n.
SO_4^{2-}	952 – 1276	665 – 891	167 – 186	100/500
Cl^-	13.6 – 20.2	29.1 – 41.3	1.51 – 1.58	300/350
F^-	1.04 – 1.42	0.48 – 0.60	1.51 – 1.58	0.75/1.5
Ca^{2+}	247 – 360	192 – 299	76.0 – 80.2	180/n.n.
Mg^{2+}	70.9 – 118	60.0 – 88.5	35.4 – 36.9	40/50
Na^+	22.5 – 32.2	29.2 – 41.7	8.61 – 9.85	120/200
K^+	9.87 – 15.7	7.54 – 14.4	4.33 – 6.07	50/n.n.
NO_2^-	0.009 – 0.04	0.01 – 1.42	0.15 – 0.16	0.08/3
NO_3^-	0.37 – 1.38	1.13 – 13.4	13.6 – 14.2	40/45
NH_4^+	0.07 – 0.89	0.10 – 1.43	0.16 – 0.41	0.5/1.5
Σ ions	1360 – 1843	1119 – 1501	528 – 541	n.n./1500
Si	5.11 – 8.51	1.16 – 5.28	11.9 – 12.3	n.n./20-25
Li	0.02 – 3.88	1.56 – 2.69	0.03	0.08/0.03
Be	0.003 – 0.01	0.00002 – 0.0004	0.00002 – 0.00003	0.0003/0.0002
Al	0.01 – 10.9	0.003 – 16.8	0.004 – 0.02	0.04/0.2
Cr	0.00003 – 0.0003	0.00003 – 0.0007	0.00004 – 0.0001	0.07/0.05
Mn	0.23 – 0.97	0.003 – 1.96	0.001	0.01/0.1
Fe	0.03 – 2.61	0.009 – 2.63	0.001-0.004	0.1/0.3
Co	0.000005 – 0.005	0.000001 – 0.001	0.00006 – 0.0001	0.01/0.1
Ni	0.008 – 0.04	0.001 – 0.01	0.0007 – 0.002	0.01/0.02
Cu	0.002 – 0.01	0.0004 – 0.006	0.002 – 0.005	0.001/1.0
Zn	0.19 – 0.46	0.01 – 0.06	0.01 – 0.09	0.01/5.0
As	0.0003 - 0.005	0.006 – 0.02	0.0006 – 0.002	0.05/0.01
Rb	0.04 – 0.07	0.05 – 0.07	0.008 – 0.01	0.1/ n.n.
Sr	1.76 – 3.04	2.93 – 4.36	0.30 – 0.39	0.4/7.0
Mo	0.0002 – 0.0005	0.0006 – 0.003	0.15 – 0.16	0.001/0.07
Cd	0.0005 – 0.002	0.00004 – 0.0005	0.002	0.005/0.001
Sb	0.000002 – 0.007	0.00001 – 0.001	0.0001 – 0.0003	n.n./0.005
Pb	0.0003 – 0.001	0.0001 – 0.001	0.00007 – 0.0004	0.006/0.01
U	0.02 – 0.07	0.05 – 0.11	0.009	n.n./0.01

Note. That a dash "-"- indicates no data, n.n. - means not regulated, H – depth, TR – transparency, MPC*- maximum permissible concentrations of substances for fishery water bodies [Federal norms "On Approval of Water Quality…", 2020], and MPC** - domestic drinking water use [Federal norms and sanitary rules 1.2.3685-21, 2021].

4 Discussion

Hydrochemical studies of the technogenic reservoirs of the Zavitinskoye deposit showed that the temperature regime of the water during the summer period varies from 6.9 to 22°C

(Table 1). According to our data, the maximum depths of the upper and lower quarries are 11.3 and 33 meters, respectively.

The waters of the quarries are neutral to slightly alkaline, with pH values close to background levels (pH 8.16 – Ingoda river). pH values range from 6.64 to 8.35 (Table 1). Redox potential (Eh) values also vary with depth: in the upper quarry, they range from 87 to 281 mV, and in the lower quarry from -30 to 157 mV. Based on salinity type, the water in the quarries is brackish with a mineralization level ranging from 1119 to 1843 mg/l, attributed to increased concentrations of sulfate and chloride ions, as well as calcium and magnesium cations. Chemically, the quarry waters belong to the sulfate-magnesium-calcium type.

Research results have shown that the mobility of many metals in neutral and slightly alkaline quarry waters is hindered, affecting their concentrations. In the microcomponent composition of the quarry waters, unusually high concentrations were noted for aluminum (up to 16.8 mg/l), strontium (up to 4.36 mg/l), lithium (up to 3.88 mg/l), as well as iron (up to 2.61 mg/l) and manganese (up to 1.96 mg/l) (Table 1). Elevated levels (in μg/l) were observed for Zn (464), U (106), Rb (65.7), Ni (41), As (23.9), and Cu (13.4). The beryllium content in the water was 10.1 and 0.35 μg/l for the upper and lower quarries, respectively, explained by the reduced water migration capacity of Be as the water pH values increase (>7) and its precipitation as hydroxide ($Be(OH)_2$).

Water in the Ermakovskoye mining quarry is slightly alkaline (pH 8.14-8.23) and fresh. The mineralization level does not exceed 0.54 g/l (Table 1). Eh values vary within the range of 197 to 289 mV. The chemical type of water is hydrocarbonate-sulfate magnesium-calcium.

Elevated values of molybdenum (164 μg/l) and zinc (87 μg/l) were recorded among the trace elements (Table 1). The beryllium content in the waters of the Ermakovskoye deposit ranges from 0.024 to 0.026 μg/l, and in one of the surveyed drill cores, the beryllium concentration was 1.03 μg/l. The fluoride ion (F^-) concentration in the quarry waters was 1.58 mg/l, with an overall site concentration of up to 2.34 mg/l.

For evaluating the ecogeochemical state of the quarry lakes of the Zavitinskoye and Ermakovskoye beryllium deposits, a comparison of the average concentrations of some components with their maximum permissible concentrations (MPC) has been conducted (Table 1) [Federal norms "On Approval of Water Quality…", 2020; Federal norms and sanitary rules 1.2.3685-21, 2021]. In the waters of the upper quarry of the Zavitinskoye deposit, the results showed exceeding the MPC for aquatic fishery objects for Mn (by 59 times), Li, Be, Zn, and Al (32-33 times), SO_4^{2-} (11 times), Fe (9 times), Sr and Cu (6 times), Ni, Ca^{2+}, and Mg^{2+} (2-3 times). Exceedances of the established norms were noted in the waters of the lower quarry for Mn (by 37 times), Li (26 times), Fe (9 times), Sr (8.5 times), SO_4^{2-} (7 times), Al and NO_2^- (4 times), Be and Zn (3 times), Cu (2 times), as well as Ca^{2+}, Mg^{2+}, and NH_4^+ ions (1.3–1.8 times). For the waters of the Ermakovskoye quarry, exceedances of the MPC were recorded for Mo – by 160 times; Zn – by 5 times, Cu – by 3 times; F- – by 2 times; SO_4^{2-} and NO_2^- - by 1.8 times.

Exceeding the Sanitary-hygienic standards for the waters of the upper quarry of the Zavitinskoye deposit was established for Li (by 89 times), Be (50 times), Al (6.4 times), Mn (5 times), U (4 times), SO_4^{2-}, Sb, and Fe (2.2-2.9 times), and minor excess for Cd, Ni, and Mg (1, 1.5, and 1.8 times). In the waters of the lower quarry, the MPC for Li (by 70 times), Al (20 times), Fe, and Mn (by 3.3 and 3.7 times), Be (2 times), SO_4^{2-} (1.5 times), Mg (1.4 times), and As (1 time) was exceeded. Minor exceedances of the sanitary-hygienic indicators were noted in the waters of the Ermakovskoye quarry for Mo (by 2.3 times) and Cd (by 2 times).

5 Conclusion

The analysis of conducted hydrogeochemical studies of the quarry waters of the Zavitinskoye and Ermakovskoye beryllium deposits showed that the waters in the quarries are brackish and fresh, belonging to the sulfate-magnesium-calcium and hydrocarbonate-sulfate magnesium-calcium types with neutral and slightly alkaline reactions, respectively. Significant variations in microelement concentrations in the identified water types indicate the significant role of the hydrogeochemical environment (pH, Eh, mineralization, etc.) in their dispersion or accumulation. The content in the water of some regulated components (Li, Be, Zn, Al, Mn, Fe, Sr, etc.) exceeds the MPC for fishery water bodies and sanitary-drinking indicators by several orders of magnitude. Their toxicity indicators belong to different classes of danger and therefore may have a direct or indirect toxic impact on aquatic ecosystems, landscapes, and human health.

Overall, the negative impact of waste from the development of the mentioned deposits is associated with disruptions to the natural landscapes in the form of preserved technogenic objects (quarries, tailings storage, large rock breakdowns not covered by vegetation, spontaneous dumps). The presented results are of significant importance not only for understanding the hydrochemistry of natural-technogenic systems but also for implementing measures for the ecological monitoring of similar mining landscapes. In this regard, it is necessary to inform the population of nearby villages about the consequences of using quarry waters for economic and recreational purposes.

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