Geochemistry of metals in hydrogeosystems of Dalnegorsky ore region (Primorsky territory, Russia)

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Abstract. This paper presents the research results of macro and micro components of water composition based on a complex analysis of geochemistry situation in the Rudnaya river basin. The research classifies the principal water geochemical types. It was proved that the chemical composition in the Rudnaya river mid-channel is stipulated by mining technogenesis. The research studies the concentration of rare-earth elements (REE) in water passages, draining industrial facilities, and the Rudnaya River receiving these passages.

1. Introduction

Hydrogeochemical research on Primorsky territory has been carried out since 1954 [1]. Considerable data have been collected till now, which provides evidence of seasonal variation of mineralization and composition of micro and macro ions in Primorsky waters. According to the research of Arzhanova and Elpatyevsky [2], Grekhnev et al. [3], Shulkin et al. [4], Elpatyevsky et al. [5] and Chudaeva [6], there are increased concentrations of Fe, Mn, Pb, Zn, Cd and As dissolved forms during low water behaviour of rivers with development pressure.

A hydrogeosystem maximum transformation is fixed in Dalnegorsky ore region. It is caused by concentration of various industrial facilities: Dalnegorsky borosilicate quarries, abandoned and working adits and mines of tin complex ore and argentums–lead–zinc ore, dumps of substandard ore and country rocks, disposals of sulphide ore enrichment (tailing dumps). The most considerable industrial impact was exerted on the Rudnaya river basin waters.

In connection with the prospects of the Rudnaya river basin recreational development, and this territory is supposed to possess obvious advantages for water tourism, it is very urgent to carry out a complex assessment of ecological and geochemical condition of waters in order to examine water chemical composition, spatial variability of metal concentration, rare-earth elements being among them.

2. Research

The research material was the data collected in June 2014 during hydrogeochemical sampling of the Rudnaya river and its feeders. To analyse main and rare-earth elements, 22 water samples of 1 to 1.5 litres each were selected in special plastic containers.

Sample selection and analytical research were conducted according to standard hydrogeochemical research methods [7] and regulatory documents [8]. To define macro and micro components composition of the waters, we used a wide variety of analytical methods, namely: ICP spectrometry, AAS with electrothermal atomization, atomic emission spectrometry with inductively coupled plasma...
(AES-ICP), which were exercised in “Ekoanalitika OOO” Ltd., Research Laboratory (accreditation certificate no. POCC RU.0001.516028), Vladivostok.

REE proportion was defined by mass spectrometry method with inductively coupled plasma on Agilent 7700 spectrometer in Geology Institute Analytic Centre, Far Eastern Branch of the Russian Academy of Science.

3. Drainage territory characteristics
The Rudnaya river springs from the foot of Skalisty heights on the Sikhote-Alin eastern slope and flows into the Rudnaya Bay, the Sea of Japan (Fig. 1).

The drainage area is 1,142 km², and it occupies Dalnegorsky region of Primorsky territory.

Water collection is characterized by disjointed low-hill and partly middle mountain terrain, and absolute marks vary from 0 to 800 m in the lower part, 100–1,165 m in the central part and 250–1,356 m in the upper part of the basin.

In the Rudnay river valley, there are four fluvial terraces above floodplain, each of them being represented by alluvial rubble-pebble, gravel pebble material with sand interlayer and lens, as well as loams and clays.

The bedrocks underlying alluvial deposits on the researched area are represented by upper cretaceous deposits of Arzamazovsky (K₂ar) and Monastyrsky (K₂mn₂) series, which are mainly composed of rhyolite tuffs, tuffits, aleurolites and conglomerate breccias. Andesite and felsite sheets are rarely marked.

![Figure 1. Research territory location scheme.](image)

Hydrographic net of the basin is widely developed. Many feeders flow into the river, the Gorbusha, the Monastyrka, the Krivaya and the Nezhdanka being the largest.
The Rudnaya recharge is predominantly pluvial, and the share of snow in total annual flow is minor. The recharge is due to a flow forming in the river basin as well as in the ground waters going from the water-bearing horizon of the sedimentation mass.

The Rudnaya river regime features mild spring flood of mixed type, summer and autumn high water and winter low water. Water discharge in the test period (June) was on average $4–6 \text{ m}^3/\text{s}$.

4. Results and discussion

The research of the macro component composition proved that the examined waters mainly have sulphate-hydrocarbonated and hydrocarbonated-sulphate magnesium–calcium structure.

Sulphate structure is typical for left-bank feeders of the Rudnaya, which drain the area adjacent to the tailing ponds of concentrating mills, and for those parts of the river which receive these feeders. The SO$_4$ source is sulphides; their considerable amount is in refinement tailings of polymetallic ore. Sulphate water mineralization is from 1.27 to 10.19 g/dm$^3$, pH values from 2.33 to 4.61, water hardness 18.58–46.99 mg-equ/l.

The analysis of water micro components proved that the highest concentration of elements is typical for sulphate waters.

Among the toxic elements which are beyond technogenic system and dissolved in the researched water are the following (mg/dm$^3$): Fe (0.12–4.386), Co (0.0226), Ni (0.062), Cu (0.012–0.014), Zn (0.07–3.131), Cd (0.011), Al (0.046–6.48), Li (0.006–0.0581), Be (up to 0.0021) and Mn (0.012–8.33).

In order to study the spatial variability of rare-earth elements’ (REE) concentration, the waters of a pond area at the upper level of Krasnorechensk mill tailing pond and its drainage on the lower horizons were examined. A pool, located to the north from the tailing pond, and the Rudnaya basin waters were tested (Figs. 2 and 3).

![Figure 2. Sample selection scheme in Rudnaya basin](image)

The amount of REE in different testing points varies from 110.99 to 0.315 mkg/dm$^3$, and it was proved that REE concentration in neutral and alkalescent waters is lower than in acid sulphate ones. Thus, in the alkalescent waters, a lake accumulating a natural flow of catchment the REE concentration is 0.273 mkg/dm$^3$.

In the process of infiltration through a sand mass of the tailing pond, these waters become more acidic. Ascensional circulation of pore solutions results in the formation of blood-red lakes on the surface of the tailing pond with pH 2.33–2.48, and the dissolved REE concentration is in the range of 44.97–55.5 mkg/dm$^3$. The highest REE value recorded in the drainage water of the lower part of the tailing pond amounts to 110.76 mkg/dm$^3$. 

| No. sample | Sum of dissolved REE, mkg/dm$^3$ |
|------------|---------------------------------|
| 1,047      |                                 |
| 8          |                                |
As the influx of the water flows into the Rudnaya river, the REE concentration decreases to 6.09 mkg/dm$^3$ and farther downstream to 2.4–0.315 mkg/dm$^3$. The data analysis demonstrates that the higher pH of the river waters, the lower the dissolved REE concentration. Obviously, it is due to the formation of alkaline geochemical barrier which arises with a sharp pH increase. At comparatively shorter distance, acid waters (pH 2.33) become neutral (pH 6.65–6.9) and even alkalescent (pH 7.76–8.48). In this situation various chemical elements are precipitated on alkaline barriers, rare-earth ones are among them.

A relationship between the amount of REE and a total water mineralization was recorded; the higher the amount, the higher the REE concentration in the researched waters. Thus, during 0.05–0.18 g/dm$^3$ water mineralization, the REE concentration ranges from 0.315 mkg/dm$^3$ to 6.09 mkg/dm$^3$, while with the increase in mineralization from 1.27 to 10.19 g/dm$^3$ the REE concentration changes from 44.97 to 110.76 mkg/dm$^3$.

Besides, in all examined samples the concentration of light REE is considerably higher than that of heavy ones and it varies from 77 to 83 % from the total REE amount. According to the data, light REE possess a little larger effective ionic radius, they are released easier in the dissolution process and, thus, enrich the aqueous solution more intensively. Together with this, the highest light REE concentration is recorded in acidic and highly acidic sulphate waters. It is due to the fact that pH increase causes a higher sorption of light REE on suspension particles than of heavy ones which changes the REE composition in the dissolved flow [9].

Therefore, REE proportion in the researched waters is controlled by elements chemical properties as well as acid–base conditions of the solution.

To examine REE behaviour in the water passages, their concentration values normalized to a definite standard were used. In this paper, their concentration values normalized in relation to North American shale composite were used (Fig. 4).
Figure 4. Spectra of REE concentration distribution in the Rudnaya river normalized to North American shale composite (NASC).

Almost all spectra demonstrate negative ceric anomaly. According to majority of scientists, Ce anomaly is caused by its oxidation (transition from Ce$^{3+}$ to Ce$^{4+}$). An oxidated ceric form becomes slow-moving, absorbs on solid particles and thus is removed from the solution.

The researched waters have both positive and negative europium anomalies. A positive anomaly is caused by chemical weathering of vulcanites of andesite rhyolitic formation.

An aqueous solution enrichment with europium results from its coming from plagioclases in which europium anomaly is the most strongly marked in comparison with other REE. A negative europium anomaly in the waters is caused by a low europium proportion in vulcanites that, according to the data [9], proves that plagioclase participates in melt fractionation processes.

5. Conclusion
A conducted hydrogeochemical research of natural and industrial water passages in Dalnegorsky ore region gives a reason to conclude the following:

- The river hydrogeochemical background is formed due to a surface flow, feeders, drainage technogenic facilities, mainly sulphide ore enrichment tailing ponds, and due to physical and chemical processes in the system “water-rock”.

- In the researched area acidic sulphate, neutral and alkalescent hydrocarbonated calcium-magnesium waters are formed.

- Absolute proportions of REE in the researched waters are controlled by acidic alkaline conditions of the solution and by general water mineralization.

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