

Geochemistry of Drainage Water of Darasun Ore Field Gold Deposits (Eastern Transbaikalia, Russia)

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Abstract – The paper presents characteristics of chemical and microelement composition of drainage water in dumps and the septic tank of the tailing dump in three gold ore deposits of Eastern Transbaikalia localized in a single ore field in the rocks of base composition. The ionic composition of all samples contains sulfate, and two of the samples contain nitrate-sulfate water due to explosives used during ore extraction and cyanide technology employed in gold extraction. Low concentrations of bicarbonate in water of the dumps at pH 7.27–7.36 allowed conclusion that the acidic potential should be neutralized by non-carbonate minerals of the host minerals, which requires special studies. The pH value plays a dominant role in distribution of microelements in water, however, the impact of geochemical features of ores and host rocks is also revealed, though for some elements this dependence is not found.

Keywords – gold ore deposits; drainage runoff; chemical composition of water; neutralization potential; microelements.

I. INTRODUCTION

Development of gold deposits is one of the main areas of modern mining industry in Eastern Transbaikalia, the Transbaikalia Territory according to administrative division. About ten ore gold deposits are currently developed in the region, and several more are being prepared for development or are temporary conserved. An open mining method predominates, and underground mine development is performed at two sites. Most significant environmental effects of gold and mineral mining include formation of vegetation free or sparsely covered technogenic areas and polluted surface and groundwater. The study of the drainage flow of the ore mining objects in Eastern Transbaikalia showed that hydrogeochemical systems formed under technogenic disturbance of the geological environment are characterized by different acid-base properties and, as a result, macro- and microelements, secondary mineral phases [1–3 and others]. The paper considers the features of these systems in three gold deposits of the Darasun ore field that differs from other gold deposits in localization of the base composition in magmatic rocks.

II. OBJECTS AND METHODS

The Darasun ore field is located within the boundaries of the gold-molybdenum belt of Eastern Transbaikalia highlighted by academician S.S. Smirnov (1961). It covers an area of about 60

km² and includes the Darasun and Talatuy gold ore deposits, Teremkin gold and silver deposit, Ust-Teremkin silver deposit and a number of ore occurrences. The ore field is composed of different-age magmatic rocks. An ancient substrate is represented by PZ₁ gabbroids, which are intruded and metamorphosed by Middle Paleozoic and Mesozoic granodiorites, diorites, granites, granosyenites, syenites, etc. [4].

The paper presents the results of hydrogeochemical sampling performed in July 2014. Samples of drainage dumps were collected in the Talatuy (Fig. 1, Points 1 and 2) and Teremkin (Fig. 1, Point 3) deposits, and water samples were collected from the brook Darasun (Points 4 and 5) and draining and tailing dumps (Point 6) in the Darasun deposit.



Fig. 1. Location of hydrogeochemical sampling sites of mining facilities in the Darasun ore field.

The Darasun deposit is a gold-quartz-sulphide formation of vein type. Veins are localized in granodiorites, granosyenites and gabbro-amphibolite, and are associated with subvolcanic complex (J₂-K) that includes fractured rock intrusions and mineral stocks of various compositions of high alkalinity (porphyrites diorite, granosienit-, sienit- and granite porphyry, felsites, trachyandesites, etc.). The main ore minerals are pyrite, arsenopyrite, chalcopyrite, pyrrhotite, faded ore, sphalerite, galena, and others. Vein minerals include quartz, tourmaline, carbonates, gypsum, anhydrite and barite. The deposit features a large amount of arsenopyrite in ores [5].

The Teremkin deposit is confined to the fracture zone, and it is characterized by development of explosive breccias with fragments of gabbro, granites, granofir and quartz veins with sulphides. The main ore minerals are chalcopyrite, pyrite, galena, sphalerite, bismuth minerals (native bismuth, bismuthin, aikinite, tetradimite), and lead sulfoantimonites [4].

The Talatuy deposit is located in the northern part of the ore field, 10–12 km north-west of Darasun ore field gold deposit. Mineralization is localized in hydrothermally modified igneous rocks of the Kruchinin intrusive complex (PZ₁) of base and medium composition (gabbro, gabbro-diorites and diorites). In mineralogy, Talatuy is distinguished by wide development of oxide-sulfide associations and Au-Cu-W-Mo bearing ores. The major minerals are magnetite, feldspar, quartz, pyrite, chalcopyrite, epidote, chlorite, tourmaline and phlogopite. Ore bearing gabbroids are enriched with boron, copper, rubidium, zirconium, and sulfur [4, 6].

The macro- and some microelement composition of water samples was analyzed using standard methods in the Laboratory of Geocology and Hydrogeochemistry, INREC SB RAS. Cations were determined by atomic absorption (Ca, Mg) and atomic emission (Na, K) methods in nitrous oxide/acetylene and air/acetylene flame using SOLAAR 6M spectrophotometer (England). Carbon dioxide components CO₂ and HCO₃⁻ were found by potentiometric titration; F⁻, Cl⁻ and NO₃⁻ were determined by potentiometry using ion-selective electrodes; SO₄²⁻ was found by turbidimetry in the form of BaSO₄; Si and P were determined by spectrophotometry. Salinity was calculated as the sum of cations and anions.

Microelements were determined by inductively coupled plasma mass spectrometry using an Instrument ELEMENT 2 (Finnigan MAT) at the Institute of Geochemistry of SB RAS (Irkutsk). The samples analyzed were filtered through a 0.45 μm membrane filter acidified with highly pure nitric acid. The resulting concentrations characterize the dissolved form.

The chemical type of water is named with respect to ions with a content of 20%-eq. in an increasing order according to the industry standard OST 41-05-263-86 adopted in Russia for hydrogeological works.

III. RESULTS

The macroelements dominating in the studied water are sulfate and calcium (Table I) with purely sulfate water in samples 3, 4 and 5, hydrocarbonate-sulfate water in sample 1, and nitrate-sulfate water in samples 2 and 6. With respect to the content of water cations, calcium water was found in samples 1, 3 and 6, and magnesium-calcium water was found in other samples.

Nitrate type of water is formed only when they are polluted. In this case, it is caused by explosives used in ore extraction (sample 2) and cyanides used in gold extraction (sample 6). Yurkevich et al. [7] report the concentration of CN⁻ in the fresh pulp in the Darasun concentration plant equal to 700 mg/l, and in the water of the old reservoir, where it attains 4.0 g/l.

TABLE I. PHYSICAL AND CHEMICAL CHARACTERISTICS OF WATER IN SAMPLING SITES (CHEMICAL COMPONENTS IN MG/L)

Index	Points					
	1	2	3	4	5	6
T, °C	11.5	15.9	13.1	16.5	22.4	25.3
pH	7.30	7.27	7.36	4.50	4.69	7.60
Eh, mV	186	160	150	292	218	188
CO ₂	7.92	5.06	4.18	28.6	22.4	4.84
HCO ₃ ⁻	158	65.9	75.6	0.61	1.83	47.3
SO ₄ ²⁻	359	1138	464	1200	1296	1175
Cl ⁻	1.16	4.71	0.97	22.1	23.7	40.6
F ⁻	0.25	0.34	0.33	0.13	0.29	0.78
NO ₃ ⁻	4.60	592	1.56	3.91	5.83	516
Ca ²⁺	145.9	353.2	170.3	365.5	375.3	362
Mg ²⁺	21.2	98.7	19.8	77.8	83.2	61.3
Na ⁺	18.3	19.3	8.29	34.2	33.7	64.9
K ⁺	2.42	6.51	2.60	2.78	3.11	24.7
Salinity	706	1887	742	1703	1817	1776
Si	3.2	<0.5	1.33	13.4	3.0	0.8
P	0.035	0.040	0.046	0.046	0.068	0.046

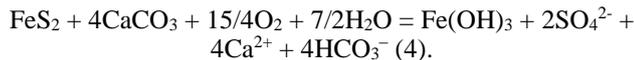
Contamination of the aquatic environment with nitrogen compounds was observed in many developed fields (Tyrynauz molybdenum-tungsten field in the Caucasus [8], Kostomuksha mine in Karelia [9], mines in Finland [10], etc.), and it is inevitable in the mining industry, where saltpeter based explosive are used. The problem of enrichment of drainage water with nitrogen compounds was the subject of special studies in the Diavik deposit in Canada [11] and at one of the ore quarries in the Urals in Russia [12], where abnormal concentrations of not only nitrates but also nitrites and ammonium were found. Therefore, along with industrial, agricultural and household types of pollution of natural water with nitrogen compounds [13], mining type should also be highlighted.

In both the gold deposits of the Baleisk ore field [1, 2] and the tungsten deposits of Eastern Transbaikalia [3], two types of hydrogeochemical systems can be distinguished with regard to the pH value – highly acidic and near-neutral and weakly alkaline water with lower metal concentrations. These differences are determined by the ratio of the acid-producing and acid-neutralizing potentials of ores and host rocks. Pyrites are considered to be the main agents of the acid-producing potential, and carbonates, in particular calcite, are the agents of the acid-neutralizing potential. Reaction (1) or the corresponding one (with the same proportions of the molar coefficients) is used to assess the acid potential, and reaction (2) or (3) is used to assess the neutralization potential [14]:



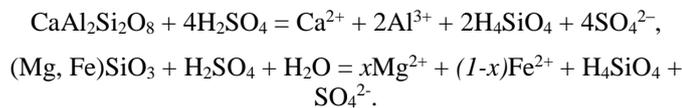
Hence, to completely neutralize the acidity, the molar ratios of pyrite and carbonate should be equal to 1:1 or 1:2. According to [15], reaction (2) is limited to pH 6.4, that is, the first dissociation constant for carbonic acid. In fact, formation of bicarbonate begins at pH 4.3, whereas prior to that, carbon in the form of CO₂ primarily passes into the gas phase. This explains insignificant concentrations of HCO₃⁻ in samples 4 and 5 (Table I) with a small but the highest for this sample content of CO₂.

The study by Castendyk et al. shows other pyrite/calcium ratios in the total reaction of pyrite oxidation and neutralization of the resulting acidity by calcite with Fe³⁺ hydroxide precipitated at pH > 6.0 [16]:



As can be seen, the ratio of pyrite and calcite is equal to 1:4, and the ratio of reaction products, sulfate and bicarbonate, is 1:2. Table I does not provide data on the ratio of SO₄²⁻ and HCO₃⁻ in drainage water of the dumps of the Talatuy and Teremkin deposits at pH 7.27–7.36 corresponding to reaction (4). The ratio is 359:158 = 1:0.44 (sample 1) at the maximum concentration of hydrocarbonate, and the ratio is 1: 0.06 (sample 2) at its minimum concentration. It is obvious that deacidizing minerals in these deposits are not carbonate. According to the quantitative mineralogical analysis of technological samples, the content of carbonates in the ores of the Talatuy deposit is insignificant, while the content of pyrites and chalcopyrites is 7–9 and 6–9 wt.%, respectively. In addition, ore-containing gabbroids contain up to 2.13% of sulfide sulfur [6]. High content of sulfates in the drainage water of the dumps indicates active oxidation of sulfide minerals.

We assume that low concentrations of CO₂ and HCO₃⁻ in drainage water show that sulfuric acid decomposition of host rocks is the main process for neutralization of the acidity resulting from oxidation of sulfide minerals. The possibility of this process is evident from the reaction of the interaction of rock-forming minerals of anorthite and hypersthene with sulfuric acid:



The reality of these reactions is confirmed by high concentrations of calcium, which, based on the above data on HCO₃⁻, is taken from the host rocks, and aluminum. The concentrations of Al in acidic water amount to tens and hundreds of mg/l. As pH increases up to more than 5.0, Al is removed from the solution to background concentrations not in the form of Al(OH)₃ hydroxide but in the form of kaolin or aluminum silicates (smectites), which does not cause secondary acidification of the system. In the diagrams of mineral equilibria, the stability fields of gibbsite and kaolin are separated by a line at the point of the H₄SiO₄ content of about 10–4.25 mol/l or 5.4 mg/l (1.6 mg/l Si).

Lawrence and Scheske attempted to determine the contribution of non-carbonate minerals to the neutralization potential [17]. The results obtained were critically evaluated by Paktunc [18], firstly, because of the use of not actual, but calculated mineral composition of the rock, and secondly, because of the relative dissolution rates of minerals used in the calculations. Thus, anorthite value in [17] is taken as 0.4 with respect to calcite, whereas in [18], the value experimentally obtained at pH 5.0 is equal to 0.018, and for other poorly soluble minerals, it is smaller by several orders of magnitude. Therefore, the neutralization potential of non-carbonate minerals is low and insufficient to neutralize the acid potential

of sulfide deposits. What provides the neutralization potential in our case? There are no other sources except for rock minerals.

TABLE II. CONCENTRATIONS OF MICROELEMENTS IN WATER SAMPLES (μG/L) DETERMINED BY ICP MS METHOD

Element	Points					
	1	2	3	4	5	6
Li	10.7	19	389	39	32	42
Be	0.012	0.015	1.48	0.56	0.23	0.0054
B	22	10.2	16	320	303	679
Al	32	13.3	32	2311	548	11.7
Sc	0.0058	0.025	0.029	0.13	0.024	0.007
Ti	1.32	5.9	0.82	7.6	5.7	6.2
V	0.15	0.19	0.076	0.034	0.052	0.11
Cr	2.77	16	1.33	20	14.9	16
Mn	5.6	738	502	5082	5138	685
Fe	30	55	2327	2126	1894	78
Co	0.27	22	1.05	82	81	13.4
Ni	0.91	30	1.54	89	82	36
Cu	9.6	16	1.96	2388	1245	302
Zn	7.2	38	30	3083	2653	37
As	0.66	0.59	0.63	21	21	18
Se	1.01	22	0.065	0.4	0.29	1.28
Br	5.51	22.9	13.3	31.4	25.9	53.1
Rb	12.9	19.5	17.5	12.1	11.2	56.8
Sr	1241	2130	1845	3227	2938	2778
Y	0.14	0.47	0.25	11.6	7.14	0.07
Zr	0.16	0.1	7.16	0.11	0.04	0.1
Mo	116	9.17	0.94	1.44	1	25.9
Ag	0.021	0.17	4.39	0.55	0.28	0.82
Cd	1.45	0.97	0.35	14.7	13.3	0.64
Sb	1.14	0.74	0.93	8.3	22	9.6
Ba	30	38	117	23	27	64
La	0.091	0.75	0.05	12.5	9.7	0.08
Ce	0.089	0.65	0.071	23	15	0.085
Pr	0.017	0.062	0.0077	2.42	1.43	0.0088
Nd	0.077	0.23	0.031	9.7	5.3	0.033
Sm	0.016	0.035	0.0075	1.88	0.88	0.0082
Eu	0.004	0.012	0.0041	0.48	0.24	0.0058
Gd	0.02	0.058	0.007	2.75	1.44	0.0077
Tb	0.0031	0.0071	0.0016	0.38	0.17	0.0016
Dy	0.019	0.035	0.014	2	0.94	0.0053
Ho	0.0037	0.0093	0.0034	0.4	0.2	0.0017
Er	0.013	0.026	0.014	1.01	0.48	0.0055
Tm	0.0017	0.0028	0.0019	0.13	0.057	0.0005
Yb	0.011	0.019	0.014	0.81	0.32	0.0031
Lu	0.002	0.0025	0.0024	0.13	0.048	0.0006
W	0.21	0.09	0.013	0.076	0.09	2.82
Re	0.69	0.46	0.0008	0.71	0.63	0.52
Pb	0.13	0.26	0.47	16	6.4	0.3
Th	0.0066	0.018	0.0098	0.023	0.015	0.0036
U	24	14.5	0.26	1.77	0.15	2.77

The distribution of microelements reveals the dependence of drainage water of ore deposits on the pH value – the highest concentrations of most elements can be observed in acidic water (Table II). At the same time, the sample from Teremkin with neutral and weakly alkaline pH values close to those in the samples from the Talatuy and the tailing dump of the processing plant is distinguished by maximum concentrations of Li, Be, Fe, Zr, Ag, Cs, and Ba at minimum Se, Br, Mo, Cd, light REEs (La–Gd), and Re. This is determined not only by water-migration characteristics of the elements, but also by geochemical characteristics of the ores and host rocks. The Ag maxima for

Teremkin and the Mo maxima for Talatuy are extremely significant. The enrichment of Darasun ores with arsenopyrite was not found in hydrogeochemical associations. This is likely due to formation of arsenates. Concentrations of boron and zirconium in the dump water of Talatuy are also at the background level, which can be attributed to poor solubility of the minerals containing these elements (tourmaline, zircon).

The concentrations of REEs in drainage water primarily depend on acid-base properties of the aquatic environment, and in acidic water, they are more than two orders of magnitude higher. The normalized spectra of lanthanides in acidic water are almost identical to a relatively rare peak in gadolinium (Fig. 2). For samples with a neutral and slightly alkaline medium, the spectra are individual, excluding complete identity of samples 3 (Talatuy) and 6 (tailing dump) from La to Tb with a positive Er anomaly. The discrepancy in the spectra of heavy REEs in these samples is most likely due to the concentration level in the sources of loss.

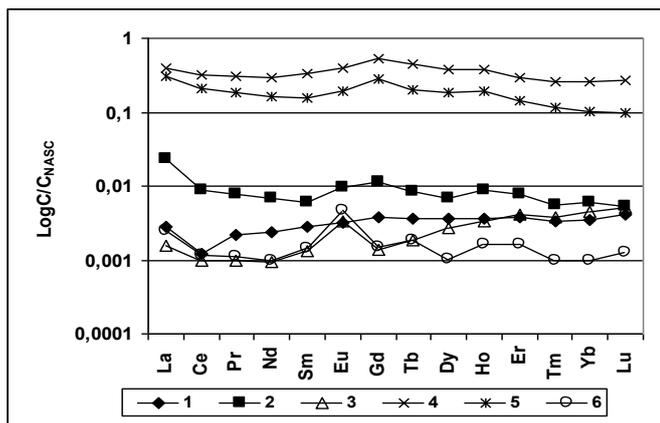


Fig. 2. Spectra of rare-earth elements normalized to NASC in the water of technogenic facilities of the Darasun ore field. Sample numbers correspond to Fig. 1 and Tables.

IV. CONCLUSION

Thus, in the considered deposits of the same industrial type, during their development, two types of hydrogeochemical environments are formed with different acid-base characteristics and the level of concentrations of ore and related chemical elements. The neutral environment of drainage water of sulphide-containing dumps with a low content of carbonates in ores and host rocks is due to acidity neutralization by rock-forming non-carbonate minerals, which requires further special studies.

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