17th INTERNATIONAL MULTIDISCIPLINARY SCIENTIFIC GEOCONFERENCE
S G E M 2 0 1 7

CONFERENCE PROCEEDINGS

VOLUME 17

ECOLOGY, ECONOMICS, EDUCATION AND LEGISLATION

ISSUE 52

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ECOLOGY AND ENVIRONMENTAL PROTECTION

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29 June - 5 July, 2017

Albena, Bulgaria

ACID ROCK DRAINAGE PREDICTION FOR HOST ROCKS OF PORPHYRY COPPER DEPOSITS IN THE BAIMKA ORE TREND (STATIC AND KINETIC TESTS)

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ABSTRACT

One of the main problems in the exploration of porphyry copper deposits is the process of acid rock drainage and metal leaching (ARD/ML), that develops during storage enclosing rock in a dump. ARD/ML is formed by the natural oxidation of sulfide minerals exposed to air and water. It leads to the production of acidic, sulfate waters and results in the heavy-metal contamination of surface and ground natural water. Standard procedures for the evaluation of waste rocks ARD/ML potential are static and kinetic tests. Static tests are used as a screening tool in the ARD prediction and include: 1) acid-base accounting (ABA) test as base; 2) multistage net acid generation (NAG) test; 3) short-term leach test that definition readily soluble components of rocks. Kinetic test (Humidity Cell Test) is used to predict long-term weathering rates and to estimate the lag time to the starting of acid generation. This study for the ARD prediction for host rocks of porphyry copper system deposits situated in the Baimka ore trend, Western Chukotka, Russia. 25 samples of enclosing rocks were collected for static tests and 3 of them (by received static tests results) for kinetic test. The mineralogy of samples was determined by scanning electron microscopy (SEM) and powder X-ray diffraction (XRPD). Trace elements were obtained by portable energy dispersive X-ray fluorescence (EDXRF) using Niton FXL-950 and inductively coupled plasma atomic emission spectrometry (ICP-AES). Content of metals in tests solutions were analyzed using inductively coupled plasma mass spectrometry (ICP-MS). All tested samples were classified as potentially acid-generating (PAG) based on the Neutralizing Potential Ratio (NPR), detected by results of static tests. But in the long-term period (30 weeks) there are no signs of acid formation: acidity (pH) of weekly leachates varies in the near neutral range (6.9-7.7).

Keywords: Acid rock drainage, acid-base accounting, net acid generation, Humidity Cell Test, porphyry copper system

INTRODUCTION

Ore objects of Baimka trend (Peschanka deposit and mineralization of Nakhodka ore field) are classified as highly profitable for development, large-volume copper-porphyry

deposits with high-tech complex ores. The Baimka trend is located in the southeastern part of the Oloi metallogenic zone and its Cu-Mo-Au porphyry ore objects are related to early Cretaceous Egdykgich Complex, whose monzonitic bodies intrude into the Upper Jurassic volcanic and volcanic-sedimentary sequence, causing extensive hydrothermal transformations of host rocks [1]. The porphyry Cu-Mo mineralization is associated with the potassic and quartz-sericite zones, that contains stockworks of quartz veins and veinlets with bornite, chalcopyrite, molybdenite and pyrite. Secondary enrichment zone with bornite and chalcozine is developed in some areas, secondary minerals are represented by magnetite, hematite, sphalerite, galena, native copper.

The high sulfidity and large volumes of porphyry Cu-Mo mineralization are determine the composition of the surface waters of the territory (figure 1). Draining water characterized by low pH (3,5-4,5), sulfate magnesium and calcium-magnesium composition, medium or high mineralization (0,5-2,2 g/l, max - 25 g/l). These waters are acidic high-metal by the relation between the complex of metals and the pH value [2]. The concentration of dissolved copper forms in the acid drainage zone are 2.2-15.9 mg/l, maximum - 24.6 mg/l. Migration of copper is carried out in the form of free ions and sulfate complexes (according by thermodynamic calculations with used HCh v.4.3) [3,4].

According to [2] in estuary of such waterways form mixed water, which are characterized by elevated concentrations of sulfates and total mineralization (up to 0.33 g/l) at neutral pH value (6,2-6,4) and low concentrations of base metals.

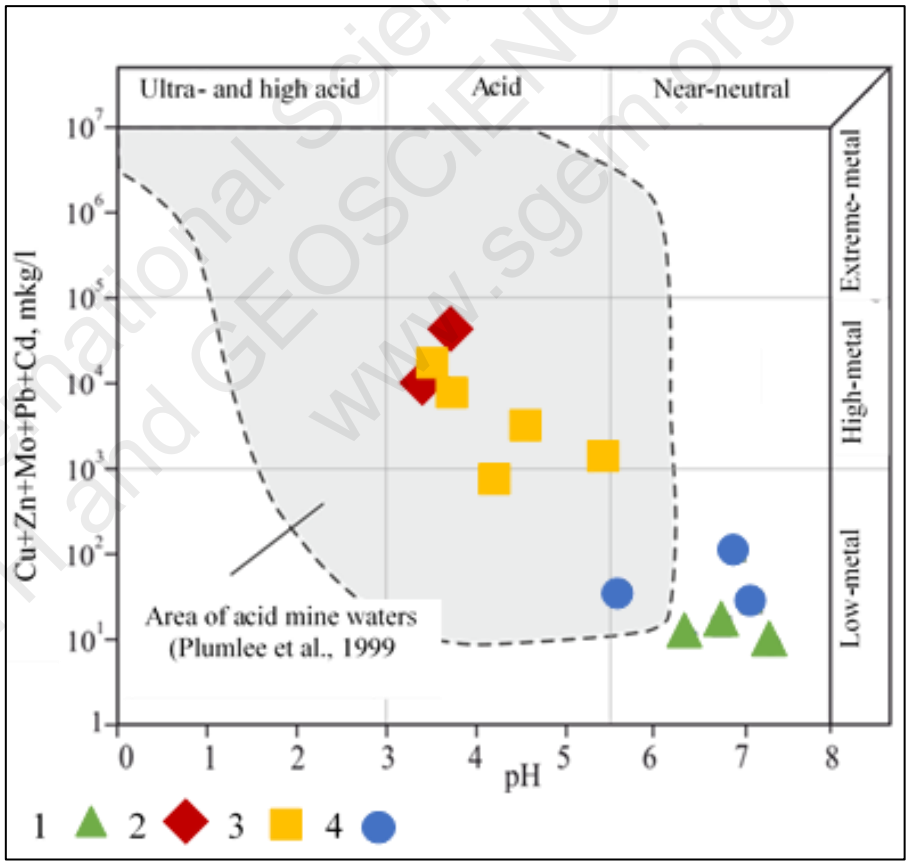

Figure 1. *Ficklin diagram showing composition of surface natural water for Baimka ore trend (by* [3], *with changes)* 1– Surface waters of background plots; 2 – Acid mine waters;

3 – Surface waters of porphyry Cu-Mo mineralization zone; 4 – Surface waters of mixing zone

Surface waters of background plots are characterized by neutral pH (6,5-6,7), sulfate-hydrocarbonate calcium composition and low mineralization (0,06-0,16 g/l). The copper concentration does not exceed 10 μg/l, and its main form in solution is the fulvate complex [3].

The acid generation processes are the main ecological problem by the development of sulfide deposits. Their activation at the extraction and storage of the sulfide-containing host rocks on the surface leads to formation acid rock drainage and metal leaching (ARD/ML) and to decrease in quality of surface waters and the degradation of the ecosystem generally. In world practice, the ARD prediction during the storage of geological materials is carried out at the exploration stage of deposits. A full review of the ARD assessment is provided in the manual to the forecast of the chemical composition of drainage from sulfide-containing geological materials [5].

MATERIALS AND METHODS

In this study total 23 samples of drill core of host rock were collected for geochemical investigations from the drill holes of the Baimka ore trend. All samples were tested for trace element analysis by portable energy dispersive X-ray fluorescence (EDXRF) using Niton FXL-950 and inductively coupled plasma atomic emission spectrometry (ICP-AES). The mineralogy of samples was determined by scanning electron microscopy (SEM) and powder X-ray diffraction (XRPD).

Standard procedures for the evaluation of waste rocks ARD/ML potential are static and kinetic tests.

Static tests allow to estimate the total potential of geological materials for acid generation and, in accordance with [5], consists of: 1) acid-base accounting or ABA test (determination of paste pH by potentiometric method, content of sulfide sulfur and carbonate carbon by LECO, calculation the acid-producing potential (AP, t $CaCO_3$/1000 t) and the neutralizing potential (NP, t $CaCO_3$/1000 t); 2) experimental determination of net acid generation of geological materials (multistage NAG-test) by accelerating the oxidation of sulfides with hydrogen peroxide in few stages; 3) determination of the readily soluble constituents of geologic materials by water extracts in static mode (Short-Term Leach Test).

The classification of host rocks was carried out, in accordance with [5], by the values of the neutralization potential ratio (NPR), equal to the ratio of NP to AP.

Kinetic tests are used to predict the rate of acid production. They are represented an imitation of weathering in laboratory conditions. Both acid generation and metal leaching can be evaluated through kinetic testing. In this study we use the Humidity Cell Test (HCT) by ASTM D5744-13, Protocol B [6]. The experiment consists of a weekly interaction of core samples (crushed to a size <6.3 mm) and a fixed volume of distilled water, followed by collection and analysis of the weekly leachates (pH, conductivity, main components). Content of metals in weekly leachates were analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

Research is carried out on the basis of the laboratory complex of the Department of Geochemistry of the Geological Faculty of the Lomonosov Moscow State University.

RESULTS AND DISCUSSION

The ABA test results

The ABA test results are summarized in Table 1. Generally, host rocks of Baimka ore trend are characterized by alkaline and near-neutral paste pH (7,2-8,5), except tuff-aleurolites of pyrite zone, that differ by low pH (3,6).

The concentrations of total sulfur and sulfide contents were measured as part of the ABA test. Sulfide content is high for all studied samples, average concentrations for different types of host rock ranges from 5,5 wt % to 23,8 wt %. The highest average concentrations observed in the tuff-aleurolites (pyrite zone) samples and the lowest average concentrations observed in the diorite samples.

At the same time, studied host rock samples show a relatively narrow range of carbonate carbon content (0,1-0,8 wt%), one or two orders less than sulfide content.

The AP, in accordance by [5], is calculated from the sulfide content by follows formula: AP (t $CaCO_3$/1000 t) = 31,25 · $S_{sulfide}$. Similarly, the NP is calculated from the carbonate carbon content by follows formula: NP (t $CaCO_3$/1000 t) = 83,3 · $C_{carbonate}$ [5]

High amounts of sulfide combined with the presence of iron sulfides in host rocks cause wide range of AP values (173 - 743 t $CaCO_3$/1000 t). Low neutralizing rock capacity (NP from 7 to 67 t $CaCO_3$/1000 t) lead to the high probability of acid rock drainage (for all samples NPR <1). Thus, based on the NPR values, all tested samples were classified as potentially acid-generating (PAG) [5].

Table 1. *Results of Acid-Base Accounting for host rocks of Baimka ore trend*

Lithology (namber of sample)	**pH_{paste}**	**Sulfur species (wt %)**		**$C_{carbonate}$ (wt%)**	**Potentials (t $CaCO_3$/1000 t)**		***NPR***
		Total	**Sulfide**		**NP**	**AP**	
Monzodiorite, monzodiorite porphyry (8)	8,1	9,4	6,8	0,3	21	211	0,1
Diorite (8)	7,2	6,3	5,5	0,5	40	173	0,2
Tuff-aleurolites (pyrite zone) (3)	3,6	>10,0	23,8	0,1	7	743	0,02
Lava and tuff-lava of andesite and andesite basalt (4)	8,5	7,3	11,3	0,8	67	352	0,2

The NAG test results

The verification of the obtained data was carried out by procedure of multistage NAG-test [7]. This is a static ARD prediction tool, corresponded a real acid forming potential. It involves the addition of hydrogen peroxide to a pulverized sample of host rock to oxidize reactive sulfide minerals, followed by measurement of the solution pH after 24 hours. A NAG pH less than 4,5 indicates that sample is acid produced, a NAG pH more than 7,0 indicates that sample is non-acid produced. If sample is defined as acid produced,

directly evaluate the generation of sulfuric acid by host rocks should by back titration to a neutral pH using hydroxide. The amount of acidity consumed is reported in tons of calcium carbonate per 1000 tons of host rock. The cycle should be repeated until there is all reactive sulfide minerals are oxidized and the NAG pH is more than 4,5 after 24 hours.

The results of the multistage NAG test for samples with different contents of sulfide are shown on Figure 2.

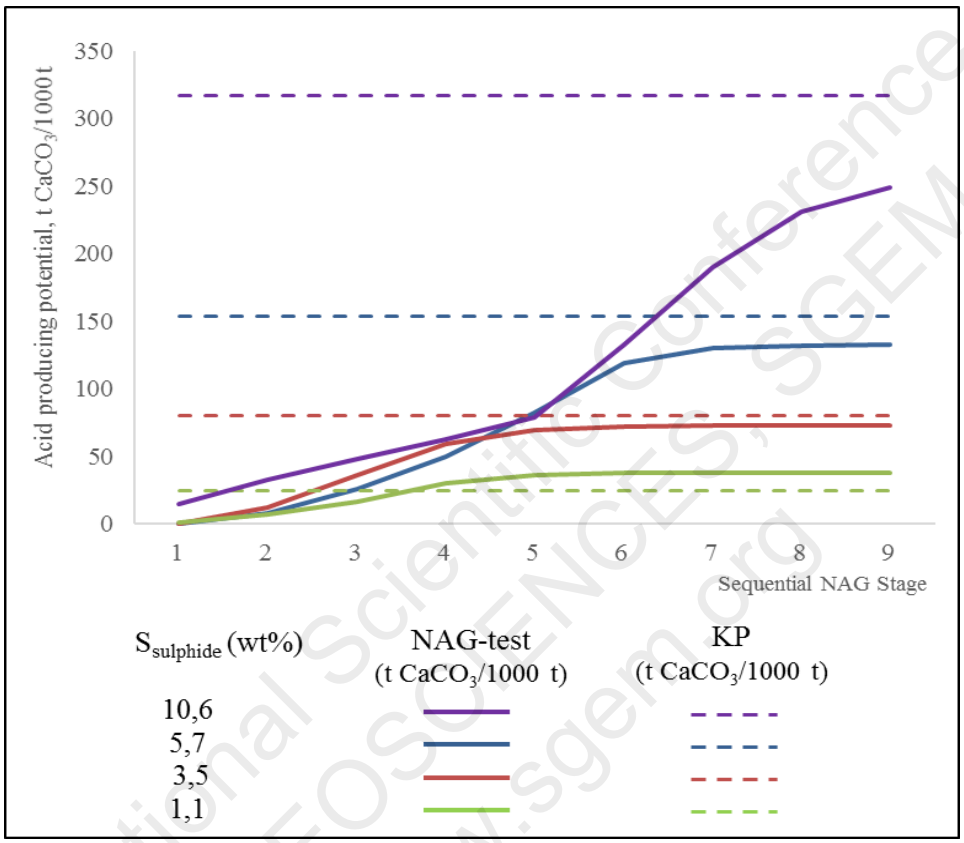

Figure 2. *The results of the multistage NAG test of host rock of Baimka ore trend with different contents of sulfide*

The results indicate that a single application of such strong oxidant as hydrogen peroxide does not confirm the high AP value of the host rocks as determined by the ABA test. The process of oxidation of sulfides develops over time and for host rocks with a sulfide content of less than 5% the achievement of calculated AP values occurs in the 4-5 stage of the multistage NAG test; further formation of sulfuric acid does not occur with the interaction of the oxidant.

For rocks with a sulfide content of 5-10% - the achievement of calculated AP values occurs in the 7-8 stage of the multistage NAG test, however, the experimentally determined total amount of sulfuric acid is slightly lower than the calculated data. The missing acidity, likely, is due to non-acid forming sulfides, which fall within calculation AP, therefore its value is overestimated.

For rocks with a sulfide content is more than 10%, it was not possible to achieve complete oxidation of sulfides, the formation of sulfuric acid continued in the 9th stage of the multistage NAG test also.

Thus, the absence in reality of such oxidizing conditions as were created during the multistage NAG test allows to speak about overassessment of the host rocks acid-producing potential established during the ABA test.

The Short-Term Leach test results

The composition of potential drainage water corresponds to the composition of water extracts from the host rocks (Short-Term Leach Test, according to [5]), in the first approximation. The composition of filtrates is obtained in the static mode, hydrocarbonate-sulfate calcium and magnesium-calcium with alkaline and near-neutral pH (6,6-7,8) and mineralization 0,3-0,4 g/l, except the tuff-aleurolites (pyrite zone). The composition of water extracts for this type of host rock is differ by elevated to 1 g/l mineralization, sulfate calcium-magnesium composition and pH values of 3,3 to 4,8.

The Humidity Cell Test results

The study of the dynamics of the composition of potential drainage waters and the rate of acid formation is carried out during the simulation of weathering (HCT, [6]) in the laboratory for three samples of host rocks selected according to the results of static tests. Despite the high probability of formation of acid rock drainage, established during static tests for these samples (NPR values less than one), there are no signs of the process of ARD/ML. At the moment, 36 cycles of weekly "water-rock" interaction have been carried out. The results of the HCT for host rocks of Baimka ore trend are shown on Figure 3.

As shown on the figure 3 (A), the pH of the leachates varies in the near-neutral range (6,9-7,7) throughout the all testing period. Data on the specific electrical conductivity of weekly leachates indicate that the main removal of readily soluble salts occurs in the first 4-6 weeks (fig.3 (B)).

The results of kinetic testing, on the whole, confirm the data of static Short-Term Leach test. The main anion of W0 filtrate is the sulfate ion, calcium and magnesium play a major role among the cations (fig.3 (C, D)).

Over time, the sulfates and products of hydrolysis of sodium- and potassium-containing silicates, those present in the host rocks, are washed out. This ensures a short-term increase in the content of sodium and potassium cations in the composition of weekly filtrates (fig.3 (D)) and an increase in the role of the hydrocarbonate ion in the anionic composition (fig.3 (C)). As a result, the composition of the filtration is changed by sulfate-hydrocarbonate magnesium-calcium.

Absence ARD processes leads to absence total metal leaching. The elements, migrating in a near neutral and slightly alkaline waters (wolfram, vanadium, cobalt, cadmium, manganese, copper, molybdenum, arsenic, stannum, zinc) are predominantly washed out in the first weeks. Concentrations of another metals in weekly leachates generally stable or slowly decreasing over time.

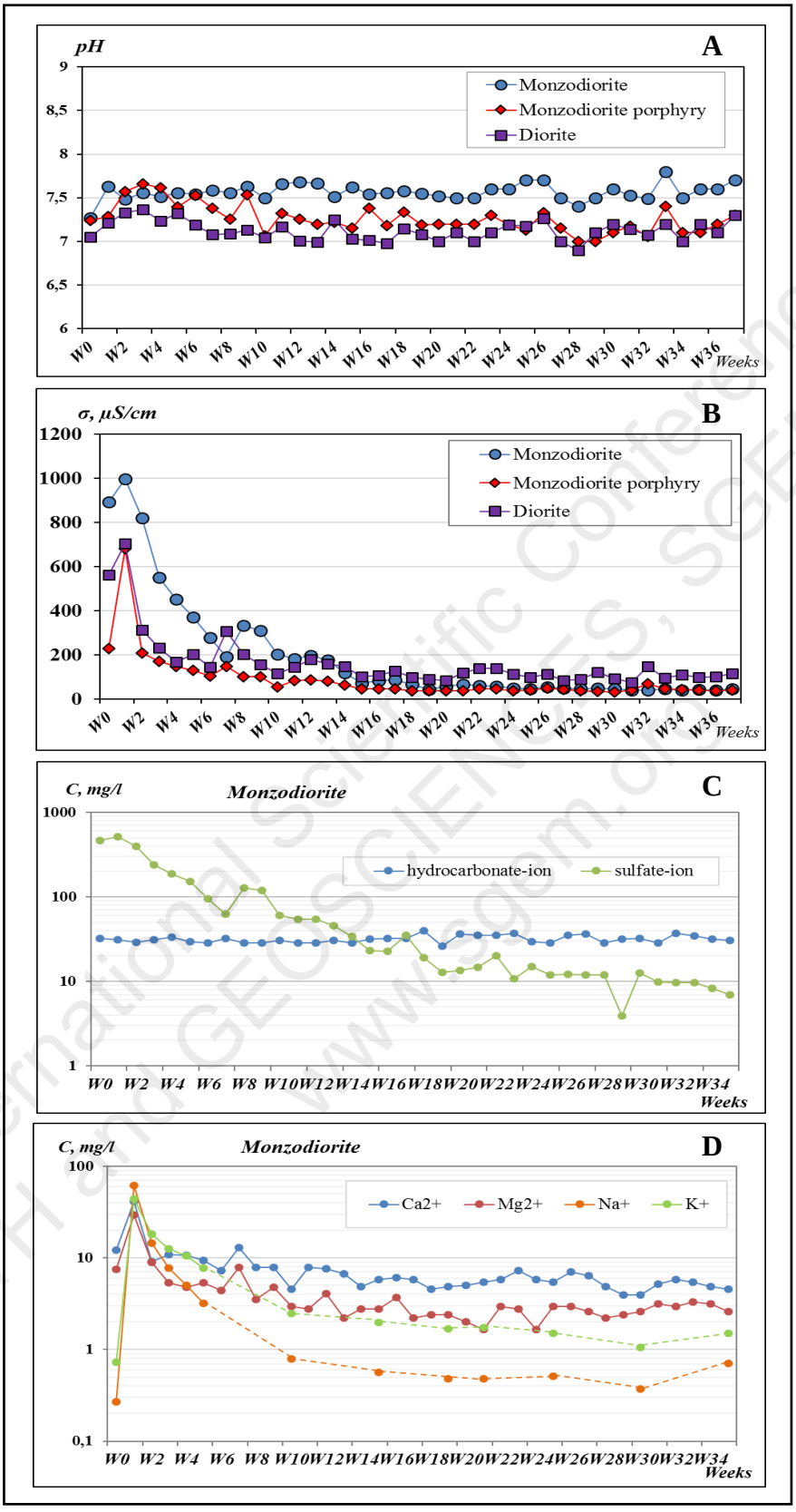

Figure 3. *The results of the Humidity Cell Test for host rock of Baimka ore trend:* **A** *- leachate pH values;* **B** *- leachate electrical conductivity values;* **C** *– leachate anionic composition;* **D** *- leachate cationic composition*

CONCLUSION

As a result of this paper, both the assessment of the potential of acid formation and the neutralizing capacity of the host rocks for the Baimka ore trend have been carried out and data have been obtained on the possible composition of acidic drainage waters when the rocks will be stored in dumps.

The total acid-producing potential of the host rocks of the Baimka ore trend, determined during the static ABA-test, is estimated as high, the NPR values for all rock types are less than one. It is indicating a significant probability of formation of acidic high-metal drainage waters when the rocks will be stored in dumps.

The study of the dynamics of the composition of potential drainage waters and the rate of acid formation is carried out during the simulation of weathering in the laboratory for three samples of host rocks selected according to the results of static tests. The pH values of the weekly filtrates from the rock samples remain at the level of 7.0-7.7 over the experimental period (36 weeks). Data on the specific electrical conductivity of solutions indicate that the basic removal of readily soluble salts occurs in the first 6-7 weeks of the cyclic "water-rock" interaction, while the anionic composition of the filtration water is replaced from sulfate to hydrocarbonate, the change in the cation composition is due to the rapid removal of sodium and potassium from rocks.

The obtained data allows to assert that there is no activation of acid flow formation processes in the long-term period despite the high potential of acid formation of the host rocks of the Baimka ore trend, established according to the results of the static ABA test. An experimental study of the dynamics of the composition of filtrates continues now.

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