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ACID GENERATION AND METAL LEACHING POTENTIAL OF SULFIDE-BEARING ROCKS IN THE VERHNE-KRICHALSKAYA AREA (WESTERN CHUKOTKA, RUSSIA)

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ABSTRACT

The natural oxidation of iron-sulfide minerals (mainly pyrite) contained in mine waste material can produce the acid rock drainage (ARD). It leads to low acidity, high sulfate and iron concentration in surface and ground water and its heavy-metal contamination.

This study investigates ARD prediction for sulfide-bearing mine waste rocks in the Verhne-Krichalskaya area, where the epithermal gold-silver deposit is located (Western Chukotka, Russia). Twenty samples of waste rocks (altered dacites, andesites and rubblerocks) were collected by drilling during exploration and analyzed to estimate their risk of acidic and contaminated drainage. Geochemical tests included acid-base accounting tests, total-metal contents tests and multiple water leach tests. Trace elements were obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES). Multiple water leachates were analyzed using potentiomentry, conductivity measurement, titration analysis, and inductively coupled plasma mass spectrometry (ICP-MS) to analyze contents of dissolved toxic elements.

According the results, altered dacites and rubblerocks generally must be considered as potentially or possible acid generating (PAG or Uncertain) compared to altered andesites which are mainly non-acid generating (Non-AG). Concentrations of some toxic elements (primarily, Al, As, Sb, Mo) in leachates are much above the Environmental design limits (EDLs) used for fishery water quality assessment.

Keywords: acid rock drainage, acid-base accounting, metal leaching potential, epithermal gold-silver deposits, Chukotka

INTRODUCTION

Sulfidic ore deposits represent a potential hazard to environment. During exploration a rapid oxidation of large masses of sulfide-bearing mineralized rocks and mine wastes can produce the acid rock drainage (ARD). It leads to low acidity, high sulfate and iron concentration in surface and ground water and its heavy-metal contamination so adversely affecting water quality.

ARD prediction based on the assessment of acid and metal leaching potentials for geological materials (such as waste rocks, mine wastes, tailings) is indispensable to develop the waste management plan for mine sites. Standard procedures for ARD

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assessment include static and kinetic tests for geological materials to determine their risk of acid generation. Samples for investigation are usually collected by drilling during exploration. Static tests are a screening tool in the ARD prediction and include the acid-base accounting (ABA) test, trace element analysis and short-term leachates [2, 3]. Kinetic tests (for example, [1]) simulate the weathering to estimate the oxidation rate of sulfides and realize in field or laboratory conditions.

This study investigates the acid generation and metal leaching potential for sulfide-bearing rocks of the Verhne-Krichalskaya area (Western Chukotka, Russia). This area comprises the Klen gold-silver deposit and some perspective ore fields. Their exploration should provide the increment of reserve base but can lead to negative changes of environment.

BRIEF OBJECT REVIEW

The Verhne-Krichalskaya area is situated on the North-East of Russia, in Chukchi autonomous district, 300 km to Bilibino city. In topography the area is represented as lowlands. It's located in cryolitic zone. The hydrographic network belongs to the Bolshoy Anuy drainage basin and includes upper streams of the Srednyaya river, the Rakovskogo river, the Krichalskaya river and its numerous creeks.

In metallogeny the Verhne-Krichalskaya area is part of the Oloi metallogenic zone included to the Verchoyano-Chukotskaya metallogenic province. It comprises the Klenovskoe ore field with the eponymous gold-silver deposit (its reserves were estimated as 18.6 t and 43.8 t for Au and Ag respectively) and some perspective ore fields (the Eol, the Unost', the Ikar, the Yasen', etc.).

In geology the Verhne-Krichalskaya area are folded from rocks of the Early Cretaceous – the Upper Jurassic volcano-plutonic complex (intrusive Hetachan gabbro-diorite-granodiorite; subvolcanic Elchechan basalt-rhyolite and Krichalsky rhyolite basaltic). Gold mineralization is related to altered propylitic and argillic rocks.

Quaternary (Q) fluvial and fluvio-lacustrine deposit is represented by pebble gravels (mainly), sands, loamy sands, loams and peats (fragmentarily). To the Upper Quaternary deposit stream gold placers are confined (reserves of one have estimated as 20-250 kg).

MATERIALS AND METHODS

Total of 20 samples of underground waste rocks from drill holes were collected for geochemical investigations. These samples characterize the altered rocks (dacite, andesite and their rubblerock) from the Unost' field and the Ikar field located in central and east ends of the Verhne-Krichalskaya area respectively. Sampling was provided by 5 samples of argillic dacites, 5 samples of propylitic dacites, 2 samples of argillic andesites, 4 samples of propylitic andesites, and 4 samples of their rubblerocks.

The mineralogy of samples was determined by scanning electron microscopy (SEM). All samples were tested for trace element analysis and acid base accounting (ABA-test). Metal leach tests were made for 9 samples (in five-stage to estimate the rate of metal eluation).

Trace elements were obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES) after oxidizing digestion in multi acids.

Acid Base Accounting was used to class the rocks on their acid generation potential. It included the determination of pH (in paste), the neutralization potential (NP) and the acid potential (AP), and the calculation of the neutralization potential ratio (NPR). Results of ABA (NP and AP) were expressed in $CaCO_3$ equivalent kg/ tons of material.

Acidity (pH in paste) was conducted by potentiomentry (the ratio of liquid to solid phase was 1:1).

The NP was made by modified [5]. The NP-test involved the addition of 0.1 N hydrochloric acid (volume 100 ml) to sample weight 2 g and the heating of solution at 80-90°C for 1-2 hours to complete the reaction (i.e. no further evolution of gas bubbles). Then the solution was back titrated to pH 6.2 to determine the amount of HCl consumed. The consumed amount of HCl was converted to units of kg $CaCO_3$/t. Relative standard deviation (RSD) was average less than 5% and 1% (to the NP estimated as less than 100 kg $CaCO_3$/t and more than 100 kg $CaCO_3$/t respectively).

The AP, in accordance to [5], was calculated from the sulfur content as:

$$AP\ (kg\ CaCO_3/t) = 31.25 \cdot S\ (\%).$$

Interpretation of ABA-test results was based on evaluation of the neutralization potential ratio (NPR=NP/AP) according to the guidelines recommended by MEND [3] and described below (Table 1).

Table 1: Acid Generation Potential Classification [3]

Acid Generation Potential	Criteria	Comments
Potentially Acid Generating	$NPR < 1$	Potentially acid generating unless sulphide minerals are non-reactive (PAG)
Possibly acid generating (or Uncertain)	$1 \le NPR < 2$	Possibly acid generating if NP is insufficiently reactive or is depleted at a rate faster than sulphides (Uncertain)
Non-Acid Generating	$2 \le NPR$	Not expected to generate acidity (Non-AG)

Metal leach tests are commonly used as a screening tool to identify leachable metals which may require further evaluation. These leach tests are designed to measure the interaction with meteoric water.

Multiple leach tests were conducted on 9 samples of waste rocks (2 samples of argillic dacites, 2 samples of propylitic dacites, 1 sample of argillic andesites, 2 samples of propylitic andesites, and 2 samples of their rubblerocks). In our study the ratio of liquid to solid phase was 5 to 1. Solids material crushed to size less 2 mm and de-ionized water were combined and shaken for an hour and were left to stand for 24-hours period. Then leachates have been filtered to get a solution and solid phase. After drying solid phases were combined with de-ionized water again to repeat the leaching. Total five stage of leaching were made to estimate the rate of metal eluation.

Filtrates of multiple leach tests have been analyzed by potentiomentry (pH, pNa), conductivity measurement and titration analysis (cations, anions in solution). The first, second and fifth filtrates have been also prepared using 0.45 um Microporous

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Membrane Filter Acetate cellulose to analyze the dissolved toxic elements by inductively coupled plasma mass spectrometry (ICP-MS, high resolution spectrometer ELEMENT 2 by Thermo Finnigan). Results of ICP-MS were compared with the Environmental design limits (EDLs) based on protection of fisheries resources and used for water quality control [6].

RESULTS AND DISCUSSION

The ore in quartz-carbonate veins consists of pyrite, arsenopyrite, freibergite, polybasite, pearceite, petzite, stibnite, native gold and electrum, molybdenite. Pyrite and arsenopyrite are the major ore minerals. Thus, there may be potential hazard to environment during the storage of underground rocks on the surface.

Sulfur content in samples varies from 0.6 wt.% to 4.3 wt.%. Altered rocks characterize the high concentration of As (mainly 1000-7000 ppm, compared to the average content in the upper crust – 2.5 ppm [4]), Sb (<5-108 ppm, in the crust – 0.2 ppm), Mo (1-96 ppm, in the crust – 0.8 ppm) and minor other elements (Cu, Pb, Zn – up to 2-5 times compared to the average content in the upper crust).

The ABA results are summarized in Table 2 and plotted in Figure 1. Results show there is no acid generation now, pH (in paste) varies from 7.6 to 9.0 (on the average 8.3 and 8.5 for altered dacites and andesites respectively). Sulfur content in altered dacites and rubblerocks is higher than in altered andesites. Therefore altered dacites and rubblerocks characterize the higher AP than andesites.

According to the NPR value more than half part of dacites and rubblerocks (from 60% to 100%) must be considered as potentially or possible acid generating (PAG or Uncertain). Altered andesites are mainly non-acid generating (Non-AG), only one of six samples is classified as possible acid generating (Uncertain).

The relation of the NPR from sulfur content shows that waste rocks with sulfur content above 2 wt.% should be assessed as potentially or possible environmental hazardous geological materials.

Table 2: Results of acid base accounting (ABA tests).

Sample type	pH_{paste}	S, wt.%	NP	AP	NPR	*PAG+ Uncertain, %*
			kg $CaCO_3$/t			
Dacite, argilic alteration (n=5)	7.6-9.0 8.3	1.7-4.2 3.0	55-208 97	53-132 94	0.4-3.9 1.0	*80*
Dacite, propylitic alteration (n=5)	7.8-8.9 8.2	1.7-4.3 2.8	75-218 147	53-134 86	0.7-3.3 1.7	*60*
Andesite, argilic alteration (n=2)	8.4-8.6 8.5	0.6-0.7 0.7	128-166 147	20-22 21	6.4-7.5 7.0	*0*
Andesite, propylitic alteration (n=4)	8.4-8.7 8.5	0.7-2.5 1.5	109-219 148	23-77 47	1.5-9.7 3.2	*25*
Rubblerock (dacite, andesite) (n=4)	7.8-8.9 8.2	1.8-3.2 2.3	46-155 92	57-100 73	0.7-1.6 1.3	*100*

The numerator contains the minimum and maximum values, the denominator - the mean values.

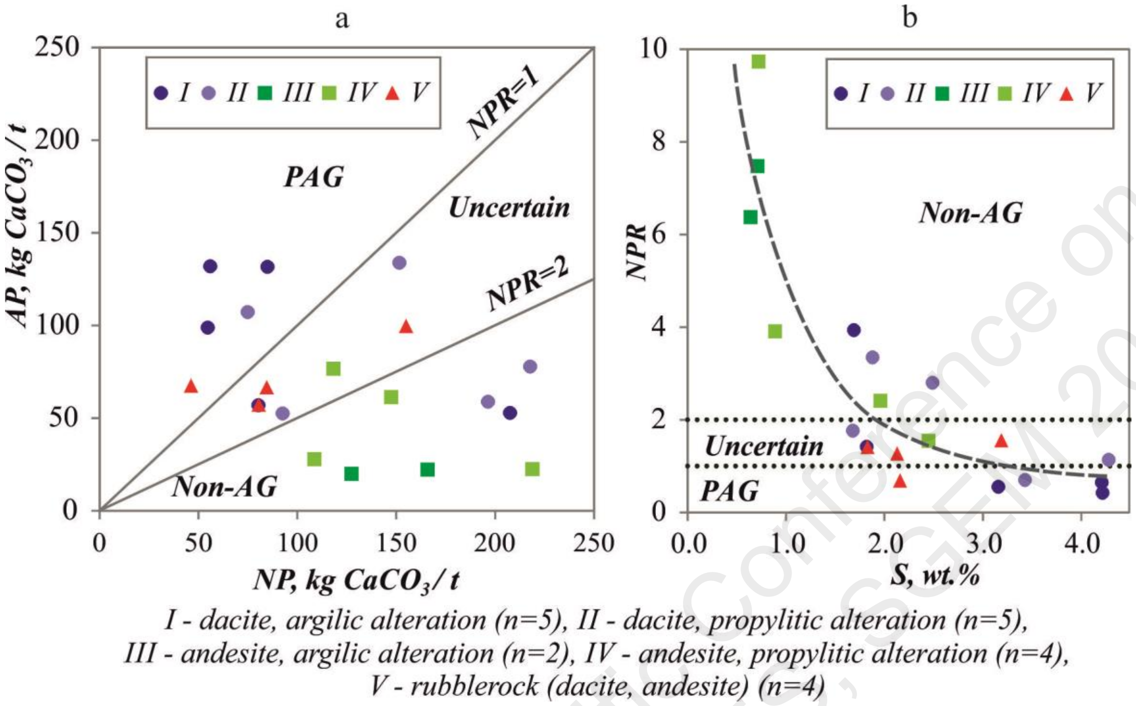

Figure 1: Ratio of the neutralization potential (NP) and the acid potential (AP) (a) and the relation of the NPR from sulfur content (b) in test samples.

Results of multiple leach tests are represented in Figure 2 and Figure 3. Data indicate that conductivity rapidly decreases from 220-300 µS/cm low to 100-150 µS/cm due to dissolution and eluation of soluble compounds such as sulfates, carbonates and others. Value of pH slowly decreases from about 8.3-8.6 to 7.8-8.0. Alkalinity of first filtrates is primarily caused by hydrolysis of albite (concentration of Na decreases from 20-35 mg/l in first filtrates to 1-2 mg/l in fifth filtrates (Figure 2).

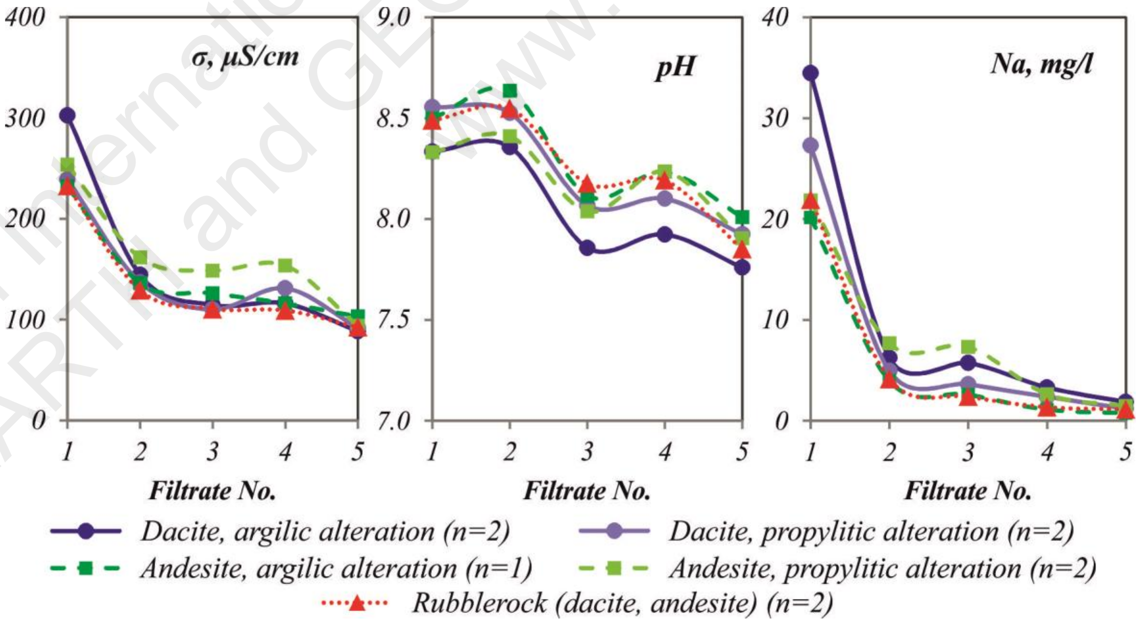

Figure 2: Conductivity, pH and Na in multiple water leachates.

Concentrations of some toxic elements (Figure 3) in leachates are much above the Environmental design limits (EDLs) based on protection of fisheries resources and used for water quality assessment [6].

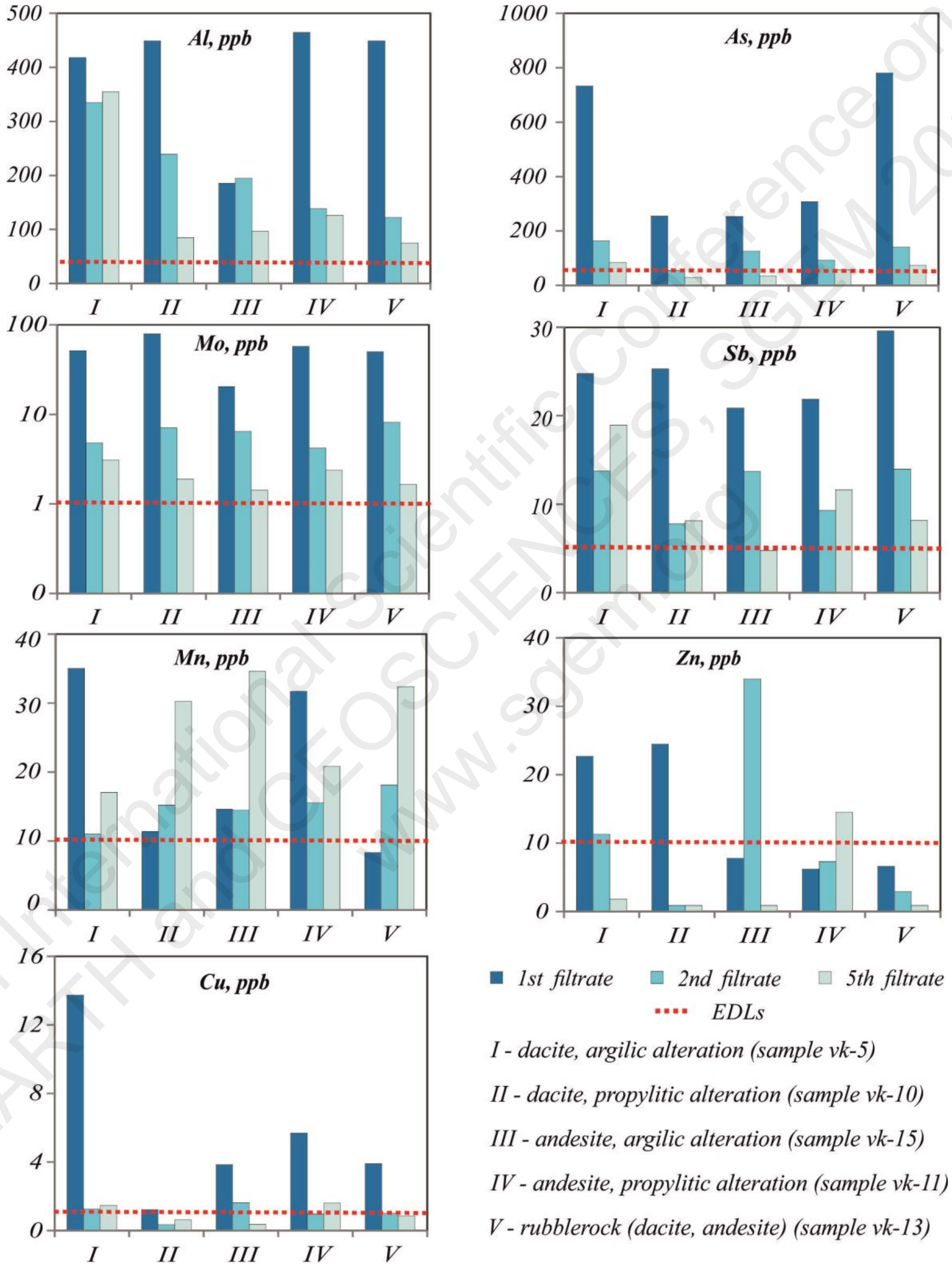

Figure 3: Concentration of toxic elements in multiple water leachates.

Elements mobile under alkaline conditions are the most dangerous to environment during the initial time of weathering (primarily Al, As, Mo, and Sb). Contents of these elements in first filtrates of all samples leachates are above the EDLs (Al - up to 10 times, As - up to 15 times, Mo - up to 80 times, Sb - up to 5 times).

Contents of Cu are above the EDLs in the most first filtrates - up to 4-14 times (excluding the propylitic dacite, 1 EDLs). Contents of Mn are also above the EDLs in the most first filtrates - up to 3.5 times (excluding the rubblerock and propylitic dacite, 0.8-1.2 EDLs). Contents of Zn in first filtrates are above the EDLs applied to altered dacites only (up to 2.5 times).

Concentrations of elements tend to decrease during weathering (excluding Mn, and locally Zn). In fifth filtrates the value of Al, Sb, Mo are usually above the EDLs up to 2-3 times (excluding the argilic dacite, 9 EDLs for Al and 4 EDLs for Sb). Contents of As, Cu and Zn are usually below the EDLs (or above them insignificantly – less than 1.5 times). The values of Mn in fifth filtrates are comparable to ones in first filtrates.

CONCLUSION

In this study the underground waste rocks of the Verhne-Krichalskaya area have been tested for ARD prediction. The area is located in Western Chukotka, Russia and comprises the Klenovskoe ore field with the eponymous epithermal gold-silver deposit and some perspective ore fields. The ore in quartz-carbonate veins contents pyrite and arsenopyrite as major ore minerals. Thus, there may be potential hazard to environment during the storage of underground rocks on the surface.

Twenty samples of waste rocks (altered dacites, andesites and rubblerocks) were analyzed to estimate their risk of acidic and contaminated drainage. All samples have been investigated to trace element analysis, ABA-tests and, particularly, multiple water leach tests.

Results of ABA-tests have shown there is no acid generation now, pH (in paste) varies from 7.6 to 9.0. Altered dacites and rubblerocks characterize the higher AP than andesites. According to the NPR value altered dacites and rubblerocks generally must be considered as potentially or possible acid generating (PAG or Uncertain). Altered andesites are mainly non-acid generating (Non-AG).

Results of multiple leach tests conducted in five stages indicate that pH slowly decreases from about 8.3-8.6 to 7.8-8.0. Conductivity decreases too due to dissolution and eluation of soluble sulfates, carbonates and others.

Contents of some toxic elements (primarily Al, As, Mo, and Sb) in leachates are much above the Environmental design limits (EDLs) based on protection of fisheries resources and used for water quality assessment (Sb, Al, As - up to 5-15 times, Mo - up to 80 times). In first filtrates contents of Mn, Cu, and Zn may be above the EDLs too (up to 2.5-14 times). Concentrations of elements generally tend to decrease during weathering.

Thus, in spite of no expected to acid runoff during the weathering at first drainage waters may contain excessive concentrations of toxic elements. It causes the ecological risk of rock drainage and requires the protecting and monitoring of environment. The

ARD prediction can be used to assist in development of waste management plan for this area.

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