Research Article

TECHNOGENIC IMPACT OF SULPHIDE-CONTAINING WASTES PRODUCED BY ORE MINING AND PROCESSING AT THE OZERNOE DEPOSIT: INVESTIGATION AND FORECAST

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ABSTRACT

The paper provides an assessment of the potential technogenic impact of sulphide-containing wastes produced by ore extraction and processing at the Ozernoe deposit, which is currently at the initial stage of mining. The analysed averaged samples of ore and wastes of mining and processing were obtained in the course of semi-industrial experimental preproduction. The results of monitoring studies in the area of sulphide-containing dumps formed at an exploring mine in the 1960s were used for assessing a potential hazard of the wastes. The origin of acid mine drainage is described. Advantages and shortcomings of tests assessing acid mine drainage are considered. The used express-method of acid indication allows to reliably determine the risk of acid mine drainage by the values of acidic and neutralising potentials formed by rocks. An estimation of acid mine drainage formation and heavy metal migration is carried out at dumps of the exploring mine. The forecast of environmental impact is given for the future wastes of mining and processing at the Ozernoe deposit.

Keywords: dumps of sulphide-containing wastes; adverse impact; environmental hazard; acid mine drainage; express-method of acid indication.

INTRODUCTION

The negative environmental impact of mining enterprises raises annually (Bwapwa et al., 2017; Pashkevich, Petrova, 2017; Simate, Ndlovu, 2014). This is due to an objectively increased consumption of material resources by mankind (Alekseenko et al., 2017a; Beloglazov et al., 2014; Cehlár et al., 2016; Gumenik et al., 1988; Pashkevich, 2017). In modern extraction conditions, the output of finished products is less than 10 %; the rest is made of mining and processing wastes, which occupy hundreds of thousands of hectares (Pashkevich, Petrova, 2015; Pavolová et al., 2016). Mineral mining wastes contain, as a rule, components that are open-stored and exposed to climatic factors and can transform into new compounds and migrate to tens and hundreds of kilometres from their source (Alekseenko et al., 2017b; Grudev, 1995; Kefeni et al., 2017).

The natural environment is subjected to the maximum technogenic load in the areas where sulphide-containing wastes are stored. Formation of acid mine drainage (AMD) waters and, respectively, litho- and hydrogeochemical pollution haloes with extremely low pH values is caused by oxidation of sulphide sulphur (Favas et al., 2016; Han et al., 2017; Nleya et al., 2016). This destructs vegetation, transforms the composition of surface sediments, surface, and ground waters. Therefore, the development and implementation of environmental protection measures to prevent the effects of sulphide-containing wastes on near-surface sediments and natural waters is necessary at the design stage and initial exploitation periods of sulphide ore mining.

The Ozernoe deposit of polymetallic sulphide ores, which is located 350 km from the specially protected area of Lake Baikal, is currently at the initial mining stage. The deposit mining will pro-

duce over 600 million tons of wastes containing sulphide sulphur and heavy metals, which are simultaneously pollutants and potential mineral raw materials. In this regard, it is necessary to assess and predict the AMD formation in areas of mineral waste storage in order to prevent acidification.

MATERIALS AND METHODS

Lead-zinc ore mineralization of the Ozernoe deposit is represented by a series of stacked and lenticular pyrite-siderite-polymetallic ore bodies arranged one above the other. The ores have pyrite-lead-zinc mineral composition. Pyrite, sphalerite, and, to a lesser extent, galena are the main ore minerals.

A distinctive feature of the deposit is the lead-zinc composition of ores with almost complete absence of copper; the ratio Pb:Zn:Cu is 1:6:0.05. The ores of the deposit contain zinc, lead, and sulphur in economic valuable concentrations; silver and cadmium are useful associated components. According to calculations, a designed plant will annually process 8 million tons of mined ores. After enriching, three concentrates are planned to be obtained:

- zinc concentrate;
- lead concentrate;
- pyrite concentrate.

Under laboratory conditions, the averaged ore samples, technological samples of zinc, lead, and pyrite concentrates, as well as tail specimens, obtained after a semi-industrial pilot production experiment, were examined. The chemical composition of the samples was determined by the X-ray fluorescence Shimadzu spectrometer XRF-1800 and the atomic absorption Shimadzu spectrophotometer AA-7000. The test results are given in Table 1.

The conducted studies showed that after enriching polymetallic ores of the Ozernoe deposit the following wastes in the total volume over 16 million m³ would be stored in the oxidizing environment: pyritic concentrate (S_{suplh} content is over 43 %) and dump tails (S_{suplh} content is over 9 %). In addition, over 25 million m³ of waste rocks, which contain 7 % of S_{suplh} at average, will be formed during ore extraction.

Monitoring studies near the Ozernoe deposit were carried out to assess the potential danger of sulphide-containing wastes at the exploration

mine worked out in the 1960s. The storage of sulphide-containing waste rocks around the exploration mine occupies 1 ha.

Four transects crossed the dumps, where averaged surface samples were taken by the envelope method from a depth of 10–15 cm [Fedorets, Medvedeva, 2009]. Each spot 2×1 m in size was sampled at the square nodes and at the intersection of diagonals. Sample quartering was performed at each point to obtain a representative specimen.

The migration capacity of toxic impurities washed by precipitation from the dump site was estimated by examining the Bezymyanny stream that drains the dump, where bottom sediment sampling was carried out each 50 m, before flowing into the Gunduy-Kholoy River at a distance of 1.5 km. A cut was made in the waste rock body and 2 wells with a depth over 2 m were drilled to assess the vertical migration of polluting components. Description of the section made it possible to characterise the constituent rocks.

Analyses of the taken dump rock samples and bottom sediments were carried out using an X-ray powder diffractometer XRD-7000 (Shimadzu) to evaluate mineral composition. The bulk elemental composition of the samples was defined using X-ray fluorescence method. A portable X-ray fluorescence spectrometer Niton Xlt 500 was used to analyse samples on site. A semiquantitative analysis of samples from the exploration mine of the Ozernoe deposit was carried out under laboratory conditions using an ED 2000 X-ray fluorescence spectrometer (Oxford Instruments, UK). To refine the results, an XRF-1800 wave-dispersive X-ray fluorescence spectrometer (Shimadzu, Japan) was used. Determination of the contents of several potentially toxic elements was carried out using atomic absorption spectrometry and inductively coupled plasma spectrometry. Analytical works were carried out on an ICPE-9000 (Shimadzu) and an atomic absorption spectrometer AA6300 (Shimadzu, Japan).

RESULTS

The investigations showed that wastes of the exploration mine mainly consist of pyrite, siderite, calcite, dolomite (Table 2) with 4.5–25.0 g/kg content of Pb, 13–35 g/kg of Zn, 170–240 g/kg of S, 215–640 mg/kg of As, 180–320 mg/kg of Cu, 40–115 mg/kg of Cd. Contrast secondary lithochemical halos of zinc, lead and other heavy

Table 1. Results of laboratory tests of ores, tailings, and zinc, lead and pyrite concentrates
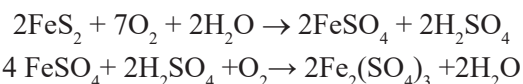
Component	Concentrations in products, %				
	Unprocessed ore	Lead concentrate	Zinc concentrate	Pyrite concentrate	Tailings
Lead	1.00	49.20	0.44	0.47	0.23
Zinc	5.83	4.91	52.20	2.05/1.25	0.57
Copper	0.07	0.46	0.20	0.11	0.03
Iron	26.33	13.83	8.15	38.57	22.35
Sulphur	22.30	26.50	34.90	43.72	9.89
Cadmium	0.01	0.011	0.10	0.0066	not determined
Gold, ppm	0.16	1.2	0.20	0.10	0.1
Silver, ppm	29.9	44.3	70.8	35.4	4.9
Thallium	0.0029	0.0032	0.0011	0.0039	0.0045
Gallium	0.00030	0.000078	0.00083	0.00015	0.00062
Germanium	not determined	not determined	not determined	not determined	not determined
Indium	0.00042	0.00063	0.00046	0.00044	0.00078
Tellurium	not determined	not determined	not determined	not determined	not determined
Rhenium	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Selenium	not determined	not determined	not determined	not determined	not determined
Cobalt	0.0016	0.0015	0.0008	0.0093	0.0008
Molybdenum	0.0002	0.0004	0.0002	0.0004	0.0001
Nickel	0.0007	0.0009	0.0003	0.0013	0.0010
Antimony	not determined	not determined	not determined	not determined	not determined
Bismuth	not determined	0.0047	not determined	not determined	not determined
Tin	0.0021	0.0013	not determined	not determined	0.0025
Arsenic	0.069	0.037	0.039	0.11	0.059
Manganese	1.44	0.07	0.084	0.50	2.08
Phosphorus	0.03	0.02	0.01	0.01	0.04
Fluorine	0.01	0.011	0.013	0.015	0.01
Barium sulphate	3.99	сл.	0.02	0.71	6.07
Titanium oxide	0.16	0.06	0.05	0.14	0.17
Magnesium oxide	1.66	0.10	0.13	0.52	2.40
Calcium oxide	6.55	0.22	2.32	1.75	9.50
Silicon oxide	12.75	0.78	0.61	3.64	18.56
Alumina	2.16	0.28	0.35	2.48	3.04
Carbon monoxide	13.30	-	-	-	13.50

metals are formed at the dump. A secondary lithochemical halo of lead drawn using the Surfer software package is presented in Figure 1.
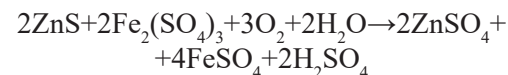
The carried out field observations and experimental studies have shown that heavy metals in acidic, oxidizing environments exist in (or transferred into) highly soluble forms, with polluting components migrating to considerable distances along the river network.

The storage of sulphide-containing rocks is associated with the danger of forming AMD due to pollution of atmospheric, surface or ground water filtered through a dump of sulphide-containing rocks or wastes by H^+ ions during the oxidation of sulphide minerals in an oxidizing environment, according to the following scheme:
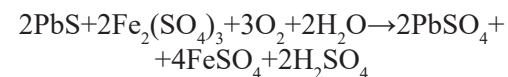
pyrite:
$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$$
$$4\,FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$$

sphalerite:
$$2ZnS + 2Fe_2(SO_4)_3 + 3O_2 + 2H_2O \rightarrow 2ZnSO_4 + 4FeSO_4 + 2H_2SO_4$$

galena:
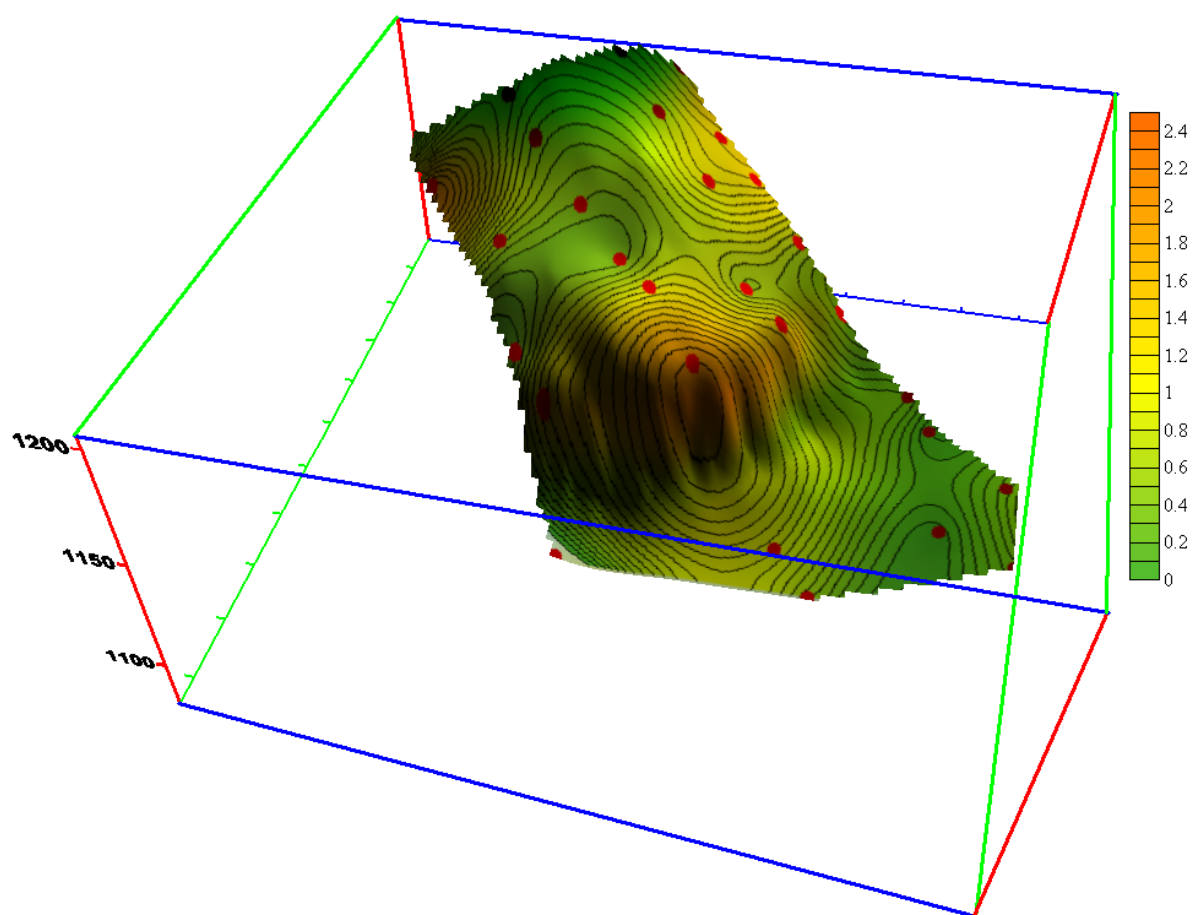$$2PbS + 2Fe_2(SO_4)_3 + 3O_2 + 2H_2O \rightarrow 2PbSO_4 + 4FeSO_4 + 2H_2SO_4$$

A process of acid formation (rate and limits of pH decrease in AMD, dependence of H^+ ion concentration on the time *pH=f(t)*) is determined by concentration of sulphide minerals in the rock; degree of crystallisation of sulphide minerals; crystallisation of pyrite; activity of biochemi-

Table 2. Composition of samples from the exploring mine

Type of analysis	Defined characteristics	Specimen burial depth, m						
		0 – 0.4	0.4 – 0.8	0.8 – 1.2	1.2 – 1.6	1.6 – 2.0	2.0 – 2.40	2.40 – 3.0
XRF	Prevailing minerals	Pyrite, quartz, siderite, magnetite, dolomite, gypsum, mica, kaolinite, zinc sulphate, lead sulphate	Siderite, quartz, pyrite, dolomite, calcite, mica, kaolinite, calcium sulphate hemihydrate	Pyrite, quartz, siderite, calcium sulphate hemihydrate, magnetite, calcite, kaolinite	Pyrite, quartz, siderite, magnetite, calcite, kaolinite, dolomite, mica	Pyrite, siderite, dolomite, quartz, gypsum, magnetite, mica, kaolinite	Pyrite, dolomite, quartz, siderite, magnetite, calcite, mica, kaolinite	Pyrite, quartz, siderite, mica, dolomite, magnetite, calcite, sphalerite, galena
XRF, AAS, and ICP	Element contents							
	Zn, g/kg	13	15	20	21	24	27	35
	Pb, g/kg	4.5	6.5	6.9	11	12.4	18.0	25
	As, mg/kg	215	298	375	425	470	534	640
	Cd, mg/kg	40	35	68	87	91	100	115
	S, g/kg	170	185	198	200	211	235	240
	Cu, mg/kg	180	192	213	230	301	266	320
	Fe, g/kg	404.9	373.6	354.5	249.6	360.4	290.4	250.5
	Ag, mg/kg	63	45	36	33	27	16	14

Fig. 1. Formation of the secondary lithochemical lead halo (the absolute height of the heap on the right, lead concentrations in technogenic deposits on the left, g/kg)

cal processes; content of minerals that neutralise acidity in rocks or wastes and their type (carbonates, clay minerals, phosphates).

The ecological hazard of sulphide-containing rock dumps is most adequately assessed by an express method of acid indication, which allows to predict the time of AMD formation, a size and a contrast of litho- and hydrogeochemical pollution halos basing on values of acid potential and neutralisation potential formed by the rock.

The express method for determining the risk of AMD occurrence is based on studying:
- acid rock potential (AP),
- neutralisation rock potential (NP),
- coefficients of the potential danger of acid contamination of the territory NNPk and NNP'k:

$$NNPk = AP–NP \qquad (1)$$

$$NNP'k = NP/AP \qquad (2)$$

The acid rock potential is determined by the results of chemical rock analysis and recalculation of the sulphide sulphur S_{sulph} percentage into the percentage of sulphuric acid formed during rock weathering:

$$S_{H_2SO_4}(\%) = S_{sulph}(\%)\frac{M.m.H_2SO_4}{A.m.S} \qquad (3)$$

where: *M* and *M* are the molecular and atomic masses, respectively.

The content of sulphuric acid is recalculated into AP, which, like NP, is measured in units equivalent to the tons of calcite $CaCO_3$ spent for neutralising kilotons of sulphide-containing rocks (t $CaCO_3$ / t rock).

The neutralisation of sulphuric acid happens according to the following reaction equation:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \qquad (4)$$

The formula for calculating the acid potential is written as follows:

$$AP = S_{sulph}(\%) \qquad (5)$$

The results of hydrochloric or sulphuric acid attack of the sulphide-containing rock up to a fixed pH value are used to calculate the neutralisation potential. If NNP ≥ 0 and NNP ' ≥ 1, the sulphide-containing rocks are not dangerous and do not have the ability to form an acid. In cases of NNPk > 0 and NNP'k < 1, rocks are dangerous and can form AMD.
- with NNP' < S, rocks form an acid (S is the content of sulphide sulphur in the sample);
- with S < NNP' < 1, rocks have the potential to form acid in the future (Figure 2).

To determine the risk of AMD formation, the express method was used. The results are shown in Table 3 and Figure 2

The results of the express analysis show the contemporary high probability of AMD formation at the dumps near the exploratory mine, and the probability increases with depth. The relatively low acid potential of waste deposited in near-surface sediments is due to the already accomplished fact of oxidation of sulphide ores and leaching of heavy metals. Nevertheless, the technogenic danger of the dumps of exploratory mines remains over the 50-year period.

According to the research, the sulphide wastes of the Ozernoe deposit have a significant acid potential (up to 41.4 t/103CaCO_3). At the concentration of sulphide sulphur in the wastes up to 10 %, there is a danger of forming more than 10 million tons of sulphuric acid. A lack of measures to protect soil and water resources will lead to infiltration of AMD through soils with the mobilisation of heavy metals from the body of the heap and formation of technochemical pollution halos.

CONCLUSION

Field observations and laboratory studies of the rocks of the exploratory mine have shown that the wastes of the Ozernoe deposit contain heavy

Table 3. Calculated acid and neutralization potentials for the tailings at the Ozernoe deposit

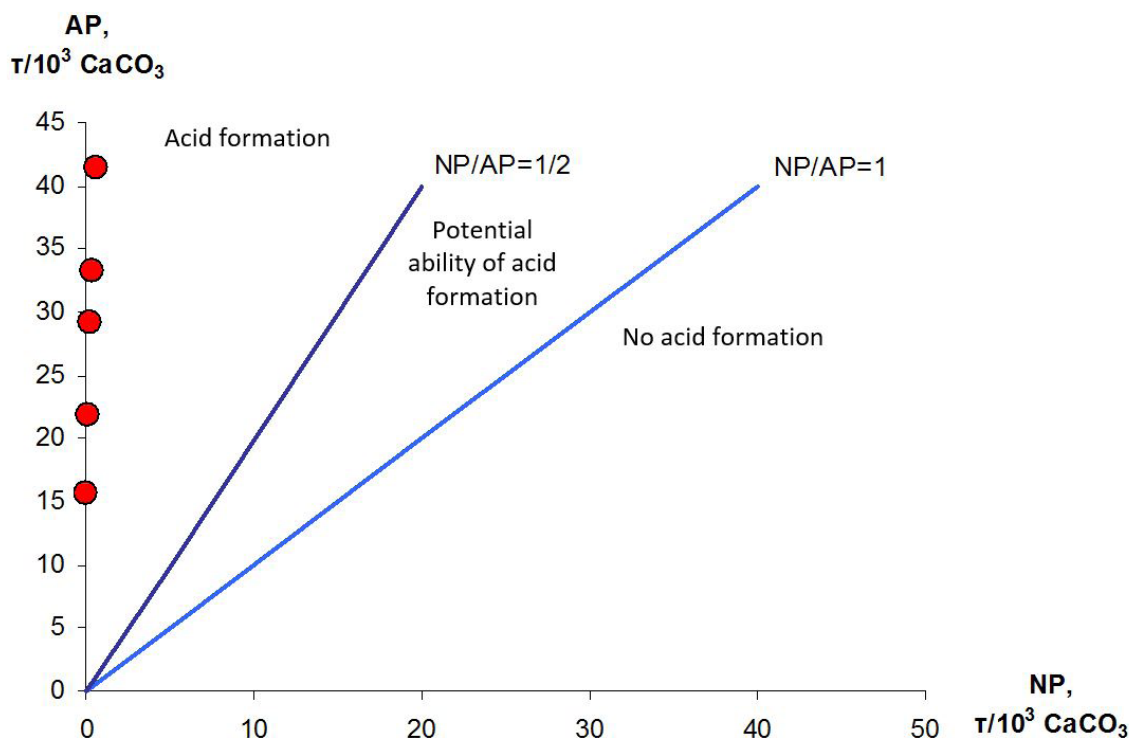| №	Properties	Specimen burial depth, m				
		0	0.8	1.4	2.0	2.6
1	Ssulph, %	5.07	7.00	9.33	10.63	13.25
2	Acid potential AP, t/(103 t CaCO3)	15.6	21.9	29.2	33.2	41.4
3	Neutralization potential NP, t/(103 t CaCO3)	0	0.1	0.3	0.4	0.6
4	NNPк = AP – NP	15.6	21.8	28.9	32.8	40.8
5	NNP'к = NP/AP	0	0.004	0.010	0.012	0.014

Fig. 2. Dependence of the ability of sulphide rocks of the Ozernoe deposit to form acid on NP and AP values

metals in the following concentrations: 13–35 g/kg of Zn, 4.5–25.0 g/kg of Pb, 180–320 mg/kg of Cu, and 215–640 mg/kg of As.

An assessment of landscape-geochemical conditions made it possible to establish that there is a danger of AMD formation in the vicinity of the spoils due to the oxidation of sulphide rocks. In addition, it is determined that more than 7.5 kg of zinc and more than 4.5 kg of lead are washed out annually from the spoil of the exploration tunnel.

The carried out researches of technogenic deposits of the exploratory mine allowed to make the forecast of the influence of the future extraction and processing wastes of the Ozernoe deposit. Thus, with the concentration of sulphide sulphur in the wastes up to 10 % of the total content, there is a danger of forming over 10 million tons of sulphuric acid. A lack of measures to protect soil and water resources will lead to infiltration of acidic waters through soils with washing heavy metals out from the dump and the formation of technochemical pollution halos.

Acknowledgments

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