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Processing Hard Coal Mining Wastes of the Luhansk Region as Man-Made Metal Deposits

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Abstract—Coal mining waste rock dumps contain a lot of rare and precious microelements and are a single complex mechanism of the chemical and biochemical transformations of substances, and the key role in such transformations belongs to sulfuric acid formed as a result of the vital functions of thionic bacteria *Th. Ferrooxidans.* The aim of the present work was to develop an environmentally friendly biotechnology for processing coal mining waste rock dumps of the Luhansk Region as man-made metal deposits. The spectral analysis of the waste rocks of the Luhansk Region revealed high concentrations of precious, rare-earth, and trace elements. A high prevalence of gallium and germanium clarkes was found, and their actual concentration in the waste was close to the minimum industrial concentration. The results of chemical analysis of the waste rock for Al_2O_3 showed that its concentration was close to that in poor bauxites, a traditional raw material for alumina. A method and technology of the biochemical leaching of aluminum, gallium, and germanium, which make use of the natural processes of sulfuric acid formation in waste rock were proposed, and their efficiency was experimentally confirmed. The proposed biochemical technology for the processing of coal mining waste rocks can serve as the basic method for diminishing their environmental impact and rational use of natural resources.

Keywords: mining waste rock, sulphuric acid, *Th. Ferrooxidans* bacteria, bioleaching, waste rock processing, aluminum, germanium, gallium

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INTRODUCTION

In the Luhansk region, 80 mines operate in coal mining regions, yielding per every 1000 tons of coal from 150 to 800 tons of mining waste rocks which are stored in dumps and heaps [1]. Such large-tonnage wastes create a large anthropogenic burden on the ecological state of the region, and, therefore, scientists are faced with the urgent issue of combating the negative consequences of dumping. In our opinion, one of ways to approach this problem consists in the processing of waste rock dumps.

The problem of processing the waste rock dumps in the region, as well as in the entire Donbass, is still unresolved and is the subject of considerable research effort.

Since the mid-1900s, much attention has been paid to the problem of processing and disposal of mining wastes. Among domestic researchers we can mention V.N. Burmistrov, Yu.V. Itkin, V.M. Ratynskii, V.R. Kler, M.Ya. Shpirta, B.F. Nifantov, L.G. Zubova, and others. In foreign countries, this problem is the subject of research of D. Leinenger, E.Raask, A.K.M. Rainbow, I. Twardowska, and others.

The most commonly proposed use of coal mining and processing waste rocks is production of building materials, fertilizers, and substitutes for soils, and as raw materials for the production of certain metals [2–7]. To minimize the negative impact of waste rock dumps on the environment, some researchers propose technologies for their conservation [8, 9].

Formulation of the problem. Coal mining waste rock dumps are a single complex mechanism of the chemical and biochemical transformations of substances, and sulfuric acid formed as a result of the vital activity of thionic bacteria *Th. ferrooxidans* plays the main role in such transformations.

As known [10, 11], the main habitat of *Th. Ferrooxidans* is acidic waters of sulfide ore and coal deposits. Here, for every ton of a chemically formed H_2SO_4, 4 tons of H_2SO_4 is formed under the action of bacteria. If

Table 1. Total alumina concentrations in the test waste rock samples

Waste rick	Concentration of Al_2O_3, %
Strongly metamorphosed (Sverdlovsk town)	20.87
Strongly metamorphosed (Antratsit town)	19.80
Middle metamorphosed (Luhansk town)	13.79
Weakly metamorphosed (Lisichansk town)	18.30

surface waters penetrates through cracks through a coal bed and is enriched with ferrous iron, then later, when these waters pass through a finely divided pyritized coal under well-aerated mine conditions, rapid pyrite oxidation with the participation of microorganisms is initiated.

The rock raised on the surface during coal mining and consisting mainly of silicate and sulfide minerals, as well as coal impurities, falls into strongly oxidizing conditions. Exposure to oxygen and atmospheric moisture drives biochemical oxidation of sulfides, mainly pyrite and marcasite. The biochemical oxidation of pyrite by *Th. Ferrooxidans* bacteria can be represented by the following reaction [10]:

$$4FeS_2 + 12O_2 + 6H_2O \rightarrow 2Fe(SO_4)_3 + 3H_2SO_4 + 2S_a.$$

The oxidation of sulfide sulfur to sulfation proceeds by bacteria can be represented by the following scheme [10]:

$$S^{2-} \xrightarrow{Th.fer} S^0_p \xrightarrow{Th.fer} S^0_B \xrightarrow{Yh.fer} SO_3^{2-} \xrightarrow{Th.fer} SO_4^{2-}$$

Microorganisms regulate the acidity of the medium by oxidizing an appropriate amount of elemental sulfur. Part of unoxidized sulfur forms a colloidal solution in the acidic medium. Therewith, per 1 mol of biochemically leached pyrite, 998–1350 kJ of heat is released. Thus, due to bacteria, the oxidative leaching of pyrite becomes an autocatalytic process [10, 11].

The aim of the present work was to develop an environmentally friendly biotechnology for processing the waste rock dumps of the Luhansk Region as man-made metal deposits.

The objects for study were four typical Donbass mining waste rock dumps, differing from each other by the brand and degree of metamorphism of the mined coal. These dumps are located in the Luhansk Region.

RESULTS AND DISCUSSION

Mineralogical analysis of the waste rock established that the main components of its ash are silicon, aluminum, and iron oxides, and the main mineral is pyrite. Therewith, the concentration of Al_2O_3 is close to its concentration in poor bauxites (Table 1).

As known, waste rocks and by-products of coal mining and processing contain a lot of rare and precious microelements. Moreover, even if the concentrations of microelements are low, due to large-scale coal mining, tens and sometimes hundreds times more of these elements are recovered and recycled than in the case of traditional raw materials [12, 13].

Spectral analysis of the waste rock revealed high concentrations of precious, rare-earth, and trace elements. A high prevalence of gallium and germanium clarkes was found, and their actual concentration in the waste rock is close to the minimum industrial concentration (Table 2).

It is known from the literature that germanium is mostly present as an isomorphous admixture (>1%) in silicate, sulfide, and sulfate minerals. Germanium was also always detected in coal [13–16]. Gallium is a component of aluminum, silicate, iron, and sulfide ores, and it is also present, together with germanium, in coal [12, 17].

Table 2. Spectral analysis of the waste rock samples

No.	Sampling site	Concentration, mg/kg waste rock	
		Ge	Ga
1	Sverdlov mine (Sverdlovsk town)	0.0020	0.010
2	Frunze mine (Antratsit town)	1.00000	1.000
3	Luganskaya mine (Luhansk town)	0.0015	1.500
4	Matrosskaya mine (Lisichansk town)	0.0150	0.015

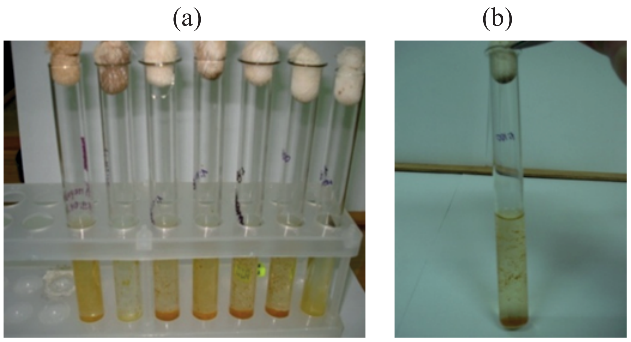

Fig. 1. *Th. Ferrooxidans* cultures: (a) temporary and (b) enriched.

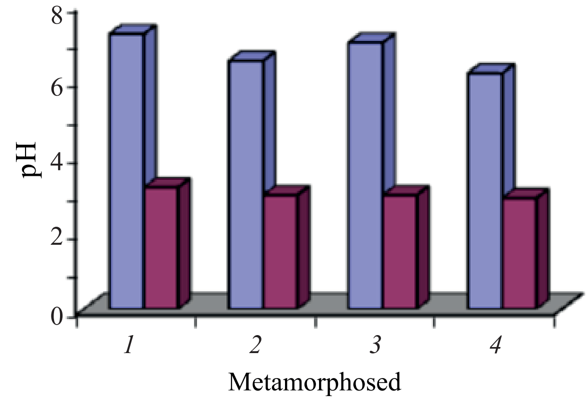

Fig. 2. Changes of pH after biochemical leaching. Waste rock: (*1*) strongly metamorphosed (Sverdlovsk town); (*2*) strongly metamorphosed (Antratsit town); (*3*) middle metamorphosed (Luhansk town); and (*4*) weakly metamorphosed (Lisichansk town). (*I*) Before leaching and (*II*) after leaching.

The aforesaid suggests that the studied waste rock dumps can be used as man-made deposits of aluminum, gallium, and germanium.

Since the current priorities for processing mining wastes, aimed at extracting industry-valuable substances and components, are complex and environmentally friendly methods. In our opinion, one of these methods is the biochemical (bacterial) production of metals using bacteria, whose vital activity products allow leaching useful metals from the waste with minimal costs and significant environmental and economic effect. Of particular interest to us is the biochemical production of gallium and germanium from the waste rock dumps of the Luhansk Region using thionic bacteria *Th. Ferrooxidans*.

To isolate microorganisms *Th. Ferrooxidans* from the mine water samples taken at the coal mining site l_1 at a depth of 640 m and waste rock samples, we used Silverman and Lundgren liquid medium [11]. The temporary and enriched cultures were isolated by conventional procedures.

Culturing was performed at 35°C in a thermostat. Bacterial growth was manifested in 2–3 days by the appearance of a film on the tube surface and a $Fe(OH)_3$ precipitate on the bottom, a change in the color of the solution from bluish green to yellow or brown, and a decrease in pH. Figure 1 presents photos of developed temporary cultures of *Th. Ferrooxidans* and enriched culture in a liquid culture medium. We started with the determination of the pH of the test rock samples. It is known from the literature that ferric iron, one of the energy sources for *Th. Ferrooxidans* bacteria, is present in solutions at pH = 3 or lower, while at pH = 4 and higher, oxidation products interfere with the subsequent cell contact with the medium, and, therefore, oxidation may slow down. At the end of the experiment, on the eighth day, a change in pH was determined. The results are shown in Fig. 2.

The resulting culture of *Th. Ferrooxidans* bacteria was used for the biochemical leaching of metals from the waste rock samples.

The test samples ground to were treated with bacterial solutions once at the beginning of the experiment. Before

Table 3. Dissolved aluminum concentrations after leaching

Run no.	Waste rock	Concentration of Al^{3+}, g/100 g waste rock	Recovery, %
1	Strongly metamorphosed (Sverdlovsk town)	5.86	30.0
2	Strongly metamorphosed (Antratsit town)	3.00	15.7
3	Middle metamorphosed (Luhansk town)	8.91	63.8
4	Weakly metamorphosed (Lisichansk town)	5.00	27.7

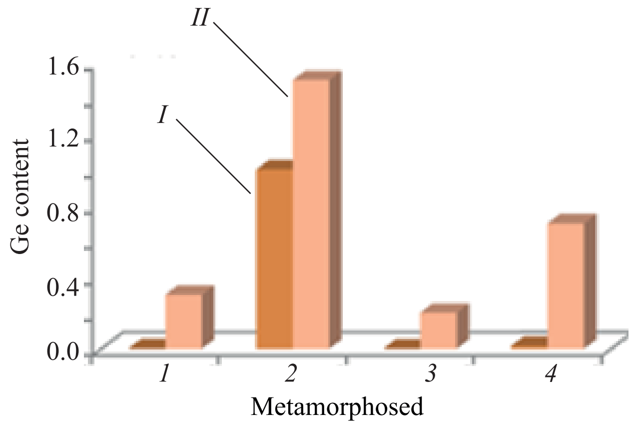

Fig. 3. Results of bacterial leaching of germanium. Waste rock: (*1*) strongly metamorphosed (Sverdlovsk town); (*2*) strongly metamorphosed (Antratsit town); (*3*) middle metamorphosed (Luhansk town); and (*4*) weakly metamorphosed (Lisichansk town). (*I*) Ge before leaching and (*II*) Ge after leaching.

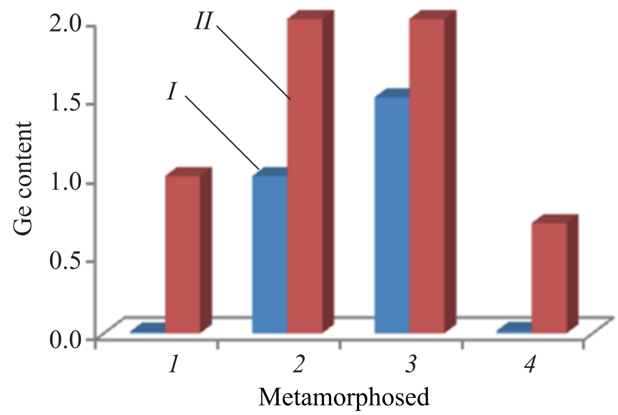

Fig. 4. Results of bacterial leaching of gallium. Waste rock: (*1*) strongly metamorphosed (Sverdlovsk town); (*2*) strongly metamorphosed (Antratsit town); (*3*) middle metamorphosed (Luhansk town); and (*4*) weakly metamorphosed (Lisichansk town). (*I*) Ga before leaching and (*II*) Ga after leaching.

treatment the samples were ground to a fraction of 1 mm to improve adsorption of bacteria in micropores and microcracks, thereby ensuring faster initiation of bacterial functioning.

The results of the biochemical leaching and the recoveries of aluminum are listed in Table 3.

The experimental results gave evidence showing that sulfuric acid formed by bacteria actively reacts with calcium carbonates and accelerates hydrolysis of feldspars at elevated temperatures. The hydrolysis of feldspars in the waste rock forms kaolin $Al_2[Si_2O_5](OH)_4$. Since the reactions of the biochemical and chemical formation of sulfuric acid occur with heat release, kaolin converts to metakaolin, and, under the action of the acid, the free ionic form of aluminum is formed. The maximum recovery of aluminum from the waste rock is 63.8%. At the 8^{th} day of leaching, the concentrations of dissolved gallium and germanium were determined. The resulting data are listed in Figs. 3 and 4, respectively.

It was found that in sulfide compounds germanium substitutes predominantly Fe^{2+}, while gallium in alumosilicates substitutes predominantly Al^{3+}. The increase in the concentrations of germanium and gallium after leaching is explained by that sulfuric acid formed due to the vital activity of *Th. Ferrooxidans* bacteria leaches trace elements isomorphically substituted in minerals, i.e. oxygen and atmospheric moisture induces in the mineral waste raised to the surface the biochemical oxidation of sulfides with *Th. Ferrooxidans* bacteria.

In our work, we propose a scheme for the biochemical production of gallium and germanium by the heap bacterial leaching of waste rock. To this end, we propose to form heaps of waste rock at prepared industrial sites and irrigate the heaps with bacterial solutions. Sulfuric acid formed by bacteria will convert sulfide and aluminosilicate minerals into soluble metal salts, which will allow leaching not only aluminum, gallium and germanium, but also other metals. The concentration of the formed acid solutions can vary from low to high. Sulfuric acid solutions of even low concentrations can leach metals from minerals and serve as an optimal factor of further bacterial growth.

CONCLUSIONS

(a) Coal mining waste rock dumps represent a single complex mechanism of the chemical and biochemical transformations of substances, and the key role in such transformations belongs to sulfuric acid formed as a result of the vital activity of thionic bacteria *Th. Ferrooxidans*. Complicated natural processes lead to the leaching of valuable metals, and such biochemical activity of bacteria can be used to produce these metals, and mining waste rocks can be considered as man-made metal deposits.

(b) Our proposed method for processing of waste rock is a new biochemical method of metal extraction (technical microbiology. The biochemical oxidation of the waste rock resulted in a fairly high recovery of aluminum (63%). It was found that the biochemical method allows processing any aluminosilicates and poor aluminum raw materials (8–20% of aluminum). The efficiency of dissolution of isomorphously substituted metals is (up to 2 mg/kg waste rock for Ga and up to 1.6 mg/kg waste rock for Ge), and even weak sulfuric acid solutions are capable of leaching metals from minerals and serve as an optimal factor of bacterial growth.

(c) The advantages the implementation of the proposed biochemical process offers in terms of environmental safety consist in reducing the release of heavy metals and hazardous chemical compounds into the environment due to the processing of the pollution source, with the subsequent possibility of releasing large areas of land occupied by waste rock dumps.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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