Biological Removal of Anorganic Pollutants from Acid Mine Drainage

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Summary

Acid Mine Drainage (AMD) is one of the significant environmental and financial liabilities of the mining industry. Currently active mines, as well as mines that have been out of production for years, produce acidic waters with high concentration of sulphates and heavy metals. Treatment methods used to mitigate impact of AMD on the environment are focused on neutralizing, stabilizing and removing pollutants through various physical, chemical and biological processes.

This paper reports the results of anorganic pollutants removal from AMD using sulphate reducing bacteria (SRB). Hydrogen sulphide produced by SRB for recovery of Cu and Zn has been used in the course of selective sequential precipitation process (SSP). In the next stage sulphates were removed from AMD by the biological anaerobic reduction. Thus, by this method removing of metals and sulphates has been achieved in successive discrete steps.

The experiments were performed at laboratory condition using water collected from the site of the AMD outflow at the shaft Pech from the enclosed and flooded Smolnik sulphidic deposit (Slovakia).

Keywords: acid mine drainage, sulphate-reducing bacteria, biogenic sulphide, heavy metals recovery

Introduction

Acid Mine Drainage (AMD) forms in the process of oxidative dissolution of the sulphide bearing minerals exposed to oxidizing conditions in coal and metal mining, mineral processing, highway and airport construction and other large-scale excavations. This process is accelerated by autochthon acidophilic microbial communities (Johnson and Hallberg, 2003). The nature of AMD varies greatly from site to site and is dependent on different factors as ore deposit geology, hydrogeology, climatology and microbiology (Nordstrom, 2011). AMD typical by low pH, high concentration of sulphates and heavy metals cause the pollution of superficial water and groundwater, contamination of soils and damage of local ecosystem. A low pH cause keeping up the solubility of metals at a high level thus permits their dispersion into the environment. Their noxious effect is enhanced by ability to persist and accumulate in natural ecosystems so providing a long-term source of contamination. Sulphates present are not considered to be toxic, however negatively affect the taste of water and concentration higher than 600 mg/L usually results in a laxative effect (INAP, 2003). Waters rich in sulphate have a high corrosive and scaling potential, moreover induces an unbalance in the natural sulphur cycle (Sarti et al., 2009).

Slovak Republic as a country with long-lasting mining activities now battle with the difficulty of AMD discharge at several localities. Various national groups of researchers reported the results of the monitoring (Kupka et al., 2012; Lintnerova et al., 2008; Luptakova et al., 2012; Singovska et al., 2013) and treatment of mine waters (Balintova and Petrilakova, 2011; Spaldon et al., 2012). While a number of treatment option have been proposed for the remediation of AMD, the use of sulphate reducing bacteria (SRB) in the bioremediation processes is increasingly of interest. These microorganisms can be defined as a mixed group of morphologically diverse, strictly anaerobic bacteria that use sulphate (or other oxidized sulphur compounds) as a terminal electron acceptor, resulting in the production of sulphide. The process is coupled with oxidation of different anorganic and organic growth substrates (hydrogen, ethanol, lactate, formate, pyruvate) (Muyzer and Stams, 2008). Sulphate reduction can be applied to remediation, such as the removal of sulphates and heavy metals in the form of low-soluble sulphides.

The objective of our work was the use of biological-chemical treatment processes, based on the

activity of sulphate reducing bacteria, for removing of selected metals (Cu, Zn) and sulphates from mine waters discharged from the closed Smolnik sulphidic deposit.

Materials and methods
Acid mine drainage
The abandoned Smolnik mine is an important and permanent source of acid mine drainage. Poly-metallic Smolnik deposit was exploited from the 14th century to 1990. The flooding in the period 1990-1994 resulted in the generation and discharge of acidic water with high content of heavy metals and sulphates (Jasko et al., 1996).

Samples used in the experiments were collected from the shaft Pech, which receives waters draining of the Smolnik deposit. Concentration of pollutants monitored in this work is listed in the Table 1.

Microorganisms
The culture of sulphate-reducing bacteria (genera *Desulfovibrio*) was used in experiments, isolated from a mixed culture of SRB obtained from the mineral water Gajdovka (Košice, Slovak Republic). For the isolation and cultivation the selective nutrient Postgate`s medium C has been used at 30°C and anaerobic conditions (Postgate, 1984).

Analytical procedures
The concentration of metals in the samples was determined by atomic absorption spectrometry (AAS) using Spectrometer Varian 240FS/240Z (Australia). The qualitative analysis of samples was done by energy dispersive spectrometry (EDX) using microanalyser MIRA3 FE-SEM (TESCAN, Czech Republic). Sulphates determi-

nation was made by nefelometric method at 490 nm utilizing Spektromom 195 (Hungary) spectrophotometer. The pH of the cultivation media and samples was measured by Radiometer Analytical PHM 210 MeterLab (France) pH-meter. For filtration membrane filters Pragopor (Czech Republic) were used with pore size 40 μm.

Removal of metals from AMD
The selected metals (Cu, Zn) were removed from AMD in the course of selective sequential precipitation process. By this manner selective recovery of iron, copper, aluminum, zinc and manganese was achieved in distinct pH regimes in the order given. As it is presented in our previous work, hydrogen peroxide as oxidizing reagent and sodium hydroxide and biologically produced hydrogen sulphide as precipitating agents were used at this method (Macingova and Luptakova, 2012). The conditions of the SSP procedure are presented in the Table 2. The particular metal precipitates were separated by filtration and air-dried after each step of the process.

Removal of sulphates from AMD
Batch studies on biological sulphates removal from AMD pre-treated in the previous process were carried out in four reactors containing 100 ml AMD and 100 ml modified Postgate`s medium C (without sulphate content). AMD serves as a source of sulphates for dissimilatory sulphate reduction. In the experiment different growth substrates has been used: sodium lactate according to prescribed media with values of COD 2.5 g/L (sample La-Na 1), and 5 g/L (sample La-Na 2); calcium lactate with values of COD 2.5 g/L (sample La-Ca 1) and 5 g/L (sample La-Ca 2). Each of

Tab. 1. Monitored parameters of AMD in comparison with national limit values

Tab. 1. Obserwowane parametry AMD w zestawieniu z wartościami narodowego limitu

Parameter	pH	SO_4^{2-}	Fe	Cu	Al	Zn	Mn
		mg/L					
value	3.8	2038	305.25	3.78	68.38	7.30	23.50
limit value	6-8.5	250	2.0	0.02	0.2	0.1	0.3

Tab. 2. The course of the SSP process

Tab. 2. Przebieg procesu SSP

step	1	2	3	4	5	6
pH	3.8→2.8	2.8→3.7	3.7	3.7→5.0	5.0	5.0→9.0
reagent	H_2O_2	NaOH	H_2S	NaOH	H_2S	NaOH
removed metals	Fe	Fe	Cu	Al	Zn	Mn

the reactors was inoculated with 10% of a 3-day SRB culture. The abiotic controls with substrates sodium lactate and calcium lactate with COD 5 g/L have been prepared (samples La-Na k and La-Ca k). The conditions for growth of the SRB were kept the same as that of the prescribed media. Daily the samples were collected over a week.

Results and discussion
By SSP selective recovery of metals (Fe, Cu, Al, Zn, Mn) was achieved in the experiment using discrete chemical and biological stages. Hydrogen sulphide produced in the process of SRB cultivation was used at third and fifth step of the process. At pH of 3.7 copper and at pH of 5.0 zinc was recovered in the form of sulphides. EDX analysis confirmed the elementary composition of obtained metal solids (Figure 1 and Figure 2). Small percentage of Na in the case of Zn-precipitates originates probably from the fourth step of the SSP, where the Al was removed from AMD using sodium hydroxide as reagent. Particular precipitates weren`t washed after filtration. Listed metals were removed from AMD to concentrations meeting the required national limit values.
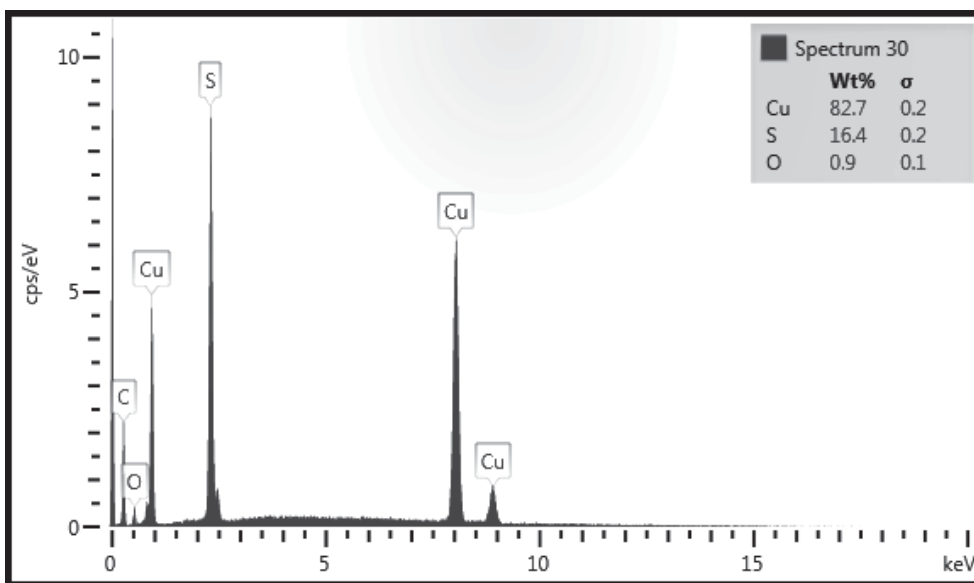

Fig. 1..Analysis of Cu-precipitates

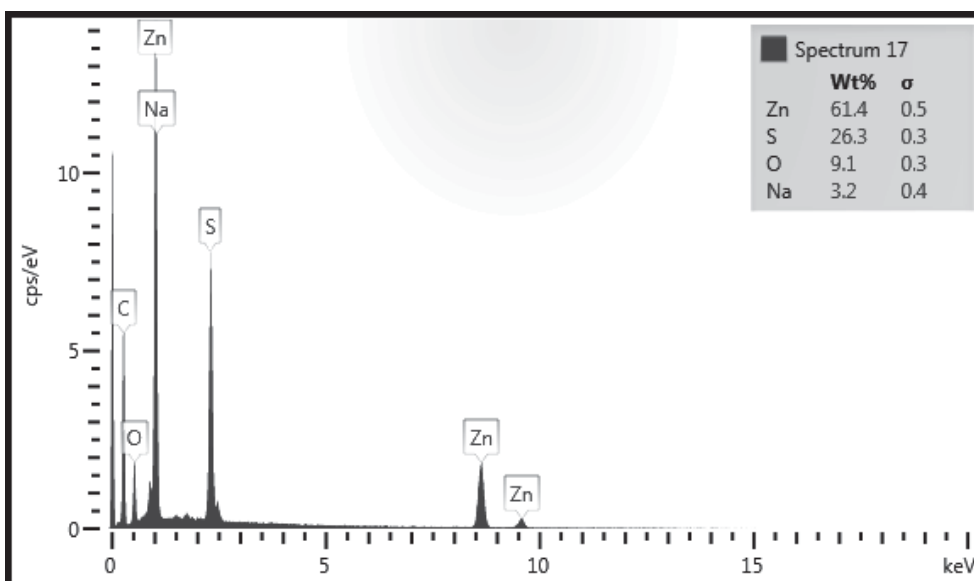Rys. 1. Analiza osadów miedzi

Fig. 2. EDX analysis of Zn-precipitates
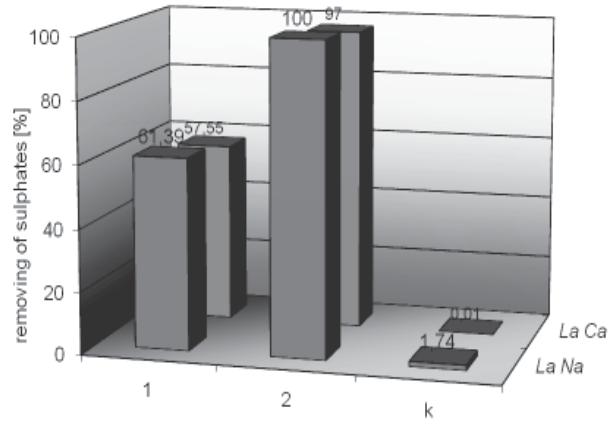
Rys. 2. Analiza metodą EDX osadów cynku

Fig. 3. Efficiency of sulphates removal
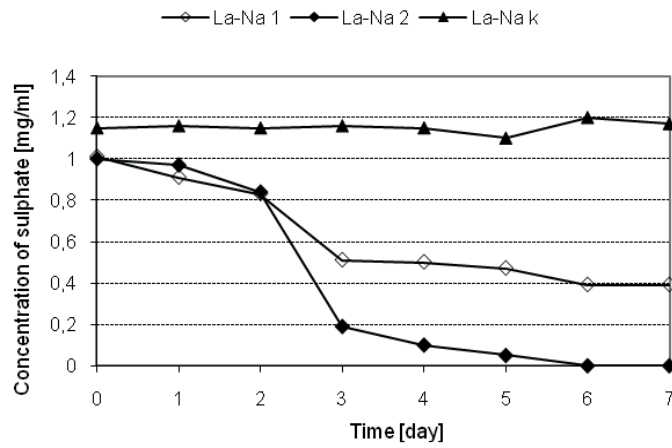
Rys. 3. Obniżenie skuteczności siarczanów

Fig. 4. Kinetic of sulphate reduction (substrate La-Na)
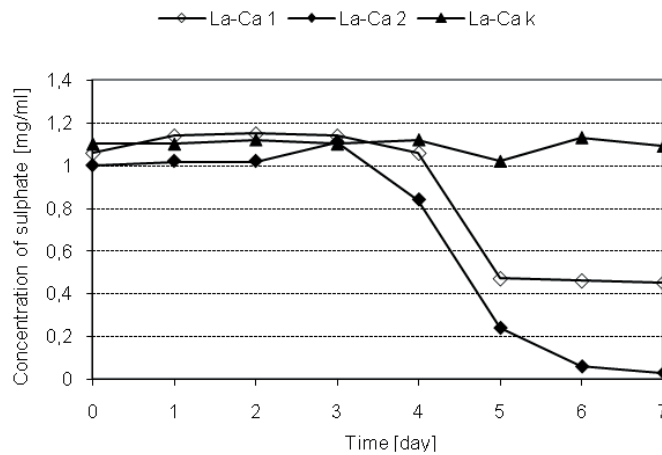
Rys. 4. Kinetyczna redukcja siarczanów (substrat La-Na)

Fig. 5. Kinetic of sulphate dreduction (substrate La-Ca)

Rys. 5. Kinetyczna redukcja siarczanów (substrat La-Ca)

In the next step the biological sulphates removal from AMD using SRB was studied. The decreasing of the sulphate concentration was monitored during the process. For the experiment different growth substrates – sodium lactate and calcium lactate were used. Due to the big number of potential substrates the chemical oxygen demand (COD) was introduced to quantify the mass or concentration of organic materials (Van Handel and Van der Lubbe, 2007). The COD/SO4^{2-} ratio in the feed is an important parameter related to electron flow in anaerobic metabolism. Experimental data showed that a lower or higher ratio results in the sulphate removal value. The ratio of 4.90 lead to 100% and 97% efficiency, the ratio 2.45 lead to 61.39% and 57.55% efficiency of sulphate removal using the sodium lactate and calcium lactate growth substrate, respectively (Figure 3). Figure 4 and Figure 5 show the influence of the substrate nature on the sulphate reduction kinetic. Concentration of sulphates in the abiotic controls did not change.

Conclusion

This work confirms the possibility of using sulphate reducing bacteria for the treatment of acid mine drainage at laboratory condition. Hydrogen sulphide produced by SRB for recovery of Cu and Zn has been used in the course of selective sequential precipitation process. In the next experiment removing of sulphates from acid mine drainage by dissimilatory sulphate reduction has been reached with 100% and 61.39% (La-Na); 97% and 57.55% (La-Ca) efficiency depend on the type and mass of used growing substrate. In these processes the monitored pollutants were removed from raw AMD discharged from the shaft Pech to levels meeting the limits established by Slovak legislation.

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Biologiczne oczyszczanie nieorganicznych zanieczyszczeń dzięki kwaśnemu drenażowi kopalni

Kwaśny drenaż kopalni (skr. AMD) to jedno z największych odpowiedzialności środowiskowych i finansowych jakie spoczywają na przemyśle kopalnianym. Zarówno obecnie działające kopalnie, jak i te niedziałające od lat, produkują wodę o dużym stężeniu siarczanu i metali ciężkich. Metody mające na celu złagodzenie działania AMD na środowisko skupiają się na neutralizacji, stabilizacji i eliminacji zanieczyszczeń przez liczne procesy fizyczne, chemiczne i biologiczne.

Niniejsza praca przedstawia wyniki z oczyszczania nieorganicznych zanieczyszczeń przy użyciu bakterii redukującej siarczany (skr. RB). Produkowany przez nią siarkowodór, dla uzupełnienia miedzi i cynku, został użyty podczas sekwencyjnego losowego procesu wytrącania (SSP). Następnie usunięto siarczany z AMD dzięki anaerobicznej redukcji. Dzięki tej metodzie udało się usunąć metale i siarczany w następnych dyskretnych etapach.

Badania zostały przeprowadzone w warunkach laboratoryjnych na wodzie uzyskanej z odpływu AMD w wale kopalnianym Pech z zamkniętego i zalanego depozytu Smolniksulphidic (Słowacja).

Słowa kluczowe: kwaśny drenaż kopalni, bakterie redukujące siarkę, biogeniczne siarczany, odzysk metali ciężkich