Combination of Chemical and Biological-Chemical Methods for Elimination of Metals from Acid Mine Drainage

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Abstract

Each acid mine drainage has a specific composition, but always contains sulphuric acid, dissolved heavy metals, sulphates, iron precipitates and their pH can be very low. The elimination of metals form the acid mine drainage is a severe environmental problem and has been a long-standing major concern to scientists, engineers, industry and governments. Various methods are used for the metals removal from waters, but any of them have been applied under commercial-scale conditions. Mostly studied are chemical and biological-chemical methods. Main aim of the paper was to interpret the combination of chemical and biological-chemical methods for the heavy metals elimination from the synthetic solution of acid mine drainage, coming from the zinc mine located in Tùnel Kingsmill outlet of the Rio Yaulì (district of Yauli – Perù). The metals selective precipitation as hydroxides (chemical method) and sulphides (biological-chemical method) at the various values of pH acid mine drainage is the fundamental of the examined process. For the hydrogen sulphide production the sulphate-reducing bacteria of genus Desulfovibrio was used. The selective sequential precipitation process reaches the selective precipitation of chosen metals with 97–99% efficiency – Fe, As, Al and Mn in the form of metal hydroxides, Cu and Zn as metal sulphides.

Keywords: *acid mine drainage, sulphate-reducing bacteria, metal sulphides, selective sequential precipitation*

Introduction

Acid mine drainage (AMD) is considered as one of the most dangerous forms of water pollution in areas of the world that have active or historic mining operations. The source of acid mine drainage is the residues of mining activity mainly after the mining of deposits with the content of sulfide minerals. AMD always contains sulfuric acid, dissolved heavy metals, sulfates and iron precipitates. Its value of pH is very low, about 1.5–2.0 (Johnson and Hallberg, 2003). AMD cause the decomposition of other minerals, the devastation of the surrounding environment, the contamination of underground water and water streams by a wide range of elements, including the toxic ones, the penetration of metals into the food chain, etc.

Generally are used two strategies for treating AMD: active and passive technologies (Skousen et al., 1998). Conventionally, hydroxide precipitation is the most commonly applied method for the treatment of metal containing waters (Kalin et al., 2006). The production of the high quantities of the unstable metal hydroxides mixture, which also lead to a greater disposal expense, is the main disadvantage of the method. The high operating costs and the production of a bulky sludge, which must be disposed, are the disadvantages of the traditional chemical treatment.

In the treatment of AMD the application of bacterially produced hydrogen sulfide by sulfate-reducing bacteria (SRB) is becoming an alternative to conventional chemical treatment (Kaksonen and Puhakka, 2007). The basic metabolic process of SRB is the anaerobic reduction of sulphates in which organic substrate (lactate, malate, etc.) or gaseous hydrogen is the electron donor and sulphate is the electron acceptor (Odom and Singleton, 1993). The research and development of the appropriate combinations of the chemical and biological-chemical methods for the metals selective recovery from AMD, suggested the interesting solving problems concerning the AMD treatment. These methods constitute the possibility of the recovery metals in a suitable form for commercial or industrial utilization (Costa et al., 2008).

The combination of the metal precipitation using the sodium hydroxide (chemical methods) with the metal precipitation using the bacterially produced hydrogen sulfide (biological-chemical method) presents the base of the selective sequential precipitation (SSP) (Tabak et al., 2003). It is the environmentally friendly way for elimination metals and metalloids from AMD.

In this study the synthetic solutions of AMD from a lead and zinc mine located in Tùnel Kingsmill outlet of the Rio Yaulì (district of Yauli – Perù) was used. The Kingsmill Tunnel was built between 1929 and 1934 by the Cerro de Pasco Copper Corporation. The tunnel drains mines Morococha mining district in Yauli River, which then flows into the Mantaro, affecting about 900000 inhabitants of the Mantaro Valley, Junín Region. Currently, an acidic water pouring Kingsmill Tunnel is approximately 1,250 liters per second, with a pH of 3.5–5.0. The river is contaminated by water of the tunnel when they are discharged into their flow, as these are oxidized prior to

Tab. 1. Metals concentration and pH of AMD sample from Tùnel Kingsmill (district of Yauli – Perù)
Tab. 1. Stężenie metali i pH próbki AMD z Tùnel Kingsmill (dystrykt Yauli – Perù)

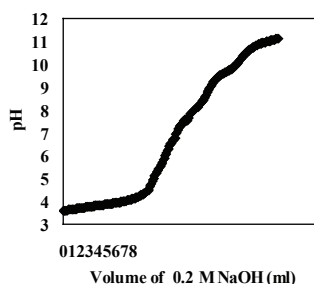|	pH	Concentration (mg/L)					
		Fe	As	Al	Cu	Zn	Mn
Value	3.0	129	2	8	12	70	50

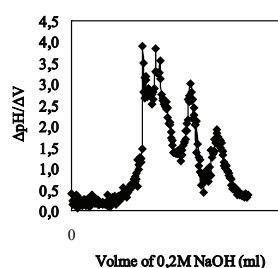Fig. 1. Integral titration curve
Rys. 1. Całkowa krzywa miareczkowania

Fig. 2. The first derivation of the integral titration curve
Rys. 2. Pierwsze wyprowadzenie całkowej krzywej miareczkowania

making contact with the minerals and metals. Peruvian mining companies are finalizing the feasibility studies using conventional remediation technologies involving the addition of lime.

The main objective of the paper was to interpret SSP as a way to separate chosen metals (Fe, As, Cu, Al, Zn and Mn) from the model solution of Peruvian AMD.

Materials and methods
Synthetic Solution of Acid Mine Drainage
The experiments were carried out at the laboratory scale using a synthetic solution of an AMD coming from the zinc mine located in Tùnel Kingsmill outlet of the Rio Yaulì (district of Yauli – Perù).

A synthetic solution with similar properties to the real sample of AMD was prepared. Reagents with a high analytical degree of purity were used (RPE Carlo Erba). Based on the concentration of metals in the real AMD sample, the corresponding salts were weighed and dissolved in deionized water. The solution with a pH of 3.0 was achieved after adjusting the pH value using 5M NaOH. The annual average metals concentration and pH values of peruvian AMD describes Table 1.

Metals precipitation by NaOH
The precipitation by 0.2M NaOH solutions was used for the informative removal of metals as hydroxides. 100ml of the AMD synthetic solution was titrated at a pH ranging from 3.0 to 10 using a 0.2M NaOH solution. During titration the

solution was continuously stirred. Changes of pH using a pH-meter PHM210 MetLab were monitored. Accrued precipitates were not removal form liquid phase. The metals concentration (Fe, As, Cu, Al, Zn and Mn) in solution by atomic absorption spectrometry (AAS) was determined.

The detailed determination of the metals precipitation pH values from studied model solution was performed by the acid-base titration – alkalimetry using automatic titrator TitraLab 850 in connection with PC program TitraMaster 85. Titration agent was 0,2M NaOH solution. After precipitation of individual metals, accrued precipitates were removed by filtration. The concentration of metals in liquid phase by the AAS was determined.

Metals precipitation by bacterially produced H₂S
The informative precipitation of heavy metals at pH 3.0 (initial pH the AMD synthetic solution), in the form of sulfides was performed in two interconnected tanks with a capacity 500 ml (the first tank - the bacterial production of hydrogen sulfide) and 250 ml (the second tank - the heavy metals precipitation by the bacterially produced H₂S) (Luptakova et al., 2002). For the hydrogen sulfide production the cultures of SRB (genus Desulfovibrio) were used. Bacteria were isolated from the potable mineral water (Gajdovka spring, Kosice-north, Slovakia). The genus Desulfovibrio was enriched from the mixed cultures SRB using the nutrient Postgate's medium C (Postgate, 1984; Luptakova et al., 2011). The SRB cultivation for the bacterial production of hydrogen sulfide was carried
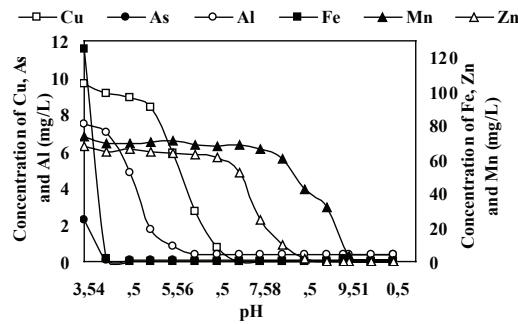
Fig. 3. Chemical analysis of the AMD synthetic solution during titration by 0.2 M NaOH

Rys. 3. Analiza chemiczna syntetycznego roztworu AMD podczas miareczkowania 0,2 M NaOH
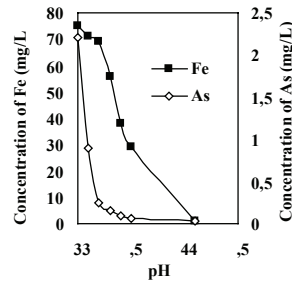

Fig. 4. The co-precipitation of Fe and As in the form of hydroxides

Rys. 1–4. Liczba turystów w prowincji Quang Ninh, Małopolsce i Krakowie [11–12]

Fig. 4. The co-precipitation of Fe and As in the form of hydroxides

Rys. 4. Współstrącanie Fe i As w postaci wodorotlenków

Time (min)	Concentration of metals (mg/L)					
	Fe	As	Al	Cu	Zn	Mn
0	129	**2.00**	8.00	**12.00**	70.00	50.00
5	128	**1.89**	7.98	**0.57**	69.80	49.98
10	129	**1.08**	8.00	**0.02**	70.00	49.96
15	127	**0.93**	8.00	**0.02**	70.00	49.98
30	127	**0.56**	7.97	**0.02**	70.00	50.00
60	128	**0.53**	7.98	**0.02**	70.00	49.97

Tab. 3. Metals precipitation by NaOH and bacterially produced H_2S (initial pH of AMD synthetic solution 3.5)

Tab. 3. Wytrącanie metali przez NaOH i bakteryjnie wytwarzany H_2S (początkowe pH syntetycznego roztworu AMD 3,5)

Step	pH	Precipitating agent	Removed metals
1.	3.5 → 4.5	NaOH	Fe, As
2.	4.5 → 3.9	H_2S	Cu
3.	4.0 → 5.8	NaOH	Al
4.	5.8 → 6.5	H_2S	Zn
5.	6.8 → 10.5	NaOH	Mn

out using the same nutrient medium. The heavy metals concentration in the liquid samples taken from the second tank by the AAS was determined.

Selective Sequential Precipitation

The selective sequential precipitation was realized to using the combined application of sodium hydroxide solution and hydrogen sulfide produced by sulfate-reducing bacteria. The bases of SSP were next principal steps: 1 – addition of 0,2M NaOH solution by the automatic titrator TitraLab 850; 2 – filtration of precipitates; 3 – addition of bacterially produced hydrogen sulfide by the equipment consist of two interconnected tanks. After each addition of the precipitating agent and metals precipitation, accrued precipitates were removal by filtration. The concentration of metals in the fil-

trates during SSP by the AAS was determined. For the hydrogen sulfide production in the framework of 2.step the same cultures of SRB (genus Desulfovibrio) were used, as in case of aforementioned experiments concerning of the metals precipitation by bacterially produced H_2S. A little amount of H_2O_2 has been added to the synthetic solution with the aim to provide the presence of Fe, As and Mn in the form of Fe^{3+}, As^{5+} and Mn^{2+}. The suitable pH values for selective precipitation of metals using automatic titrator TitraLab 850 in connection with PC program TitraMaster 85 were performed. Titration agent was 0,2M NaOH solution.

Results and discussion

Each metal in aqueous solution precipitates by addition of sodium hydroxide solution or hydrogen sulfide at specific pH

levels (Tabak et al., 2003). The acid-base titration – alkalimetry is simple and convenient method for the suitable pH values determination of the metals selective precipitation from aqueous solution (Totsche et al., 2003). It helps to explain the AMD forming procedure and helps to find the treat method. The issue of alkalimetry is the titration curve. Its shaped likes a staircase. Vertical part shows the process OH- ions neutralizing H$^+$ ions, which increases the pH of water. Horizontal part indicates OH- ions precipitate metal ions into metal hydroxides, which will act as a buffer, using hydroxide from the titrant, keeping the pH constant for a brief time until a specific metal has completely precipitated. When pH reaches certain level the metal ions will precipitate and be eliminated from the water. This forms the stair steps of the titration curve.

For all that the first part of experiments was oriented on the metals precipitation pH values determination using the acid-base titration with 0.2 M NaOH. The initial pH of AMD solution was 3.5. Figure 1 describes the shapes of the AMD synthetic solution integral titration curve and Figure 2 its the first derivation. The chemical analysis of the AMD synthetic solution during titration (Figures 3 and 4) documented the co-precipitation of Fe and As at pH <3.5–4.0>. Next the successive precipitation of Al (pH 5.8), Cu (pH 6.5), Zn (pH 8.5) and Mn (10.2) were observed. The co-precipitation of Fe and As is in accordance with results of many authors (Kaksonen and Puhakka, 2007), because the arsenic compounds have the high affinity for adsorption on the iron hydroxide.

During the metals precipitation by bacterially produced hydrogen sulfide at the initial pH of the AMD synthetic solution, the co-precipitation of Cu and As were observed. Table 2 presents that at pH 3.0 Cu was effectively recovered using biologically produced H2S. After 10 minutes the concentration of Cu was 0.02 mg/L. The selective precipitation of Cu

was not achieved because was evidenced the decreasing of As concentration too (Table 2.).

After determination of the suitable pH values for metals selective precipitation were realized experiments concerning of the SSP. The metals selective precipitation as hydroxides or sulphides at the various values of pH AMD is the fundamental of the examined process. The working conditions, occurrence of metal precipitates and obtained results of the selective sequential precipitation of heavy metals form AMD synthetic solution illustrates Table 3. Bacterially produced hydrogen sulphide reacts with the available metal ions in AMD to form insoluble metal sulphides at the appropriate values of pH. When pH of the studied solution is adjusted by sodium hydroxide come to consequent precipitation of metals in the form of hydroxides.

Conclusion

SSP process demonstrates the removal of heavy metals from aforementioned AMD synthetic solution by the combined application of sodium hydroxide solution and bacterially produced hydrogen sulfide. SSP is able to sequentially precipitate of Fe^{3+}, As^{5+}, Al^{3+} and Mn^{2+} in the form of hydroxides; Cu^{2+} and Zn^{2+} in the form of sulfides. For the removal of Cu and Zn in the form of sulfides were received excellent results. For the removal of Al and Mn in the form of hydroxides were received good results (the minor co-precipitation was observed). Was not come to good results point of view of the Fe and As the selective precipitation, because was determined the co-precipitation of Fe and As.

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Połączenie chemicznych i biologiczno-chemicznych metod eliminacji metali z kwaśnego drenażu kopalnianego

Każdy kwaśny drenaż kopalniany ma określony skład, ale zawsze zawiera kwas siarkowy, rozpuszczone metale ciężkie, siarczany, osady żelaza, a jego pH może być bardzo niskie. Eliminacja metali z kwaśnego drenażu kopalnianego jest poważnym problemem środowiskowym i od dawna stanowi poważny problem dla naukowców, inżynierów, przemysłu i rządów. Różne metody są stosowane do usuwania metali z wód, ale żadna z nich została zastosowana w warunkach komercyjnych. Przeważnie badane są metody chemiczne i biologiczno-chemiczne. Głównym celem pracy była interpretacja połączenia chemicznych i biologiczno-chemicznych metod eliminacji metali ciężkich z syntetycznego roztworu kwaśnego drenażu kopalnianego pochodzącego z kopalni cynku zlokalizowanej w wylocie Tùnel Kingsmill w Rio Yaulì (dzielnica Yauli – Peru). Podstawą badanego procesu jest selektywne wytrącanie metali w postaci wodorotlenków (metoda chemiczna) i siarczków (metoda biologiczno-chemiczna) przy różnych wartościach pH kwaśnego drenażu kopalnianego. Do produkcji siarkowodoru wykorzystano bakterie redukujące siarczany z rodzaju Desulfovibrio. Proces selektywnego sekwencyjnego wytrącania osiąga selektywne wytrącanie wybranych metali z wydajnością 97–99% – Fe, As, Al i Mn w postaci wodorotlenków metali, Cu i Zn jako siarczków metali.

Słowa kluczowe: *kwaśny drenaż kopalniany, bakterie redukujące siarczany, siarczki metali, selektywne sekwencyjne wytrącanie*