

STUDY OF PRECIPITATING METHODS FOR ELIMINATION OF HEAVY METALS FROM ACID MINE DRAINAGE

ALENA LUPTÁKOVÁ¹, STEFANO UBALDINI²,
EVA MAČINGOVÁ¹, INGRIDA KOTULIČOVÁ¹

¹*Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, Košice,
SK-043 53, Slovak Republic (luptakal@saske.sk)*

²*Institute of Environmental Geology and Geoengineering, CNR, Roma, Italy
(stefano.ubaldini@igag.cnr.it)*

Abstract: The submitted paper deals with the study of combination of chemical and biological-chemical methods for the heavy metals elimination from the acid mine drainage. The experiments were carried out at the laboratory scale using a synthetic solution with similar properties to the real sample of acid mine drainage, originating from the zinc mine located in Túnel Kingsmill outflow of the Rio Yauli (district of Yauli – Perú). The successive repetition of the metal precipitations as hydroxides (chemical method) and sulphides (biological-chemical method) at the various acid mine drainage pH was the basis of the examined processes. For the hydrogen sulphide production the sulphate-reducing bacteria of genus *Desulfovibrio* were used. Results confirmed the precipitation of Fe, As, Al and Mn in the hydroxide form; Cu and Zn in the form of sulphides. For the selective removal of Cu, Zn, Al and Mn the excellent results were received. Selective precipitation of Fe and As was not so successful since the co-precipitation of Fe and As was later determined as a main mechanism of the precipitate forming.

Keywords: acid mine drainage, metals, selective sequential precipitation

1. Introduction

Acid mine drainage (AMD) represents the major environmental problem especially associated with mining activities. The basis of the AMD generation is the oxidation of pyrite and other sulphidic minerals exposed to both oxygen and water. Each AMD has a specific composition, but always contains high concentration of the sulphuric acid, dissolved heavy metals, sulphates, iron precipitates and their pH values can be very low. Consequently AMD must be collected and treated before it can be discharged (YOUNGER *et al.*, 2002; KADUKOVA and STOFKO, 2009).

Various methods are used for the treatment of AMD but any of them have not been applied under the commercial-scale. Chemical and biological-chemical methods are mostly studied with the aim to eliminate metals, sulphates and achievement the neutral pH (PRASCAKOVA, 2005; KAKSONEN and PUHAKKA, 2007; JENCAROVÁ, 2008; KAVULICOVA *et al.*, 2009; IVANOVA *et al.*, 2010). In general two strategies - active and passive technologies - for treating AMD are used: (SKOUSEN *et al.*, 1998; BALINTOVA and LUPTAKOVA, 2012). In the conventional treatment system alkaline materials and other chemicals are added to the AMD to neutralize it and enhance hydroxide precipitation. Gradually the pH increases and the metal ions precipitation (for example as hydroxides) are achieved. Each metal in aqueous solution contributes to the AMD acidity. Additionally, individual metals precipitate at specific

pH levels. For example, hydroxides of Fe^{3+} precipitate at about pH 3 and of Al^{3+} at pH ranging from 3.7 to 4.5. Divalent metal ions precipitate in the alkaline range, Ni^{2+} at about pH 8, Fe^{2+} at pH ranging from 8 to 9 and Zn^{2+} at more than pH 9 (SKOUSEN *et al.*, 1998). The precipitation process is affected not only by reaction time but also by the thermodynamic considerations. The general importance of pH in an AMD system is not the only important factor in metal removal but also ionic strength, temperature, redox potential, and concentrations of suitable complexing agents (e.g. humic substances) and interactions of the precipitated solids play a significant role. The treatments using alkaline materials involve some serious limitations of application and effectiveness. They usually result in production of unstable metal hydroxides mixture, also leading to a greater disposal expense. The high operating costs and production of a bulky sludge, which must be disposed, are the disadvantages of the traditional chemical treatment.

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 solution of problems concerning the AMD treatment. These methods constitute the possibility of metals recovery in a suitable form for commercial or industrial utilization. The combination of the metal precipitation using the sodium hydroxide (chemical methods) and metal precipitation using the bacterially produced hydrogen sulphide (biological-chemical method) presents the base of the selective sequential precipitation (SSP) (TABAK *et al.*, 2003). The base of SSP is the evidence that metals in aqueous solution precipitate by addition of sodium hydroxide solution or hydrogen sulphide at specific pH levels. The acid-base titration by the sodium hydroxide solution is a simple and convenient method for the suitable pH determination of the metals selective precipitation from aqueous solution. The issue of alkalimetry is the titration curve (the vertical part shows the process OH^- ions neutralizing H^+ ions; the horizontal part indicates OH^- ions precipitating metal ions into metal hydroxides, which will act as a buffer keeping the constant pH for the short time until the specific metal will completely precipitate). When pH reaches at the certain level the metal ions will precipitate and be eliminated from the water. SSP is the environmentally friendly way for the metals and metalloids elimination from AMD.

The main objective of the paper was to interpret the SSP process that is the combination of chemical and biological-chemical methods as a way of chosen metals (Fe, As, Cu, Al, Zn and Mn) separation from the model solution of Peruvian AMD.

2. Materials and methods

2.1 Synthetic solution of acid mine drainage

The experiments were carried out at the laboratory scale using a synthetic solution of AMD coming from the zinc mine located in Túnel Kingsmill outlet of the Rio Yauli (district of Yauli – Perú). The synthetic solution with the 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 metal concentrations in the real AMD sample,

the model solution with the same metal concentrations was prepared. The corresponding salts were weighed and dissolved in deionized water. The solution pH value was adjusted to 3 using 5 M NaOH. A little amount of H₂O₂ was added to the synthetic solution with the aim to get Fe, As and Mn in the form of Fe³⁺, As⁵⁺ and Mn²⁺. The annual average metals concentration of Peruvian AMD is outlined in Table 1.

Table 1. Concentration of chosen elements of AMD sample from Peru with the annual average pH value 3.1.

Element	Al	Cd	Cu	Zn	As	Mn	Fe	Ca	Mg
Concentration (mg.l ⁻¹)	7.80	0.16	10.80	69.15	1.96	62.35	127.86	381	49.50

2.2 Chemical and biological-chemical methods combination

The successive repetition of the metal precipitation as hydroxides (chemical method) and sulphides (biological-chemical method) at the acid mine drainage various pH were the fundamental of the examined processes. This selective sequential precipitation (SSP) was realized in two principal steps: 1 – addition of 0,2M NaOH solution by the automatic titrator TitraLab 850; 2 – addition of bacterially produced H₂S by the nitrogen gas continuous transfer from the cultivation tank. The determination of suitable pH values for selective precipitation of metals from studied model solution was performed in the previous experiments by the acid-base titration – alkalimetry using automatic titrator TitraLab 850 in connection with PC program TitraMaster 85. The strains of SRB (genus *Desulfovibrio*) were used for the hydrogen sulphide production. Bacteria were isolated from the potable mineral water (LUPTAKOVA *et al.*, 2002; MACINGOVA, 2010). At the end of SSP respective steps the formed precipitates of the individual metals were removed by filtration from the AMD solution. In the filtrates the metal concentrations were analysed by atomic absorption spectrometry (AAS).

3. Results and discussions

Table 2 illustrates particular steps of the experimental procedure and obtained results of the selective sequential precipitation of heavy metals from the AMD synthetic solution.

Table 2. Metals precipitation by NaOH and bacterially produced H₂S.

	1-Step	2-Step	3-Step	4-Step	5-Step
pH	3.0→4.5	4.5→3.9	3.9→5.8	5.8→5.0	5.0→10.5
Precipitating agent	NaOH	H ₂ S	NaOH	H ₂ S	NaOH
Removed metals (precipitates)	Fe, As	Cu	Al	Zn	Mn

In the 1-Step of process the addition of 0.2 M NaOH into the AMD solution from initial pH 3.0 to pH 4.5 by the automatic titrator was realized. The addition was

performed slowly (0.1ml/min) and with the solution magnetic agitation. Formation of the orange precipitates was observed at pH around 3.5. Figure 1 outlines co-precipitation of As and Fe. This behaviour is in accordance with the results of many authors since the arsenic compounds are known to have the high affinity to adsorb on the iron hydroxide (KAKSONEN and PUHAKKA, 2007).

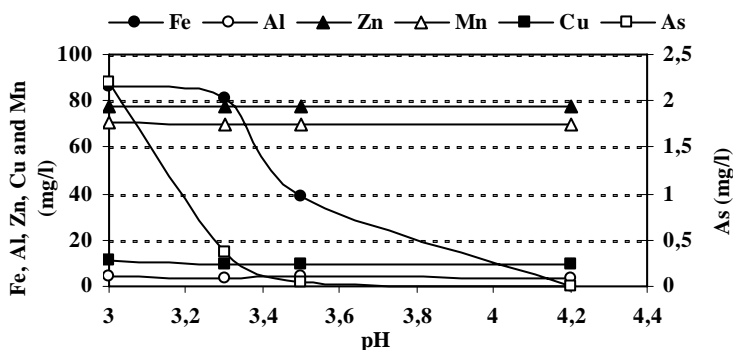


Fig. 1. Co-precipitation of As and Fe during the 1-Step of SSP process.

Bacterially produced H_2S was transferred by means of the nitrogen gas continuous flow from the bacteria cultivation tank into the filtrate (after the removal of As and Fe hydroxides by filtration) (2-Step). This step lasted for 30 minutes. The brown precipitates were observed shortly after 5 minutes. The pH of AMD solution decreased from 4.5 to 3.9 under the influence of the hydrogen sulphide (KAKSONEN and PUHAKKA, 2007). Cu was probably eliminated in the form of sulphide (Table 3).

Table 3. Precipitation of Cu by bacterially produced H_2S (2-Step of SSP process)

Time (min)	pH	Concentration (mg.ml ⁻¹)			
		Cu	Zn	Al	Mn
0	4.5	9.25	78	3,8	70.5
5	4.0	< 0.03	77,9	3,9	69.9
10	3.9	< 0.03	77,8	3,8	69.5
15	3.8	< 0.03	77,6	3,8	69.4
20	3.8	< 0.03	77,9	3,7	69.6
25	3.8	< 0.03	77,8	3,8	69.5
30	3.9	< 0.03	77,7	3,7	69.4

After the removal of Cu precipitates by filtration, 0.2 M NaOH solution was added into the filtrate by the automatic titrator until pH of 5.8 was reached (3-Step). The precipitation of Al was detected (Fig. 2). White Al precipitates were obtained after filtration. Bacterially produced H_2S was again added into the remaining filtrate (4-Step). The white precipitates were observed after 10 minutes. The decrease of AMD solution pH values from 5.8 to 5.0 was probably due to the influence of the hydrogen sulphide (Table 3). The white precipitates were removed and the last step of the

process, the addition of 0.2 M NaOH into the filtrate with consequent pH increase from 5.0 to 10.5, followed. The precipitation of Mn was identified (Fig. 3.).

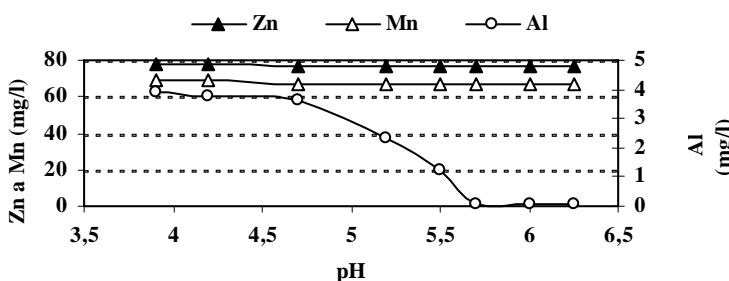


Fig. 2. Precipitation of Al during the 1-Step of SSP process.

Table 4. Precipitation of Zn by bacterially produced H₂S (4-Step of SSP process).

Time (min)	pH	Zn	Mn
		(mg.ml ⁻¹)	
0	5.8	75.4	69.8
5	5.4	22.6	69.6
10	5.2	0.6	69.5
15	5.1	0.6	69.4
20	5.0	0.6	69.6
25	5.2	0.5	69.5
30	5.0	0.5	69.4

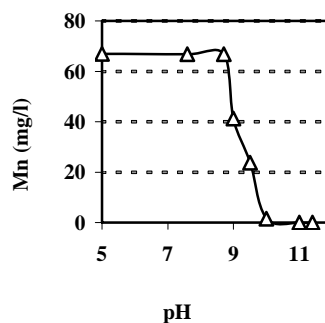


Fig. 3. Precipitation of Mn during the 5-Step of SSP process.

4. Conclusions

The combination of chemical and biological-chemical precipitating methods for the heavy metals elimination from the acid mine drainage was studied. The chemical method was realised by the metal precipitation using the sodium hydroxide and the biological-chemical method using the bacterially produced hydrogen sulphide. Their suitable combination presents the basis of the selective sequential precipitation (SSP). Achieved results demonstrated the possibility of heavy metals removal from the synthetic solution simulating the composition of acid mine drainage coming from the zinc mine located in Túnel Kingsmill outlet of the Rio Yauli (district of Yauli – Perú). In SSP process Fe³⁺, As⁵⁺, Al³⁺ and Mn²⁺ precipitated in the form of hydroxides and Cu²⁺ and Zn²⁺ in the form of sulfides. Excellent results were received for the removal of Cu, Zn, Al and Mn. Selective precipitation of Fe and As was not possible because of the co-precipitation of Fe and As.

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