

Physical-chemical and Biological-chemical Methods for Treatment of Acid Mine Drainage

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The main goal of the article was to demonstrate the technical feasibility of the heavy metals removal from the acid mine drainage coming from a lead and zinc mine located in Tùnel Kingsmill outlet of the Rio Yauli (district of Yauli – Perù) using physical-chemical and biological-chemical methods. The base of the physical-chemical method was the electrowinning. The principle of the biological-chemical method was the selective sequential precipitation of metals with the application of H₂S produced by the sulfate-reducing bacteria and NaOH solution. The experimental tests were conducted by the synthetic solutions of the acid mine drainage. Electrowinning tests were carried out after the chemical iron-aluminum precipitation that permitted a complete Fe-Al removal. By electrochemical experiments, high metals removal were achieved: in particular, by Zn and Mn electrodeposition, it was possible to achieve about 95 - 97% Zn and Mn removal (as MnO₂), with a relatively low energetic consumption. The results of the selective sequential precipitation documented that the pre-treatment of the synthetic solution by the H₂O₂ addition improved the selectivity of the process, except Fe and As. 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 sulfides.

1. 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 (Younger et al., 2002). The source of AMD is the residues of the mining activity mainly after the mining of deposits with the content of the sulfide minerals (Luptakova et al., 2002). AMD results when the metal sulfide minerals particularly pyrite come in contact with oxygen and water in the presence of a naturally occurring Fe- and S-oxidizing bacteria such as *Acidothiobacillus ferrooxidans* which acts as a biological catalyst (Akcil and Koldas, 2006). AMD always contain sulfuric acid, dissolved heavy metals, sulfates and iron precipitates. Its value of pH is very low, about 1.5 – 2.0. These components of AMD have a deleterious influence on the biota of streams receiving AMD and very negative influence on the surrounding environment (Balintova et al., 2010). Generally are used two strategies for treating AMD: active and passive technologies. Conventionally, hydroxide precipitation is the most commonly applied method for the treatment of metal containing waters. The high operating costs and the production of a bulky sludge, which must be disposed, are the disadvantages of the traditional chemical treatment. Recent research and development is focused on the physical, chemical (Plasari and Muhr, 2007; Balintova and Petrilakova, 2011) and biological methods for the selective recovery of metals from AMD (Prascakova,

2005; Luptakova et al., 2007). The goal is to recover metals in a suitable form for commercial or industrial utilization (Tabak et al., 2003; Kaksonen and Puhakka, 2007).

In this regards, the applications of the physical-chemical and biological-chemical methods like the electrowinning and the combination of chemical precipitation with the bacterial sulfate-reduction are interesting. Electrowinning as a technology is relatively cheap and environmentally friendly and produces metals with a high degree of purity (Ubal dini et al., 2008; Beolchini et al., 2009). The combination of the metal precipitation using the solution of sodium hydroxide (NaOH) with the metal precipitation using the bacterially produced hydrogen sulfide (H₂S) presents the base of the selective sequential precipitation (SSP) (Tabak et al., 2003; Kaksonen and Puhakka, 2007). It is the environmentally friendly way for elimination metals and metalloids from AMD. This process is based on the ability of sulfate-reducing bacteria (SRB) to perform reduction of sulfates on hydrogen sulfide. This bacterially produced H₂S reacts with the available metal ions occurring in AMD to form insoluble metal sulfides at appropriate pH values. When the pH of AMD is adjusted by NaOH metals precipitate in the form of hydroxides. The using of the bacterially produced H₂S for the sulfide precipitation has been demonstrates to have several benefits over the chemical sulfide precipitation e.g. the below cost of chemicals for the H₂S production, no need require process tanks to be closed and vacuum-evacuated for the H₂S storage, the better regulation of the H₂S production (Skousen et al., 1998; Kaksonen and Puhakka, 2007).

In this study the synthetic solutions of AMD from a lead and zinc mine located in Túnel Kingsmill outlet of the Rio Yauli (district of Yauli – Perú) 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 making contact with the minerals and metals. Peruvian mining companies are finalizing the feasibility studies using conventional remediation technologies involving the addition of lime. However, these methods present negative drawbacks - the production of secondary solid wastes. The main aim of the present experimental work was to test alternative technologies in order to remove heavy metals (Zn, Cu, Al, As, Mn and Fe) from Peruvian AMD, in a relatively cheap and environmentally friendly way, by means of the electrowinning (Ubal dini et al., 2010a) and the selective sequential precipitation (Luptakova et al., 2002).

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 (due to the unavailability of real AMD at the Italian and Slovak workplace) of an AMD coming from the zinc mine located in Túnel Kingsmill outlet of the Rio Yauli (district of Yauli – Perú). 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 3.5 was achieved after adjusting the pH value using 5 M NaOH. The annual average metals concentration and pH value of Peruvian AMD describes Table 1.

Table 1: Concentration of chosen elements and pH of AMD sample from Perú

pH	Concentration of metal (mg/L)							
	Zn	Cu	Al	As	Mn	Fe	Ca	Mg
3.5	69.15	10.80	7.80	1.96	62.35	127.86	381.00	49.50

2.2 Electrowinning

With the aim to oxidize Fe²⁺ eventually present to Fe³⁺ 0.1 ml of the 5 M HNO₃ was added to the synthetic solution. In a subsequent step, 5 M NaOH was added to reach pH 4.0. Successively, the

deposit was separated by filtration (Ubaladini et al., 2010b). Electrowinning tests were performed in a cylindrical glass laboratory cell of 200 cm³ volume (Ubaladini et al., 2006; Luptakova et al., 2010). The cell was connected to a potentiostat-galvanostat (Ubaladini et al. 2006; Luptakova et al., 2010a; Ubaladini et al., 2010b). With the scope to study the electrodeposition kinetic, liquid samples of 5 cm³ have been drawn and submitted to chemical analysis by ICP-MS. Purity of the solid deposit, was determined by X-Ray Diffraction technique (XRD). Metallic content of the deposit was analysed by ICP-MS (Beolchini et al., 2007).

2.3 Selective sequential precipitation

With the aim to provide the presence of Fe, As and Mn in the form of Fe³⁺, As⁵⁺ and Mn²⁺ 0.1 ml of 30 % H₂O₂ was added to the synthetic solution. The determination of suitable pH for the selective precipitation of metals was selected according to the literature (Kaksonen and Puhakka, 2007; Luptakova et al., 2010) and the results of the acid-base titration using automatic titrator TitraLab 850. Titration agent was 0.2 M NaOH. For the H₂S production the cultures of SRB (genus *Desulfovibrio*) were used. Bacteria were isolated from the potable mineral water (Gajdovka spring, Slovak Republic). The genus *Desulfovibrio* was enriched from the mixed cultures SRB using the nutrient Postgate's medium C (Postgate, 1984). The SRB cultivation for the bacterial production of H₂S was carried out in the anaerobic cultivation tank using the same nutrient medium. The combined application of NaOH and H₂S produced by sulfate-reducing bacteria i.e. the selective sequential precipitation (SSP) metals in the form of metal hydroxides or metal sulfide was realized in two principal steps: 1 – addition of 0.2 M NaOH by the automatic titrator; 2 – addition of bacterially produced H₂S by the nitrogen gas continuous transfer from the cultivation tank (Luptakova et al., 2010). The particular procedure was following: the addition of 0.2 M NaOH into the AMD solution with initial pH 3.5 up to the achievement pH 4.5; the metal hydroxides filtration; the addition of bacterially produced H₂S into the filtrate from the previous step for the duration of 60 minutes; the metal sulfides filtration; the addition of 0.2 M NaOH into the filtrate from the previous step up to the achievement pH 5.8; the metal hydroxides filtration; the addition of bacterially produced H₂S for the duration of 60 minutes; the metal sulfides filtration; the addition of 0.2 M NaOH up to the achievement pH 10.5; the metal hydroxides filtration. After each precipitation and filtration step the metal concentrations were analyzed in the liquid sample by AAS.

3. Results and discussions

3.1 Electrowinning

Preliminary chemical-pretreatment by NaOH, permitted precipitation of Fe together with Al and others toxic metals, while energetic consumption decreases during the electrowinning. Innovative technology such as electrowinning was developed during the experimental work with recovery of purified useful metals as Zn and Mn (Table 2). All metals deposited on the cathode, while Mn deposited on the anode as MnO₂.

Table 2: Main results achieved by Zn cathodic and MnO₂ anodic electrodeposition

Chemical species	Recovery (%)	Faradic current efficiency (%)	Energetic consumption (kWh/kg)
Zn	97.50	1.89	118.00
MnO ₂	95.00	1.75	619.05

In the first stage of the process, cathode deposition of Zn was achieved. In this phase, Cu and traces of Cd, Ni, Mn (as metallic Mn) metals co deposited with the Zn. Parameters reported in Table 3, permitted a decreasing of all metals concentrations (data not shown here) under the recommended limit suggested from Peruvian law directives (Quality III), with the exception of Ni, which is still a little high and requires further electrochemical experiments.

MnO₂ anodic deposition was achieved on the residual solution (Table 4), adding a little amount of concentrated H₂SO₄ for pH adjusting at the main experimental conditions.

Table 3: Main experimental conditions achieved for metallic cathode electrodeposition

Factors	Value
Cathode Vs. SCE (V)	-1.00 ÷ -1.23
Cell voltage (V)	2.50 ÷ 3.0
Current intensity (mA)	84 ÷ 90
Current density (mA.cm ⁻²)	0.84 ÷ 0.90
pH	4.0
Bath temperature (°C)	40
Electrolysis time (h)	6
Stirring conditions (rpm)	200

Table 4: Main experimental conditions achieved for MnO₂ anodic electrodeposition

Factors	Value
Cathode Vs. SCE (V)	1.33
Cell voltage (V)	1.73 ÷ 1.76
Current intensity (mA)	40 ÷ 300
Current density (mA.cm ⁻²)	0.4 ÷ 3.0
pH	0.97
Bath temperature (°C)	95
Electrolysis time (h)	6
Stirring conditions (rpm)	200

3.2 Selective sequential precipitation

Metals in aqueous solution precipitate by addition of sodium hydroxide solution or hydrogen sulfide at specific pH levels (Tabak et al., 2003). The acid-base titration by the sodium hydroxide solution is simple and convenient method for the suitable pH values determination of the metals selective precipitation from aqueous solution (Totsche et al., 2006). 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 precipitate metal ions into metal hydroxides, which will act as a buffer, 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. 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. The chemical analysis of the AMD synthetic solution during titration (Figure 2) documented the co-precipitation of Fe and As at pH <3.5 - 4.0>.

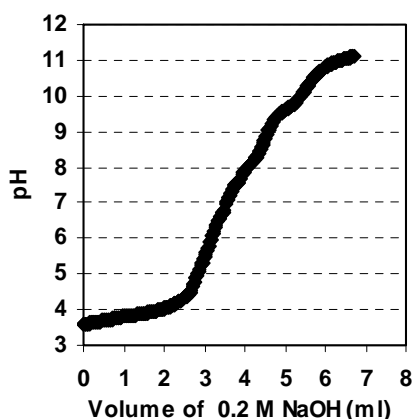


Figure 1: Integral titration curve

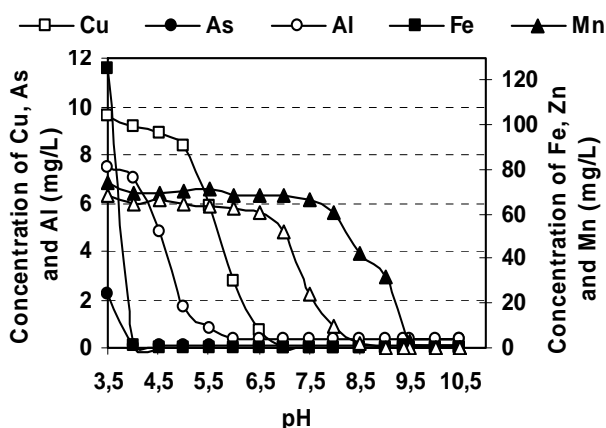


Figure 2: Chemical analysis of the AMD synthetic solution during titration by 0.2 M NaOH.

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.

After determination of the suitable pH values for the metals selective precipitation were realized experiments concerning of the SSP. The initial pH of AMD synthetic solution was 3.5. The working conditions, occurrence of metal precipitates and obtained results of the SSP of heavy metals from AMD synthetic solution illustrates Table 5 and Figure 3.

Table 5: Metals precipitation by 0.2 M NaOH and bacterially produced H₂S

	Step 1	Step 2	Step 3	Step 4	Step 5
pH	3.5 → 4.5	4.5 → 3.9	4.0 → 5.8	5.8 → 6.5	6.8 → 10.5
Precipitating agent	NaOH	H ₂ S	NaOH	H ₂ S	NaOH
Removed metals	Fe, As	Cu	Al	Zn	Mn
Metals in liquid phase	Cu, Al, Zn, Mn	Al, Zn, Mn	Zn, Mn	Mn	

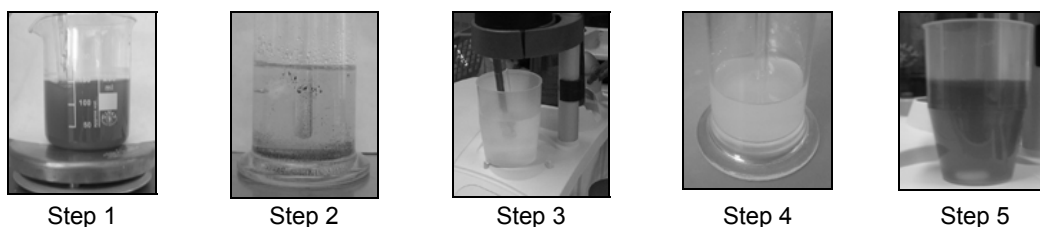


Figure 3: The metal precipitates formation by the selective sequential precipitation. by the sodium hydroxide solution and the bacterially produced hydrogen sulphide. Step 1 – the formation of Fe and As hydroxides; Step 2 – the formation of Cu sulphides; Step 3 – the formation of Al hydroxides; Step 4 – the formation of Zn sulphides; Step 5 – the formation of Mn hydroxides.

4. Conclusions

Biohydrometallurgical process constituted by chemical precipitation/electrowinning has demonstrated the technical feasibility of the process aimed at the removal of toxic metals from Peruvian AMD samples; in fact, at the end of the process, the metals' concentration decreased under the recommended legislation limit. It was possible to achieve 90 – 95 % metals removal. In particular, 97.50 % of Zn was recovered with an energetic consumption 118 kWh/kg, while 95 % of manganese was recovered as MnO₂ at grade of purity, with an energetic consumption 619.05 kWh/kg. SSP process demonstrates the removal of heavy metals from AMD synthetic solution by the combined application of NaOH solution and bacterially produced H₂S. SSP is able to sequentially precipitate of Fe, As, Al and Mn in the form of hydroxides and Cu and Zn in the form of sulfides. For the removal of Cu and Zn in the form of sulfides and Al and Mn in the form of hydroxides were received excellent results. But the high co-precipitation of Fe and As was detected. In this case the selectivity was not confirmed.

Acknowledgements

Work was supported by: Joint Project n.1 of the CNR/SAV (2010/2012); Project CNR RSTL n. 0042.0005; Joint Project n.2 of the CNR/CONCYTEC (Perù) (2009/2011); Slovak Research and Development Agency contract SRDA-0252-10 and the Scientific Grant Agency No. 2/0166/11.

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