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Application of Innovative Remediation Processes to Mining Effluents contaminated by Heavy Metals

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Abstract. The scope of the paper was to demonstrate the technical feasibility of the remediation processes by electrowinning and selective sequential precipitation, for toxic metals removal from acid mine drainage. By electrochemical experiments, high metals removal has been achieved: in particular, by Zn and Mn electrodeposition, it was possible to achieve about 93-99% Zn and Mn removal (as MnO_2), with a relatively low energetic consumption. The principle of the heavy metals selective sequential precipitation is the combined application of sodium hydroxide solution and hydrogen sulfide produced by sulfate-reducing bacteria. For the hydrogen sulfide production the sulphate-reducing bacteria of genus *Desulfovibrio* was used. The selective sequential precipitation process reaches the selective precipitation of chosen metals with 99% efficiency – Fe, As, Al and Mn in the form of metal hydroxides, Cu and Zn as metal sulfides.

Key words: heavy metals, Acid Mine Drainage, bioprecipitation, electrowinning, selective sequential precipitation.

Introduction

The elimination of metals from the mining effluents is a severe environmental problem and has been a long-standing major concern to scientists, engineers, industry, and governments, both in this country and throughout the world (Beolchini et al., 2007; Beolchini et al., 2009a; Beolchini et al., 2009b; Vegliò et al., 2003).

Various methods are used for the metals removal from waters, but any of them have been applied under commercial-scale conditions. Applications of methods depend on geochemical, technical, natural, financial and other factors. In addition each mining effluent i.e. acid mine drainage (AMD) is unique in regard to different chemical status and require different methods of treatment (Ubaldini et al., 2010). The AMD under study coming from a lead and zinc mine located in Tùnel Kingsmill outlet of the Rio Yaulì (district of Yauli – Perù). 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 (Luptakova et al., 2010). However, these methods present negative drawbacks - the production of secondary wastes (e.g. lime precipitation generates high volumes of solid wastes).The main aim of the present experimental work was to test innovative remediation processes in order to remove heavy metals (Al, As, Cu, Fe, Mn, Zn) from Peruvian AMD, in a relatively cheap and environmentally friendly way, by means of electrowinning and selective sequential precipitation (SSP) (Luptakova et al., 2011; Ubaldini et al. 2009).

Materials and Methods

The experimental activity has been carried out at laboratory scale by synthetic solutions, starting from AMD coming from the lead and zinc mine located in Tùnel Kingsmill outlet of the Rio Yaulì - Perù. The elemental composition of the peruvian AMD is reported in Table 1. The natural pH was of 3.5.

A little amount of nitric acid (HNO3) has been added to the synthetic solution, with the aim to oxidise Fe2+ eventually present to Fe3+. In a subsequent step, sodium hydroxide (NaOH) was added to reach pH 4.0 (Ubaldini et al., 2010b).

Electrowinning tests have been performed in a cylindrical glass laboratory cell of 200 cm3 volume. The cell was connected to a potentiostat-galvanostat (Luptakova et al., 2012).

Liquid samples have been whit 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 (Vegliò et al., 2003).

Table 1. Characterization of mine waste water samples from Perù (concentrazioni in μg/L).

Al	7778
Ni	29.9
Cd	156
Cu	10750
Zn	69144
Cr	4.9
As	1957
Sb	28.8
Pb	648
Mn	62353
Fe	127857
Hg	0.3
Ca	381.0 mg/L
Mg	49.5 mg/L
Na	3.8 mg/L
K	1.1 mg/L

The combined application of sodium hydroxide solution and hydrogen sulfide produced by sulfate-reducing bacteria i.e. selective sequential precipitation (SSP) was realized in too principal steps: 1 – addition of 0,2M NaOH solution by the automatic titrator TitraLab 850; 2 – addition of bacterially produced hydrogen sulfide by the equipment consist of too interconnected bioreactors. A little amount of H2O2 has been added to the synthetic solution with the aim to provide the presence of Fe, As and Mn in the form of Fe3+, As5+ and Mn2+. The determination of suitable pH values for selective precipitation of metals from studied model solution was performed by the acid-base titration – alkalimetry using automatic titrator TitraLab 850 in connection with PC program TitraMaster 85.

For the hydrogen sulphide production in the framework of 2.step the cultures of SRB (genus Desulfovibrio) were used. Bacteria were isolated in Kosice-north, Slovakia. The genus Desulfovibrio was enriched from the mixed cultures SRB using the nutrient Postgate's medium C (Luptakova et al., 2008). The SRB cultivation for the bacterial production of hydrogen sulfide was carried out using the same nutrient medium. After precipitation of individual metals accrued precipitates were removed from AMD by filtration. The concentration of metals during SSP was determined by AAS.

Results and Discussion

Innovative technology such as electrowinning has been developed during the experimental work with recovery of purified useful metals as Zn and Mn (Table 2). All metals deposited on the cathode, while manganese deposited on the anode as MnO_2.

In the first stage of the process, cathodic deposition of Zn was achieved. In this phase, Cu and traces of Cd, Ni, Mn (as metallic Mn) metals codeposited with the Zn. A decreasing of all metals concentrations (Table 2) under the recommended limit suggested from Peruvian law directives (Quality III).

MnO_2 anodic deposition was achieved on the residual solution, adding a little amount of concentrated H_2SO_4 for pH adjusting at the main experimental conditions.

The selectivity of the metals precipitation from AMD depends on the buffering systems. Its strength provides the titration curves, which determines the range of pH values for precipitation of individual metals. For all that the first part of experiments was centered on the study of titration curve by acid-base titration of the AMD synthetic solution with 0.2M NaOH. The results of alkalimetry were prepared in the form of titration curves. The shapes of the AMD synthetic solution integral titration curve (data not shown), its the first derivation (data not shown) and chemical analysis of the AMD synthetic solution during titration allocated five points of inflexion for precipitation metals: Fe + As (pH 4.5); Al (pH 5.8); Cu (pH 6.5); Zn (pH 8.5) and Mn (10.2). 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 sulfides at the various values of pH AMD is the fundamental of the examined process. The working conditions and obtained results of the selective sequential precipitation of heavy metals form AMD synthetic solution (Table 2). Bacterially produced hydrogen sulfide reacts with the available metal ions in AMD to form insoluble metal sulfides 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.

Table 3 describes some characteristics, advantages, disadvantages and improvements of studied processes.

Conclusion

Biohydrometallurgical applications constituted by bioprecipitation/electrowinning have 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.

In particular, electrowinning permitted 99 % of Zn recovery, whit an energetic consumption of 118 kWh/kg, while 93 % of manganese was recovered as MnO2 at grade of purity, with an energetic consumption of 619.05

Table 2. The metal removal efficiency of the integrated process applied to synthetic AMD sample.

Metal	Fe	As	Cu	Al	Zn	Mn
Input concentration (mg/L)	127.86	1.96	10.75	7.78	69.14	62.35
Output concentration (mg/L)	0.21	0.01	<0.005	0.08	<0.005	0.60

Table 3. Comparison of the studied processes (Luptakova et al., 2012).

	Electrowinning	Selective sequential precipitation
Pretreatment of the acid mine drainage (Oxidation Fe^{2+} to Fe^{3+})	Yes	Yes
Precipitates of the acid mine drainage pretreatment	Mixture of Fe and Al hydroxides	Mixture of Fe and As hydroxides
Removal efficiency of metals	Fe, Zn, Cu > 99% Al, Mn > 93%	Al, As, Cu, Fe, Mn, Zn > 99%
Form of the end product	Zn^0, MnO_2	Fe, Al, As, Mn – hydroxides Cu, Zn – sulfides
Selectivity of the processes	High for Zn and Mn	High for all metals
Degree of purity end product	Over 90%	Over 95%
Utilization of the products method	Anticorrosive protection Alloy production	Pigments production Metallurgical metal production[3]
Time of the realizations	2 hours	12 – 24 hours
Advantages	Production of Zn in the metallic form High purity of Zn	High selectivity, Simultaneous removing acidity, metals an sulfates Sulfur production
Disadvantages	Cost of electric energy	Cost of substrates for cultivation of sulfate-reducing bacteria
Improvements	Stabilization of pH using suitable salts	Cheap substrates for cultivation of sulfate-reducing bacteria

kWh/kg. SSP process demonstrates the removal of heavy metals from aforementioned AMD, by the combined application of sodium hydroxide solution and bacterially produced hydrogen sulfide.

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