# APPLICATION OF BIOHYDROMETALLURGICAL PROCESSES FOR HEAVY METALS REMOVAL FROM ACID MINE DRAINAGE

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**Abstract:** The main scope of this study was to remediate Acid Mine Drainage (AMD) by application of biohydrometallurgical processes, environmentally friendly, to remove heavy metals such as Zn, Cu, Mn, Cd, Al and Fe. The processes studied have been electrowinning and bioprecipitation. The samples utilised were collected from the zinc mine located in Italy and from a cooper – iron ore deposit in Slovakia. By electrochemical experiments, high metals removal, with a low energetic consumption, has been achieved: in particular, by Zn electrodeposition, it was possible to achieve 95-99% Zn removal. Culture of sulphate-reducing bacteria (SRB) of genera *Desulfovibrio sp.* was used for the bioprecipitation tests. The precipitation kinetic of metals at the original pH of aforementioned AMD by SRB has been investigated. This method has been performed in two interconnected reactors. Achieved results indicate the 98-99% selective elimination of Cd from AMD - Italian mine, and the 98-99% selective elimination of Cu from AMD - Slovak mine by bacterially produced $H_2S$. Both the electrowinning and bioprecipitation processes have been demonstrated the technical feasibility to decrease the heavy metals concentration.
The experimental work has been carried out in the framework of the agreement of scientific cooperation between the Institute of Environmental Geology and Geoengineering of the CNR, Italy and the Institute of Geotechnics of Slovak Academy of Sciences, Slovakia (years 2007-2009).

**Key words:** heavy metals, biohydrometallurgical processes, Acid Mine Drainage, *Desulfovibrio sp.*

## 1. Introduction

In contrast to most organic pollutants, heavy metals are never degraded. The only ways to remedy heavy metals-polluted lands are stabilization or extraction using the suitable methods (VEGLIÓ *et al*., 2003; KADUKOVA and STOFKO, 2006); BEOLCHINI *et al*., 2007). Various methods are used for redevelopment of soils and waters in the world (APHA, 1989), but any of them are universal (PAGNANELLI *et al*., 2003; BÁLINTOVA and KOVALIKOVÁ, 2008; UBALDINI *et al*., 2009). Classical treatments for the removal of heavy metals from contaminated waters are precipitation with lime or more expensive chemicals (EPSTEIN, 2003). However, these methods present negative drawbacks - the production of secondary wastes (e.g. lime precipitation generates high volumes of solid wastes) (UBALDINI *et al*., 2009). There is a need for new and low-cost technologies in the field of elimination metals from environment. With respect to involved proposition various authors have studied, at laboratory scale, the application of physicochemical and biological-chemical processes. Between the innovative and unconventional technologies belong for example the electrowinning and the bioprecipitation. Electrowinning process is

currently used at large scale to purify process solutions and to recover precious metals. Microorganisms play important roles in the environment fate of heavy metals (RONALD, 1995) with a multiplicity of physical, chemical and biological mechanisms effecting transformations between soluble and insoluble phases (BEOLCHINI *et al*., 2009a; BEOLCHINI *et al*., 2009b).

The biggest environmental problems relating to mining and processing activities in the worldwide is the formation and treatment of acid mine drainage (DIKMAN and BUISMAN, 1999). The source of acid mine drainage (AMD) is the residues of mining activity mainly after the mining of deposits containing of sulphide minerals. AMD contains sulphuric acid, metals in the soluble form and its pH can be very low (UBALDINI *et al*., 2006a). In Italy and Slovakia there are some localities with existing AMD generation conditions (UBALDINI *et al*., 2007a; UBALDINI *et al*., 2007b).

## 2. Materials and methods

### *2.1 Samples*

The investigation has been carried out at laboratory scale by synthetic solutions, starting from AMD from the zinc mine located in Montevecchio Mine (Italy) and Slovak Mine located in Smolník. The AMD characterisation is reported in Tables 1 and 2.

Table 1. Composition of the AMD Italian sample in mg/l.

| Zn | Cd | Cu | Ni | As | Sb | Pb | Mn | Fe | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1600 | 3.50 | 0.50 | 4.00 | 0.006 | 0.005 | 0.076 | 86 | 190 | 1800 |

Table 2. Composition of AMD Slovak sample in mg/l.

| Zn | Cd | Cu | Ni | As | Al | Pb | Mn | Fe | $SO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|
| 10.13 | 0.1 | 4.31 | 0.32 | 0.042 | 79.50 | 0.019 | 20 | 270 | 2938 |

### *2.2 Physical-chemical process: electrowinning*

Nitric acid ($HNO_3$) has been added to the synthetic solution, with the aim to oxidise $Fe^{2+}$ to $Fe^{3+}$. In a subsequent step, sodium hydroxide (NaOH) was added to reach pH 4.0. Successively, the deposit has been separated by filtration.

Electrowinning tests have been performed in a cylindrical glass laboratory cell of 200 $cm^3$ volume according to UBALDINI *et al*., 2008. The cell was connected to a potentiostat-galvanostat. With the scope to study the electrodeposition kinetic, liquid samples of 3 $cm^3$ have been whit drawn and submitted to chemical analysis by ICP-MS, while the purity of the solid deposit was determined by X-Ray Diffraction technique (XRD). Metallic content of the deposit was analysed by ICP-MS.

## *2.3 Biological-chemical processes: bioprecipitation*

The cultures of SRB (genera *Desulfovibrio sp.*) were used which were isolated from a mixed culture obtained from the potable mineral water (LUPTAKOVA *et al.*, 2002; LUPTAKOVA *et al*., 2008). Scanning electron micrographs of sulphate-reducing bacteria is reported in Figure 1.

The precipitation of heavy metals form AMD sample was performed in two interconnected bioreactors with a capacity 1000 ml (the first bioreactor) and 250 ml (the second bioreactor) (UBALDINI *et al*., 2006a; LUPTAKOVA *et al*., 2008a). The heavy metals concentration in the liquid samples taken from the bioreactor was determined by atomic absorption spectrophotometry. The qualitative analysis of precipitates obtained by bacterial produced hydrogen sulphide was realized by energy dispersive spectrometry (EDS) analysis. Samples of precipitates were dried and coated with gold prior to the EDS analysis.

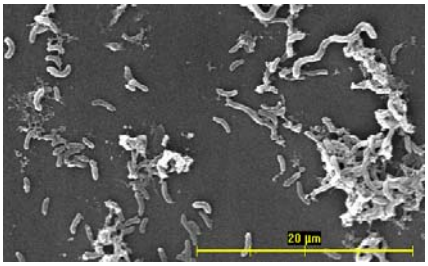


Fig. 1. Scanning electron micrographs of sulphate-reducing bacteria (*Desulfovibrio sp.)* (LUPTAKOVA *et al.*, 2002).

# 3. Results and discussion

## *3.1 Physical-chemical process: electrowinning*

Preliminary precipitation step has been carried out before electrowinning. During this phase, also Al deposition has been achieved. The liquor prepared was treated by using an electrowinning lab-scale operation, to verify the technical feasibility of the metals deposition.

The average results of the electrowinning tests on Montevecchio (initial pH 4.6) and Smolnik samples (initial pH 3.5), show that, after 30', Zn deposit was of low quality. After 1 h, Zn deposit was uniform, while on counter electrode surface $MnO_2$ deposited. Manganese deposited to the anode as $MnO_2$ and to the cathode as $Mn^+$. After 2 hours, 90-95% of the metals have been removed by a quantitative cathodic deposition. The high grade purity of the metallic deposit has been achieved, such as it was demonstrated from the results of analysis conducted by XRD.

At the end of the processes, all the metals concentrations decrease under the recommended limit suggested from EC (data not shown here) (Ubaldini *et al*., 2006a; UBALDINI *et al*., 2006b; UBALDINI *et al*., 2006c). Table 3 and Table 4 show the main results of Zn electrowinning from synthetic solution (AMD Italian and Slovak

samples, respectively), while Table 5 shows the results attained after chemical precipitation by NaOH (AMD from Slovak sample).

Table 3. Main results of Zn electrowinning of synthetic solution (AMD Italian sample).

| Time (min) | R (%) | η* (%) | E* (kWh/kg) |
|---|---|---|---|
| 90 | 97.98 | 21.65 | 16.23 |
| 120 | 99.85 | 13.05 | 30.21 |

***** *η - Faradic current efficiency, E - energetic consumption*

Table 4. Main results of Zn electrowinning of synthetic solution without chemical precipitation (AMD Slovak sample).

| Time (min) | R (%) | η* (%) | E* (kWh/kg) |
|---|---|---|---|
| 90 | 92.18 | 20.10 | 17.13 |
| 120 | 96.89 | 11.92 | 31.21 |

***** *η - Faradic current efficiency, E - energetic consumption*

Table 5. Main results of Zn electrowinning of synthetic solution after chemical precipitation (AMD Slovak sample).

| Time (min) | R (%) | η* (%) | E* (kWh/kg) |
|---|---|---|---|
| 90 | 97.07 | 25.94 | 12.00 |
| 120 | 99.71 | 14.99 | 24.91 |

***** *η - Faradic current efficiency, E - energetic consumption*

## *3.2 Biological-chemical processes: bioprecipitation*

During the metals bioprecipitation at the original pH of aforementioned AMD, only the precipitation of Cd (in the case of the AMD sample from Montevecchio Mine) and Cu (in the case of AMD sample from Smolnik - adit Pech) were observed.

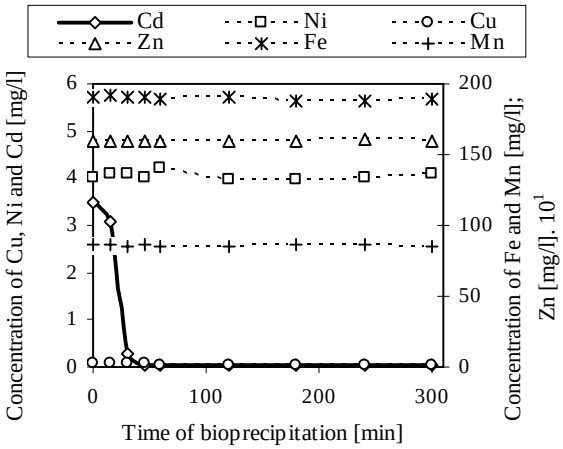


Fig. 2. Precipitation of heavy metals by biologically produced $H_2S$ by SRB from AMD - Italian mine at original pH value of AMD.

Fig. 2 presents that at pH 4.6 Cd was effectively recovered from AMD of Montevecchio Mine using biologically produced $H_2S$. After 30 minutes the concentration of Cd was 0.03 mg/L. On the basis of the results of EDS qualitative analysis, Cd was precipitated in the form cadmium sulphides.

In the event of the AMD Smolnik at pH 3.5, the initial copper concentration 4.31 mg/l was decreased to less than 0.05 mg/l after 4 hours (Fig. 3). EDS qualitative analysis of precipitates demonstrates that Cu was precipitated in the form sulphides CuS.

Concentration changes of other metals (Zn, Fe, Ni, Mn), were not significant or remained without changes in case of both aforementioned AMD.

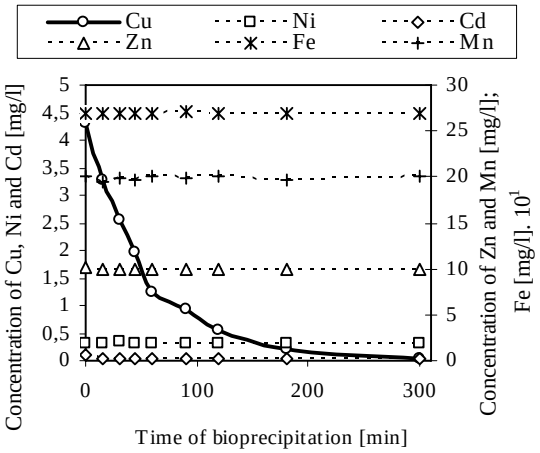


Fig. 3. Precipitation of heavy metals by biologically produced $H_2S$ by SRB from AMD – Slovak mine at original pH value of AMD.

## 4. Conclusions

By application of biohydrometallurgical processes, the technical feasibility to decrease the heavy metals concentration on the AMD studied has been determined.

In particular, through electrowinning, it was possible to achieve high Zn removal with a low energetic consumption, while bioprecipitation process demonstrates the selective precipitation of heavy metals by SRB from the AMD samples. At original pH value of AMD from Italian Mine was achieved only the precipitation of Cd. From AMD of Slovak mine was achieved only the precipitation of Cu at original pH value. Obtained results indicate the 98-99% elimination of Cd or Cu by bacterially produced $H_2S$.

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