



Recovery of Metals from Acid Mine Drainage

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Acid Mine Drainage (AMD) poses a severe pollution problem attributed to current and past mining activities. Low pH, high concentrations of sulphates and various heavy metals makes AMD treatment a major concern because of possible deleterious effects of the effluent on the surroundings. Treatment methods to address AMD focus on neutralizing, stabilizing and removing problem pollutants through various physical, chemical and biological processes. This paper reports the results of studies conducted to develop and optimize the process of selective sequential precipitation (SSP) of selected metals (Fe, Cu, Al, Zn, Mn) to produce high recoveries of metals from AMD. Remediation options involve both chemical and biological strategies. At the SSP process abiotic system uses sodium hydroxide to raising pH with consequential precipitation of metal hydroxides. Biological system exploits hydrogen sulphide produced by sulphate-reducing bacteria in order to precipitate metals as sulphides at the various values of AMD pH. In the optimized SSP process the iron was removed from AMD as first to improve the selectivity of the operation.

1. Introduction

Acid Mine Drainage (AMD), resulting from the uncontrolled oxidation of sulphide minerals greatly accelerated by certain lithotrophic prokaryotes (Johnson and Hallberg, 2003) is a serious environmental problem associated with mining activities and mineral processing. This drainage characterised by high concentration of sulphates and dissolved metals pollutes receiving streams and subsurface waters and causes degradation of surrounding soils. Due to the low pH, the solubility of the toxic metals contained in the AMD keeps up at a high level thus permits their dispersion into the environment (Hallberg, 2010). Precipitation using alkaline reagents is the most widely used treatment method for removing metals as hydroxides (Johnson and Hallberg, 2005; Balintova and Petrilkova, 2011). This technology is cost effective, easy of automatic pH control and can be applied to large operating units. However large volumes of hazardous concentrated sludge are generated requiring further treatment and controlled final disposal. The suitable alternative methods recover metals from AMD in the form of sulphides using precipitating agent as H_2S , Na_2S and $NaHS$. The superior sulphide precipitation is reasoned by the sparingly soluble nature of sulphide precipitates, better thickening and dewatering characteristics as corresponding metal hydroxides, the production of lower sludge volumes (6 to 10 times) and stability of formed sulphides over a wide pH range. Additionally, sulphide precipitates can be processed by existing smelters for metal recovery. Chemical sulphide precipitation has not been widely used for AMD treatment due to high cost of chemicals and the hazard associated with their manipulation. Promising approach is based on the use of sulphate-reducing bacteria (SRB), which use sulphate as terminal electron acceptor in the metabolism of the organic matter, reducing it to sulphide at anaerobic condition. The generation of sulphide by SRB is favourable method eliminating of safety concerns related to precipitating agent transport, handling and on-site storage. The process is self-controlling, high sulphide concentrations become inhibitory to the bacteria that subsequently stop

producing and a dangerous runaway is impossible. This is an interesting option, especially when besides heavy metals sulphate is also present in the wastewater (Veeken et al, 2003; Huisman et al., 2006).

The recent treatment processes focus on recovery of metals as the metal resources are depleting. Reuse of metals can only become economically and technically feasible when metals are removed selectively and relatively pure metal sludge is produced.

The aim of our study was to develop and optimise the process of selective sequential precipitation (SSP) of iron, copper, aluminium, zinc and manganese from real AMD. In this paper the possibility of selective removal of heavy metals using discrete chemical and biological operation is evaluated. Abiotic system uses solution of sodium hydroxide to raise pH of AMD with simultaneous precipitation of metal hydroxides. Biological system uses hydrogen sulphide produced by SRB to precipitate metals in the form of sulphides at various values of pH.

2. Materials and methods

2.1 Acid mine drainage

The experiments were carried out by raw AMD discharged from the shaft Pech that receives the waters draining the enclosed and flooded Smolnik sulphidic deposit (Slovakia). The concentration of pollutants is season and rainfall dependent. The concentration of monitored parameters of AMD and general requirements for surface water quality according to Regulation of the Government of the Slovak Republic (2010) is shown in the Table 1.

Table 1: The monitored parameters of AMD discharged from the shaft Pech in comparison with (*) national limit values.

parameter	pH	SO ₄ ²⁻ mg/L	Fe mg/L	Cu mg/L	Al mg/L	Zn mg/L	Mn mg/L
value	3.8	2938	405.25	8.38	108.38	12.00	35.50
value*	6-8.5	250	2	0.02	0.2	0.1	0.3

2.2 Microorganisms

In the experiment the culture of sulphate-reducing bacteria (genera *Desulfovibrio*) has been used, isolated from a mixed culture of SRB obtained from the mineral water Gajdovka (Košice, Slovak Republic). For their isolation and cultivation the selective nutrient medium C according to Postgate has been used at 30 °C and anaerobic conditions (Postgate, 1984).

2.3 Analytical procedures

The concentration of metals in the samples was determined by atomic absorption spectrometry using Spectrometer Varian 240FS/240Z. Radiometer Analytical PHM 210 MeterLab pH-meter was used to determination of the samples pH. The precipitates were filtered using 0.40µm membrane filters Pragopor. The mineralogical composition was analyzed by powder XRD using a Bruker D8 Advance diffractometer with CuKα radiation and equipped with a secondary graphite monochromator. The diffraction data were collected over an angular range 10<2θ<80° with step 0.08 and counting time of 30 s. Diffraction patterns were treated with the Diffra^{plus} Basic analysis program. IR absorption spectra were recorded with a Bruker Tensor 27 spectrometer from 4000 to 400 cm⁻¹ using KBr pellets method. The qualitative analysis of precipitates obtained by SSP process was done by energy dispersive spectrometry analysis using microanalyser CAMECA SX 100. Precipitates were dried and coated by gold before the EDS analysis.

3. Experiments

The selective sequential precipitation of selected metals from sample of real AMD was performed under semi-continual conditions. The process consists of two stages – a chemical and a biological. Within the biological stage the hydrogen sulphide was produced by sulphate-reducing bacteria in the reactor via cultivation using Postgate's medium C (microbial H₂S generation). In the chemical stage the sulphide was transported to the contactor by the help of nitrogen gas purged through the reactor. The

contactor was filled by AMD and precipitation of metal sulphide occurred here. After filtration of precipitate the filtrate pH was adjusted to higher value in the beaker using NaOH (1 mol/L). In this step the simultaneously precipitation of metal hydroxide was observed. After filtration of precipitate the filtrate was returned in the contactor and the whole process was repeated at the higher pH value. After each of precipitation and filtration step the concentration of metals was analyzed in the liquid sample and a qualitative EDS analysis of precipitates was done to confirm the elementary composition of precipitates.

The selectivity of the introductory SSP process was not satisfactory. In this reason in the optimized SSP process the iron in the ferric form was removed from AMD as first. The ferrous iron was oxidized using 30 % hydrogen peroxide in the continuously stirred beaker. The required amount of used hydrogen peroxide was determined in our previous experiments (Macingova, 2010). Within this step the decreasing of pH value and partial iron precipitation were observed. Total iron precipitation was achieved using NaOH (1 mol/L). After filtration of ferric precipitates the solid-phase products were identified by X-ray diffraction. The process continued according to foregoing mode.

4. Results and discussion

The operating condition of SSP process is presented in the Table 2. As is shown in the Table 4 the introductory SSP process the partially selective precipitation of Fe and Al with more than 99 % efficiency and Mn with more than 72 % efficiency were achieved using solution of NaOH. Cu and Zn with about 99 % efficiency were removed using biologically produced hydrogen sulphide.

Table 2: The conditions and results of the SSP process

step	1	2	3	4	5	6
pH	3.8	4.5	4.5	6.0	6.0	9.0
reagent	H ₂ S	NaOH	H ₂ S	NaOH	H ₂ S	NaOH
removed metals	Cu	Fe, Al	Zn	Al, Fe	Fe	Fe, Mn
proportionment (%)	99.99	19.38:80.61	99.99	33.14:66.85	99.99	5.08:94.91

The selectivity of the introductory SSP process was not satisfactory, co-precipitation of Fe with Al and Mn was observed. The results documented the iron precipitation in broad range of pH (from 4.5 to 9.0) due to the presence of iron in the AMD in both, ferrous and ferric forms. According to known data, ferric iron precipitates at pH 3-4 while ferrous iron not precipitate at pH<6. In this reason removal of iron from AMD at low pH requires oxidation of ferrous to ferric iron. After oxidation using hydrogen peroxide certain decrease of pH and partial iron precipitation was observed. Only after addition of NaOH solution total iron precipitation was achieved. The operating condition of improved SSP process is presented in the Table 3. At the optimized SSP process the selective precipitation of Fe, Al and Mn using solution of NaOH ; Cu and Zn using bacterially produced hydrogen sulphide with more than 99 % efficiency was achieved with enhanced selectivity and purity of obtained precipitates (Table 4).

Table 3: The conditions and results of the optimized SSP process

step	1	2	3	4	5	6
pH	2.8	3.7	3.7	5.0	5.0	9.5
reagent	H ₂ O ₂	NaOH	H ₂ S	NaOH	H ₂ S	NaOH
removed metals	Fe	Fe	Cu	Al, Zn	Zn	Mn
proportionment (%)	99.99	99.99	99.99	98.94:1.05	99.99	99.99

Table 4: The efficiency of metal removal

	Fe	Cu	Al	Zn	Mn
SSP process metal removing (%)	99.97	98.55	99.93	99.63	72.75
improved SSP process metal removing (%)	99.99	99.76	99.63	99.92	99.92

The precipitates formed when raw AMD is neutralized may include both oxyhydroxides and hydroxisulphates (Lee et al., 2002). The formation of schwertmannite after oxidation and precipitation step of Fe in the improved SSP process was verified with X-ray diffraction (data not shown). Identification of schwertmannite as oxidation and precipitation product of real AMD sample are consistent with results of Bigham et al. (1996) who reported that schwertmannite is the dominant Fe phase precipitated from mine waters having pH values between 2.0 and 4.0. In addition to a variable composition (it is commonly admixed with other nanophase Fe minerals), schwertmannite is also poorly crystalline and producing low intensity, but unique XRD patterns (Bigham and Nordsrom, 2000; Loan et al., 2004). Other precipitates obtained by improved SSP process were X-ray amorphous; however the results of EDS analysis confirm their elementary composition (data not shown). Infrared spectroscopy gives additional useful information about the composition of schwertmannite. The comparison of absorption bands for schwertmannite obtained in experiment and literature data (Bigham et al., 1990) is shown in the Table 5. FTIR spectra of schwertmannite samples are shown on Figure 1 – sample 1 was obtained after oxidation step and sample 2 was obtained after precipitation step of iron.

Table 5: Position of absorption bands in the FTIR spectrum of schwertmannite – measured data and literature data ()*

Position (cm ⁻¹)	Position (cm ⁻¹) *	Interpretation*
470	483	ν -FeO
604	608	ν_4 SO ₄
695	704	ν -FeO
845	800-880	δ -OH
985	976	ν_1 SO ₄
1051, 1135	1038, 1124, 1186	ν_3 SO ₄
1640	1634	H ₂ O
3350	3300	ν -OH

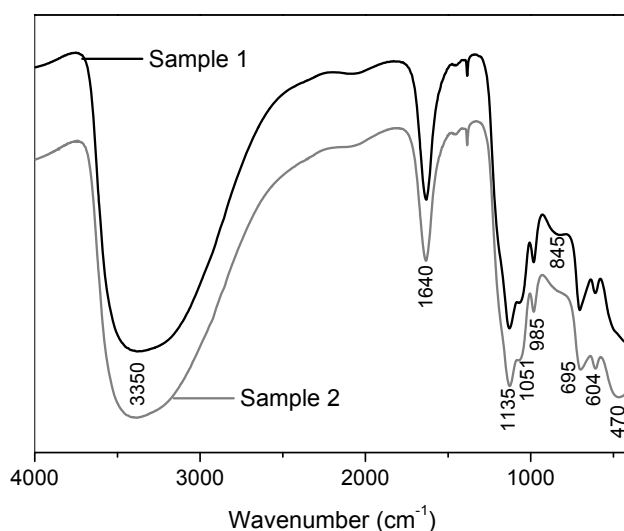


Figure 1: Infrared spectra of schwertmannite samples

Impact of hydrogen peroxide addition on the other selected metals was monitored by titration of AMD (with and without addition of hydrogen peroxide) using solution of NaOH (0.2 mol/L) up to pH 12. As it is illustrates on Figures 2 and 3, pretreatment of AMD with addition of hydrogen peroxide did not affects the precipitation of other metals.

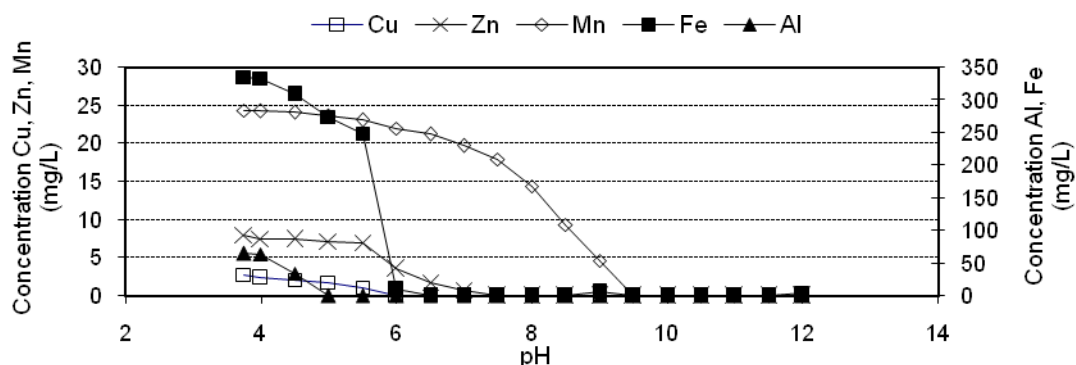


Figure 2: Metals precipitation during titration of AMD (without addition of H₂O₂) with NaOH solution

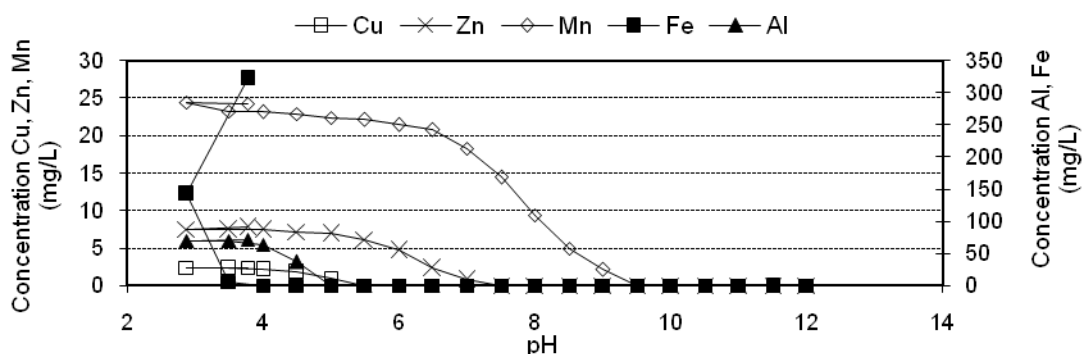


Figure 3: Metals precipitation during titration of AMD (with addition of H₂O₂) with NaOH solution

5. Conclusion

The selective precipitation and recovery of iron, copper, aluminium, zinc and manganese from raw AMD discharged from shaft Pech (Slovakia) was studied in this work. At the introductory SSP process the partially selective precipitation Fe and Al with more than 99 % efficiency and Mn with more than 72 % efficiency were achieved using solution of NaOH. Cu and Zn with about 99 % efficiency were removed using biologically produced hydrogen sulphide. Insufficient selectivity of precipitation has been reached in this proceeding. The optimised SSP process in the first step completely removed iron in the ferric form after oxidation using hydrogen peroxide. The improved SSP process was able to separate Fe, Al and Mn using solution of NaOH; Cu and Zn using bacterially produced hydrogen sulphide with 99 % effectivity and high precipitate purities. The combination of metal precipitation

by hydrogen sulphide produced by sulphate-reducing bacteria and solution of sodium hydroxide has been shown as means for selective and effective recovery of selected metals from AMD.

Acknowledgement

This work was supported by the Operational Programme Research and Development through the project: Centre of Excellence for Integrated Research of the Earth's Geosphere (ITMS: 26220120064), which is co-financed through the European Regional Development Fund and by the Slovak Grant Agency VEGA for project No. 2/0166/11.

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