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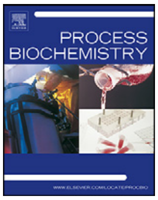

Application of physical–chemical and biological–chemical methods for heavy metals removal from acid mine drainage

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ABSTRACT

Acid mine drainage (AMD) represents a serious environmental problem related to sulfide minerals and coal mining. High content of toxic metals and high acidity in AMD adversely affects surface water, groundwater and soil. The abandoned mine of the Smolník deposit in Slovakia is a typical example in this respect. The quality of AMD needs to be monitored and suitable treatment methods need to be developed.

The aim of this paper was to demonstrate the technical feasibility of heavy metals removal from AMD using physical–chemical and biological–chemical methods. The base of the physical–chemical method was electrowinning. The principle of the biological–chemical method was the selective sequential precipitation (SSP) of metals with the application of hydrogen sulfide produced by sulfate-reducing bacteria and sodium hydroxide solution. Both the electrowinning and SSP processes decrease the content of heavy metals in AMD. The pre-treatment of AMD by chemical iron–aluminum precipitation (in the case of electrowinning tests) and chemical iron precipitation (in the case of SSP tests) improved the selectivity of the processes. A further aim of the work was the improvement of the SSP.

During the electrochemical experiments, 99% Zn removal – under metallic form – and 94% Mn removal – under MnO_2 form – both with a high degree of purity, were achieved. The SSP process reached the selective precipitation of chosen metals with 99% efficiency – Fe, Al and Mn in the form of metal hydroxides, Cu and Zn as metal sulfides. The results achieved may be used for designing a process appropriate for the selective recovery of metals from the AMD discharged from the Smolník deposit.

1. Introduction

Mining influenced water (MIW) is a term for any water that has had its chemical composition affected by mining or mineral processing. There are several types of MIW: acid mine drainage (AMD), mineral processing waters, marginal waters and residual waters [1]. AMD is a MIW with mineral acidity formed at the sites of active and abandoned mines by the dissolution of products resulting from the oxidation (chemically and microbiologically mediated) of sulfide minerals, mainly pyrite or iron disulfide [2–4]. The amount and toxicity of AMD depends on several factors such as the mineralogy of the rock material, the surface area, the oxygen concentration and the amount of water contacting the material, etc. The high acidity, elevated levels of heavy metals and salts such as sulfates and chlorides in AMD, has a negative impact on the environment. Therefore, AMD should be collected and treated before the outflow [5,6].

In this study a sample of AMD from the Pech shaft of the abandoned and flooded Smolník deposit was used. Smolník is historically one of the best-known and richest Cu–Fe ore deposits in Slovakia. It is geomorphologically located in the Slovenské Rudohorie Mountains (West Carpathians). The main minerals of the deposit are pyrite and chalcopyrite. In 1990 mining was stopped. The mine was flooded until 1994. At some year an ecological collapse occurred. Consequently the fish kill and the decline of the Smolník stream quality were observed. At the present time AMD drains from the flooded mine through the Pech shaft into the Smolník stream and is negatively affecting the stream biotope [7–9]. In addition, the gradual neutralization of AMD as it comes into contact with the surface water causes the precipitation of Fe and Al oxy-hydroxides that are carried by water into the Hnilec river and further to the Ružín water-basin [10–12]. The generation of AMD at the Smolník location is not possible to stop. It is necessary to develop methods for its treatment [13,14].

Generally there are two main approaches for AMD remediation: active and passive treatments [15,16]. Both types use various physical, chemical and biological methods to reduce the

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concentration of metals in AMD [17–21]. None of them have been applied universally, because AMD has different chemistries and requires different methods of treatment. Recent research and development is focused on a suitable combination of physical, chemical and biological methods for the selective recovery of metals from AMD [21–24]. The goal is to recover metals in a suitable form for commercial or industrial utilization. Therefore, the applications of physical–chemical and biological–chemical methods like electrowinning and bioprecipitation were studied.

The electrowinning process is currently used on a large scale to purify, concentrate and treat solutions containing heavy metals. Moreover, it is applied, in combination with other methods, for the recovery of precious metals from gold bearing minerals, valuable metals such as copper and nickel from electronic and galvanic industrial wastes, and zinc and manganese from spent alkaline batteries. Electrowinning as a technology is relatively cheap and environmentally friendly and produces metals with a high degree of purity [25–28].

The most efficient biological–chemical method for AMD treatment seems to be the combined removal of acidity, metals and sulfates using a bacterially mediated sulfate-reduction [4]. These processes are based on the ability of sulfate-reducing bacteria (SRB) to perform dissimilatory reduction of sulfates on hydrogen sulfide with simultaneous oxidation of organic substrates [29]. Bacterially produced hydrogen sulfide in the bioreactor 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 sodium hydroxide, metals precipitate in the form of hydroxides. The process of selective removal of metals from AMD in the form of sulfides and hydroxides is called selective sequential precipitation (SSP). It is based on complete segregation of both the biological sulfate reduction step and the metal precipitation step. SSP is a suitable method for the recovery of metals from AMD in a marketable form [23].

Iron frequently presents in AMD as both ferrous (Fe^{2+}) and ferric iron (Fe^{3+}). According to Soeyink and Jenkins [30], Fe^{3+} precipitates at pH 3–4, while Fe^{2+} does not precipitate at $pH < 6$. It is desirable that iron in the ferric form improves the selectivity of the SSP process and the purity of the obtained precipitates. Several different chemical and biological routes can achieve the oxidation of Fe^{2+} to Fe^{3+}. Chemical oxidants include, for example, atmospheric oxygen, hydrogen peroxide and HNO_3. Biological oxidation may be affected by *Acidithiobacillus ferrooxidans* [15,31,32].

The main objective of this paper was to study electrowinning and SSP as a way to separate chosen metals (Fe, Cu, Al, Zn and Mn) from an AMD synthetic solution and real AMD, respectively. The specific goal of this research was to define the main parameters of the electrowinning process and to determine optimum conditions for the SSP process with the aim of achieving high a recovery of metals with a high degree of purity.

2. Materials and methods

2.1. Acid mine drainage

The experiments were carried out at the laboratory scale using a synthetic solution in the case of electrowinning (due to the unavailability of real AMD at the Italian workplace) and by real AMD in the case of SSP. 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 synthetic solution with pH of 3.8 was achieved after adjusting the pH value using 5 M NaOH [24,32]. The sample of AMD was taken from the abandoned and flooded deposit in Smolník (from the Pech shaft). After the collection, the samples were stored in closed polyethylene bottles and kept at 4 °C.

2.2. Physical–chemical processes

HNO_3 was added to the process solution with the aim of oxidizing Fe^{2+} to Fe^{3+}. In the subsequent step, sodium hydroxide was added to reach a pH of 4.0. The precipitates were successively separated by filtration [32].

The electrowinning tests were performed in a 200 cm^3 cylindrical glass laboratory cell, at constant cathode potential, under magnetic agitation (200 rpm), for an electrolysis time of 2 h, according to Fornari and Abbruzzese [33].

Three electrodes were used: a cathode of platinum mesh, an anode of platinum wire and a saturated calomel electrode, as a reference. The cell was connected to the potentiostat–galvanostat (AMEL, Mod. 568) and equipped with an instrument system to automatically control the process parameters (programmable function generator AMEL, Mod. 568, interface Mod. 560/A, integrator Mod. 721, differential electrometer Mod. 631).

With the aim of calculating for the experimental margin of error, each test was repeated three times [34].

2.3. Biological–chemical processes

A bacterial culture of SRB (*Desulfovibrio* sp. and *Desulfotomaculum* sp.) was used for the experiments. It was isolated using the nutrient Postgate's medium C from potable mineral water (Gajdovka spring, Kosice-north, Slovakia) [13,29]. The SRB cultivation for the bacterial production of hydrogen sulfide (used in the SSP experiments) was carried out using the same nutrient medium. The chemical composition of the medium was as follows (in g/L): 0.5 K_2HPO_4, 1.0 NH_4Cl, 1.0 Na_2SO_4, 0.1 $CaCl_2{\cdot}2H_2O$, 2.0 $MgSO_4{\cdot}7H_2O$, 3.5 sodium lactate, 1.0 yeast extract, 0.5 $FeSO_4{\cdot}7H_2O$, 0.1 ascorbic acid and 0.1 thioglycolic acid. The pH of the medium was adjusted to 7.5 using 5 M NaOH.

In the SSP experiments real AMD was used. The AMD was pretreated applying chemical Fe^{2+} oxidation by H_2O_2 and the subsequent addition of sodium hydroxide that resulted in complete Fe removal.

To investigate the influence of a H_2O_2 addition on the precipitation of metals as hydroxides, various pH values, using a titration procedure, were studied. Samples of 100 ml AMD and 100 ml AMD with 50 μl of 30% hydrogen peroxide were titrated at a pH ranging from 3.8 to 12 using a 0.2 M NaOH solution. During titration the AMD solution was continuously stirred and samples were drawn off regularly to determine the concentration of metals (Fe, Cu, Al, Zn and Mn).

SSP of heavy metals using bacterially produced hydrogen sulfide from the AMD sample was performed in two coupled batch reactors under semi-continuous conditions. The first reactor was filled with the nutrient medium and inoculated with the SRB culture. After the anaerobic cultivation, nitrogen gas was purged through the reactor to strip the hydrogen sulfide formed due to sulfate reduction. The biogenic hydrogen sulfide was transferred into the second reactor filled with a pretreated sample of AMD with a pH of 3.7. The formation of a metal sulfide precipitate (CuS) was visually observed. The precipitate suspension was then filtered. Afterwards, a 5 M NaOH solution was added to the filtrate in order to adjust the pH to a higher value (5.0) and to obtain the precipitation of metal hydroxides ($Al(OH)_3$). After the filtration of the precipitate the filtrate was returned to the second reactor and the whole process was repeated at a higher pH. The precipitates of ZnS and $Mn(OH)_2$ at pH 5.0 and pH 9.5 were obtained, respectively. After each precipitation and filtration step the metal concentrations were analyzed in the liquid sample and an EDS qualitative analysis of the precipitate was performed. Optimal values of pH for the heavy metals precipitation were selected according to the literature and our previous experiments [4,14,35].

2.4. Analytical procedures

To study the electrodeposition kinetics, liquid samples of 5 cm^3 were withdrawn and submitted for chemical analysis by ICP-MS, while the purity of the solid deposit was determined by X-ray diffraction (XRD) technique. The metallic content of the deposit was analyzed by ICP-MS after dissolution by HCl. The concentration of metals during SSP was determined by atomic absorption spectrometry (AAS) using a Varian 240FS/240Z spectrometer. The concentration of Fe^{3+} was determined by method based on absorption of ferric iron at 300 nm [36], using a Helios Gamma photometer (Thermo Electron Corporation, England). pH was measured using a pH-meter PHM210 MetLab (Radiometer Analytical, France). The qualitative analysis of precipitates obtained by the SSP process was done using energy dispersive spectrometry (EDS) analysis using instruments, which included a scanning electron microscope BS 300 (Tesla, Czechoslovakia) and an X-ray microanalyser EDAX 9100/60 (Philips, Holland). The precipitates were dried and coated with gold before the EDS analysis.

3. Results and discussion

The mine water from the Pech shaft represents the typical AMD outflow with low pH values, high concentration of sulfates, Fe, Al, Mn, Zn and Cu. The chemical composition of the mine water is shown in Table 1 in comparison with the limits allowed by Regulation No. 296/2005 Coll. of the Government of the Slovak Republic

Table 1
Examined parameters of AMD sample collected from the Pech shaft.

Parameter	pH	Concentration (mg/L)					
		SO_4^{2-}	Fe	Al	Mn	Zn	Cu
Value	3.8	2938	405.25	108.38	35.50	12.00	8.38
Value[a]	6–8.5	250	2	0.2	0.3	0.1	0.02

[a] Limit values of Government Regulation No. 296/2005 Coll.

[37]. The AMD may be considered as secondary sources of metals and be treated with clean technologies. The aim of our experiments was the recovery of chosen metals in a suitable form for subsequent industrial use. Therefore, the removal of Fe, Al, Mn, Zn and Cu was studied using both the electrowinning and SSP methods.

3.1. Physical–chemical processes

During preliminary electrowinning tests low adherence of Fe deposits were observed on the cathode and deposition was low after 1 h. Based on these results, preliminary precipitation steps were carried out before the electrowinning because the Fe remaining in the solution interfered negatively with the electrolytic process, masking the electrodes surface and decreasing the current efficiency [25–28]. Together with Fe precipitation (about 99% of precipitated Fe) Al precipitation also occurs (about 94% of precipitated Al).

In a subsequent step, the solution was treated to verify the technical feasibility of the metal deposition using an electrowinning lab-scale operation.

The optimum operating parameters as determined during the experimental tests are reported in Table 2.

The average results of the electrowinning tests on synthetic Smolník samples show that Zn deposits were of low quality after 30 min.

After 90 min, Zn deposits were uniform, while on the surface of the counter electrode MnO_2 deposited. Manganese was deposited on the anode as MnO_2, while only a small amount was deposited on the cathode as Mn^0. After 2 h, 94–99% of the metals were removed by the quantitative electrodeposition. A high-grade purity deposit was achieved (MnO_2 and Zn up to 90%), as demonstrated from the results of the quantitative chemical analysis by ICP-MS. Main peaks of the XRD spectrum reported in Fig. 1, demonstrate the presence of manganese mainly in the form of MnO_2 (large curvature in less than 20° is due to plastic samples holders used in XRD analysis, while the broad peak in around 22° is produced by the background noise, due to amorphous species in the sample). Fe and Al were removed before the electrowinning process by precipitation – Zn^0 was recovered from the solution using cathodic deposition after MnO_2 anodic deposition; consequently, only metallic Mn^0 traces co-deposited with Zn^0 on the cathode.

Table 3 shows the metals' concentration of the synthetic AMD sample after the Fe/Al precipitation–electrowinning process.

As seen in Table 3, at the end of the process, the efficiency of the removal ranged from 93.72 to 99.96% for all metals.

Table 2
Best experimental conditions of the electrowinning tests.

Factors	Value
Cathode vs. SCE (V)	−1.47
Cell voltage (V)	3.7–5.0
Current intensity (mA)	400–1000
Current density (mA cm^{-2})	4.0–10
pH	3.5
Bath temperature (°C)	35
Electrolysis time (h)	2
Stirring conditions (revolution per minute)	200

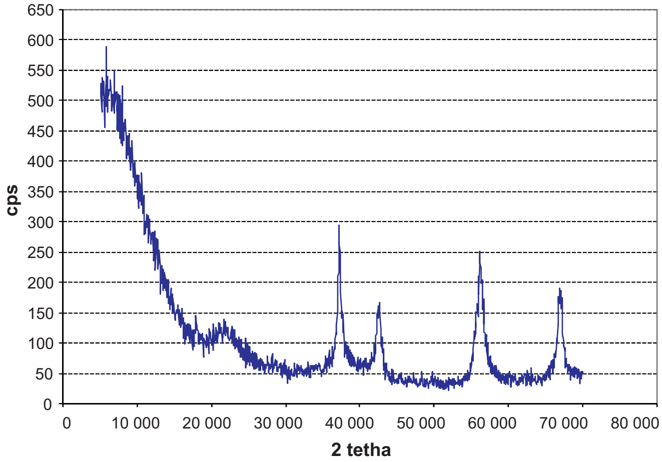

Fig. 1. X-ray diffraction spectrum. Main peaks of MnO_2 identified as 294, 167, 250 and 190 cps.

Table 3
The metal removal efficiency of precipitation–electrowinning process applied to synthetic AMD sample.

Metal	Fe	Cu	Al	Zn	Mn
Input concentration (mg/L)	405.25	8.38	108.38	12.00	35.50
Output concentration (mg/L)	0.21	<0.005	6.80	<0.005	1.95
Metal removing (%)	99.95	99.94	93.72	99.96	94.51

The highest efficiency was achieved during the removal of zinc (see Table 4).

Analysis of the data demonstrates the influence of preliminary Fe/Al precipitation: the chemical pre-treatment permitted the decreasing of energetic consumption during the electrowinning.

Electrochemical kinetics was studied in batch operations. The first large scale use will allow, through continuous operations, for better control of the process parameters and for better efficiency of the process.

It is possible to suppose that, in a continuous system, the deposition parameters will be improved. In particular, applying the process to a continuous system and stabilizing the values of pH by the use of salts such as $Al_2(SO_4)_3{\cdot}18H_2O$ or $KAl(SO_4)_2{\cdot}12H_2O$, decreases the energy consumption.

Moreover, with the aim to increase the low $ZnSO_4$ conductivity, salts such as Na_2SO_4, that increase the cathode polarization, can be added to the electrolytic bath. These salts are added in very low concentrations. One part will be recycled in the electrolytic

Table 4
Main results of Zn electrodeposition without and with chemical precipitation of synthetic AMD sample.

Time [min]	Without chemical precipitation			With chemical precipitation		
	R [%]	η [%]	E [kWh/kg]	R [%]	η [%]	E [kWh/kg]
90	91.88	19.90	18.53	96.08	25.84	13.86
120	95.35	11.32	32.61	99.96	14.70	25.01

R = Zn recovery; η = Faradic current efficiency; E = energetic consumption.

Table 5
Results of the non-optimized heavy metals selective sequential precipitation.

Step	1	2	3	4	5	6
pH	3.8	4.5	4.5	6.0	6.0	9.0
Added reagent	H_2S	NaOH	H_2S	NaOH	H_2S	NaOH
Removed metals	Cu	Fe, Al	Zn	Al, Fe	Fe	Mn, Fe
Form of removed metals	CuS	$Fe(OH)_3Al(OH)_3$	ZnS	$Al(OH)_3Fe(OH)_2$	FeS	$Mn(OH)_2Fe(OH)_2$

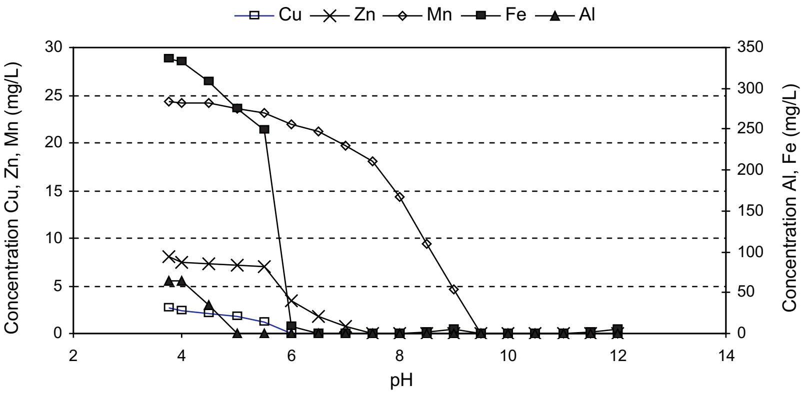

Fig. 2. Residual concentration of selected metals in AMD at different pHs without oxidation of Fe^{2+} to Fe^{3+}.

cell, while the remaining fraction will be subjected to precipitation with alkaline agents before being discharged into the environment [24,28].

3.2. Biological–chemical processes

Results of our previous work relating to the treatment of AMD from the Pech shaft by the successive running of two sequential steps (the hydrogen sulfide bacterial production and the metals precipitation by the bacterially produced hydrogen sulfide) demonstrate that under the natural pH of the studied AMD, i.e. pH 3.8, only Cu was effectively recovered in the form of sulfides [14].

Therefore, in the subsequent SSP experiments the combination of metals precipitation by bacterially produced hydrogen sulfide and the adjustment of the pH values with sodium hydroxide were accomplished using the aforementioned real AMD. The selective removal of Cu and Zn in the form of sulfides and Fe, Al and Mn in the form of hydroxides was achieved here. However the co-precipitation of Fe, Al and Mn was observed (Table 5) [21,35,38].

As a consequence, we have performed further experiments with the aim to improve the selectivity of the non-optimized SSP process.

The AMD acidity includes two components: hydrogen ions and dissolved metal ions. This can be observed in the AMD acidity titration curves [39,40]. The influence of the pH on metal solubility in AMD was investigated using endpoint titration using a 0.2 M NaOH solution. The gradual addition of NaOH caused AMD neutralization and successive precipitation of metal ions in the form of hydroxides. Hydroxides of Fe, Al, Zn, Cu and Mn are insoluble in water and have specific solubility products. When pH reaches a certain level the metal ions precipitate and they are eliminated from the water. Residual concentrations of Fe, Al, Zn, Cu and Mn as a function of pH during the NaOH titration tests, are shown in Fig. 2.

The maximum precipitation of metals in the form of hydroxides during the titration process was observed at different pH values: Al (pH ~ 5), Cu (pH ~ 6), Fe (pH ~ 6.5), Zn (pH ~ 7.5) and Mn (pH ~ 9.5). Results indicated that iron precipitation occurs in a broad range of pH, from 3.8 to 6.5. Determinations of the total iron and Fe^{3+} in the collected AMD confirmed the dominant presence of Fe^{2+}. The presence of Fe^{2+} does not allow the selective recovery of metals. Oxidation of Fe^{2+} to Fe^{3+} is essential in order to obtain the precipitation of iron at a low pH [30,31]. Therefore the Fe^{2+} oxidation in the studied AMD was achieved using hydrogen peroxide (H_2O_2) [35]. The precipitation of Fe, Al, Cu, Zn and Mn in pretreated AMD is

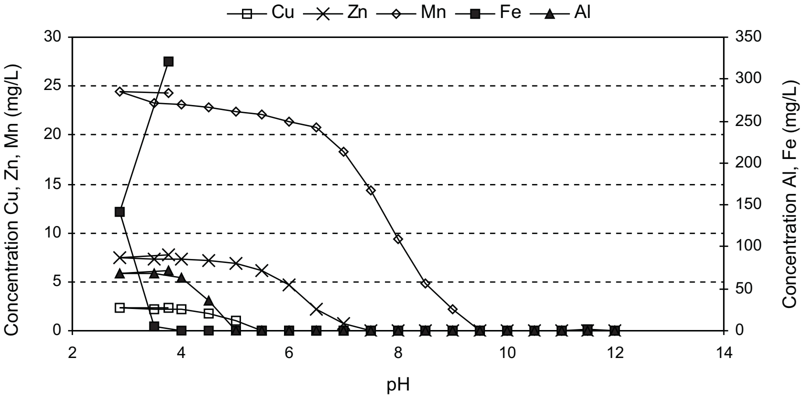

Fig. 3. Residual concentration of selected metals in AMD at different pHs after oxidation of Fe^{2+} to Fe^{3+}.

Table 6
Results of the optimized heavy metals selective sequential precipitation.

Step	1	2	3	4	5	6
pH	2.8	3.7	3.7	5.0	5.0	9.5
Added reagent	H_2O_2	NaOH	H_2S	NaOH	H_2S	NaOH
Removed metals	Fe	Fe	Cu	Al	Zn	Mn
Form of removed metals	$Fe(OH)_3$	$Fe(OH)_3$	CuS	$Al(OH)_3$	ZnS	$Mn(OH)_2$

Table 7
The metal removal efficiency from real AMD of optimized SSP process.

Metal	Fe	Cu	Al	Zn	Mn
Input concentration (mg/L)	405.25	8.38	108.38	12.00	35.50
Output concentration (mg/L)	<0.05	<0.02	<0.04	<0.01	<0.03
Metal removing (%)	99.99	99.76	99.96	99.92	99.92

presented in Fig. 3. In this case the effective pH values for selective precipitation of metals in the form of hydroxides were the following: Fe (pH ~ 3.5), Al (pH ~ 5.0), Cu (pH ~ 5.5), Zn (pH ~ 7.5) and Mn (pH ~ 9.5).

The pretreatment of AMD with the addition of H_2O_2 did not affect the concentration and precipitation of other metals (Figs. 2–3). A certain pH decrease and partial iron precipitation was observed. Total iron precipitation was achieved only after the addition of NaOH.

The next experiments were oriented toward the SSP process using the pretreated AMD. The oxidation and precipitation of iron represented the first and second steps of optimized SSP (Table 6). Metals were precipitated in the form of sulfide and hydroxide at various values of AMD pH that were assigned on the ground of the aforementioned results of titration and our previous experiments [21,38]. Table 6 summarizes the operating steps, conditions, and the results of optimized SSP, while Table 7 shows the metal removal efficiency from AMD. EDS qualitative analysis confirmed the elemental composition of precipitates. Examples of the obtained EDS spectrum are shown in Figs. 4 and 5.

The comparison of Table 5 with Table 6 demonstrates the improvement of the metal precipitation selectivity by the SSP optimization. After oxidation the iron was completely removed from AMD.

The development of the six steps of the optimized SSP process permitted the iron, aluminum and magnesium recovery as metal hydroxides and copper and zinc as metal sulfides. The removal efficiency for all the metals was more than 99%.

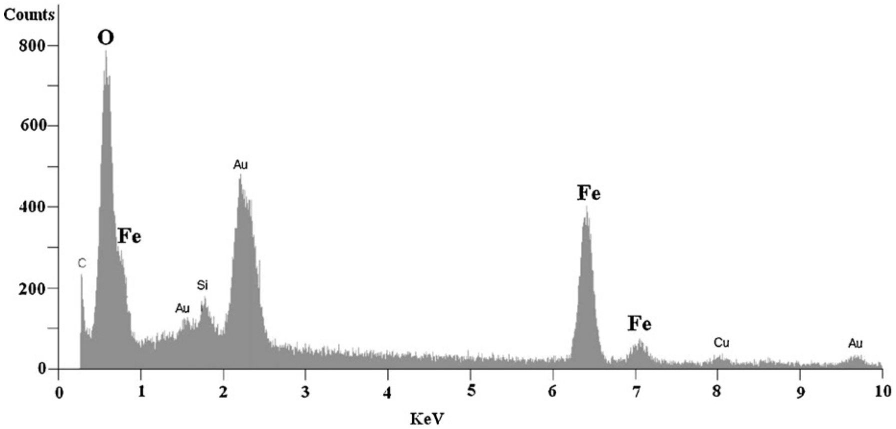

Fig. 4. EDS spectrum of iron hydroxide precipitates—the products of optimized SSP process.

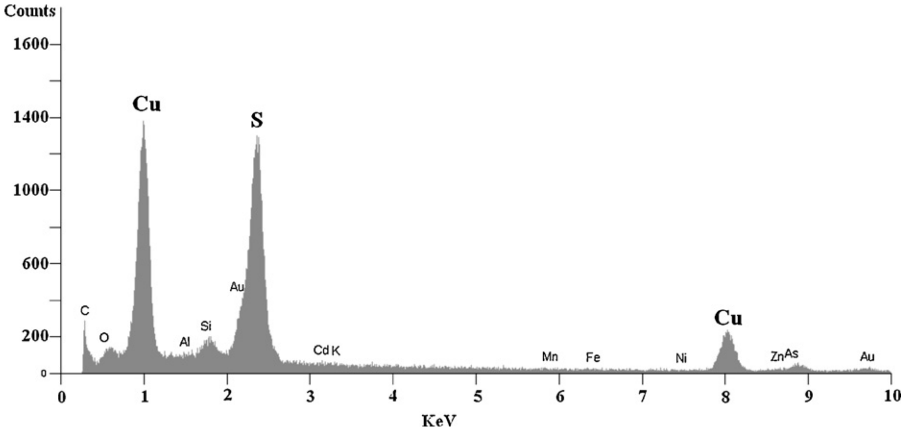

Fig. 5. EDS spectrum of copper sulfide precipitates—the products of optimized SSP process.

Table 8
Comparison of the studied physical–chemical and biological–chemical processes.

	Electrowinning	Selective sequential precipitation
Form of precipitates after pretreatment of AMD	Mixture of Fe and Al hydroxides	Fe hydroxides
Removal efficiency of metals	Fe, Zn, Cu > 99% Al, Mn > 93%	Fe, Al, Zn, Cu, Mn > 99%
Form of the end product	Zn^0, MnO_2	Fe, Al, Mn-hydroxides Cu, Zn-sulfides
Selectivity of the processes	High for Zn and Mn	High for all metals
Purity of the end product	Over 90%	Over 95%
Utilization of the products	Anticorrosive protection[a] Alloy production	Pigments production[b] Metallurgical industry[c]
Time of the realization	2 h	12–24 h
Advantages	Production of Zn in the metallic form[d] High purity of Zn[d]	High selectivity[e]; simultaneous removing of acidity, metals an sulfates; sulfur production[e]
Disadvantages	Cost of electric energy	Cost of substrates for cultivation of sulfate-reducing bacteria[f]
Improvements	Stabilization of pH using suitable salts[g]	Cheap substrates for cultivation of sulfate-reducing bacteria[f]

[a] Kalendová [46].
[b] Kaksonen and Puhakka [4], Wei et al. [22], and Tabak et al. [24].
[c] Lewis [41].
[d] Ubaldini et al. [26] and Vegliò et al. [28].
[e] Kaksonen and Puhakka [4] and Skousen et al. [15].
[f] Liamleam and Annachhatre [42], Friedl et al. [43], and Martins et al. [44].
[g] Andrés and Cortijo [45].

3.3. Comparison of studied physical–chemical and biological–chemical processes

Table 8 describes some characteristics, advantages, disadvantages and improvements of studied processes. The list of comparisons suggests the application of electrowinning for the treatment of AMD containing the major concentrations of Zn and Mn, while the selective sequential precipitation may be used for the selective removal of metals from AMD. Both processes have demonstrated high efficiency in removal of metals with high degree of purity. Realization time of electrowinning process is shorter compared to the selective sequential precipitation process. The study of inscribed improvements will be decreasing the energetic consumption (in the case of the electrowinning) or the cost of substrates for cultivation of sulfate-reducing bacteria (in the case of the selective sequential precipitation).

4. Conclusions

Samples of real acid mine drainage collected from the Pech shaft of the abandoned and flooded Smolník deposit (Slovakia) and synthetic AMD were used in this study. The characteristics are typical of acid mine drainage, with low pH values and a high concentration of sulfates and heavy metals (mainly Fe, Al, Mn, Zn and Cu).

Heavy metals can be usefully separated and recovered for industrial applications. The experiments were oriented for the removal of the metals using selected physical–chemical and biological–chemical methods. Electrowinning was used as physical–chemical method.

SSP of metals with the application of the bacterially produced hydrogen sulfide by sulfate-reducing bacteria, in combination with the precipitation of hydroxides using sodium hydroxide, was performed as the biological–chemical method.

In the collected samples of the acid mine drainage, it was confirmed that Fe was predominantly found in the divalent state. Due to the speciation of Fe, it was not possible to achieve selective precipitation of the other metals. The pre-treatment of acid mine drainage samples with the aim to oxidize Fe^{2+} to Fe^{3+} and the subsequent Fe^{3+} precipitation by NaOH addition, improved the applied processes. Iron oxidation was carried out using HNO_3 in the case of electrowinning tests, while H_2O_2 was used in the SSP tests. It was demonstrated that both studied processes are able to bring the heavy metal concentration below the limits recommended by the Regulation of the Government of the Slovak Republic No. 296/2005 Coll.

The main advantage of the electrowinning process is the high recovery of Zn (99% of Zn in metallic form) and Mn (94% of Mn in MnO_2 form), together with a high degree of purity (over 90% in both cases).

The benefit of using the biological–chemical method is the possibility for selective recovery of the chosen metals (iron, aluminum and magnesium as metal hydroxides; copper and zinc as metal sulfides) with more than 99% efficiency. Based on the experimental results achieved, the scaling up of this process in a continuous system will be carried out with the main objective of evaluating the feasibility of an integrated physical–chemical/biological–chemical process at an industrial scale.

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