



# Alternative Approach to Selected Metals Removal/Recovery from Mine Waters Flowing from the Flooded Siderite Mine Nižná Slaná

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## Abstract

*The objective of this work was the application of innovative method for metals recovery from metalliferous mine water released from the flooded siderite ore deposit Nižná Slaná. Although the metals contained in mine drainage are considered environmental pollutants, they may also be recognised as valuable resources. Several techniques can be used to obtain them by precipitation. Conventional processes using alkaline reagents produce huge amounts of mixed sludge with appropriate storage and management requirement, void of possibility of individual metals subsequent processing. This study examined the feasibility of Fe and Mn selective retrieval from real mine water. After oxidation and partial precipitation of iron using hydrogen peroxide, precipitation by sodium hydroxide was applied to the residue iron removal from mine water. In the next step potassium permanganate was used to eliminate manganese by oxidative precipitation. ORP and pH values of processed mine water was recorded in the course of oxidation/precipitation processes. The morphology and elemental composition of obtained products were studied by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). The recovery efficiencies of Fe and Mn from mine water reached 99.87 % and 99.25%, respectively. Target metals were removed with high selectivity to levels that comply with environmental requirements.*

*Keywords: Mine water, Selective removal of metals, siderite mine, nižná slaná*

## Introduction

Recovery of metals from mine waters is not a new approach to mine waste management. The combination of increasing global demands for metals, high mining costs, stringent environmental regulations and the depletion of historically important resources has led to a re-evaluation of alternative metal retrieval options. Mine waters are considered as a possible sources of components with a potential economic value (transition metals, rare earth elements, sulfuric acid, freshwater). Various sophisticated processes have been developed with purpose to obtaining them. The choice of suitable techniques is conditioned by chemistry of mine water, which depend on many factors, including geology, composition and mineralogy of ore deposits, mining methods, climatic conditions and hydrology of the site. The used separation methods can be divided into basic categories: chemical (precipitation, reduction, extraction), physical-chemical (reverse osmosis, ion exchange, evaporation), electrochemical (electrolysis, electrocoagulation, electrodialysis), microbiological (sulfate reduction, metal reduction) and their combinations (electrochemical cells with semipermeable membranes, bioelectrochemical systems, extraction with ion exchange, sulfide precipitation with alkali neutralization) [1]. Some of proposed treatment methods are yet at the level of basic research, others are verified in pilot plants [2-6].

Based on the specific local conditions and requirements, several companies are capable to prepare tailored solutions that are successfully applied in practice (BQE Water, Clean TeQ Water, Paques).

Our investigations were focused on the selective removal/recovery of iron and manganese from mine water flowing out of the flooded mine areas of Nižná Slaná siderite ore deposits (Slovakia).

## Materials and Methods

Water discharging from a former mine to the river Slaná near the village of Nižná Slaná was used in our study. Mining activity in the vicinity of Nižná Slaná was in progress on ore deposits of various genetic types. From the 14th century silver, copper, mercury ores and, to a large extent, iron ores limonite and siderite were mined here. The greatest growth of mining activity occurred at the turn of the 18th and 19th centuries related to the establishment of a big iron smelter focused on the siderite processing [7]. From the middle of the 20th century until 2008 two iron-ore bodies were exploited in Nižná Slaná ore field with subsequent processing of siderite, using a unique technology for blast furnace pellet production. After the mining activity finishing, spontaneous flooding of the mine began in August 2011. A hydrogeological study carried out in 2011 estimated its duration on yield of 7–12 l/s at 20 years [8]. In February 2022 massive release of polluted water with extremely high concentration of metals

and sulfates from the deep level of mine to the river Slaná was observed [9]. Ecological accident caused a multiple increase of dangerous elements concentration in the river, its rusty colouring and death of fishes and other creatures.

Water used in the experiments was taken from discharge pipe, which serves to drain water from flooded mining areas into the stream of river Slaná over March 2022. The physical-chemical characteristics of mine water are presented in the table 1.

Tab. 1. The selected physical-chemical parameters of mine water from Nižná Slaná location

	pH	ORP (mV)	Fe (mg/l)	Mn (mg/l)	Mg (mg/l)	SO <sub>4</sub> <sup>2-</sup> (mg/l)	flow rate (l/s)
value	5.6	-6.7	4 762	533	5 492	35 796	20

The experiments were carried out in laboratory conditions, using two liters of mine water. They were performed repeatedly and the individual results were almost identical. Process of iron and manganese selective recovery involves the next steps:

- 1) The ferrous iron present in mine water was oxidized using a corresponding amount of 30 % hydrogen peroxide. In this process decreasing of pH value and partial precipitation of iron was observed.
- 2) Neutralization of filtrate by 10M NaOH resulted in nearly complete iron removal by precipitation.
- 3) Manganese was retrieved from the mine water by oxidative precipitation using a proportional volume of 5 % KMnO<sub>4</sub> solution.

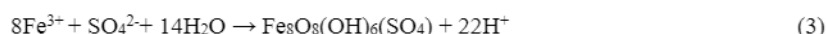
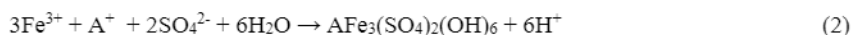
The reagents were added to the processed water in each phase of the experiment under stirring. The pH and ORP values (oxidation-reduction potential, values compared to the Ag-AgCl reference electrode) were monitored (recorded) during oxidation/precipitation processes. Gained data were recorded using a LabVIEW software (National Instruments, Austin, Texas, USA). In the individual steps of experiment, sedimentation of resulting precipitates took place to the next day. After filtration through membrane filters Prapopor with a pore size of 0.40 µm (Pragochema, Czech Republic), they were washed with distilled water and air-dried at ambient temperature. The morphology of obtained products was studied by scanning electron microscope (SEM) MIRA 3 FE-SEM (TESCAN, Czech Republic) and their composition was evaluated by energy dispersive X-ray spectroscopy (EDX) (Oxford Instrument, Oxford, UK). Concentration of metals in mine water was determined using atomic absorption spectrometer VARIAN AA240FS (Melbourne, Australia).

## Results and Discussion

In our study iron and manganese were recovered selective from real mine water by redox precipitation. Due to the complexity of Fe and Mn chemistry in solutions, iron was separated in the first step of the treatment process. In acid mine water, manganese is present primarily in the soluble divalent form and iron occurs in two oxidation states, Fe(II) and Fe(III). If iron is present in water in a reduced form, oxidation and precipitation of manganese is inhibited or reductive redissolution of present Mn precipitates appears ( $Mn^{4+} + 2Fe^{2+} \rightarrow Mn^{2+} + 2Fe^{3+}$ ) [10, 11]. Manganese removal in acid mine drainage does not significantly occur until iron is reduced to low concentrations. Trivalent iron precipitates at pH values of 2.5-4, while divalent iron does not precipitate at pH lower than 6. For this reason, its removal at low pH requires oxidation of Fe(II) to Fe(III). In our experiment, a stoichiometric amount of hydrogen peroxide was used as an oxidizing agent (equation 1) [12,13]. Based on our previous study [14], oxidation of Mn(II) by this reagent was not expected. Reaction of manganese and hydrogen peroxide is favored in alkaline medium ( $Mn^{2+} + H_2O_2 + 2OH^- \rightarrow MnO_2 + 2H_2O$ ) [15, 16].



In this step of experiment, formation of precipitate was noticed. Concentration of iron and manganese in mine water dropped from 4 762 mg/l to 2 180 mg/l and from 533mg/l to 520 mg/l, respectively. Simultaneously, decrease of pH from 5.6 to 2.3 and increase of ORP value from 218 mV to 800 mV was noticed. In theory, after oxidation, by subsequent hydrolysis of ferric iron in the presence of sulfate, secondary Fe precipitates are generated in acid producing reaction. The nature of formed precipitates is determined by the composition of aqueous phase with pH, iron and sulfate concentration as master variables. According to Jönsson et al. [17], at pH below 3, different forms of jarosite precipitate (equation 2), where A<sup>+</sup> is a monovalent cation, such as ammonium, potassium, sodium or hydronium. At the values of pH 3-4 schwertmannite is the most common formed phase (equation 3). Kaksonen et al. [18] reported the occurrence of jarosite at pH < 2 and schwertmannite at pH 2-4. Bigham et al. [19] state schwertmannite as the dominant Fe-phase over the pH range of 2.5–4.5.



The generated solid phase (sample Fe-1) was removed by filtration. In follow, by controlled addition of NaOH, the pH value of processed water gradually increased to 4.05 with simultaneous precipitation of Fe(III) (sample Fe-2). Iron and manganese concentration in mine water decreased to 6 mg/l and 510 mg/l, respectively. At both processes of iron removal, relatively rapid sedimentation of formed precipitates occurred, but the filtration of both samples was time-consuming. After washing and drying, the precipitates were homogenized in a mortar and subjected to a further analyses. Their mineralogical composition was evaluated using elemental EDX analysis (figure 1, figure 2). The mass percentage in sample Fe-1 confirmed the presence of elements corresponding presumably the mineral jarosite. In sample Fe-2 the mass ratio of components conforms probably to ferric hydroxide with a partial adsorption of sulfates. As figure 3 and figure 4 demonstrate, no specific morphological characteristics were observed in the Fe-precipitates. Mild decrease of manganese concentration at both steps of iron removal could be related to its adsorption onto Fe-solid particles [10] For explicit determination of composition and structure of obtained iron products comprehensive mineralogical analysis is needful.

In our previous work, by analogical procedure, iron in the form of schwertmannite was recovered from the mine water draining the enclosed and flooded Smolník sulfidic deposit (Slovakia). Hematite was obtained by its thermal decomposition at a temperature of 800°C [20]. The physical-chemical properties of both mine waters and the EDX profiles of the acquired precipitates are different. However, Kaksonen et al. [21] referred the conversion of jarosite formed in a two-stage continuous stirred tank reactor to hematite and acid by conventional autoclaving (225 °C). Also, in the process described by Ristić and al. [22] hematite was



produced from synthetic ammonium jarosite upon heating at 600°C. The opportunity of applying similar processes in the processing of Fe-precipitates received from Nižná Slaná mine water requires further experiments and analyses.

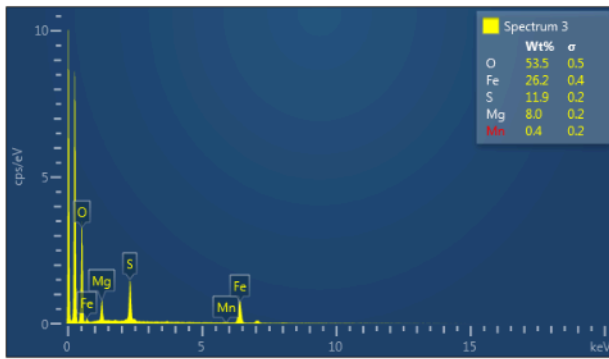


Fig. 1. EDX spectrum of sample Fe-1

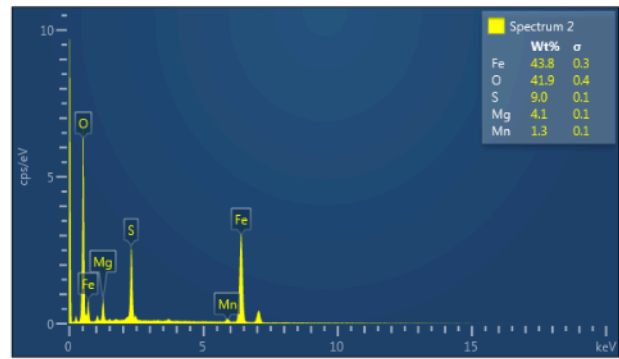


Fig. 2. EDX spectrum of sample Fe-2

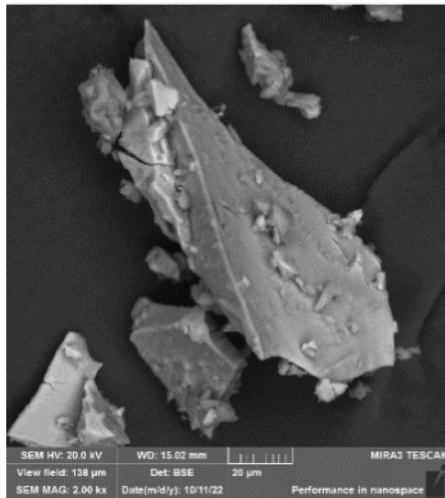


Fig. 3. SEM micrograph of sample Fe-1

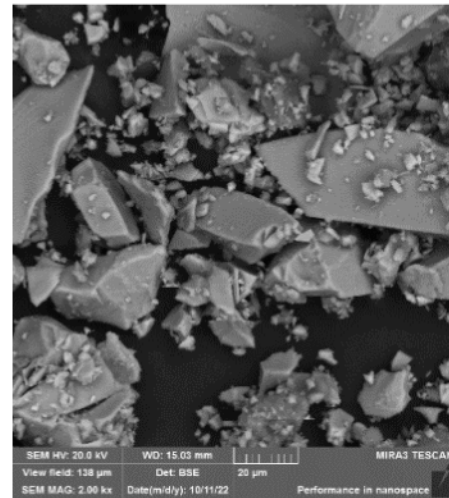
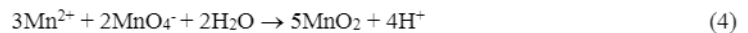


Fig. 4. SEM micrograph of sample Fe-2

Manganese occurs in the water environment in soluble and insoluble form in oxidation states Mn(II), Mn(III) and Mn(IV), depending on the redox conditions and pH of the environment. The transition between these forms appears through oxidation and reduction reactions, which can be abiotic or conditioned by microbial processes. In acid mine water, manganese is present predominantly in the soluble divalent form, and alkalization is a commonly used method for its removal. However, uncatalyzed oxidation and precipitation of Mn is favoured at high value of pH at about 10 [11]. Moreover, during this process manganese coprecipitates with different metals present in the mine water [23]. In this relation, oxidative precipitation seems to be a more suitable alternative for manganese removal using different oxidizing agents (hypochlorite, Caro's acid, SO<sub>2</sub>/air (O<sub>2</sub>), potassium permanganate) [24, 25]. To effectively precipitate dilute manganese from solution at lower pH ranges, a powerful oxidizing agent has to be used [24]. Considering our previous experiences [23], an equimolar amount of potassium permanganate was used as a reagent in our experiments. During the process, precipitation of manganese occurred via synproportionation reaction (equation 4). Its concentration in the mine water dropped to a value of 4 mg/l. Simultaneously, a decline of pH from 4.05 to 2.27 and rise of the ORP value from 552 mV to 934 mV were recorded.



Fast-acting sedimentation and dynamic filtration of resulting precipitates was observed. After drying and homogenization, the morphology and elemental composition of the obtained sample (Mn-1) were evaluated. Smooth spherical aggregates were observed on SEM images (figure 5). EDX analysis of the specimen presented in figure 6 confirmed the presence of elements corresponding to manganese oxide with a non-stoichiometric composition with minor ratio of magnesium.

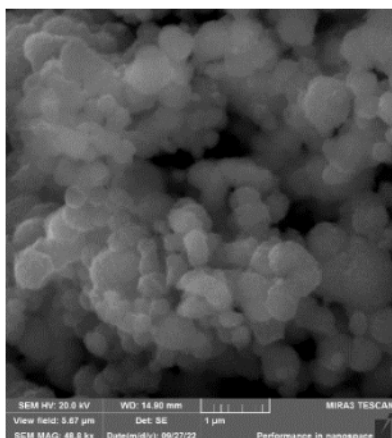


Fig. 5. SEM micrograph of sample Mn-1

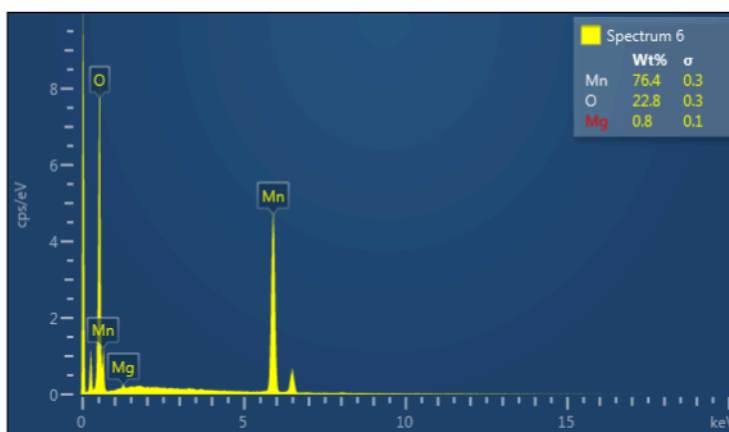


Fig. 6. EDX spectrum of sample Mn-1

Aqueous precipitation of transition metal oxides often proceeds through non-equilibrium phases. The manganese oxides are a remarkable example of structural and oxidation-state diversity, include more than 30 phases over oxidation states from Mn(II) to Mn(VII) [26]. Howe et al. [27] reported, that the sequence of reactions involving Mn(II) oxidation and subsequent precipitation as manganese dioxide involves the simultaneous occurrence of several forms of manganese (dissolved Mn(II), hydrated Mn(III) oxides, Mn(II) adsorbed on particles, and Mn(II) complexes with ligand). Future research on the exact identification of the obtained Mn-product is necessary.

### Conclusions

The results of our work confirmed the possibility of iron and manganese removal from real mine water with high selectivity, reaching efficiency of 99.87% and 99.25%, respectively. Further analyses remain necessary to precise physical and chemical characterization of retrieved Fe- and Mn-products. Based on the obtained results, it will be possible to consider their following processing and potential use.

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