ALTERNATIVE OPTIONS FOR REMOVING/RECOVERING SELECTED METALS FROM MINE WATERS FLOWING OUT FROM THE FLOODED MINING WORKINGS OF THE NIŽNÁ SLANÁ SIDERITE ORE DEPOSIT

ALTERNATIVE OPTIONS OF SELECTED METALS REMOVAL/RECOVERY FROM MINE WATERS FLOWING OUT FROM THE FLOODED MINING WORKINGS OF SIDERITE ORES DEPOSIT NIŽNÁ SLANÁ

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Abstract

The objective of this work is the application of an innovative method for metals recovery from metalliferous mine water released from the flooded siderite mine Nižná Slaná. Although the metals contained in mine drainage are considered environmental pollutants, they may also be valuable resources. Conventional chemical precipitation processes produce huge amounts of sludge with storage and management requirements, without the possibility of waste metals processing. This study comprehensively investigated the selective recovery of Fe and Mn from 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 of the solutions were recorded in the course of oxidation/precipitation processes. The morphology and elemental composition of the 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 98.4% and 96.7%, respectively. Targeted metals were removed with high selectivity to levels that meet water quality criteria for safe discharge to the environment.

Keywords: *metalliferous mine water, selective metals removal, SEM, EDX*

Introduction

Recovering metals from mine water is not a new approach to mine waste management. The combination of high extraction costs, increasingly stringent environmental commitments and the depletion of historically important metal resources has led to a re-evaluation of alternative options for metal recovery. Mine water is now viewed in a new light and treated as a potential resource, often as part of a broader water treatment solution for a given site. Many sophisticated processes have been developed to recover components of this water that have potential economic value. The choice of a suitable method depends on the physical and chemical properties of the mine water, which are influenced by many factors, including the geology, composition and mineralogy of the ore deposits, mining methods, climatic conditions and hydrology of the site. The separation methods used can be divided into basic categories: chemical (precipitation, reduction, extraction), physical-chemical (reverse osmosis, ion exchange, evaporation), electrochemical (electrolysis, electrocoagulation, electrodialysis), microbiological (sulphate reduction, metal reduction) and combinations thereof (electrochemical cells with semi-permeable membranes, bioelectrochemical systems, ion exchange extraction) [1]. Some methods are still at the basic research stage, while others have been verified in pilot operations. Based on specific local conditions and requirements, several companies are able to prepare tailor-made solutions that are successfully applied in practice (Clean TeQ Water, BQE Water, Stantec, Paques).

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In our work, we focused on the selective removal/recovery of iron and manganese from mine water flowing out of flooded mine areas of the Nižná Slaná siderite ore deposit.

Materials and methods

The experiments used mine water flowing from the Marta drainage tunnel into the Slaná River near the former Siderit Nižná Slaná plant. Mining activity took place in the vicinity of Nižná Slaná on ore deposits of various genetic types. From the 14th century onwards, silver, copper and mercury ores were mined here, as well as large quantities of limonite and siderite iron ores. The greatest boom in mining activity occurred at the turn of the 18th and 19th centuries in connection with the creation of a large ironworks focused on the processing of siderite [2]. From the mid-20th century until 2008, two iron ore bodies were mined in the Nižná Slaná ore field, with the siderite subsequently processed using a unique technology for the production of blast furnace pellets. After mining operations ceased, the mine began to flood spontaneously in August 2011. A hydrogeological study conducted in 2011 estimated the flooding time of the mine at 20 years and the amount of mine water flowing out at 7–12 l/s [3]. In February 2022, a massive leak of contaminated water from the deep level of the mine into the Slaná River was observed. An evaluation of laboratory analyses of water samples taken on 24 February 2022 found that several monitored indicators exceeded the permissible limits for surface water pollution [4] in the leaking mine water and in the Slaná river [5] by several times.

Water samples used in the experiments were taken from the discharge pipe, which serves to drain water from flooded mining areas of the deposit into the Slaná River during March 2022. The water had a pH value of 5.60 and concentrations of selected metals Fe and Mn were 4762 mg/l and 459.5 mg/l. The experiments were carried out under laboratory conditions using one litre of mine water. They were repeated, with the results of each experiment being almost identical.

Iron was removed from the mine water in two steps. After adding an appropriate amount of 30% hydrogen peroxide, rapid oxidation of divalent iron occurred, with partial precipitation of Fe^{3+}observed. Using 10M NaOH, almost complete precipitation of iron was achieved. Manganese was removed from the mine water by oxidation and precipitation by adding an adequate volume of 5% $KMnO_4$solution . During the oxidation processes, pH and ORP (oxidation-reduction potential, values relative to the Ag-AgCl reference electrode) values were monitored. The data obtained were recorded using a software application in the LabVIEW environment (National Instruments, Austin, Texas, USA).

The precipitates were separated in individual steps of the process using a Pragopor filter with a pore size of 0.40 µm, washed with distilled water and dried at laboratory temperature. Their morphology and composition were evaluated using a scanning electron microscope (MIRA 3 FE-SEM, TESCAN, Czech Republic) and elemental analysis using an EDX detector (Oxford Instrument, Oxford, UK). The concentrations of metals in mine water and filtrates were determined using a VARIAN AA240FS atomic absorption spectrometer (Melbourne, Australia).

Results and discussion

Due to the interactions between Fe and Mn in solutions, iron was separated from the water first. If it is present in the water in a reduced form, the precipitated manganese is resolubilised ($Mn^{4+} + 2Fe^{2+} \rightarrow Mn^{2+} + 2Fe^{3+}$) [6].

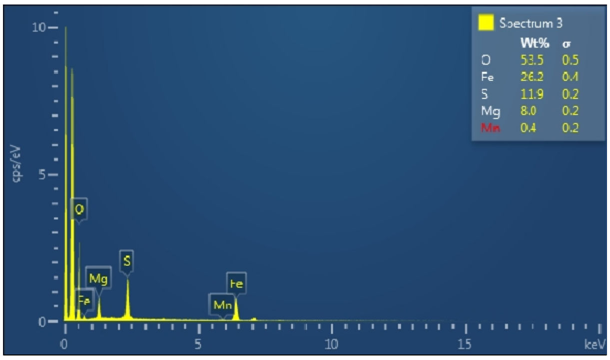
Iron is present in mine water in two oxidation states, Fe^{2+} and Fe^{3+} . Trivalent iron precipitates at pH values of 2.5-4, while divalent iron does not precipitate at pH values below 6. For this reason, its removal at low pH requires oxidation of the ferrous form to ferric. After oxidation, partial hydrolysis of the resulting trivalent iron occurs, with the soluble Fe^{3+}ion precipitating in the form of ferric hydroxide and hydroxysulfates [7]. In our work, an equimolar amount of hydrogen peroxide (8.5 ml of 30% H_2O_2) (1) [8] was used as the oxidising agent. After oxidation and subsequent precipitation of iron (sample Fe-1), its concentration in mine water decreased from the original 4762 mg/l to 2680 mg/l. At the same time, a decrease in pH from 5.60 to 2.32 and an increase in ORP from 218 mV to 800 mV were recorded.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \cdot OH + OH^- \qquad /1/$$

In the next step, after adding NaOH to the mine water, an increase in pH to 3.33 was observed. At the same time, iron precipitation (sample Fe-2) occurred and its concentration decreased to 7.5 mg/l.

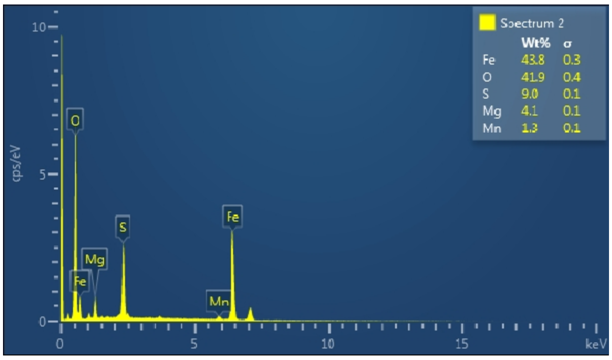
In both processes, the resulting precipitates sedimented relatively quickly, but the filtration of both samples was time-consuming. After drying, the precipitates were homogenised in a mortar and subjected to further analysis. Their mineralogical composition was evaluated using elemental EDX analysis (Figs. 1–2). The mass percentage in sample Fe-1 confirmed the presence of elements corresponding to jarosite, while in sample Fe-2, the presence of elements probably corresponds to ferric hydroxide with partial adsorption of sulphates. No specific morphological characteristics were observed in either sample (Figs. 3–4).

Using a similar procedure, iron in the form of schwertmannite was removed from the Smolnícka mine water flowing out of the Pech shaft [9]. Hematite was obtained by its thermal decomposition at 800°C. However, the physical and chemical properties of both mine waters and the EDX profiles of the obtained precipitates are different. The possibility of applying this process in the further processing of Fe precipitates obtained from water from Nižná Slaná therefore requires further analysis and experimentation.



	Wt%	σ
O	53.5	0.5
Fe	26.2	0.4
S	11.9	0.2
Mg	8.0	0.2
Mn	0.4	0.2

Fig. 1 EDX spectrum of sample Fe-1



	Wt%	σ
Fe	43.8	0.3
O	41.9	0.4
S	9.0	0.1
Mg	4.1	0.1
Mn	1.3	0.1

Fig. 2 EDX spectrum of sample Fe-2

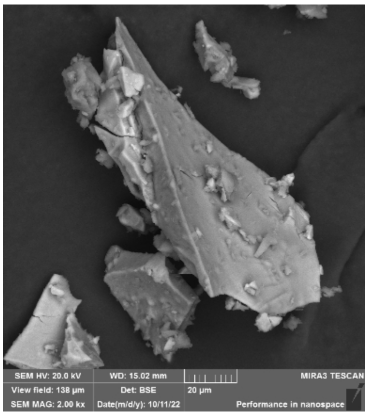


Fig. 3 SEM image of sample Fe-1

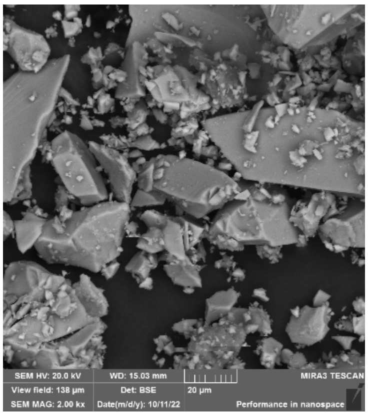


Fig. 4 SEM image of sample Fe-2

Manganese occurs in the aquatic environment in soluble and insoluble forms in oxidation states +2, +3 and +4, depending on the redox conditions and pH of the environment. The transition between these forms occurs through oxidation and reduction reactions, which can be abiotic or caused by microbial processes. In acidic mine water, manganese is mainly present in soluble divalent form, and alkalisation is a commonly used method for its removal. However, this process causes co-precipitation of manganese with magnesium, which is present in high concentrations in the treated mine water [10]. A 5% potassium permanganate solution (9.3 ml) was therefore used as the reagent. During the oxidation process, manganese precipitated (2), and its concentration in the mine water decreased to 1.5 mg/l. At the same time, a decrease in the pH of the water from 3.33 to 2.35 and an increase in the ORP value from 552 mV to 934 mV were recorded.

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2 + 4H^+ \qquad /2/$$

The resulting precipitates sedimented very quickly and their filtration was dynamic. After drying and homogenisation, the morphology and elemental composition of the obtained sample (Mn-1) were evaluated. Smooth spherical aggregates were observed in the SEM images (Fig. 5). Howe et al. (2004) report that the sequence of reactions involving Mn^{2+}oxidation and subsequent precipitation in the form of manganese oxide involves the simultaneous occurrence of several forms of manganese (dissolved Mn^{2+}, hydrated Mn^{3+}oxides, Mn^{2+}adsorbed on particles, and Mn^{2+}complexes with ligands). EDX analysis confirmed the presence of elements corresponding to manganese oxide with a non-stoichiometric composition (Fig. 6). Further analyses, such as Raman spectroscopy or X-ray photoelectron spectroscopy (XPS), will be necessary to accurately identify the Mn product obtained.

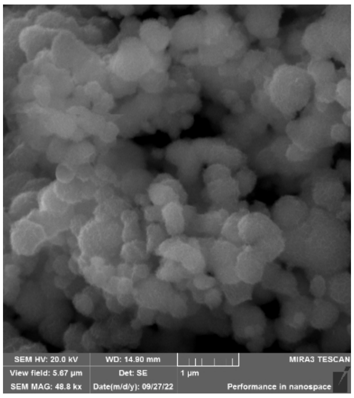


Fig. 5 1SEM image of the Mn-1 sample

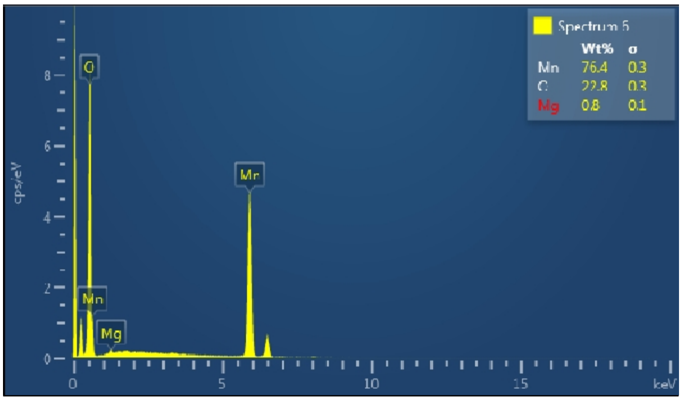


Fig. 6 EDX spectrum of the Mn-1 sample

Conclusion

The results of our work confirmed the possibility of selective removal of iron and manganese from real mine water with an efficiency of 98.4% and 96.7%. However, further analyses are needed to accurately identify the Fe and Mn products. Based on the results obtained, it will be possible to consider their potential use.

Acknowledgements

This work was supported by a financial contribution from the Agency for the Support of Research and Development under contract no. APVV-20-0140 and the VEGA grant agency as part of project no. 2/0142/19. The authors would like to thank the scientific institutions SAV and CNR for supporting this study through the Mobility CNR-SAV-20-02 programme.

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