ECOLOGICAL DISASTER ON THE SLANÁ RIVER – CHARACTERISTICS OF MINE WATERS AND PROPOSED REMEDIATION PROCEDURES

ECOLOGICAL DISASTER ON THE SLANÁ RIVER – GEOCHEMISTRY OF MINE WATERS AND REMEDIATION PROCEDURES

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Abstract

The discharge of mine water from the flooded deposit of siderite ores in Nižná Slaná (Slovakia) caused an ecological disaster on the Slaná River. Mine impacted effluents transport a huge amount of metals and metalloids to the river recipient. The high iron content resulted in a significant red colouration of the river, which is observed several tens of kilometres downstream. The pH, alkalinity, and associated properties of mine water change as the water equilibrates to atmospheric conditions because of the degassing of dissolved $_{CO_2,}$dissolution of $_{O_2}$, oxidation of Fe(II) and Mn(II), and hydrolysis of Fe(III) and Mn(IV). Although many different biological and chemical technologies are considered for treatment of acid mine drainage (AMD), lime neutralisation remains by far the most widely applied method. The principle of AMD neutralisation lies in the insolubility of metals in alkaline conditions. A common by-product of lime neutralisation is gypsum, as AMD is often rich in sulphate.

Keywords*: mine impacted water, siderite, AMD remediation, Fe-oxidising bacteria, lime, neutralisation*

Introduction

The Nižná Slaná – Kobeliarovo deposit area lies west of the Slaná River valley, in the triangle between the villages of Nižná Slaná, Gočovo and Kobeliarovo (Fig. 1). The Nižná Slaná ore field is part of the Hanková – Volovec – Holec carbonate belt, which is a relatively narrow belt of the Betliar Formation of black phyllites with lydite and carbonates of the older Gemerian Palaeozoic [1]. Carbonates, crystalline limestone, dolomite, ankerite and siderite form a significant part of the productive formation itself. The locations of limestone, ankerite and siderite are repeated many times in the vertical section of the deposit and are stratiform in nature. The basic types of carbonates are very similar in terms of their chemical composition, degree of contamination and trace element content. The increased Mn content in siderite, ankerite and limestone also indicates that sedimentary, diagenetic and metamorphic processes played a significant role in their formation [2].

The main Manó deposit has been regularly mined underground since the second half of the 19th century. Until 1975, mining of the deposit was carried out through the 1,300 m long Manó hereditary adit. From 1975, the deposit was accessed through the Gabriela shaft, which was also the main mining facility.

Based on verified ore reserves, the Siderit Nižná Slaná mining and processing complex was built with a capacity of 700,000 to 1 million tonnes per year. The mined ore was processed by roasting in rotary kilns and magnetic separation. The final product was blast furnace pellets with a content of Fe 55.8 ± 0.4% and Mn 3.5 ± 0.1% [3].

The Kobeliarovo deposit has been mined since 1994. The deposit was opened by two mining works: the Transport Tunnel, which is a continuation of the former Manó heritage tunnel at the VI horizon level, and a new opening work – a decline in Kobeliarovo. Two significant sources of drinking water with a yield of 4–5 l/s were also tapped in the transport tunnel section. The deposit was explored above the VI horizon. Two productive carbonate locations with balanced metasomatic mineralisation were found at the deposit [4]. Both deposits were mined using caving mining methods.

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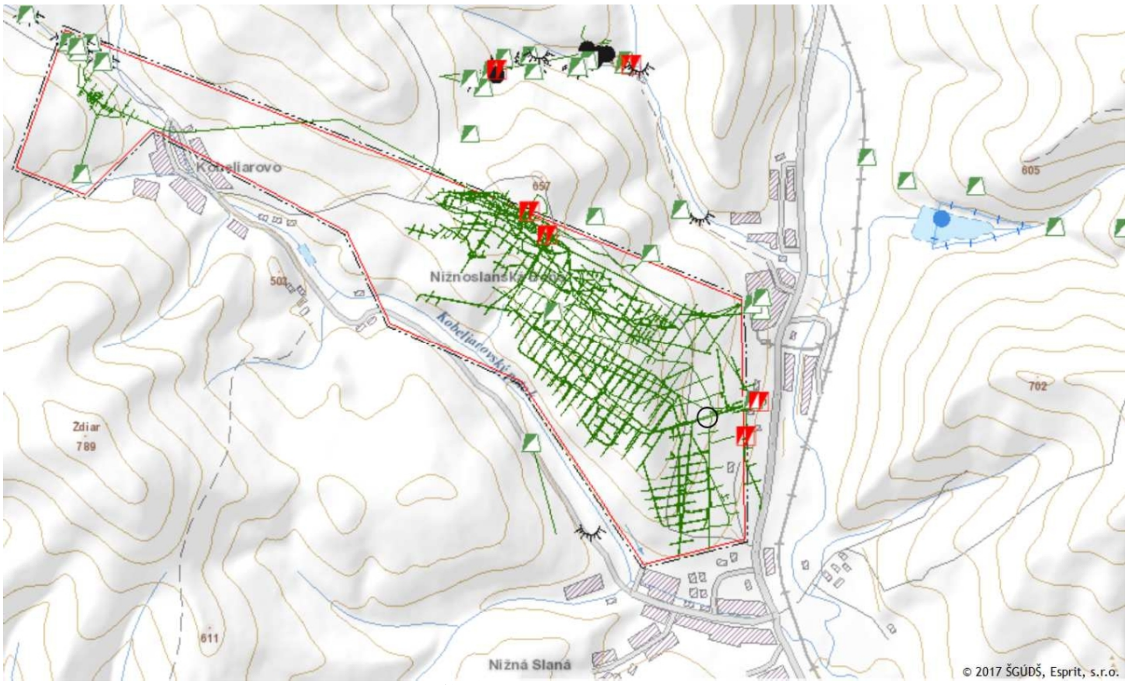

Fig. 1. Topographic map of the Nižná Slaná - Kobeliarovo area with mining areas marked
source: https://apl.geology.sk/geofond/sbd/

Nižnoslanský siderite has a reduced iron content and increased Mn, Mg and Ca content, which are isomorphously bound in the siderite lattice. The average content of useful components in the raw ore is: Fe 33.50%, Mn 2.18% and SiO_2 8.50%. The ore was mainly contaminated by black phyllites overlying the ore deposit, but also by inserts of unbalanced carbonates – ankerites and limestones. The ore mined from Kobeliarovo was transported through a 4 km long underground transport tunnel Manó – Kobeliarovo and the Jozef adit to the Gabriela mine yard, where it was further processed together with the ore from the Manó – Gabriela deposit [3]. Polysulphide mineralisation is present to a small extent. Locally, higher sulphide contents were found mainly in sericitic-graphitic and graphitic phyllites in the Manó-Gabriela deposit. The following ore minerals were identified: pyrite, arsenopyrite, pyrotite, marcasite, sphalerite, chalcopyrite, galena, tetrahedrite, ullmannite, jamesonite, boulangerite, magnetite, hematite, limonite and others [5].

In 2001, work began on deepening the Gabriela mining shaft from its original depth of 300 m by a further 65 m. m. The opening of the XIII horizon made additional siderite ore reserves available, which, with planned annual production of one million tonnes, was expected to extend the mine's life by ten to twelve years.

In 2008, Siderit, s.r.o. Nižná Slaná was declared bankrupt due to its long-term inability to pay for gas and electricity, and mining was terminated. In 2009–2010, the drainage of the deposit continued by pumping mine water. Despite its efforts and negotiations, Siderit was unable to ensure the continuation of mining activities – the opening, preparation and extraction of the exclusive deposit in the Nižná Slaná mining area after 8 September 2011, which was the date of expiry of the District Mining Office's decision authorising mining activities while securing the main mining works in the said mining area.

The District Mining Office in Spišská Nová Ves ordered Siderit s.r.o. to prepare a hydrogeological study of the flooding of the mine and subsequently a plan for the liquidation of the main mining works, which was to take this study into account. The hydrogeological study of the flooding of the mine in Nižná Slaná, or rather the Manó – Gabriela deposit, was prepared for Siderit, s. r. o., by Ing. Marián Bachňák ENVEX Rožňava [6]. The study estimated that the mine would take 20 years to flood and that the amount of mine water flowing out would be 7–12 l/s. The pumping of mine water was finally stopped in August 2011, and the mine has been flooding ever since. To prevent unwanted leaks in the built-up area between the Gabriela shaft and the Slaná River, where the state road passes, a drainage tunnel (Marta) was excavated from the surface to the Gabriela pit with a total length of 110 m at the height of the local erosion base of 360 m above sea level. In 2017–2019, water management facilities were constructed in front of the mouth of the Marta tunnel and the portal of this tunnel was built [7].

Current status of the issue

On 24 February 2022, the District Office of Rožňava reported pollution of the Slaná watercourse in the Nižnoslanská Baňa area. The source of the pollution was a discharge structure used to drain water from flooded mining areas of the Nižná Slaná siderite ore deposit. The high iron content caused a significant red discolouration of the water, which can be observed for several tens of kilometres (Fig. 3). The values of some indicators exceeded the limits for surface water quality requirements (NV SR No. 269/2010 Z. z.) several times over. The solution is to treat the mine water by precipitating iron and other elements in the form of suitable minerals and then separating them by sedimentation or filtration.

Fig. 2. Outflow of mine water from the flooded siderite ore deposit in Nižná Slaná, 15 March 2022.

Fig. 3. Red colouring of the Slaná River, 13 km from the site of pollution (Rožňava, Nadabula, 15 March 2022).

Genesis of mine water

The dissolution and mobility of metals in rock environments containing ores are influenced by two main, essentially antagonistic geochemical processes: acidity-forming processes of oxidative weathering of sulphides and neutralisation reactions of acidic waters with carbonates. The oxidation of pyrite by oxygen proceeds according to equation 1 [8].

$$FeS_2 + 3.5O_2(aq) + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \rightarrow FeSO_4 + H_2SO_4 \quad (1)$$

The oxidation of disulphide sulphur S_2^{2-} to the sulphate form $2S^{6+}$ is associated with the transfer of 14 electrons and the formation of two H^+ protons. Further acidification of the environment occurs as a result of the formation of hydrolytic products of trivalent iron after the oxidation of Fe^{2+} to Fe^{3+}.

$$Fe^{2+} + 0.25O_2(aq) + 2.5\,H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \quad (2)$$

The neutralisation of acidic drainage water upon contact with carbonates – siderite and ankerite – and the mobilisation of metal cations occurs (in the case of congruent dissolution of the above minerals) in accordance with equations 3 and 4, respectively.

$$Fe_x Mn_{(1-x)} CO_3 + H_2SO_4 \rightarrow xFe^{2+} + (1\text{-}x)Mn^{2+} + SO_4^{2-} + H_2O + CO_2 \quad (3)$$

$$\mathrm{Ca}_x\mathrm{Mg}_y\mathrm{Fe}_z, \mathrm{Mn}_w(\mathrm{CO}_3)_2 + \mathrm{H_2SO_4} \rightarrow x\mathrm{Ca}^{2+} + y\mathrm{Mg}^{2+} + z\mathrm{Fe}^{2+} + w\mathrm{Mn}^{2+} + \mathrm{SO_4}^{2-} + 2\mathrm{HCO}^-_3 \quad (4)$$

Siderite has zero net neutralisation capacity because the two hydrogen protons consumed in reaction 3 are subsequently produced during the hydrolysis of oxidised iron (equation 2) and manganese.

In the flooded areas of the Nižná Slaná siderite deposit, other sulphides and carbonates are transformed and a whole series of exothermic reactions take place, including the spontaneous combustion of black shales containing pyrite and other sulphides. Black shales form the immediate surroundings of carbonate deposits in the Spišsko-Gemerské Ore Mountains [9]. Graphitic shales form layers several metres to tens of metres thick in the bedrock and overburden of the siderite deposits of the Nižná Slaná deposit. Thanks to the sorption capacity of carbon, they play an important role in the concentration of various elements [10]. These porous structures allow the permeability of rocks for various types of fluids, thereby increasing their reactivity. In the presence of oxygen,spontaneous temperature increases and self-ignition may occur [1] [11]. These processes are probably the cause of the abnormally high temperature of the mine water (36.5 °C), which, at a yield of approximately 20 l/s, represents an enormous amount of geochemically generated heat. The products of sulphide oxidation are water-soluble metal sulphates, which are gradually washed out by drainage mine water.

Materials and methods

Samples of mine water were taken from the outlet of the Marta drainage tunnel into the Slaná River (Fig. 2) and from the Gabriela pit (Fig. 10). Water samples from the Gabriela pit were taken using a submersible electric sampling pump at a rate of approximately 150 litres per hour from a depth of 3 m. As part of the sampling, in-situ measurements of physical and chemical parameters (pH, conductivity, temperature, ORP, oxygen saturation) were performed using a WTW – Multi 3630 field device in a flow-through vessel. At the same time, filtered and unfiltered water samples were collected in sample bottles for laboratory analysis of selected metals, anions, dissolved substances, H_2S and others. The total concentrations of metals were determined using a VARIAN AA240FS atomic absorption spectrometer. The Fe^{3+} and Fe^{2+} species were determined spectrophotometrically using the UV method [12, 13] and the VIS method with o-phenanthroline [14], respectively.

Results and discussion

The leaking mine water is of the ferric-sulphate type with a high concentration of dissolved iron and high total mineralisation (concentration of dissolved substances RL_{105}~ 53 g l^{-1}) (Table 1). The major elements are magnesium, dissolved iron in the reduced divalent form Fe^{2+} and manganese. Sulphates are the most abundant anions. At a yield of ~ 20 l $^{s^{-1}}$(72 $^{m^3h^{-1}}$), the amount of pollutants discharged into the Slaná recipient between March and June was ~ 90 t per day. The mine water has an acidic reaction, pH 5.7, and exhibits high acidity values ($ZNK_{8.3}$~ 160–180 mmol $^{l^{-1}}$), which translates to a consumption of approximately 9 g $_{CaCO_3}{}^{l^{-1}}$. Approximately 52 litres of water from the Slaná River are needed to neutralise 1 litre of mine water. From the moment the mine water is mixed with water from the Slaná recipient, ferric hydroxide will precipitate. Its concentration will decrease as the mine water is diluted with river water.

The geochemical parameters of mine water from NS rule out the possibility of using so-called "passive technology" treatment using anoxic limestone drainage (ALD). Mine water is highly supersaturated with ferric hydroxide and alkaline metal jarosite. *Although the concentrations of Fe(3+)* in *the filtered* and stabilised *samples* were in the order of tens of mg/l, any movement of the pH towards the alkaline region will cause a significant increase in the concentration of Fe(3+) in the filtered and stabilised samples. Although the concentrations of Fe^{3+} in filtered and stabilised samples were in the order of tens of mg/l, any movement of the pH towards the alkaline range will cause $Fe(OH)_{(3)}$ $_{to}$ precipitate. This will passivate the surface of the limestone with precipitated ferric hydroxide and reduce its reactivity.

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[1] Processes of "spontaneous combustion" were also recorded at the Nižný Slanský deposit during the extraction of siderite ores: *"The extractability, as well as occupational safety and hygiene, are also very adversely affected by the as yet unlocated heat accumulation in a large part of the underlying blocks of the XI horizon, accompanied by $_{SO_2}$and CO emissions. The cause of this heat accumulation has not yet been reliably explained. The cause of the gas is probably the flow of mine winds through not completely collapsed mined areas, which oxidises the overburden rocks – black phyllites and lydites rich in pyrite" (Rozložník et al., 1990).*

Table 1. Physical and chemical parameters of mine water from the Nižná Slaná site (2022).

Date of sampling	t C	pH	ORP mV	EK µScm	O_2 % sat	RL105 mg/l	Fe mg/l	Mg mg/l	Mn mg/l	Ni mg/l	Co mg/l	As mg/l	SO_4^{2-} mg/l	HCO_3^- mg/l
15. 3.*	24.7	5.5	-6.7	26,400	25.4	56,162	4709		527	15.9	3.2	14.7	31135	
5.	36.1	5.1	-15.6	24,800	< 2		5020	7110	592	23.4	3.1	16.8	34108	72
18.5	35	5.7	-12	22600	< 1	50,794	5012	4858	595	33.9	3.4	17.8	35460	134
12. 8.	23.9	5.6	-11.1	21300	< 1	40,328	4190	4296	484	21.1	3.4	11.2	26100	487
Limit	< 26	6 8.5		1100	> 5 mg/l	900	2	100	0.3	0.02	0.5	0.02	250	-

* outlet – Marta adit

Options for cleaning mine water

The solution for the water treatment process is to remove Fe, As, Ni and other elements. It is also necessary to reduce the concentration of sulphates and eliminate the acidity of mine water using neutralising agents. The removal of iron in the form of Fe(III) precipitates, together with co-precipitating elements (As, Co), requires the oxidation of Fe^{2+} to Fe^{3+} followed by the separation of precipitates by sedimentation or filtration. An alternative option is alkaline precipitation of iron in the form of ferrous hydroxide $Fe(OH)_2$ without the need for Fe^{2+} oxidation.

Oxidation of Fe^{2+} in mine water

After anoxic mine water emerges from underground, several of its physical and chemical parameters change rapidly. Mine water is >100 times supersaturated with carbon dioxide compared to the partial pressure $_{\text{of } CO_2}$in atmospheric air. The degassing of CO_2reduces the total dissolved carbonate content. Under the influence of atmospheric oxygen, Fe^{2+} is oxidised to Fe^{3+} , Fe^{3+} is hydrolysed and the pH is subsequently reduced. As Fe oxidation/precipitation progresses, a new equilibrium is established between the liquid, gaseous and precipitating solid phases.

The rate of chemical oxidation of Fe^{2+} in natural waters depends on the pH value. At higher pH values, hydrolysed forms of ferrous ions predominate in the solution, which oxidise much faster than non-hydrolysed Fe^{2+} ions: $Fe(OH)_2^0(aq) >> Fe(OH)^+ >> Fe^{2+}$. In waters with pH values in the range 5 < pH < 9, the rate of iron oxidation is directly proportional to the concentration of iron and the partial pressure of oxygen and increases proportionally with the square of the concentration of $[OH^-$ions [15].

$$\frac{-\mathrm{d}[\mathrm{Fe}^{2+}]}{\mathrm{d}t} = k_{pH5-9}[\mathrm{Fe}^{2+}][\mathrm{OH}^-]^2\, p\mathrm{O}_2$$

When the pH value increases by one unit (the concentration $[OH^-]$ increases tenfold[2]), the oxidation rate of Fe increases a hundredfold. The oxidation rate of Fe^{2+} in pH-neutral waters is high, with a reaction half-life of minutes.

At pH values < 4, unhydrolysed Fe^{2+} ions predominate and the oxidation rate decreases dramatically (Fig. 4). In solutions with pH < 3, the iron oxidation rate is extremely slow, with a rate constant that is 5 orders of magnitude lower. The presence of $HCO_3^-$and SO_4^{2-}anions reduces the oxidation rate of Fe due to the formation of complexes. In acidic sulphate solutions, the rate is directly proportional to the partial pressure of oxygen and proportional to the square of the Fe^{2+}concentration.

Fig. 4 shows the course of iron oxidation in a real sample of mine water from Nižná Slaná upon contact with atmospheric air. Iron oxidation in mine water was monitored using online gas analysis and liquid phase chemical analysis (Fig. 5). The rate of iron oxidation was calculated from the rate of oxygen consumption using the stoichiometry of equations 2 and 7. The molar ratio of oxidised iron to oxygen consumed, $Fe/O_2 = 4$. Oxidised trivalent iron precipitates in the form of ferric hydroxide. The H^+ion, which is a product of hydrolytic reactions (equation 2), causes the pH to drop below 3. As a result of the pH drop, the rate of this oxidation reaction decreases rapidly.

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[2] (pH 5 $[OH^-] = 10$^$^{-9}$ mol L^$^{-1}$; pH 6 $[OH^-] = 10^{-8}$ mol L^{-1} ; pH 7 $[OH^-] = 10^{-7}$ mol L^{-1} ; pH 8 $[OH^-] = 10^{-6}$ mol L^{-1})

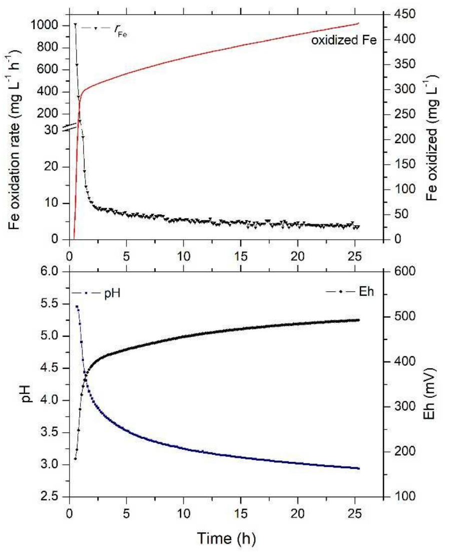


Fig. 4. Time record of Fe oxidation in mine water from Nižná Slaná, change in pH and oxidation-reduction potential (Eh). The rate of iron oxidation decreases sharply when the pH value falls below 4.

Fig. 5. Laboratory tests of chemical and bacterial oxidation of iron in mine water with online analysis of gases, pH and ORP.

The Fe^{2+}oxidation rate decreased from an initial value of > 1000 mg/l/h (pH 5.5) to a value of ~ 5 mg/l/h at pH < 3. The total amount of oxidised iron in 25 hours is approximately 450 mg/l, which represents less than 10% of the original Fe^{2+}concentration. To increase the oxidation rate, it is necessary to increase the pH of the solution by adding neutralising agents (NaOH, KOH, $Ca(OH)_2$, $CaCO_3$) or using oxidising agents (H_2O_2, ozone, Fe-oxidising bacteria).

When the pH drops below 3, a significant portion of the trivalent iron in the mine water remains dissolved in the form of sulphate complexes, and with the continued oxidation of $Fe^{(2+)}$,the concentration of dissolved Fe^{3+}in the solution gradually increases.

$$Fe^{2+} + SO_4^{2-} + 0.25\, O_2(aq) + H^+ \rightarrow FeSO_4^{+} + 0.5\, H_2O \tag{5}$$

After complete oxidation of Fe^{2+} to $Fe^{(3+)}$,the pH of the mine water drops to a value of pH < 2 (Fig. 6). The original concentration of Fe^{2+} was approximately 5000 mg/l. The concentration of dissolved Fe^{3+} in the solution was ~ 2500 mg/l, with approximately the same amount of Fe^{3+} precipitating in the form of hydroxides (equation 2) or hydroxysulfates (Fig. 7).

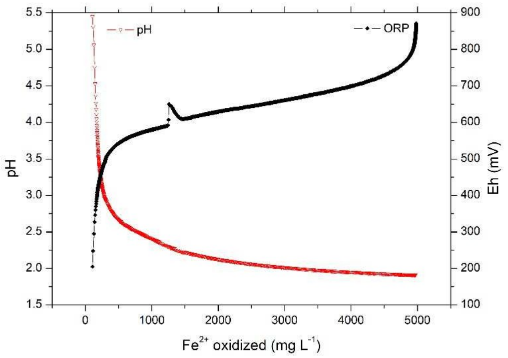


Fig. 6. Change in pH and oxidation-reduction potential of mine water during the oxidation of $Fe^{2+}$to Fe^{3+}.

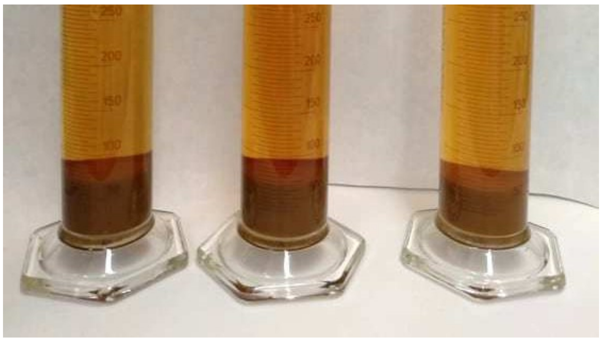
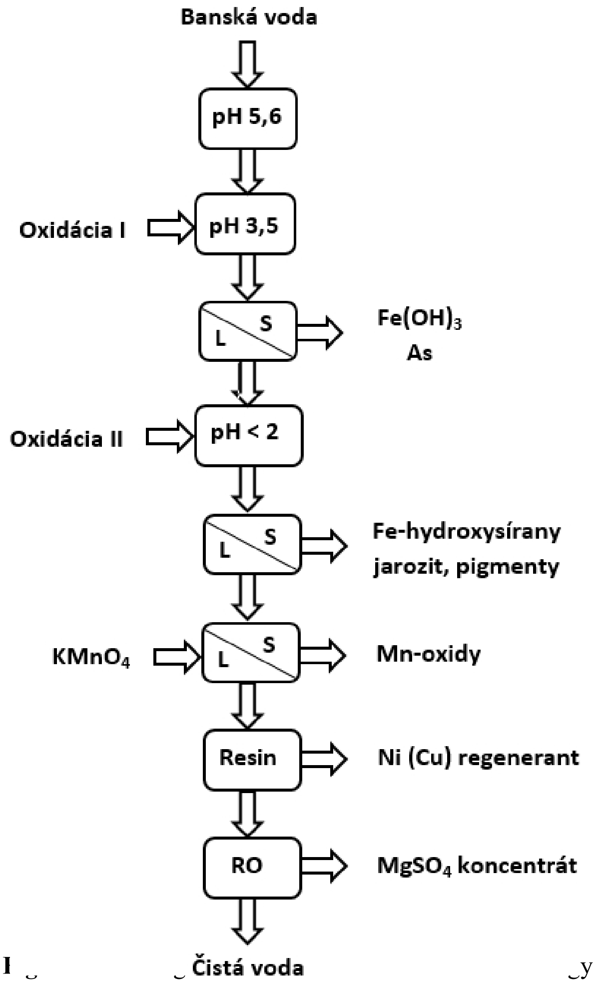


Fig. 7. Mine water after complete oxidation of Fe^{2+} to Fe^{3+} and precipitation of Fe(III).

Water purification technologies using Fe^{2+} to Fe^{3+} oxidation apply various physical-chemical and biological processes to accelerate the oxidation of iron and its subsequent precipitation. By adjusting the pH value > 6, the rate of iron oxidation increases by several orders of magnitude. At the same time, complete precipitation of Fe(III) occurs (Mačingová et al., 2022, this collection, pp. 13-17). A similar process can be observed when mixing water in the Slaná reservoir as a result of the neutralisation of acidic mine water with river water containing alkalinity and dissolved oxygen.

Precipitation of Fe^{3+}in an acidic environment in the form of jarosite, $KFe_3(SO_{42}OH_6)$,makes it possible to remove not only iron but also a significant portion of sulphate anions from water. A diagram of the technology with controlled iron oxidation, with the possibility of selective recovery of metals from mine water, is shown in Figure 8. In the first oxidation step, rapid chemical oxidation of $Fe^{2+}$to $Fe^{3+}$by atmospheric oxygen takes place. As a result of hydrolysis and precipitation of $Fe(OH)_3$, the pH drops to 3.5. In this step, approximately 10% of iron and practically all arsenic are removed from the water by sorption and coprecipitation with Fe hydroxides. In the second oxidation step, using Fe-oxidising bacteria, $Fe^{2+}$is oxidised to $Fe^{3+}$with subsequent hydrolysis and controlled precipitation of Fe(III) in the form of jarosite, resulting in a decrease in pH to < 2. In this step, Fe and a significant amount of sulphates corresponding to the molar ratio of Fe/S in jarosite are removed. The separation of Fe precipitates is followed by the oxidative precipitation of Mn (Mačingová et al. 2022, this collection, pp. 13-17). The next step is the reversible adsorption of Ni using chelating sorbents with the possibility of regeneration. In the final step, reverse osmosis is used to obtain a concentrated $MgSO_4$solution and pure water (permeate).



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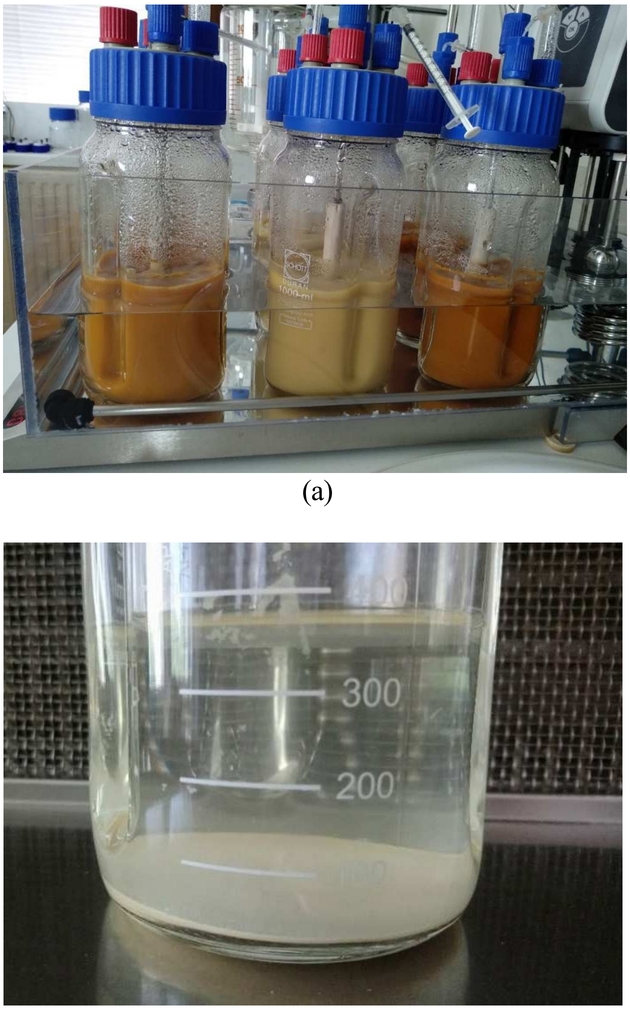
with Fe oxidation and selective sequential extraction of individual elements.


(a)

(b)

Fig. 9. (a) Bacterial Fe oxidation in mine water with controlled precipitation of Fe in the form of various types of Fe hydroxides (schwertmannite and jarosite).
(b) Sediment after bacterial oxidation of Fe^{2+} and precipitation of K-jarosite. Fe^{2+} at the beginning 5087 mg/l. Residual concentration of Fe^{3+} in the liquid phase 208 mg/l, pH 1.9.

Treatment of mine water without Fe^{2+}oxidation

Mine water pumped from the Gabriela pit (Fig. 10) is anoxic, clear, with a low oxidation-reduction potential and a pH value of 6.5 (Table 1). During the extraction of mine water, contact with atmospheric air causes CO_2 to escape, rapid oxidation of iron and precipitation of $Fe(OH)_3$, which manifests itself in the form of cloudiness and red colouration of the water within a few minutes.

When mine water is mixed with $Ca(OH)_2$, a blue-green $Fe(OH)_2$precipitate forms (Fig. 10c). Geochemical modelling of the "titration" of mine water with calcium hydroxide showed the formation of a small amount of $Fe(OH)_3$, followed by the formation of a precipitate of divalent iron $Fe(OH)_2$, gypsum ($CaSO_4 \cdot 2H_2O$) and calcite $CaCO_3$. The physical and chemical parameters of the mine water before and after mixing with $Ca(OH)_2$and separation of precipitates are shown in Table 2. The treated water does not meet the limit values for Mg, Mn and Ni. The table also shows the values after mixing the treated water (Q = 3 l/s) with water from the Slaná recipient (Q_{355}= 444 l/s).

Table 2. Physical and chemical parameters of mine water after neutralisation with$Ca(OH)_2$

Sample	Fe mg/l	Mg mg/l	Mn mg/l	Ca mg/l	Ni mg/l	Co mg/l	Al mg/l	Zn mg/l	As mg/l	COD_{Cr} mg/l	pH
Gabriela	4006	4296	483.9	636	21.1	3.40	3.5	3.5	11.2		5.05
$Ca(OH)_2$	0.14	**2542**	**8.5**	**633**	**0.17**	0.13	<0.02	0.06	0.008	25.8	8.4
*Q355	0.14	25.7	0.13	**633**	**1.9**	0.13	0.12	0.026	0.013	11.1	
Limit	2	100	0.3	200	0.02	0.5	0.2	0.1	0.02	35	6-8.5

*recipient Slaná – Nižnoslanská mine (river km 67.75) above the discharge of mine water Q_{355} = 444 l/s, design flow of untreated mine water from the Gabriela shaft = 3 l/s

Fig. 10 (a) Mining water intake from the Gabriela pit

(b) Mine water pumped by a submersible pump from a depth of 3 m below the surface

(c) Mine water after mixing with $Ca(OH)_2$. Formation of blue-green ferric hydroxide precipitate

Conclusion

The geochemical parameters of mine water from NS rule out the possibility of using passive water treatment with anoxic limestone drainage (ALD). Mine water is highly supersaturated with ferric hydroxide and alkaline metal jarosite. The concentrations of dissolved Fe^{3+}in filtered and stabilised samples from the Gabriela pit were in the order of tens of mg/l. Any movement of the pH towards the alkaline range causes $Fe(OH)_3$precipitation. Similar experiences have been observed by colleagues from the Czech Republic at mining sites (Zlaté Hory, Běstvina, Kaňk near Kutná Hora). In the case of processing mine water pumped from deeper parts of the mine, conveyed to the ALD via piping without contact with the atmosphere, the reactivity of the ALD decreased within a few weeks due to the passivation of the limestone surface by precipitated ferric hydroxide. Attempts to inoculate sulphate-reducing bacteria and laboratory tests of passive water treatment by biological sulphate reduction and precipitation of metals in the form of sulphides have so far been unsuccessful at our workplace. Controlled oxidation of Fe in mine water requires the construction of a fluidised bed bioreactor with iron-oxidising bacteria oxidising bacteria, or other processes to accelerate iron oxidation. The use of hydrogen peroxide and ozone is uneconomical due to the high concentrations of Fe^{2+}. Neutralisation of mine water with CaO or $Ca(OH)_2$ and subsequent precipitation of metals in the form of hydroxides appears to be an advantageous treatment process, which could form the basis for the design of mine water treatment technology in Nižná Slaná. Eliminating the oxidation step prevents acidification of the water as a result of the hydrolysis of ferric ions. Fe^{2+} is removed in the form of $Fe(OH)_2$. At the same time, there is a significant reduction in the concentration of sulphates by precipitation in the form of gypsum $CaSO_4 \cdot 2H_2O$. The precipitates are easily separable by sedimentation or filtration.

Acknowledgements
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