CHEMISTRY OF MINE WATER FROM THE GABRIELA SHAFT IN NIŽNÁ SLANÁ AND PROPOSED TECHNOLOGIES FOR ITS TREATMENT

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INTRODUCTION

The metasomatic siderite deposit Nižná Slaná–Kobeliarovo is part of the Hanková–Volovec–Holec carbonate belt, Betliar Formation (formation of black phyllites with lydite and carbonates of the older Palaeozoic). The deposit area extends west of the Slaná River valley in the triangle between the villages of Nižná Slaná, Gočovo and Kobeliarovo. In the deposit strip, siderite forms several locations separated from each other by various interlayers (black phyllites, limestones, ankerites) (Grecula et al., 1995).

The main deposit of the Nižná Slaná ore field, the Manó–Gabriela deposit, has been mined underground since the second half of the 19th century. Until 1975, siderite was mined through the 1,300 m long Manó adit. From 1975, the deposit was accessed via the Gabriela pit, which was also the main mining facility. Iron ore mining and processing was carried out by Siderit, s. r. o. Nižná Slaná. The Kobeliarovo deposit has been mined since 1994. Siderite ore was transported in mining carts through an underground transport tunnel at the VI horizon level, which is a continuation of the former Manó heritage tunnel, to the Gabriela pit mining yard (extraction horizon). The deposit was opened by the Gabriela shaft to the XIII horizon level. The deposit lies beneath a local erosive base with low-permeability rocks in the overburden. The average inflow of groundwater into the deposit during the mining period was 4 l/s. Mining was terminated in 2008 when Siderit, s.r.o. Nižná Slaná was declared bankrupt due to long-term insolvency. In 2011, the flooding of the mine began (Kolektív_autorov, 2012).

To eliminate leaks in the built-up area between the Gabriela shaft and the Slaná River, through which a state road passes, a drainage tunnel called Marta, with a total length of 110 m, was excavated from the surface to the shaft body at an elevation of 360 m above sea level. (Zvrškovec, 2020).

On 24 February 2022, the Slovak Environmental Inspection Authority in Košice received a report of pollution of the Slaná watercourse in the Nižnoslanská Baňa area. Nižnoslanská Baňa. 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 measured values of some indicators exceeded the limits for surface water quality requirements (NV SR No. 269/2010 Z. z.) several times over. The high iron content caused a significant red discolouration of the water, which can be observed for several tens of kilometres (Fig. 1).

Fig. 1: Red colouration of the Slaná River, 13 km from the site of contamination (Rožňava, Nadabula Bridge, 15 March 2022).

Ferrous minerals in the form of suspensions are transported further downstream over long distances and sediment in places where the kinetic energy of the water flow is reduced.

METHODOLOGY

nd banskej water samples were taken from the outlet of the Marta drainage tunnel into the Slaná River (Fig. 2) and from the Gabriela pit. Water samples from the Gabriela pit were taken with 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, RL content, H_2S and others.

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

GEOCHEMICAL MODELLING

Geochemical modelling of mine water and the processes that occur during its contact with the atmosphere and alkalisation was performed using the Geochemist's Workbench 2022 software package.

RESULTS AND DISCUSSION

The leaking mine water is of the magnesium-sulphate type with a high concentration of dissolved iron and high total mineralisation. In the period from mid-March to 9 June 2022, the concentration of dissolved substances RL_{105} ~ 53 g l^{-1} (Table 1). The major elements are: magnesium Mg^{2+}~ 6 g l^{-1}, dissolved iron in divalent form Fe^{2+}~ 5 g l^{-1}, manganese Mn^{2+}~ 0.6 g l^{-1}. The most abundant anions are sulphates ~ 34 g l^{-1}. At a yield[1] ~ 20 l s^{-1} (72 m^3 h^{-1}), the indicative balance of pollutant inputs into the Slaná recipient was ~ 90 t per day. Mine water has an acidic reaction, pH 5.7, and exhibits high acidity values ($ZNK_{8.3}$~ 160 - 180 mmol l^{-1}). When mixed with water from the Slaná River, approximately 52 litres of water from the Slaná River are needed to neutralise 1 litre of mine water.

After flowing out of the mining environment, the water undergoes rapid chemical changes. Upon contact with atmospheric air, Fe^{2+} oxidises to Fe^{3+} . As a result of the hydrolysis of the ferric ion and its subsequent precipitation in the form of ferric hydroxide iron hydroxide, the turbidity and red colouration of the water increase.

Parameter	Outflow 15.3.2022	Jama Gabriela 18 May 2022	Gabriela Pit 30 June 2022	Jama Gabriela 12 August 2022
t (°C)	24.7	35	25.9	23.9
pH	5.53	5.7	5.6	5.63
ORP (mV)	-6.7 201 | 3.394	-12 186 | 3.038	-	-11.1 197 | 3.341
O_2 (% sat)	25.4	< 1	< 1	< 1
EC (µS cm)	26,400	22600	20400	21300
RL_{105} (mg/l)	56,162	50,794	45,138	40328
Fe (mg/l)	4709	5012	4316	4190
Mg (mg/l)		4858		4296
Mn (mg/l)	527	595	458	484
Ni (mg/l)	15.9	24.3		21.1
Co (mg/l)	3.2	3.46		3.4
As (mg/l)	14.67	17.80	11.31	11.2
SO_4^{2} (mg/l)	31135	34108		26100

Table 1: Physical and chemical parameters of mine water.

In terms of basic typology, mine water is relatively simple and at the same time extreme in its chemical composition. Sulphates account for 99.7% of anions (Fig. 3), and magnesium ions account for almost 93% of the usual main cations. However, when all cations are taken into account, a significant proportion is also made up of usually minor components, namely dissolved iron and manganese (24.1 and 3.1 eq. %, respectively).

[1] The flow rate of mine water at the outlet into the Slaná River in the period from March to 9 June 2022 was approximately 20 l $s^{(-1)}$.

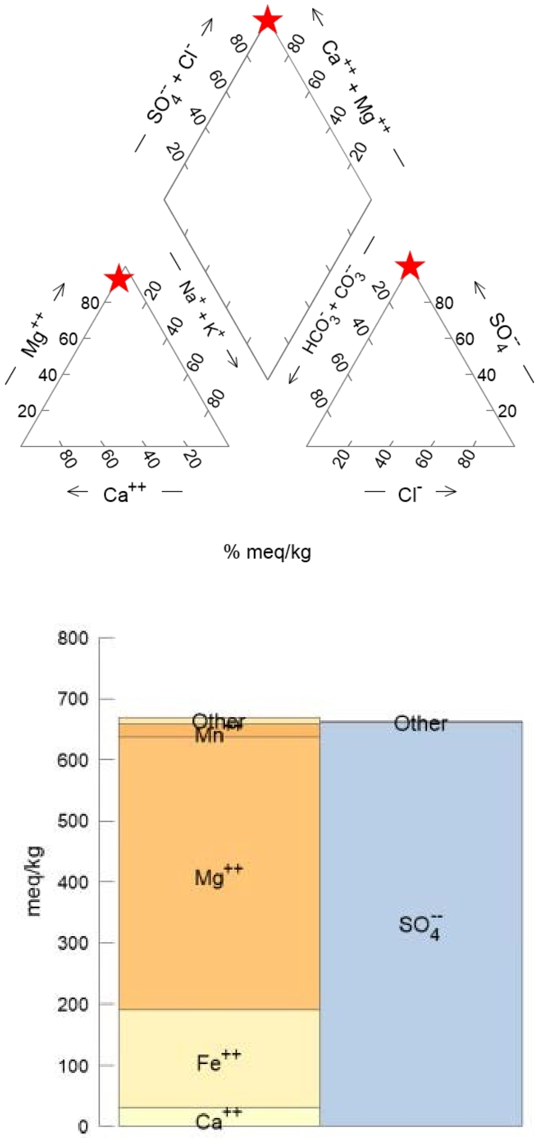

Fig. 3: Piper's and bar chart for mine water from Nižná Slaná.

The mine water is extremely supersaturated with respect to oxyhydroxides and hydroxides of trivalent iron (10^{10}times with respect to goethite, 10^{3}times with respect to ferric hydroxide), but also with respect to jarosites (10^{11}times with respect to potassium, sodium 10^{7}times), siderite (10^{4}times) and slightly supersaturated with respect to gypsum (1.2 times) (Fig. 4). The mine water is significantly pressurised by dissolved $CO_2(aq)$, its partial pressure reaching five hundred times the normal partial pressure of carbon dioxide in the atmosphere.

If mine water is allowed to reach equilibrium spontaneously by precipitation of supersaturated minerals without contact with the atmosphere, then 51.8 mg of goethite and 487.6 mg of gypsum will be precipitated from each litre of mine water. The pH value will shift to a more acidic range of 5.19 as a result of the reaction:

$$FeSO_4(aq) + HCO_3^- \rightarrow FeCO_3(s) + SO_4^{2-} + H^+$$

After oxidation by atmospheric oxygen, the pH value drops to 2.37 due to the oxidation of divalent iron to trivalent iron and the formation of the $Fe(OH)^{2+}$complex, which is the most abundant trivalent iron species in water in this pH range.

$$FeSO_4 + 1.5H_2O + 0.25O_{2(aq)} \rightarrow Fe(OH)_2 + SO_4^{2-} + H^+$$

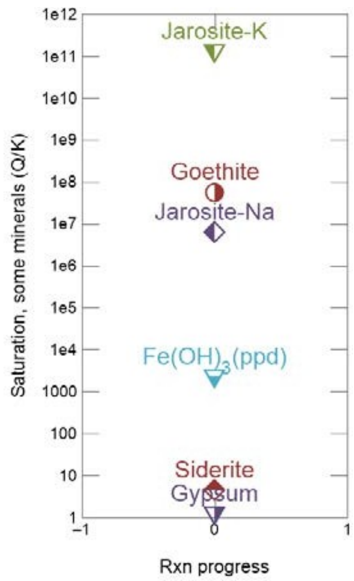

Fig. 4: Degree of supersaturation of mine water with respect to minerals

This was verified in the laboratory by accelerated oxidation of mine water with hydrogen peroxide, when the pH value dropped to around 2.0–2.2 (Fig. 5). Although divalent iron is oxidised to trivalent iron, goethite precipitation practically does not occur because the solubility of goethite increases with decreasing pH, and the change in pH-Eh conditions follows the equilibrium between the $FeSO_4$ sulphate complex and goethite.

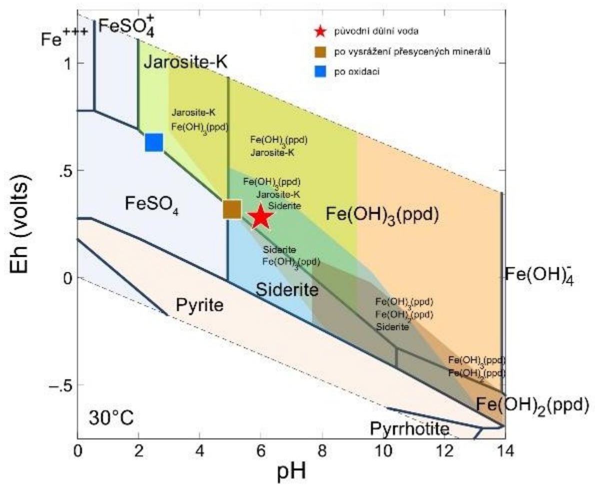

Fig. 5: Speciation diagram for mine water from Nižná Slaná. The diagram was constructed for the activities of components in the original mine water. The coloured fields indicate areas of conditions under which the mine water is supersaturated with respect to individual minerals.

Only strong alkalisation of mine water leads to the precipitation of goethite (or alternatively ferric hydroxide or one of the oxyhydroxides) and manganese oxides (model hausmannite Mn_3O_4) and a reduction in high concentrations of dissolved iron and manganese (Fig. 6).

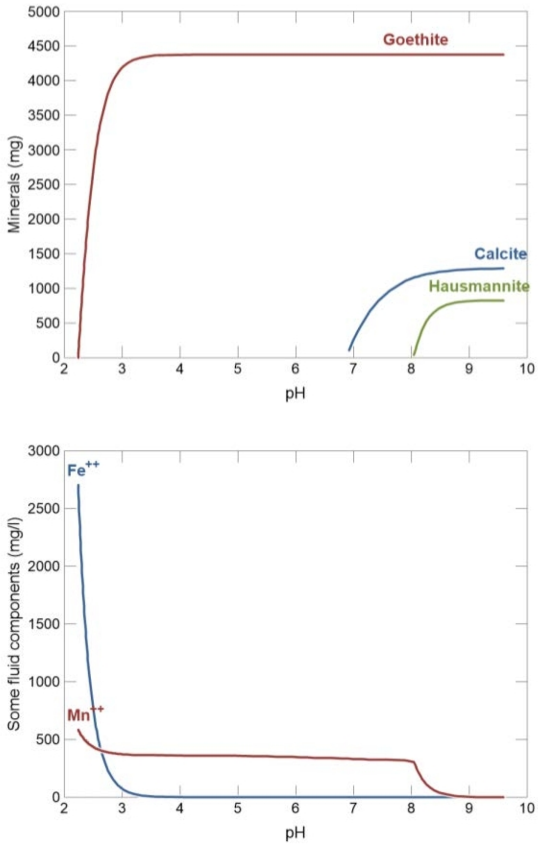

Fig. 6: Development of mineral precipitation and concentrations of dissolved iron , manganese and , and manganese in mine water during its alkalisation.

The described behaviour of mine water was experimentally verified by titration with sodium hydroxide. The experimentally obtained titration curves are shown in Fig. 7 together with the model titration curve of mine water.

Geochemical models for mine water from Nižná Slaná show how mine water will behave when equilibrium is reached and subsequently the processes that will be associated with its oxidation by atmospheric oxygen. When interpreting the processes and, in particular, the precipitation of individual minerals, it is necessary to take into account that the areas of conditions for their precipitation significantly overlap for the given conditions, and the rate of their precipitation may determine which of the minerals will precipitate. A faster precipitating mineral removes a given component from the water, and thus the water may become unsaturated with respect to a thermodynamically more stable (less soluble) mineral. This is particularly true for oxide forms of trivalent iron. However, the basic direction of the processes will remain comparable.

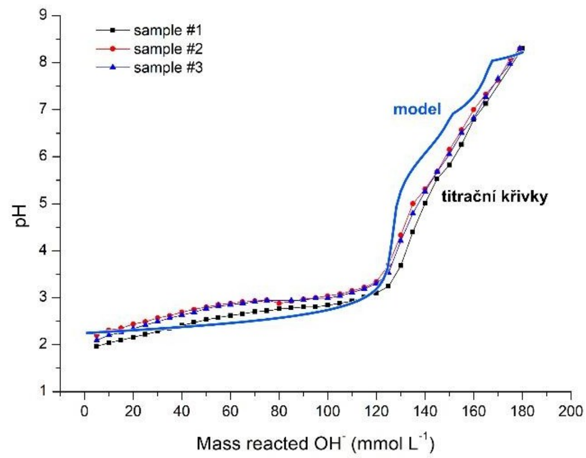

Fig. 7: Experimental titration curves of mine water and their geochemical model.

CONCLUSION

The mine water from Nižná Slaná is extreme in terms of its type, overall mineralisation and high concentrations of iron, manganese and other metals. In addition, when it rises to the surface, it is significantly supersaturated with ferric oxyhydroxides, jarosite and siderite. Although the pH value of the mine water is only slightly acidic, its purification and reduction of environmental impacts will require more than just oxidation, which leads to its strong acidification. Its purification will require significant alkalisation in combination with intensive aeration.

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