The Smolnik Mining Site in Slovakia: its Potential Use for the Production of Mineral Pigments

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Abstract

A batch cultivation of mine impacted water from the Smolnik mining site was carried out comparing the autochthonous microbial consortia to three pure acidophilic chemolithoautotrophic bacterial species. They were inoculated into the mine water together, as a bacterial consortium, in order to remove dissolved iron from the liquid phase while monitoring changes in various geochemical parameter (pH, ORP).

Overall, the final total iron concentration decreased from the initial 228.5 mg/L to 67 mg/L when bacteria were added. After a final pH increase (20% KOH) and filtration of the Fe-precipitates, the final concentration of total dissolved Fe was 2.11 mg/L.

Keywords: Mine Impacted Waters, Acidophilic bacteria, Mineral Pigments, Circular economy, Historical Mining Sites

Introduction

The riverbed of adjacent water bodies in the Smolnik region is discernibly coloured from the presence of ochreous precipitates, typical for mine impacted waters, especially in abandoned historical mining areas. This is caused by an elevated iron concentration in the mine water (237 mg/L^{-1}) and its precipitation when mixed with river freshwater.

On the walls of a sedimentation basin built for iron precipitation close to the main mine outflow, the secondary mineral Schwertmannite (Fig. 1) is naturally formed in big pieces, showing its earthy colours and hues potentially usable as a naturally reclaimed pigment.

Iron ochre precipitates are mainly formed on surfaces that are in contact with mine water, particularly in regions where flow is reduced. The dominant mineral in the outflow is the aforementioned Schwertmannite ($Fe_8O_8(OH)_8{-}2x(SO_4)x \bullet nH_2O$) (Fig. 1) (Lintnerová *et al.* 2009). Together with elements such as iron and sulfur, metalloids such as arsenic or antimony also co-precipitate with iron. After drying, its structure becomes brittle and can be easily crushed into a fine powder. It can be easily mixed with a base medium, such as oil, and the resulting colour is intense and rich. Smolnik mine waters can therefore be considered a rare raw material, which shows potential as a source of natural pigments and metals through the innovative use of bio-hydrometallurgical approaches.

Smolnik mine water contains metals, some of which are on the list of Critical Raw Materials (CRMs) issued by the European Union (European Commission 2023). CRMs are a cornerstone of circular economy and independent, self-sufficient EU. The primary pollutants in this AMD (Acid Mine Drainage) are iron, sulfates, manganese, aluminum, copper, zinc and arsenic.

The Smolnik deposit is one of only a few where mine waters were intensively used for the extraction of copper since the Middle Ages. During favourable periods, it was possible to obtain more metal from the mine water than from the ore (Jaško *et al.* 1998). Cementation technology was unique in the world at that time. According to historical records, China (1086 A.D.) was the first to use this technology (Lung 1986), but it is the Smolnik location that holds this primacy within Europe. The oldest written mention of copper production by cementation in Smolnik is from 1346 (Juck 1984). This record was therefore the second in the

Figure 1 *Secondary mineral Schwertmannite; Left – formed in the mine water on the wall of the sedimentation basin; Right – detail with its porous structure.*

world to mention the practice of copper cementation.

Mining activities at Smolnik ceased in 1994, and the area was subsequently flooded. The mining complex itself began to behave like a bioreactor, producing large amounts of acid mine drainage, where the predominant microorganism belongs to the genus *Gallionella* (Bártová 2020).

Under normal conditions, the flow of mine water reaches 10 L/s, with an average temperature of 14 °C. Sulfates and ferrous iron, which are products of pyrite leaching, are the dominant ions in this water (Kupka *et al*. 2012).

At the outflow from the main discharge shaft (Pech shaft), the total Fe concertation is currently 228.5 mg/L (225 mg/L Fe^{2+} and 3.5 mg/L Fe^{3+}) with a decreasing tendency over the years (Tab. 1). The mine water flows from underground in an anoxic form, and thus the biggest moiety of the iron is present in its Fe^{2+} form, serving as an energy substrate for iron oxidising microorganisms.

Iron is the fourth most abundant element in the Earth's crust by percent mass (Rösler and Lange 1972) and thus a common contaminant in natural waters occurring in various types of environments. Nowadays, the necessity of iron removal and recovery from such water and wastewater is currently emphasised in order to protect human health and critical infrastructure (Kaksonen and Janneck 2024). Huge opportunities connected to this endeavour lie in the use of microbial consortia facilitating iron cycling. Oxidised iron forms such as Schwertmannite can be used as valuable products (pigments, sorbents) (Reichel *et al*. 2017) and increase the value of such a material.

An example of good practice in this sector is the social enterprise True Pigments LLC in Appalachian Ohio, US (Pigments 2024).

The Truetown Discharge, located in the Sunday Creek watershed, is the largest single acid mine drainage discharge in the state of Ohio, with a flow rate of 62 L/s. The AMD treatment facility is able to treat approximately

Table 1 *Change in the composition of mine water over the years.*

Shaft Pech	SO_4^{2-} mg/L	Fe mg/L	Al mg/L	Mn mg/L	Zn mg/L
2011	2082	272	57.9	22.6	8.4
2020	1722	232	40.3	16.5	4.4
2025	1766	229	44.1	17.1	5.4

Shaft Pech	Cu µg/L	Li µg/L	Co µg/L	Pb µg/L	As µg/L	Cd µg/L	Sb µg/L	Cr µg/L
2011	1710	312	861	20.8	22	16,4	-	2.9
2020	498	253	308	36.4	73	3.8	11.2	0.4
2025	1070	290	410	12.1	28.4	0.85	<0.1	<0.1

5.3 million litres of acid mine drainage daily, cleaning up Sunday Creek while processing iron oxide for professional-grade paint pigment production and employing at least five full-time workers (Enforcement 2023).

Methods

Bacterial strains and incubation conditions

Three strains of chemolithotrophic, acidophilic, iron-oxidizing bacteria were used in the experiments: *Acidithiobacillus ferrivorans* SS3 (DSM 17398), *Acidithiobacillus ferrooxidans* (DSM 14882) and Leptospirillum feriphilum (DSM 14647). Detailed description of their growth and iron oxidation kinetics is described in detail elsewhere (Kupka *et al.* 2023). Bacteria were incubated in natural mine water from the outflow of the main discharge shaft (Pech). The cultivation took place in magnetically stirred and properly aerated baffled reaction vessels with the working volume 0,5 L with the set temperature of 25 °C and 240 RPM.

Mine water parameters

pH/ ORP analysis

A combined glass electrode (InLab Micro Mettler Toledo) was used for pH measurement. The oxidation-reduction potential (ORP) of the liquid phase during bacterial iron oxidation was measured with a combined Pt-Ag/AgCl redox electrode (InLab Redox Micro Mettler Toledo). In both cases, the Seven2Go S2 (Mettler Toledo) was used.

Iron speciation

Ferric iron was determined with a UV-spectrophotometric method at 300 nm (Basaran and Tuovinen 1986). Ferrous iron concentrations were determined by a modified o-phenantroline spectrophotometric method, insensitive to Fe^{3+} interference (Herrera *et al.* 1989).

Cell monitoring

Presence of microbial cells was confirmed by direct microscopic count using a Neubauer counting chamber with a depth of 0.01 mm. Higher densities of pure cultures facilitated faster Fe^{2+} oxidation and therefore also higher oxidation-reduction potential.

Chemical analyses

Elemental analysis of the water was done using AAS (Varian AA240Z, AA240FS) and ICP-MS 7700 (Agilent). Sulfate concentration was analyzed by ion chromatography (Dionex ICS 5000).

Results

In order to oxidise Fe^{2+} from acid mine drainage, three strains of chemolithotrophic, acidophilic, iron-oxidizing bacteria were used in a batch cultivation process. This was compared to batch cultivation without any microbial inoculation, so only natural microbial consortia were present. All batch cultivations were carried out in triplicate, with the mean value for each point plotted (Fig. 2).

Inoculation of bacterial consortium consisting of A. ferrivorans SS3, A. ferrooxidans and L. feriphilum on the third day of cultivation, accelerated Fe^{2+} complete oxidation in a span of 24 hours. Compared to the water with only native microorganisms available, even after 120 hours approximately 76 mg/L of Fe^{2+} was still present.

Once all Fe^{2+} is successfully oxidised to Fe^{3+}, the water can be used for the secondary minerals precipitation.

In order to precipitate out dissolved Fe^{3+}, pH of the oxidised solution in both cases (S; S+bb) was adjust by 20% KOH to 3.7. The pH of the Smolnik AMD from the Pech Shaft spans from 3,7 to 4,1 (Bálintová *et al.* 2019). In the experiment, the lowest value from this range was used as it is already sufficiently high for Fe precipitation.

***Table 2** Parameters of the Smolnik mine water (2025).*

pH	ORP mV	Conductivity mS/cm	Temperature °C	Flow rate L/s
4,12	289	2,09	12,1	10

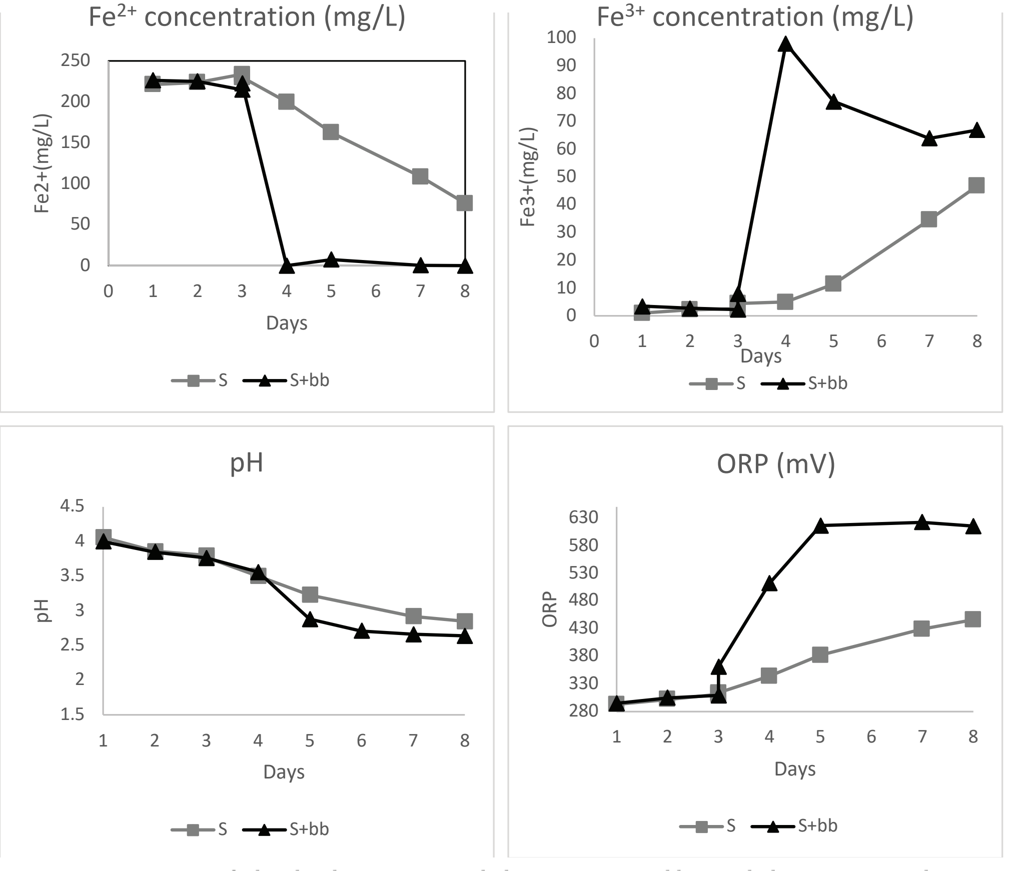

***Figure 4** Process of a batch cultivation; S- Smolnik mine water; S + bb – Smolnik mine water with 3 inoculated bacterial cultures.*

After pH adjustment to 3.7, Fe^{3+} concentration dropped to 2,11 mg/L (S+bb) and 1,74 mg/L (S), respectively.

The Fe^{2+} concentration in “S+bb” was below the detection limit already after 24 hours of bacterial inoculation but for the “S” cultivation there was still 76 mg/L present even on the 8th day. After raising the pH and subsequent filtration of precipitates (vacuum filtration through 0,23 μm membrane filter), there was still 46,75 mg/L Fe^{2+} present in the filtrate. This far exceeds the norm of 2mg/L for surface water quality according to Regulation of the Government of the Slovak Republic (269/2010 2010). The oxidized water, where inoculated bacterial consortium was used, exceeded this threshold value by only 0,11 mg/L.

Conclusion

The main purpose of this study was to remove dissolved iron by the process of bio-oxidation from the original mine water and thus minimise the risk of further iron precipitation, when mine water mixes with freshwater. To minimize the addition of chemical agents, only bacterial iron oxidation was performed.

The use of properly grown iron oxidisers in their exponential phase can effectively substitute the use of a chemical agent such as hydrogen peroxide.

Subsequently, after effective Fe2+ oxidation, selective precipitation and recovery of metals of interest can be achieved with high yields through the process of

Optimized Selective Sequential Precipitation (Macingova E. 2012) without the need for hydrogen peroxide.

Compared to the aforementioned True Pigments social enterprise, where pigments are produced from the sediments in the creek, in this research the crude mine water is being used before it reaches the water body. Intensive research is currently underway. Preliminary results show great potential for novel use of the Smolnik mine waters.

Acknowledgments

This study was funded by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the projects No. 09I03-03-V04-00697

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