

Microbial synthesis of schwertmannite from lignite mine water and its utilization for removal of arsenic from mine waters and for production of iron pigments

E. JANNECK¹, I. ARNOLD², T. KOCH², J. MEYER³, D. BURGHARDT⁴, S. EHINGER¹

¹G.E.O.S. Ingenieurgesellschaft mbH, PO Box 1162, D-09581 Freiberg, Germany, e.janneck@geosfreiberg.de

²Vattenfall Europe Mining AG, Vom-Stein-St. 39, D-03050 Cottbus, Germany, ingolf.arnold@vattenfall.de

³Wismut GmbH, Jagdschänkenstr.29, D-09177 Chemnitz, Germany, j.meyer@wismut.de

⁴Technische Universität Dresden, Institute for Groundwater Management, D-01062 Dresden, Germany, diana.burghardt@tu-dresden.de

Abstract In collaboration with the Vattenfall Europe Mining AG, the G.E.O.S. Freiberg mbH has designed a pilot plant for microbiological synthesis of schwertmannite (SHM). This pilot plant has been in operation since 2007 in the lignite open pit mine of Nochten in Germany. By means of microbiological oxidation of ferrous iron, a pure schwertmannite is precipitated in the pilot plant under pH conditions between 2.85 and 3.1. During the process, a maximum load of 2.5 m³/h and an oxidation rate of 55 g Fe(II)/(m³·h) were achieved. The produced schwertmannite has a low content of impurities and can be used as a sorbent for removing arsenic from mine waters. For this purpose a pilot scale test in a mine water treatment plant of an abandoned uranium mine was successfully performed. It was also shown that schwertmannite is an expedient substance for production of iron pigments. For this purpose schwertmannite has to be processed by drying, calcination and milling. In cooperation with partners from the ceramic and coating industry we have produced samples of roofing tiles, floor tiles and concrete cobblestones as well as lacquer, synthetic resin paints and corrosion-protective coatings.

Key Words schwertmannite, microbial oxidation, lignite mine water

Introduction

Schwertmannite can be precipitated from iron and sulphate rich mine waters by means of microbial oxidation of ferrous iron. No treatment chemicals are needed in this process to perform the oxidation of ferrous iron and the subsequent precipitation of schwertmannite. The water only has to be aerated for the oxidation process. The oxidation process is enhanced by naturally occurring bacteria in the groundwater which can grow and proliferate under acidic pH conditions. No nutrients have to be provided for the autotrophic iron oxidizing bacteria that use dissolved carbon dioxide as sole carbon source.

Due to the advantages of the microbial oxidation, the process efficiency should be evaluated in a pilot plant under practice-related conditions. Another purpose of the investigations presented here was to identify the requirements for a possible utilization of schwertmannite as raw material for producing saleable products such as sorbents for As removal and iron pigments.

Lignite mine waters in Lusatia as a source of schwertmannite

The Lusatian mining area is located in southeast Germany. This area comprises five active opencast mines operated by the Vattenfall Europe Mining AG which produces more than 60 Mio t Lignite per year. The production of coal in the Lusatia requires a huge water lift between 4.4 to 11 m³ per ton coal. The total amount of lifted water in the Lusatian mining area accounted for 392 Mio m³ in 2005 differing in the specific opencast pits (Figure 1).

In the opencast mine Nochten about 115 Mio m³ mine water per year are pumped from the subsurface and have to be treated using lime milk for precipitation of ferric hydroxide and neutralizing the water. 20–25 Mio m³ mine water per year are purified in the treatment plant Tzschelln. This groundwater is lifted from the dump area and has high iron and sulphate concentrations. A typical analysis of this water is given in Table 1. The iron(II) and sulphate concentration vary between 300 to 400 mg/L and 1,700 to 2,100 mg/L, respectively. Such kinds of high iron containing waters are suitable for schwertmannite recovery. If 2/3 of the iron load in the treatment plant Tzschelln could be precipitated as schwertmannite a recovery between 8,000 and 14,000 t/a of schwertmannite would be possible over a period of at least 30 years.

Table 1 Exemplary analysis of the Tzschelln treatment plant's inflow

Table 2 Exemplary analysis of the Schlema-Alberoda treatment plant's inflow

Parameter	Value	Unit
pH-value	5.30	
electr. Conductivity (25°C)	2,930	µS/cm
TIC	65	mg/L
Chloride	34	mg/L
Sulphate	1,970	mg/L
Iron, total	382	mg/L
Iron, dissolved	324	mg/L
Iron(II), dissolved	324	mg/L
Acidity	14.0	mmol/L

Parameter	Value	Unit
pH-value	6.95	
electr. Conductivity (25°C)	2,260	µS/cm
TIC	120	mg/L
Chloride	57	mg/L
Sulphate	780	mg/L
Iron, total	5.7	mg/L
Arsenic	1.0	mg/L
Uranium	2.0	mg/L
Radium	1,580	mBq/L

Pilot plant for microbial oxidation of ferrous iron

The designed pilot plant (Figure 1) consists of an oxidation basin with removable growth carriers as well as an aeration and a precipitation tank. The overall volume is about 10.5 m³ and the oxidation basin has a capacity of 8.14 m³. Due to the high flow rate of the circulation pump (approximately 30 m³/h) low gradients of process parameters can be guaranteed. The water inflow is intensively aerated by a CENTROX aerator. A chain cleaner assembled at the bottom of the oxidation basin removes dropping schwertmannite to the sludge collecting channel. From there the sludge is pumped to a storage tank where the sludge can sediment and thicken. The thickened sludge can be recycled to the oxidation basin or pumped into big bags for dewatering by gravity.

From the chemical engineering point of view, the designed pilot plant is a hybrid type of bioreactor. It has physical characteristics of a fixed-bed reactor in parallel with a circulation reactor. The advantages of this special reactor design are avoiding plugs in the fixed-bed (growth carrier) and a free circulation inside the oxidation basin.

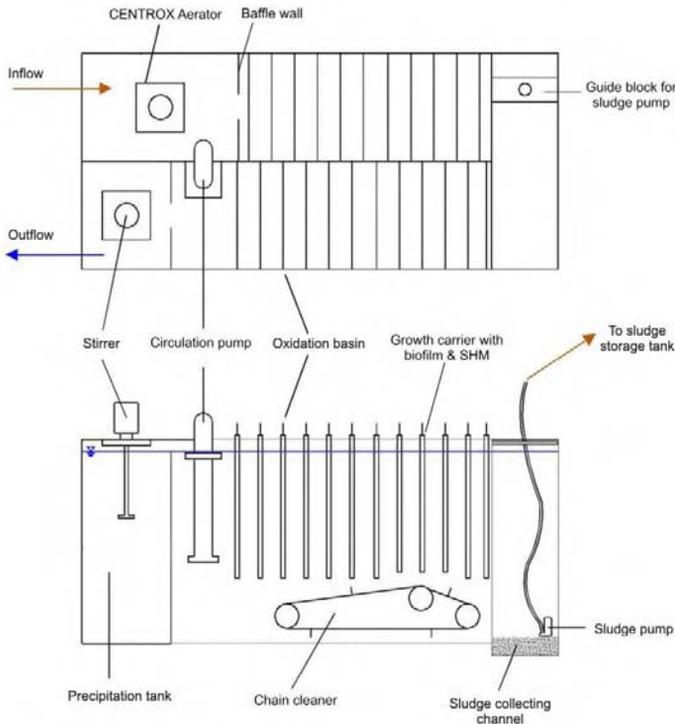


Figure 1 Schematic drawing of the pilot plant

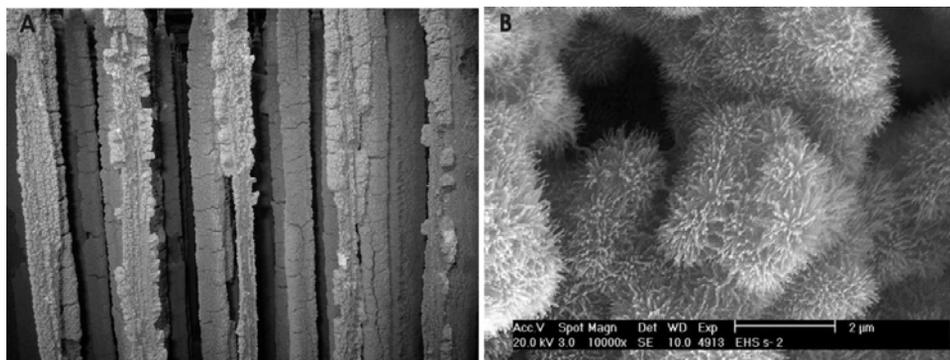
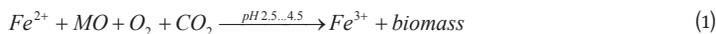


Figure 2 Schwertmannite produced in the pilot plant by microbial treatment of Lusatian minewater, A) Encrustations on the growth carrier material, B) SEM picture of the formed mineral schwertmannite

Characteristics of schwertmannite

The mineral Schwertmannite precipitates at a pH between 2.8 and 4.5 (see equation 1, 2; Bigham et al. 1996) and exhibits a molar ratio of $\text{Fe} : \text{SO}_4^{2-}$ of 8.00 : 1 or 4.57 : 1, respectively.



The mineral is composed of fine, 10 to 20 nm long and 2 to 5 nm wide needles, which form hedgehog-like aggregates. The crystalline structure is related to the tunnel structure of akaganeite. The first de-tailed characterisation of the mineral was carried out by Bigham and Schwertmann at the beginning of the 1990s (Bigham et al. 1990, 1994).

The schwertmannite generated microbiologically in the pilot plant (Figure 3) is a very pure mineral nearly free of impurities and with a high specific surface. The Schwertmannite sludge exhibits a better dewatering capacity in comparison to the iron hydroxides. Dewatering by gravity yields a dry matter content of 35–45%.

Determination of the oxidation rate

The microbially enhanced oxidation process in the pilot plant occurs both on the surface of the biofilm carriers and in the free volume of the oxidation basin. The oxidation rate is influenced by various parameters, e.g. oxygen supply, pH, temperature, sludge circulation, composition of the inflowing mine water and surface area of the biofilm carrier. At technical scale only the sludge circulation and the amounts of carriers can be used to accelerate the oxidation rate. So in a first step the oxidation rate was determined in the pilot plant at different surface areas of the growth carrier. In these experiments the oxidation rate was calculated according to Eq. (3) from the total amount of ferric iron ($\text{Fe(III)}_{\text{ges}}$) formed during microbial oxidation and the residence time τ . The results are presented in Figure 3. By drawing the oxidation rate as a function of A_F/V_F ratio it was possible to distinguish $v_{\text{Ox-F}}$ and $v_{\text{Ox-V}}$ and to estimate these values.

In the next step sludge circulation was applied for increase of oxidation rate. At a ratio of surplus to recycled sludge of 1:1 a overall oxidation rate of 55 g/(m³·h) at 2.5 m³/h inflow was achieved. However, the results could not be reproduced. Probably differences in the microbial activity of the sludge are responsible for the low reproducibility. Heinzel et al. (2009) identified *Ferribacter polymyxa* and *Gallionella ferruginea* as the most dominating strains in the pilot plant. Presently we are elaborating a method for determination of bacterial counts and identification of *F. Polymyxa* by FISH to get more information about the microbial activity of the sludge.

$$v_{\text{Ox}} = \frac{\text{Fe(III)}_{\text{ges}}}{\tau} = \frac{\text{Fe(III)}_{\text{ges}}}{V_R} \cdot Q_{\text{Zu}} = v_{\text{Ox-F}} \cdot \frac{A_F}{V_R} + v_{\text{Ox-V}} \left[\frac{\text{g}}{\text{m}^3 \cdot \text{h}} \right] \quad (3)$$

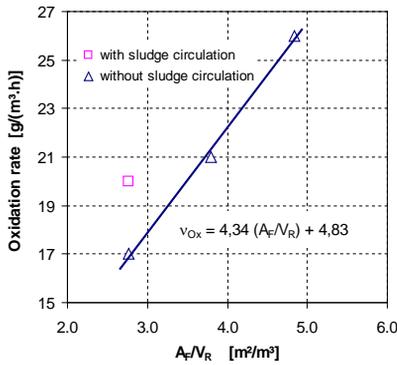


Figure 3 Oxidation rate as a function of A_F/V_R ratio

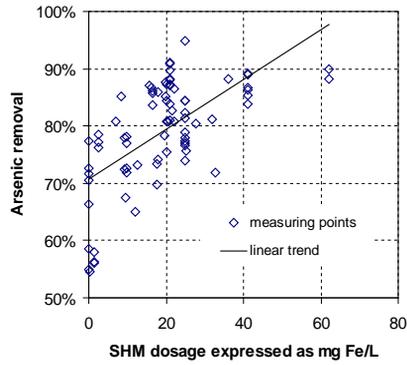


Figure 4 Enhancement of arsenic removal by dosage of schwertmannite suspension

A_F	Surface of the growth carriers and all other surfaces inside the reactor	[m ²]
Fe	(III) _{ges} Total amount of ferric iron formed by microbial oxidation	[g/m ³]
Q_{Zu}	Inflow	[m ³ /h]
V_R	Reactor volume	[m ³]
v_{Ox}	Total (overall) oxidation rate	[g/(m ³ ·h)]
v_{Ox-F}	Oxidation rate caused by oxidation at the carrier	[g/(m ² ·h)]
v_{Ox-V}	Oxidation rate caused by oxidation in free reactor volume	[g/(m ³ ·h)]
τ	Residence time of water in the oxidation basin and aeration chamber	[h]

Pilot test for removal of arsenic from mine water

The schwertmannite produced in the pilot plant Tzschelln was used to enhance the arsenic removal from mine water in the abandoned uranium mine of Schlema-Alberoda (East Germany). The uranium mine water has to be purified from iron, arsenic, uranium and radium, iron and manganese. The installed treatment technology is described by Meyer, et al. (2009). The average composition of mine water inflow is shown in Table 2. The required limit of arsenic for discharging into the river Mulde is $\leq 0.1\text{--}0.3$ mg/L (dependent on flow rate of the Zwickauer Mulde river). The naturally occurring iron concentration is not sufficient for complete arsenic removal or to meet the prescribed maximum value. Thus it was investigated, whether it is possible to enhance the arsenic removal by dosing SHM as a diluted aqueous suspension. The results are given in Figure 4. It was possible to improve the arsenic removal from 60% to nearly 90% by dosing 20–40 mg/L Fe or 35–70 mg/L SHM (dry mass).

Acknowledgements

The authors thank the Federal Ministry of Education and Research of Germany and the European Commission’s 7th Framework Programme for financial support under contract no. FKZ 03Go714D (Project: SURFTRAP) and CP-IP 228559 (Project: ProMine), respectively.

References

Bigham, J.M.; Schwertmann, U.; Carlson, L.; Murad, E. (1990): A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. – *Geochimica et Cosmochimica Acta* 54, 2743–2758

Bigham, J.M.; Carlson, L.; Murad, E. (1994): Schwertmannite, a new iron oxyhydroxysulphate from Pyhäsalmi, Finland, and other localities. – *Mineralogical Magazine* 58, Dec., 641–648.

Bigham, J.M.; Schwertmann, U.; Pfab, G. (1996): Influence of pH on mineral speciation in a bioreactor simulating acid mine drainage. – *Applied Geochemistry* 11: 845–849.

Heinzel, E.; Hedrich, S.; Janneck, E.; Glombitza, F.; Schlömann, M. (2009): Bacterial Diversity in a Mine Water Treatment Plant. – *Applied and Environmental Microbiology*, 75(3), 858–861

Meyer, J (2009): Wasser am Standort Schlema-Alberoda. – *Rundschau / Dialog* 62, 6–8 (Company newsletter of Wismut GmbH, issue 62/2009)